BANSAL CLASSES

CHEMISTRY

TARGET IIT JEE 2007

XI (P, Q, R, S)

ATOMIC STRUCTURE

CONTENTS

Physical Constants[a]

Constant and Symbol[b]		SI Value	Gaussian Value
Speed of light in vaccum	c	2.99×10^{8} m/s	2.99×10^{10} cm/s
Proton & electron charge	e	1.60×10^{-19} C	4.8×10^{-10} statC
Permittivity of vaccum	ε_0	8.85×10^{-12} $C^2/N\text{-}m^2$	
Avogadro constant	N_A	6.02×10^{23} mol^{-1}	6.02×10^{23} mol^{-1}
Electron rest mass (0.000548 amu)	m_e	9.10×10^{-31} kg	9.10×10^{-28} g
Proton rest mass (1.00757 amu)	m_p	1.67×10^{-27} kg	1.67×10^{-24} g
Neutron rest mass (1.00893 amu)	m_n	1.67×10^{-27} kg	1.67×10^{-24} g
Planck constant	h	6.62×10^{-34} J s	6.62×10^{-27} erg s
Permeability of vaccums	μ_0	$4\pi \times 10^{-7}$ NC^{-2} s^2	
Bohr radius	a_0	5.29×10^{-11} m	0.529×10^{-8} cm
Bohr's velocity		$2.188 \times 10^{6} \times \frac{Z}{n}$ m/sec.	$2.188 \times 10^{8} \times \frac{Z}{n}$ cm/sec.
Bohr's energy (–13.6 eV/atom)		$-21.8 \times 10^{-19} \frac{Z^2}{n^2}$ J/atom	-21.8×10^{-12} erg/atom
Bohr magneton (BM)	β_e	9.27×10^{-24} J/T	
Gas constant	R	8.3145 J/mol-K	8.3145×10^{7} erg/mol-K
Boltzmann constant	k	1.38×10^{-23} J/K	1.30×10^{-16} erg/K
Gravitional constant	G	6.67×10^{-11} $m^3/kg\text{-}s^2$	6.67×10^{-8} $cm^3/g\text{-}s^2$

Energy Conversion Factors[a]

1 erg = 10^{-7} J

1 cal = 4.184 J

1 eV = 1.602177×10^{-19} J = 1.602177×10^{-12} erg = 23.0605 kcal/mol

Greek Alphabet

Alpha	Α	α	Beta	Β	β
Gamma	Γ	γ	Delta	Δ	δ
Epsilon	Ε	ε	Zeta	Ζ	ζ
Eta	Η	η	Theta	Θ	θ
Iota	Ι	ι	Kappa	Κ	κ
Lambda	Λ	λ	Mu	Μ	μ
Nu	Ν	ν	Xi	Ξ	ξ
Omicron	Ο	ο	Pi	Π	π
Rho	Ρ	ρ	Sigma	Σ	σ
Tau	Τ	τ	Upsilon	Υ	υ
Phi	Φ	ϕ	Chi	Χ	χ
Psi	Ψ	ψ	Omega	Ω	ω

KEY CONCEPT

STRUCTURE OF ATOM

Rutherford's Model
Bohr's Model
Wave mechanical model

EXTRA NUCLEAR PART (e^-)

Electrons,protons & neutrons are the most important fundamental particles of atoms of all elements (Except hydrogen)

Some uncommon Fundamental particles :

1. ${}_{Z}X^{A}$, A = Z + n

2. $m = m_0/[1-(v/c)^2]^{1/2}$

3. Reduced mass $\frac{1}{\mu} = \frac{1}{M} + \frac{1}{m} = \frac{mM}{m+M}$ m = mass of e^- ; M = Mass of nucleus

4. Photon is considered massless bundle of energy. But to find its mass use $m = \frac{h}{\lambda c}$

5. $E = mc^2$, $E = h\nu = hc/\lambda = hc\,\bar{\nu}$

6. Quantum efficiency or Quantum Yield = $\frac{\text{no. of molecules reacting}}{\text{no. of quanta absorbed}}$

7. $R_n = R_1 (A)^{1/3}$, $R_1 = 1.33\text{x}10^{-13}$ cm A = mass number

8. $d_{\text{neucleus}} = \frac{A}{N_A} \frac{1}{4/3\,\pi r^3}$ $\frac{1}{2} m_\alpha v_\alpha^2 = K \frac{Z_e . 2e}{r}$; $\text{Tan}\frac{\theta}{2} = \frac{K.z_e Z_e}{mv^2 .b}$

number of a particles at $\theta = K \frac{1}{\sin^4 \theta/2}$; b = impact parameter

9. Rydberg's Equation $\frac{1}{\lambda} = \bar{\nu} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{x}\, Z^2$

10. Limiting spectral line (series limit) means $n_2 = \infty$

11. H_α line means we know n_1 , n_2 (longest λ , shortest ν , least E) [H_α , H_β , H_γ , H_δ]

12. No. of wavelengths observed in the spectrum = $\frac{n(n-1)}{2}$

when e^- deexcites to ground state , n = no. of higher orbit

13. $1/2\, mv^2 = h\nu - h\nu^0$(w) (work function or B.E.)

ν^0 = Threshhold frequency $W = h\nu_0 = \frac{hc}{\lambda_0}$

14. Accelerating potential = eV = KE = $\frac{1}{2} mv^2$

15. λ = hc/E = 1240 ev. nm

16. $\nu = \frac{2KE}{h}$

17. $F = \frac{K}{D}\frac{q_1 q_2}{r^2}$; $K = \frac{1}{4\pi\varepsilon_0}$, P.E. = $\frac{K q_1 q_2}{r}$ D = dielectric constant, centrifugal force = $\mathbf{mv^2/r}$

18. $mvr = n \cdot \frac{h}{2\pi} = n.\hbar$

19. $E_n = \frac{E_1}{n^2} z^2 - \frac{2\pi^2 me^4}{n^2h^2} z^2$; $E_1 = \frac{-2\pi^2 me^4}{h^2}$

20. $r_n = \frac{n^2}{Z} \times \frac{h^2}{4\pi^2 e^2 m}$

21. $v = \frac{z}{n} \times \frac{2\pi e^2}{h}$

22. revolutions per sec = $v/2\pi r$

23. Time for one revolution = $2\pi r/v$

24. Separation energy = $E_{n_\infty = \infty} - E_{n \text{ given } = 2,3,4,\ldots\ldots}$

25. No. of waves = n = no. of shells

26. I.E. = $E_{n=\infty} - E_{\text{ground state of e-}}$ (K, L, M, N)

27. $n = n_r + n_\phi$ (Sommerfeld model)

28. $\lambda = h/mv = h/p$

29. $\lambda = \sqrt{\frac{150}{V \text{in volts}}}$ Å

30. $E_n \neq KE$ $KE = 1/2\, mv^2$, $E = h\nu$

31. $\Delta x.\Delta p > h/4\pi$

32. $\nu^{1/2} = a(z-b)$ b = screening constant

33. Radius of $e^- = 2.8 \times 10^{-13}$ cm $\left[\frac{e^2}{r} = mc^2\right]$

34. Nucleons

35. Isotopes, Isobars, Isotones (A – Z)

36. Isoelectronic

37. Isosters

38. Isodiaphers (A – 2Z)

39. paramagnetic

40. Diamagnetic

41. Core, Kernel, core charge, optical e^-
[Valence shell, outermost shell, pentultimate shell]

42. $L = \frac{h}{2\pi}\sqrt{l(l+1)}$

43. $S = \frac{h}{2\pi}\sqrt{S(S+1)}$; $S_z = s\frac{h}{2\pi}$

44. $\mu = \sqrt{n(n+2)}$ B.M. n = number of unpaired e^- ;

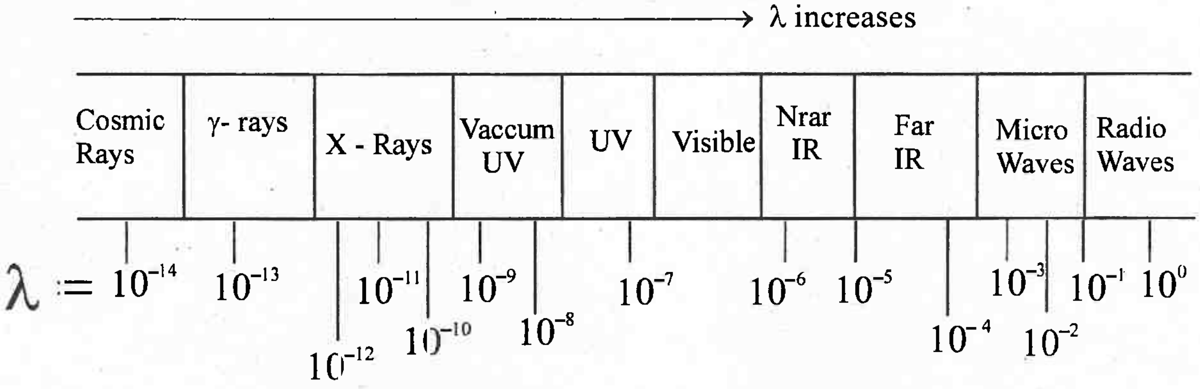
45.

Radial Nodes ;	Angular nodes ;	Total nodes
$(n - l - 1)$	l	$(n-1)$

46. Total no. of e^- in an energy level = $2n^2$
Total no. of e^- in a sublevel = 2(2l+1)
Maximum no. of e^- in an orbital = 2
Total no. of orbitals in a sublevel = (2l+1)
No. of subshells in main energyshell = n
No. of orbitals in a main energy shell = n^2

l =	0	1	2	3	4
	s	p	d	f	g

47. ELEECTROMEGNETIC SPECTRUM



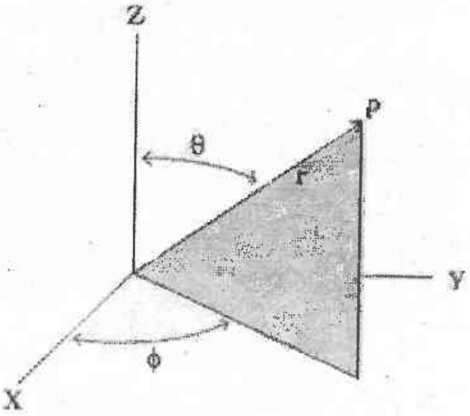
λ in meters.

Distinction between the wave – particle nature of a photon and the particle–wave nature of sub-atomic particle.

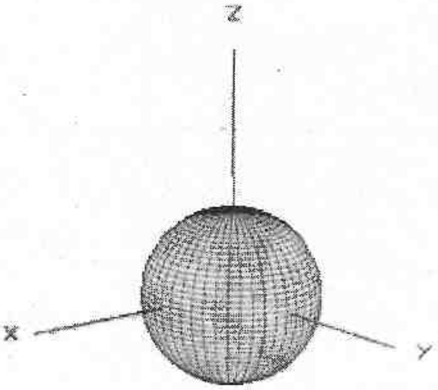
	PHOTON	SUB ATOMIC PARTICLE
1.	Energy = $h\nu$	Energy = $\frac{1}{2} m\nu^2$
2.	Wavelength = $\frac{c}{\nu}$	Wavelength = $\frac{h}{m\nu}$

Note: We should never interchange any of the above and to write electronic conf. of Cation first write for neutral atom & then remove e^- from outermost shell.

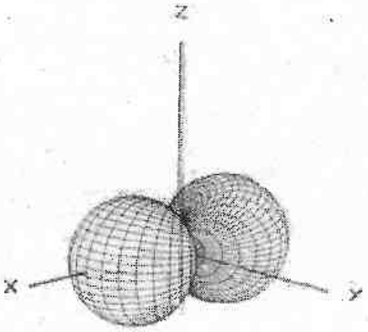
SHAPES OF ATOMIC ORBITALS



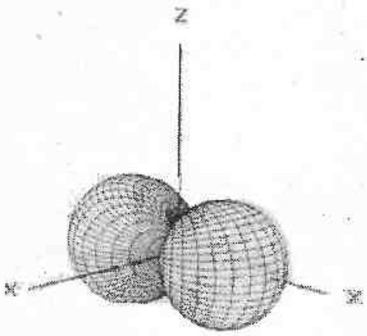
The spherical Polar Coordinates



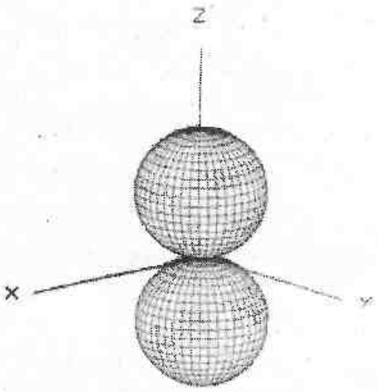
S



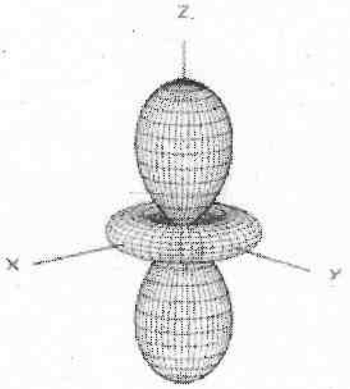
p_x



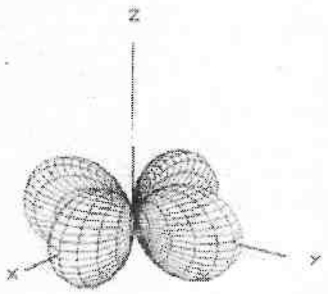
p_y



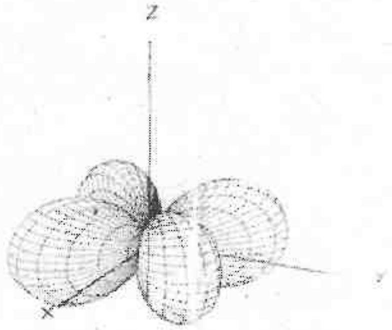
p_z



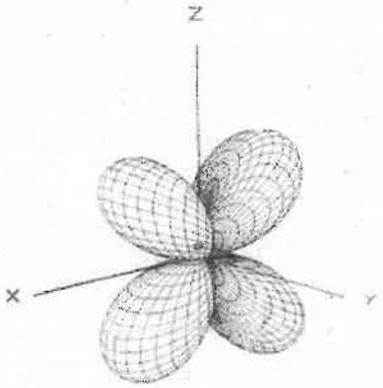
d_{z^2}



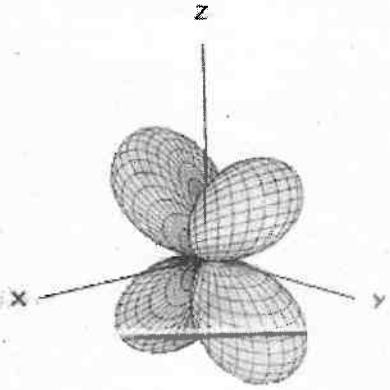
$d_{x^2-y^2}$



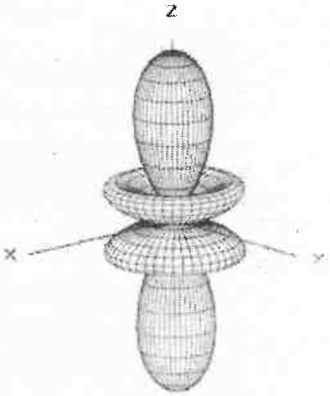
d_{xy}



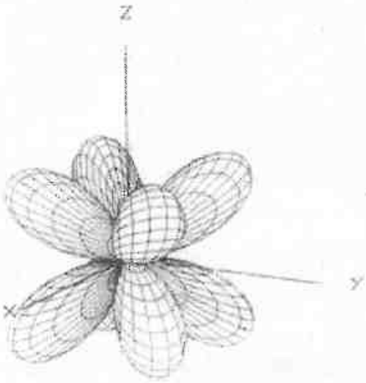
d_{xz}



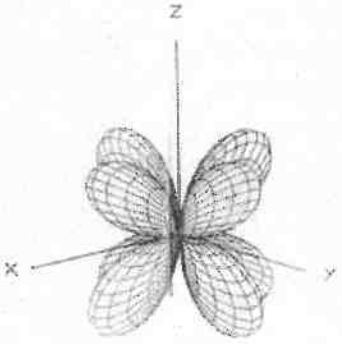
d_{yz}



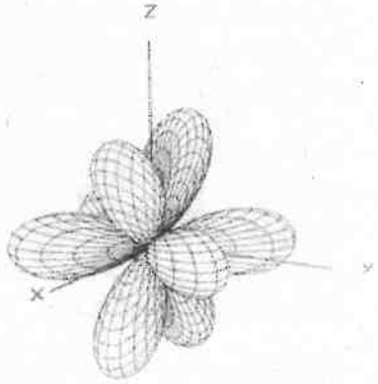
f_{z^3}



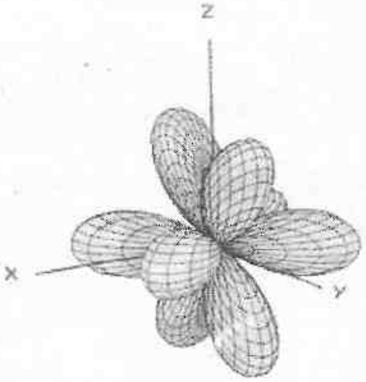
f_{xyz}



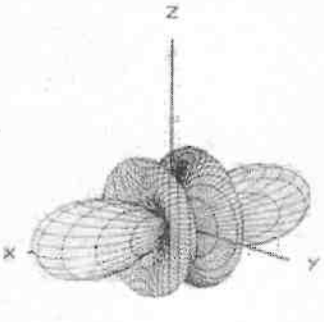
$f_{z(x^2-y^2)}$



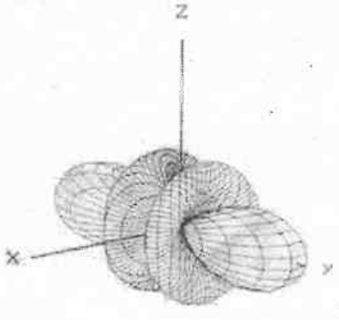
$f_{x(y^2-z^2)}$



$f_{y(z^2-x^2)}$



f_{x^3}



f_{y^3}

Angular part of the wave function : The figures show shapes of atomic orbitals as polar plots. The direction in which the angular part is positive (negative) is indicated in blue (red). A surface on which the angular part of the wave function vanishes is called an angular node. It may be a plane or the surface of the conc. The s, p, d and f orbitals have 0, 1, 2, and 3 angular nodes respectively.

EASY GO

Q.1 Atoms consists of protons, neutrons and electrons. If the mass of neutrons and electrons were made half and two times respectively to their actual masses, then the atomic mass of ${}_6C^{12}$.
(A) Will remain approximately the same (B) Will become approximately two times
(C) Will remain approximately half (D) Will be reduced by 25%

Q.2 Which of the following is not true in Rutherford's nuclear model of atom
(A) Protons and neutrons are present inside nucleus
(B) Volume of nucleus is very small as compared to volume of atom
(C) The number of protons and neutrons are always equal
(D) The number of electrons and protons are always equal

Q.3 When α – particles are sent thought a thin metal foil, most of them go straight through the foil because (one or more are correct)
(A) Alpha particles are much heavier than electrons
(B) Alpha particles are positively charged
(C) Most part of the atom is empty space
(D) Alpha particles move with high velocity

Q.4 Bohr's model can explain
(A) The spectrum of hydrogen atom only
(B) Spectrum of atom of iron containing one electron only
(C) The spectrum of hydrogen molecule
(D) The solar spectrum

Q.5 The ratio of the energy of a photon of 2000 Å wavelength radiation to that of 4000 Å radiation is
(A) 1 / 4 (B) 4 (C) 1 / 2 (D) 2

Q.6 Bohr model of an atom could not account for
(A) Emission spectrum (B) Absorption spectrum
(C) Line spectrum of hydrogen (D) Fine spectrum

Q.7 The maximum energy is present in any electron at
(A) Nucleus (B) Ground state
(C) First excited state (D) Infinite distance from the nucleus

Q.8 Which electronic level would allow the hydrogen atom to absorb a photon but not to emit a photon
(A) 3s (B) 2p (C) 2s (D) Is

Q.9 The third line in Balmer series corresponds to an electronic transition between which Bohr's orbits in hydrogen
(A) $5 \rightarrow 3$ (B) $5 \rightarrow 2$ (C) $4 \rightarrow 3$ (D) $4 \rightarrow 2$

Q.10 Correct set of four quantum numbers for valence electron of rubidium(Z = 37) is
(A) $5, 0, 0, +\frac{1}{2}$ (B) $5, 1, 0, +\frac{1}{2}$ (C) $5, 1, 1, +\frac{1}{2}$ (D) $6, 0, 0, +\frac{1}{2}$

Q.11 The correct set of quantum numbers for the unpaired electron of chlorine atom is

	n	l	m		n	l	m
(A)	2	1	0	(B)	2	1	1
(C)	3	1	1	(D)	3	0	0

Q.12 The orbital diagram in which the Aufbau's principle is violated is

	2s	$2p_x$	$2p_y$	$2p_z$		2s	$2p_x$	$2p_y$	$2p_z$
(A)	↑↓	↑↓	↑		(B)	↑	↑↓	↑	↑
(C)	↑↓	↑	↑	↑	(D)	↑↓	↑↓	↑↓	↑

Q.13 The total number of neutrons in dipositive zinc ions with mass number 70 is
(A) 34 (B) 40 (C) 36 (D) 38

Q.14 Principal quantum number of an atom represents
(A) Size of the orbital (B) Spin angular momentum
(C) Orbital angular momentum (D) Space orientation of the orbital

Q.15 Which of the following sets of quantum numbers represent an impossible arrangement

	n	l	m	m_s		n	l	m	m_s
(A)	3	2	–2	$\frac{1}{2}$	(B)	4	0	0	$\frac{1}{2}$
(C)	3	2	–3	$\frac{1}{2}$	(D)	5	3	0	$\frac{1}{2}$

Q.16 CO has same electrons as or the ion that is isoelectronic with CO is
(A) N_2^+ (B) CN^- (C) O_2^+ (D) O_2^-

Q.17 The explanation for the presence of three unpaired electrons in the nitrogen atom can be given by
(A) Pauli's exclusion principle (B) Hund's rule
(C) Aufbau's principle (D) Uncertainty principle

Q.18 The maximum number of electrons that can be accommodated in the Mth shell is
(A) 2 (B) 8 (C) 18 (D) 32

Q.19 Elements upto atomic number 103 have been synthesized and studied. If a newly discovered element is found to have an atomic number 106, its electronic configuration will be
(A) $[Rn]5f^{14}, 6d^4, 7s^2$ (B) $[Rn]5f^{14}, 6d^1, 7s^2 7p^3$
(C) $[Rn]5f^{14}, 6d^6, 7s^0$ (D) $[Rn]5f^{14}, 6d^5, 7s^1$

Q.20 Which quantum number will determine the shape of the subshell
(A) Principal quantum number (B) Azimuthal quantum number
(C) Magnetic quantum number (D) Spin quantum number

Q.21 An isostere is

(A) NO_2^- and O_3 (B) NO_2^- and PO_4^{3-} (C) CO_2, N_2O, NO_3^- (D) ClO_4^- and OCN^-

Q.22 The electronic configuration of an element is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$. This represents its
(A) Excited state (B) Ground state (C) Cationic form (D) Anionic form

Q.23 Which of the following has maximum number of unpaired electron (atomic number of Fe 26)
(A) Fe (B) Fe (II) (C) Fe (III) (D) Fe (IV)

Q.24 Which quantum number is not related with Schrodinger equation
(A) Principal (B) Azimuthal (C) Magnetic (D) Spin

REFRESH YOUR CONCEPTS

LIGHT

Q.1 H- atom is exposed to electromagnetic radiation of 1028 Å and gives out induced radiations. Calculate λ of induced radiations.

Q.2 The wavelength of a certain line in the Paschen series in 1093.6 nm. What is the value of n_{high} for this line. $[R_H = 1.0973 \times 10^{+7}\ m^{-1}]$

Q.3 A certain dye absorbs 4530 A^0 and fluoresces at 5080 A^0 these being wavelengths of maximum absorption that under given conditions 47% of the absorbed energy is emitted. Calculate the ratio of the no. of quanta emitted to the number absorbed.

Q.4 The reaction between H_2 and Br_2 to form HBr in presence of light is initiated by the photo decomposition of Br_2 into free Br atoms (free radicals) by absorption of light. The bond dissociation energy of Br_2 is 192 KJ/mole. What is the longest wavelength of the photon that would initiate the reaction.

Q.5 Wavelength of the Balmer H_α line (first line) is 6565 A^0. Calculate the wavelength of H_β (second line).

Q.6 Calculate the Rydberg constant R if He^+ ions are known to have the wavelength difference between the first (of the longest wavelength) lines of Balmer and Lyman series equal to 133.7nm.

Q.7 The quantum yield for decomposition of HI is 2. In an experiment 0.01 moles of HI are decomposed. Find the number of photons absorbed.

Q.8 The light radiations with discrete quantities of energy are called ______.

Q.9 What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition, n=4 to n=2 of He^+ spectrum.

Q.10 Calculate the energy emitted when electrons of 1.0 g atom of hydrogen undergo transition giving the spectral line of lowest energy in the visible region of its atomic spectrum.

PLANK'S QUANTUM THEORY

Q.11 Calculate the wavelength of the radiation that would cause photo dissociation of chlorine molecule if the Cl- Cl bond energy is 243 KJ/mol.

Q.12 Suppose 10^{-17} J of light energy is needed by the interior of the human eye to see an object. How many photons of green light ($\lambda = 550$ nm) are needed to generate this minimum amount of energy.

Q.13 A photon having $\lambda = 854\ A^0$ causes the ionization of a nitrogen atom. Give the I.E. per mole of nitrogen in KJ.

Q.14 Calculate the threshold frequency of metal if the binding energy is 180.69 KJ mol^{-1} of electron.

Q.15 Calculate the binding energy per mole when threshold frequency to the wavelength of 240 nm.

Q.16 A metal was irriadated by light of frequency $3.2 \times 10^{15}\ S^{-1}$. The photoelectron produced had its KE, 2 times the KE of the photoelectron which was produced when the same metal was irriadated with a light of frequency $2.0 \times 10^{15}\ S^{-1}$. What is the ionization Energy of metal.

Q.17 U.V. light of wavelength 800 Å & 700 Å falls on hydrogen atoms in their ground satte & liberates electrons with kinetic energy 1.8 eV and 4 eV respectively. Calculate planck's constant.

Q.18 The dissociation energy of H_2 is 430.53 KJ/mol. If H_2 is exposed to radiant energy of wavelength 253.7 nm, what % of radiant energy will be converted into K.E.

Q.19 A potential difference of 20 KV is applied across an X-ray tube. Find the minimum wavelength of X-ray generated.

Q.20 The K.E. of an electron emitted from tungstan surface is 3.06 eV. What voltage would be required to bring the electron to rest.

BOHR'S MODEL

Q.21 Calculate energy of electron which is moving in the orbit that has its rad. sixteen times the rad. of first Bohr orbit.

Q.22 The electron energy in hydrogen atom is given by $E_n = \frac{-21.7 \times 10^{-12}}{n^2}$ ergs. Calculate the energy required to remove an e^- completely from n = 2 orbit. What is the largest wavelength in cm of light that can be used to cause this transition.

Q.23 Calculate the wavelength in angstrom of photon that is emitted when an e^- in Bohr orbit n=2 returns to the orbit n=1. The ionization potential of the ground state of hydrogen atom is 2.17×10^{-11} erg/atom.

Q.24 The radius of the fourth orbit of hydrogen atom is 0.85 nm. Calculate the velocity of electron in this orbit.

Q.25 The velocity of e^- in a certain Bohr orbit of the hydrogen atom bears the ratio 1:275 to the velocity of light. What is the quantum no. "n" of the orbit and the wave no. of the radiation emitted for the transition from the quatum state (n+1) to the ground state.

Q.26 Electrons of energy 12.09 eV can excite hydrogen atoms. To which orbit is the electron in the hydrogen atom raised and what are the wavelengths of the radiations emitted as it drops back to the ground state.

Q.27 A doubly ionised lithium atom is hydrogen like with atomic number z = 3. Find the wavelength of the radiation required to excite the electron in Li^{2+} from the first to the third Bohr orbit.

Q.28 Estimate the difference in energy between I and II Bohr Orbit for a hydrogen atom. At what minimum at no. a transition from n=2 to n=1 energy level would result in the emission of X–rays with $\lambda = 3.0 \times 10^{-8}$ m? Which hydrogen like species does this at no correspond to.

Q.29 Find out the no. of waves made by a Bohr electron in one complete revolution in its 3rd orbit.

GENERAL

Q.30 What is de-Broglie wavelength of a He-atom in a container at room temperature.

Q.31 Through what potential difference must an electron pass to have a wavelength of 500 Å.

Q.32 A proton is accelerated to one- tenth of the velocity of light. If its velocity can be measured with a precision ± 1%. What must be its uncertainity in position.

Q.33 To what effective potential a proton beam be subjected to give its protons a wavelength of 1×10^{-10} m.

Q.34 Calculate magnitude of angular momentum of an e^- that occupies 1s, 2s, 2p, 3d, 3p.

Q.35 Calculate the number of exchange pairs of electrons present in configuration of Cu according to Aufbau Principle including d and s electrons.

Q.36 He atom can be excited to $1s^1 2p^1$ by $\lambda = 58.44$ nm. If lowest excited state for He lies 4857cm^{-1} below the above. Calculate the energy for the lower excitation state.

Q.37 Wave functions of electrons in atoms & molecules are called________.

Q.38 The outermost electronic conf. of Cr is___________.

TOUGH ROAD

Q.1 X-rays emitted from a copper target and a molybdenum target are found to contain a line of wavelength 22.85 nm attributed to the K_α line of an impurity element. The K_α lines of copper (Z = 29) and molybdenum (Z = 42) have wavelength 15.42 nm and 7.12 nm respectively. Using Moseley's law, $\gamma^{1/2} = a\,(Z - b)$ calculate the atomic number of the impurity element.

Q.2 Calculate the energy emitted when electrons of 1.0 g atom of hydrogen undergo transition giving the spectral lines of lowest energy in the visible region of its atomic spectra.

Q.3 1.8 g hydrogen atoms are excited to radiations. The study of spectra indicates that 27% of the atoms are in 3rd energy level and 15% of atoms in 2nd energy level and the rest in ground state. If I.P. of H is 21.7×10^{-12} erg. Calculate –

(i) No. of atoms present in III & II energy level.

(ii) Total energy evolved when all the atoms return to ground state.

Q.4 One mole He^+ ions are excited. Spectral analysis showed existence of 50% ions in 3rd orbit, 25% in 2nd and rest in ground state. Calculate total energy evolved when all the ions return to the ground state.

Q.5 The energy of an excited H-atom is –3.4 eV. Calculate angular momentum of e^-.

Q.6 The vapours of Hg absorb some electrons accelerated by a potential diff. of 4.5 volt as a result of which light is emitted. If the full energy of single incident e^- is supposed to be converted into light emitted by single Hg atom, find the wave no. of the light.

Q.7 The hydrogen atom in the ground state is excited by means of monochromatic radiation of wavelength x A^0. The resulting spectrum consists of 15 different lines. Calculate the value of x.

Q.8 The eyes of certain member of the reptile family pass a single visual signal to the brain when the visual receptors are struck by photons of wavelength 850 nm. If a total energy of 3.15×10^{-14} J is required to trip the signal, what is the minimum number of photons that must strike the receptor.

Q.9 If the average life time of an excited state of H atom is of order 10^{-8} sec, estimate how many orbits an e^- makes when it is in the state n = 2 and before it suffers a transition to n =1 state.

Q.10 Calculate the frequency of e^- in the first Bohr orbit in a H-atom.

Q.11 What is de Broglie wavelength associated with an e^- accelerated through P.D. = 100 KV.

Q.12 A single electron orbits around a stationary nucleus o f charge +Ze where Z is a constant from the nucleus and e is the magnitude of the electric charge. The hydrogen like species required 47.2 eV to excite the electron from the second Bohr orbit to the third Bohr orbit. Find

(i) the value of Z and give the hydrogen like species formed.

(ii) the kinetic energy and potential energy of the electron in the first Bohr orbit.

Q.13 A stationary He^+ ion emitted a photon corresponding to a first line of the Lyman series. The photon liberated a photon electron from a stationary H atom in ground state. What is the velocity of photoelectron.

Q.14 To what series does the spectral lines of atomic hydrogen belong if its wave number is equal to the difference between the wave numbers of the following two lines of the Balmer series 486.1 and 410.2 nm. What is the wavelength of this.

Q.15 A particle of charge equal to that of an electron and mass 208 times the mass of the electron moves in a circular orbit around a nucleus of charge +3e. Assuming that the Bohr model of the atom is applicable to this system, (a) derive an expression for the radius of the nth bohr orbit, (b) find the value of n for which the radius of the orbit is approximately the same as that of the first Bohr orbit for th ehydrogen atom, and (c) find the wavelength of the radiation emitted when the revolving particle jumps from the third orbit to the first.

Q.16 A neutrons breaks into a proton and an electron. This decay of neutron is accompanied by release of energy. Assuming that 50% of the energy is produced in the form of electromagentic radiation, what will be the frequency of radiation produced. Will this photon be sufficient to cause ionization of Aluminium. In case it is able to do so what will be the energy of the electron ejected from the Aluminium atom. IE_1 = of Al = 577 KJ/mol

Q.17 Find the number of photons of radiation of frequency 5×10^{13} s^{-1} that must be absorbed in order to melt one gm ice when the latent heat of fusion of ice is 330 J/g.

Q.18 A base ball of mass 200 g is moving with velocity 30×10^2 cm/s. If we can locate the base ball with an error equal in magnitude to the λ of the light used (5000 Å), how will the uncertainty in momentum be compared with the total momentum of base ball.

Q.19 The dye acriflavine, when dissolved in water, has its maximum light absorption at 4530 Å and its maximum fluorescence emission at 5080 Å. The number of fluorescence quanta is, on the average, 53% of the number of quanta absorbed. Using the wavelengths of maximum absorption and emission, what % of absorbed energy is emitted as fluorescence?

Q.20 An electron has a speed of 40 m/s, accurate up to 99.99%. What is the uncertainity in locating its position.

Q.21 Hydrogen atom in its ground state is excited by means of monochromatic radiation of wavelength 975Å. How many different lines are possible in the resulting spectrum? Calculate the longest wavelength amongst them.

Q.22 An alpha particle after passing through a potential difference of 2 x 10^6 volt falls on a silver foil. The atomic number of silver is 47. Calculate (i) the K.E. of the alpha-particle at the time of falling on the foil. (ii) K.E. of the α – particle at a distance of 5 x 10^{-14}m from the nucleus, (iii) the shortest distance from the nucleus of silver to which the α–particle reaches.

Q.23 Calculate the de-broglie wavelength associated with motion of earth (mass 6 × 10^{24} Kg) orbiting around the sun at a speed of 3 × 10^6 m/s.

Q.24 Suppose the potential energy between electron and proton at a distance r is given by $-\frac{ke^2}{3r^3}$. Use Bohr's theory to obtain energy of such a hypothetical atom.

Q.25 An energy of 68 eV is required to excite a hydrogen like atom from its second Bohr orbit to the third. The nuclear charge is Ze. Find the value of Z, the kinetic energy of the electron in the first Bohr orbit and the wavelength of the radiation required to eject the electrons from the first Bohr orbit to infinity.

Q.26 A proton captures a free electron whose K.E. is zero & forms a hydrogen atom of lowest energy-level (n = 1). If a photon is emitted in this process, what will be the wavelength of radiation? In which region of electromagnetic spectrum, will this radiation fall? (Ionisation potential of hydrogen = 13.6 volt, h = 6.6 x 10^{-34}K/s, C = 3.0 x 10^8 m/s)

Q.27 The ionisation energy of the hydrogen atom is given to be 13.6 eV. A photon falls on a hydrogen atom which is initially in the ground state and excites it to the (n = 4)state.

(a) show this transition in the energy-level diagram &

(b) calculate the wavelength of the photon.

Q.28 Calculate Total spin and the multiplicity for each possible configuration of N-atom.

(A) 
(B) 

(C) 
(D) 

Q.29 Find the wavelength of the first line of He$^+$ ion spectral series whose interval between extreme line is

$$\left[\frac{1}{\lambda_1}-\frac{1}{\lambda_2}=2.7451\times10^4\ \text{cm}^{-1}\right]$$

Q.30 The ionisation energy of a H-like Bohr atom is 4 Rydbergs

(i) What is the wavelength of radiation emitted when the e$^-$ jumps from the first excited state to the ground state.

(ii) What is the radius of first Bohr orbit for this atom. [1 Rydberg = 2.18 × 10^{-18} J]

ENJOY

1995

Q.1 Iodine molecule dissociates into atoms after absorbing light of 4500A^0. If one quantum of radiation is absorbed by each molecule, calculate the K.E. of iodine atoms
(Bond energy of I_2 = 240 KJ/mol)

Q.2 Calculate the wavelength of radiation emitted, producing a line in Lyman series, when an electron falls from fourth stationary state in hydrogen atom.

1996

Q.3 Calculate the wave no. for the shortest wavelength transition in the Balmer series of atomic hydrogen.

Q.4 The orbital angular momentum of an electron in 2s orbital is:

(A) $+\frac{1}{2}.\frac{\hbar}{2\pi}$ (B) Zero (C) $\frac{\hbar}{2\pi}$ (D) $\sqrt{2}.\frac{\hbar}{2\pi}$

Q.5 Consider the hydrogen atom to be a proton embedded in a cavity of radius a_0 (Bohr radius) whose charge is neutralised by the addition of an electron to the cavity in vacuum, infinitely slowly. Estimate the average total energy of an electron in its ground state in a hydrogen atom as the work done in the above neutralisation process. Also, if the magnitude of the average K.E. is half the magnitude of the average P.E., find the average potential energy.

1997

Q.6 An electron can undergo diffraction by crystals. Through what potential should a beam of electron be accelerated so that its wavelength become equal to 1.54 A°.

Q.7 With what velocity should an α–particle travel towards the nucleus of a Cu atom so as to arrive at a distance 10^{-13} m.

Q.8 The first use of quantum theory to explain the structure of atom was made by :
(A) Heisenburg (B) Bohr (C) Planck (D) Einstein

Q.9 A compound of Vanadium has magnetic moment of 1.73 BM work out electronic configuration of Vanadium Ion in the compound.

1998

Q.10 The energy of an electron in the first Bohr orbit of H atom is – 13.6 eV. The possible energy value(s) of the excited state(s) for electrons in Bohr orbits of hydrogen is/are :
(A) – 3.4 eV (B) – 4.2 eV (C) – 6.8 eV (D) + 6.8 eV

1999

Q.11 The electrons, identified by n & l ; (i) n = 4 , l = 1 (ii) n = 4 , l = 0 (iii) n = 3 , l = 2 (iv) n = 3 , l = 1 can be placed in order of increasing energy, from the lowest to highest as :
(A) (iv) < (ii) < (iii) < (i) (B) (ii) < (iv) < (i)
(C) (i) < (iii) < (ii) < (iv) (D) (iii) < (i) < (iv) < (ii)

Q.12 Gaseous state electronic configuration of nitrogen atom can be represented as:

(A) ↑↓ ↑↓ ↑ ↑ ↑ (B) ↑↓ ↑↓ ↑ ↓ ↑

(C) ↑↓ ↑↓ ↑ ↓ ↓ (D) ↑↓ ↑↓ ↓ ↓ ↓

2000

Q.13 The electronic configuration of an element is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$. This represents its:
(A) excited state (B) ground state (C) cationic form (D) anionic form

Q.14 The number of nodal planes in a p_x orbital is:
(A) one (B) two (C) three (D) zero

Q.15 Calculate the energy required to excite one litre of hydrogen gas at 1 atmp and 298K to the first excited state of atomic hydrogen. The energy for the dissociation of H – H is 436 KJ mol^{-1}.

2001

Q.16 The wavelength associated with a golf weighing 200g and moving at a speed of 5m/h is of the order
(A) 10^{-10}m (B) 10^{-20}m (C) 10^{-30}m (D) 10^{-40}m

Q.17 The quantum numbers +1/2 and –1/2 for the electron spin represent:
(A) rotation of the electron in clockwise and anticlockwise direction respectively.
(B) rotation of the electron in anticlockwise and clockwise direction respectively.
(C) magnetic moment of the electron pointing up and down respectively.
(D) two quantum mechanical spin states which have no classical analogue.

2002

Q.18 If the nitrogen atom had electronic configuration $1s^7$, it would have energy lower that of normal ground state configuration $1s^2 2s^2 2p^3$, because the electrons would be closer to the nucleus. Yet $1s^7$ is not observed because it violates :–
(A) Heisenberg uncertainity principle (B) Hunds rule
(C) Pauli's exclusion principle (D) Bohr postulate of stationary orbits

Q.19 Rutherfords experiment, which established the nuclear model of atom, used a beam of :–
(A) β - particles, which impinged on a metal foil and get absorbed.
(B) γ - rays, which impinged on a metal foil and ejected electron.
(C) Helium atoms, which impinged on a metal foil and got scattered.
(D) Helium nuclie, which impinged on a metal foil and got scattered.

2003

Q.20 Wavelength of high energy transition of H-atoms is 91.2 nm. Calculate the corresponding wavelength of He atoms.

2004

Q.21 The sping magnetic moment of cobalt of the compund $Hg[Co(SCN)_4]$ is [Given : Co^{+2}]
(A) $\sqrt{3}$ (B) $\sqrt{8}$ (C) $\sqrt{15}$ (D) $\sqrt{24}$

Q.22 The radius of which of the following orbit is same as that of the first Bohr's orbit of hydrogen atom?
(A) He^+ (n = 2) (B) Li^{2+} (n = 2) (C) Li^{2+} (n = 3) (D) Be^{3+} (n = 2)

Q.23(i) The wave function of 2s electron is given by

$$\Psi 2s = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_o}\right)^{3/2}\left(2-\frac{r}{a_o}\right)e^{2-\frac{r}{a_o}}$$

It has a node at $r = r_0$, find relation between r_0 and a_0.

(ii) Find wavelength for 100 g particle moving with velocity 100 ms^{-1}.

ANSWER KEY

EASY GO

Q.1	D	Q.2	A	Q.3	C	Q.4	B	Q.5	D	Q.6	D	Q.7	D
Q.8	D	Q.9	B	Q.10	A	Q.11	C	Q.12	B	Q.13	B	Q.14	A
Q.15	C	Q.16	B	Q.17	B	Q.18	C	Q.19	D	Q.20	B	Q.21	A
Q.22	B	Q.23	C	Q.24	D								

REFRESH YOUR CONCEPTS

LIGHT

Q.1 6563 Å ; 1216 Å ; 1026 Å Q.2 6 Q.3 0.527 Q.4 6235 Å Q.5 4863 Å
Q.6 1.096×10^7 m^{-1} Q.7 3×10^{21} Q.8 photons Q.9 $n_1 = 1, n_2 = 2$ Q.10 1.827×10^5 J/mol

PLANK'S QUANTUM THEORY

Q.11 4.9×10^{-7} m Q.12 28 photons Q.13 1403 KJ/mol Q.14 4.5×10^{14} s^{-1} Q.15 497 KJ/mol
Q.16 319.2 KJ/mol Q.17 6.57×10^{-34} Js Q.18 8.68 % Q.19 0.62 Å Q.20 3.06 V

BOHR'S MODEL

Q.21 -1.36×10^{-19} Joules Q.22 -5.425×10^{-12} ergs, 3.7×10^{-5} cm Q.23 1220 Å
Q.24 5.44×10^5 m/s Q.25 2 ; 9.75×10^4 cm^{-1} Q.26 3 , 6563 Å , 1215 Å , 1026 Å
Q.27 113.74 Å Q.28 10.2 eV , z = 2 Q.29 3

GENERAL

Q.30 14 pm Q.31 6.03×10^{-4} volt Q.32 1.05×10^{-13} m
Q.33 0.0826 volts Q.34 $0 ; 0 ; \sqrt{2}\frac{h}{2\pi} ; \sqrt{6}\frac{h}{2\pi} ; \sqrt{2}\frac{h}{2\pi}$ Q.35 25
Q.36 3.3×10^{-18} J Q.37 orbitals Q.38 $3s^2\ 3p^6\ 3d^5\ 4s^1$

TOUGH ROAD

Q2. 182.5 KJ Q3. 292.68×10^{21} atoms, 162.60×10^{21} atoms, 832.50 KJ Q4. 331.13×10^4 J
Q5. h/π Q6. 3.63×10^6 m^{-1} Q7. 938 Å Q8. 1.35×10^5 Q9. 8×10^6
Q10. 6530×10^{12}Hz Q11. 3.88 pm Q12. 5 ; 340 ev , – 680 eV Q13. 3.09×10^8 cm/sec
Q14. Brackett ; 2.63×10^{-4} cm Q15. $r_n = \dfrac{n^2 h^2}{4\pi^2 \times 3e^2 \times 208 m_e}$ n = 25 ; 55.2 pm
Q16. 8.83×10^{19} Hz , yes, 58.5×10^{-15} J Q17. 10^{22}
Q18. 1.75×10^{-28} Q19. 47.26% Q.20 0.0144 m Q21. six , 18800 Å
Q22. 6.4×10^{-13} J, 2.1×10^{-13}J, 3.4×10^{-14}m Q23. 3.68×10^{-65} m Q24. $E = \dfrac{n^6 h^6}{384\, m^3\, K^2\, e^4\, \pi^6}$
Q25. 6 ; 489.6 eV , 25.28 Å Q26. 910 Å ;U.V. Q27. 973.5 Å
Q28. +1/2 , +1/2 , +1/2 , +3/2 and 2,2,2,4 Q29. 4689 Å Q30. 303.89 Å , 2.645×10^{-9} cm

ENJOY

Q.1 2.186×10^{-20} Joules Q2. 9.7×10^{-8} m Q3. 27419.25 cm^{-1} Q4. B
Q5. $-\dfrac{e^2}{4\pi\varepsilon_0 a_0} ; -\dfrac{2e^2}{4\pi\varepsilon_0 a_0}$ Q6. 63.12 volts Q7. 6.3×10^6 m/s Q8. B
Q9. [Ar] $3d^1$ Q10. A Q11. A Q12. A and D Q13. B, C Q14. A
Q15. 97.819 KJ Q16. C Q17. D Q18. C. Q19. D Q20. 22.8 nm
Q21. C Q22. D Q.23 (i) $r_0 = 2a_0$, (ii) 6.626×10^{-35} m

BANSAL CLASSES

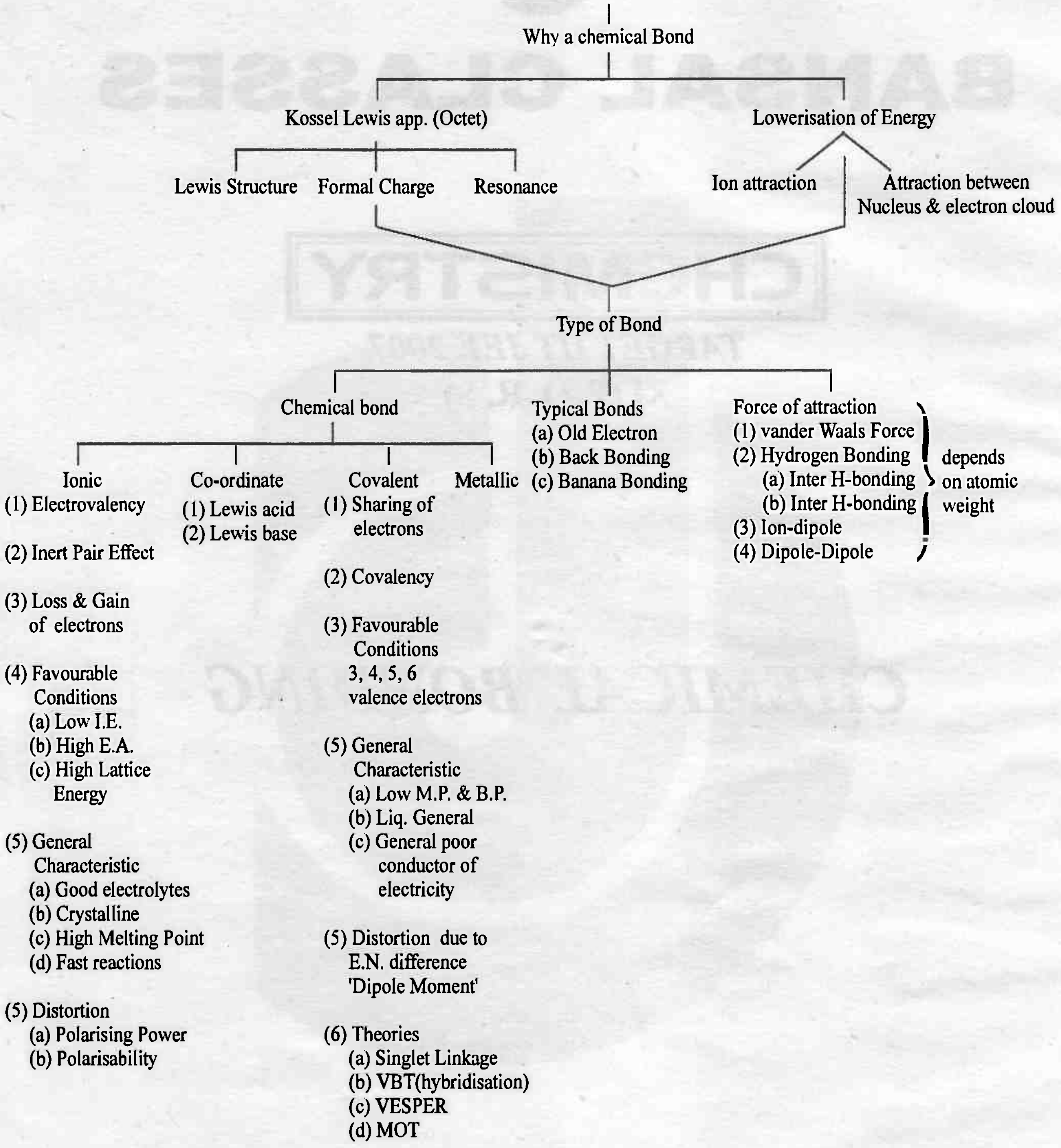
CHEMISTRY

TARGET IIT JEE 2007
XI (P, Q, R, S)

CHEMICAL BONDING

CONTENTS

Flowchart to Chemical Bonding



KEY CONCEPT

Reasons for Bond formation:

- Attainment of Octet [$ns^2\ np^6$], assumed to be most stable.
- Lowerisation of energy due to attractions.

Types of bonds : Ionic, covalent, co-ordinate

IONIC BOND [ELECTROVALENT]

- Complete loss of e^- to form ions.
- Electrostatic attraction between ions.
- Elements of 'p' & 'd' block may show variable electrovalency due to

(a) **Inert Pair effect (for p block):** The reluctance of 's' electron pair to take part in bond formation on moving down a group in 'P' block elements.

Finds application in

- Stability of oxidation state of a particular metal atom.
- Oxidizing & reducing power of compounds.

(b) **Unstability of core:** For 'd' block elements the core may either have pseudo inert configuration or any other & as such no "extra stable" or inert gas configuration.

Properties of Ionic compounds

- Uniform crystal lattice
- High Melting points / Boiling points.
- Good electrolytes
- Soluble in Polar solvents
- Show isomorphism.

☺ No sp. theories to understand bond formation.

☺ characteristics like various crystal lattices to be done in solid state.

Polarisation of ions: Polarising power (+), Polarisability (–)

Fajan's Rule: [For Polarisation]
More Polarisation : Cation size small, anion size large, charge on cation & large, cation having Pseudo inert gas configuration cause more polarisation of anion.

$$\text{IONIC POTENTIAL } \phi = \frac{\text{charge on cation}}{\text{radius of cation}} \propto \text{covalent character of ionic compound}$$

$$\propto \text{tendency to form complexes}$$

$$\propto \text{hydration \& solvation energy}$$

$$\propto \frac{1}{\text{M Pt.}},\ \frac{1}{\text{B Pt.}},\ \frac{1}{\text{Thermst.}}$$

COVALENT BOND

- Sharing of electrons
- Overlapping of orbitals
- Types : single, double, triple, polar, non–polar, directional.
- Show isomerism.
- Variable covalency : Shown by elements having vacant 'd' orbitals (caused due to excitation of the electron.)

Properties:

- Low melting point & boiling point. (except Diamond / Graphite)
- Electrical conductivity either due to auto-protolysis or self ionisation.

Dipole moment

Dipole moment is a vector quantity = $\mu = q \times d$. Units = col m (S.I.) or esu cm(cgs) or Debey(common unit) $1\ D = 10^{-18}$ esu cm $= 3.33 \times 10^{-30}$ col. m

$$\%\ \text{ionic character} = \frac{\text{observed D.M.}}{\text{calculated D.M. for 100\% ionic}} \times 100\ \%$$

$$\%\ \text{ionic character} = [\,16\,(X_A - X_B) + 3.5\,(X_A - X_B)^2\,]\ \%$$ [Hanny & Smyth equation]

Dipole moment depends on

- Electronegativity difference between atoms
- Angle between various bonds
- Magnetic of polarity of the molecule
- Direction of bond dipole moment
- Influence of unshared e^- pairs
- Symmetrical / Unsymmetrical shape.

Bond Moments:

H–F (1.9 D)	H–O (1.5 D)	C – C (0 D)	C–F (1.4 D)
H–Cl (1.1 D)	H–N (1.3 D)	C = O (2.3 D)	C–Cl (1.5 D)
H – Br (0.8 D)	H– C (0.4 D)		C – Br (1.4 D)
H – I (0.4 D)			C – I (1.2 D)

CO-ORDINATE BOND

Bonding between lewis acid & lewis base or electron deficient & electron rich species.

Lewis base: Species with lone pair on 'central atom' available for donation. eg. NH_3, H_2O

Lewis acid: Electron deficient due to incomplete octal, vacant P or d orbital & high + ve $\frac{\text{charge}}{\text{size}}$ ratio.

Lewis Dot structures:

- Arrangement of various atoms & types of bonding present but no idea of geometry.
- Selection of central atom [least E.N. of all elements excluding hydrogen]
- All atoms bonded to central atom except in case of typical linkages.(peroxides)
- In hydrogen containing oxy acids all 'H' are attached to oxygen except in H_3PO_3(dibasic) & H_3PO_2(monobasic).

Applications:

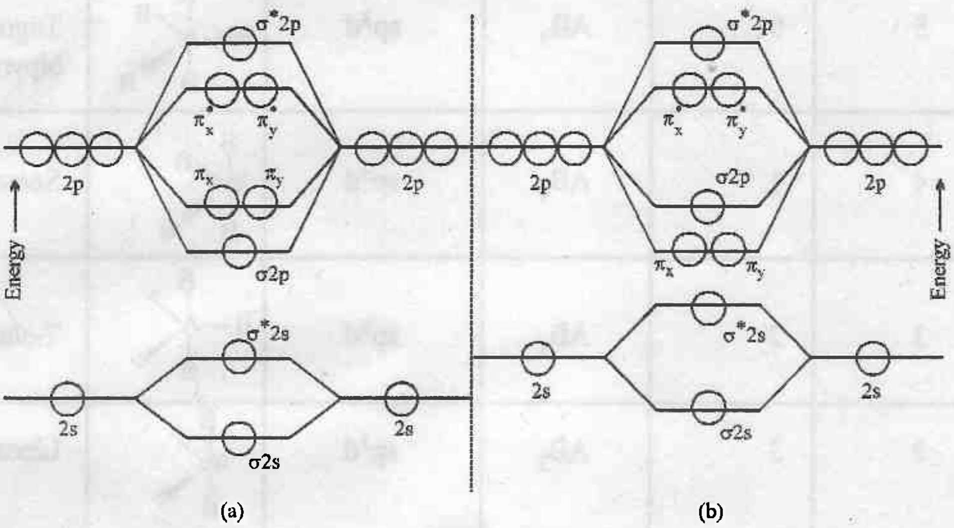
- To know various linkages present
- To calculate O.S. of various elements.

It is essential to learn some common Lewis structures

- ✦ Electronic theory of valency (Kossel, Lewis) ;Singlat linkages
- ✦ Valence bond theory (Heitler, London, Pauling, Slater).
- ✦ M.O.T. (Hund , Mulliken).

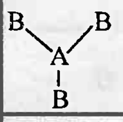
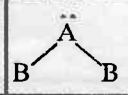
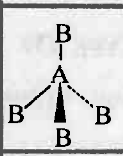
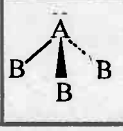
MOT : M.O.diagram, bonding, anti bonding & non bonding electron.

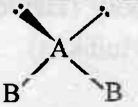
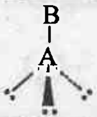
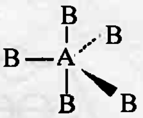
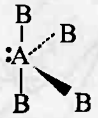
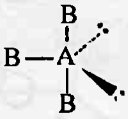
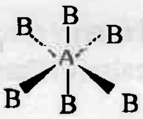
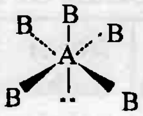
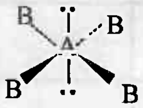
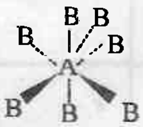
bond order = $\frac{1}{2}(N_b - N_a)$.



Molecular-orbital energy patterns for homonuclear diatomic molecules .(a) Diagram for molecules with low-lying 2s-orbitals. (b) Diagram for N_2 and lighter homonuclear diatomics.

SHAPES OF MOLECULES BASED ON VSEPR THEORY

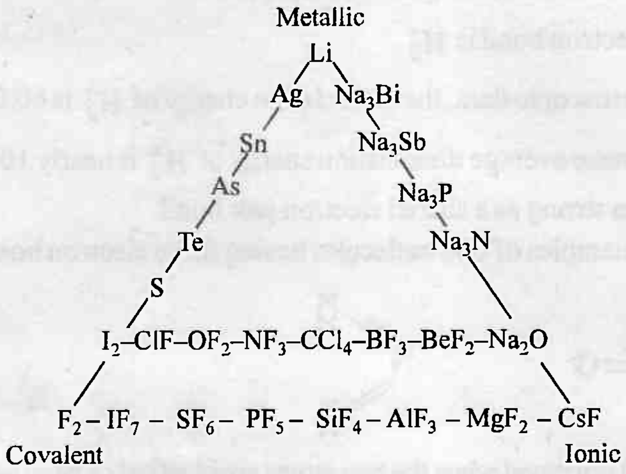
Total no. of hybrid orbitals	No. of b.p. (bond pairs)	No. of unshared pair i.e. l_p	General formula	Type of hybridisations	Stereo chemical formula	Shape	Exam.
2	2	0	AB_2	sp	B–A–B	linear	$BeCl_2$
3	3	0	AB_3	sp^2		Trigonal planar	BCl_3, GaF_3
3	2	1	AB_2	sp^2		Bent or angular	GeF_2, O_3
4	4	0	AB_4	sp^3		Tetrahedral	CH_4
4	3	1	AB_3	sp^3		Trigonal pyramid	NH_3

Total no. of hybrid orbitals	No. of b.p. (bond pairs)	No. of unshared pair i.e. l_p	General formula	Type of hybridisations	Stereo chemical formula	Shape	Exam.
4	2	2	AB_2	sp^3		Bent or angular	H_2O
4	1	3	AB	sp^3		linear	HF
5	5	0	AB_5	sp^3d		Trigonal bipyramidal	PF_5, $NbBr_5$
5	4	1	AB_4	sp^3d		Seesaw	SF_4
5	3	2	AB_3	sp^3d		T-shaped	ClF_3, BrF_3
5	2	3	AB_2	sp^3d		Linear	ICl_2^- XeF_2
6	6	0	AB_6	sp^3d^2		Octahedral	SF_6
6	5	1	AB_5	sp^3d^2		Square pyramidal	IF_5
6	4	2	AB_4	sp^3d^2		Square planar	IF_4 XeF_4
7	7	0	AB_7	sp^3d^3		Pentagonal bipyramidal	IF_7

How To Decide The Type Of Hybridisation :

Type of hybridisation = (number of σ bonds + number of lone pairs)

SUMMARY OF THE THREE MAIN TYPES OF BONDS



RESONANCE

- Delocalisations of π electron cloud in between orbitals of various atoms in a molecule (provided all the atoms are in the same plane)
- Exists where more than one Lewis dot structure are possible for a molecule.
- Resonance causes stablisation of the molecule & difference in the energies of hybrid & other structure is termed as Resonance energy.
- R.E. → Experimental heat of formation-Theoretical heat of formation.
- The properties of the actual structure (Resonance hybrid) are decided by the weighed average (depending on stability) of the contributing molecule.
- More the resonating structure more stable the molecule becomes.

FORCES OF ATTRACTION (WEAKER BONDS)

- **Metallic bonds:** Electron gas model or sea model, with metal atom existing as kernels along with less firmly held valence e^{-s} & bonds between various kernels (at the lattice site) & valence e^{-s} is known as metallic bonds.
- **Hydrogen bonding:** When a hydrogen atom is linked to a highly electronegative atom (like F, O or N) comes under the influence of another strongly electronegative atom, then a weak bond is developed between them, which is called as hydrogen bond.

Types of H-bonding:

- Intermolecular
- Intramolecular

Applications in:

(a) Association of a molecule as in carboxylic acid.
(b) Dissociation of a polar species.
(c) Abnormal melting point & boiling point.
(d) Enhanced solubility in water.

- **Ion dipole attraction**
- **Dipole-dipole attraction**
- **Ion-induced dipole attraction**
- **Dipole-Induced Dipole attraction**
- **Induced -dipole Induced Dipole attraction**

SOME TYPICAL BONDS

1. ***Odd electron bond:***

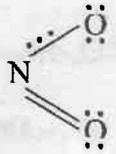
✦ These include one electron bond and three electron bond.

✦ The example of one electron bond is H_2^+.

✦ According to the spectroscopic data, the dissociation energy of H_2^+ is 60.0 cals which means that it is one electron bond because average dissociation energy of H_2^+ is nearly 100 cals.

✦ The bond is only half as strong as a shared electron pair bond.

✦ NO and NO_2 are the examples of odd molecules having three electron bonds e.g.



✦ The three electron bond is formed when the two atoms are identical or have nearly same electronegativity.

✦ The three electron bonds is also about half as strong as a normal bond.

2. ***Back bonding:***

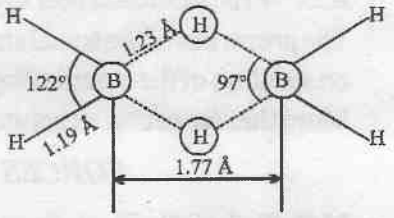
✦ If among the bonded atoms, one atom has a vacant orbital & another has excess of e^{-s} then a sort of π bonding takes place between he two. If this is between 'P' orbitals of the two, this is known as pπ-pπ back bonding.

✦ Most efficient when the atoms are very small & the orbitals involved of the two are of same energy level.

3. ***Banana bond:***

✦ This type of bonding is present in B_2H_6.

✦ This structure shows that there are two types of hydrogen atom-Terminals and bridging.

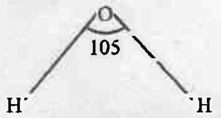


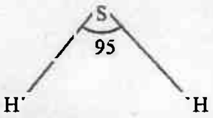
MISCELLANEOUS CONCEPT

1. ***Comparison of bond angles.***

(a) In case central atoms are having different hybridisation then it can be compared.

(b) If same hybridisation but different central atom then bond angle would be more of the molecule in which C.A. is more E.N. eg. H_2S & H_2O.





(c) If C.A. is same & bonded atoms different then bond angle increases as the attached atom size increases.

2. ***Paramagnetic nature.***

(a) Use of MOT for diatomic molecules

(b) Use of Lewis dot structure for the rest.

3. ***Bond strength & Bond length.***

(a) Using bond order as calculated in MOT

(b) Using concepts of resonance.

EXERCISE - I

IONIC BOND

Q.1 An ionic bond A^+B^- is most likely to be formed when :
(A) the ionization energy of A is high and the electron affinity of B is low
(B) the ionization energy of A is low and the electron affinity of B is high
(C) the ionization energy of A and the electron affinity of B is high
(D) the ionization energy of A and the electron affinity of B is low

Q.2 Which of the following compounds of elements in group IV is expected to be most ionic ?
(A) $PbCl_2$ (B) $PbCl_4$ (C) CCl_4 (D) $SiCl_4$

Q.3 Which of the following is in order of increasing covalent character ?
(A) $CCl_4 < BeCl_2 < BCl_3 < LiCl$ (B) $LiCl < CCl_4 < BeCl_2 < BCl_3$
(C) $LiCl < BeCl_2 < BCl_3 < CCl_4$ (D) $LiCl < BeCl_2 < CCl_4 < BCl_3$

Q.4 The hydration of ionic compounds involves :
(A) Evolution of heat (B) Weakening of attractive forces
(C) Dissociation into ions (D) All of these

Q.5 The correct order of decreasing polarizability of ion is :
(A) Cl^-, Br^-, I^-, F^- (B) F^-, I^-, Br^-, Cl^- (C) I^-, Br^-, Cl^-, F^- (D) F^-, Cl^-, Br^-, I^-

Q.6 Which has the lowest anion to cation size ratio :
(A) LiF (B) NaF (C) CsI (D) CsF

Q.7 Which of the following statement(s) is/are correct regarding ionic compounds?
(A) They are good conductors at room temperature in aqueous solution.
(B) They are generally soluble in polar solvents.
(C) They consist of ions.
(D) They generally have high melting and boiling points.

Q.8 Which of the following compounds contain/s both ionic and covalent bonds?
(A) NH_4Cl (B) KCN (C) $CuSO_4 \cdot 5H_2O$ (D) NaOH

Q.9 Which of the following compound is/are predominantly ionic?
(A) KCl (B) Na_2S (C) H_2 (D) CaO

Q.10 On heating to 400-500° C, relatively unstable hydrides and carbonates decompose. Which of the following will decompose when heated to 400-500°C ?
(A) LiH (B) NaH (C) Li_2CO_3 (D) Na_2CO_3

Q.11 Which of the following statements is/are true for BaO and MgO ?
(A) BaO is more ionic than MgO (B) MgO is more ionic than BaO
(C) BaO has a higher melting point than MgO (D) MgO has a higher melting point than BaO

Q.12 Whether this reaction is possible or not.

$$Tl^+ + Al^{3+} \longrightarrow Al^+ + Tl^{3+}$$

Q.13 Most ionic compounds have :
(A) high melting points and low boiling points
(B) high melting points and nondirectional bonds
(C) high solubilities in polar solvents and low solubilities in nonpolar solvents
(D) three-dimensional network structures, and are good conductors of electricity in the molten state

Q.14 Among the following, the element which show inert-pair effect are :
(A) Bi (B) Sn (C) Pb (D) C

Q.15 Which of the following have an $(18+2)$ electron configuration ?
(A) Pb^{2+} (B) Cd^{2+} (C) Bi^{3+} (D) SO_4^{2-}

COVALENT BOND

Q.16 A sigma bond may be formed by the overlap of 2 atomic orbitals of atoms A and B. If the bond is formed along as the x-axis, which of the following overlaps is acceptable ?
(A) s orbital of A and p_z orbital of B (B) p_x orbital of A and p_y orbital of B
(C) p_z orbital of A and p_x orbital of B (D) p_x orbital of A and s orbital of B

Q.17 The maximum covalency is equal to
(A) the number of unpaired p-electrons
(B) the number of paired d-electrons
(C) the number of unpaired s and p-electrons
(D) the actual number of s and p-electrons in the outermost shell.

Q.18 How many bonded electron pairs are present in IF_7 molecule :
(A) 6 (B) 7 (C) 5 (D) 8

Q.19 PCl_5 exists but NCl_5 does not because :
(A) Nitrogen has no vacant 2d-orbitals (B) NCl_5 is unstable
(C) Nitrogen atom is much smaller than P (D) Nitrogen is highly inert

Q.20 Which of the following has/have a strong covalent bond?
(A) Cl-F (B) F-F (C) C-Cl (D) C-F

Q.21 Which of the following statements is/are true?
(A) Covalent bonds are directional
(B) Ionic bonds are nondirectional
(C) A polar bond is formed between two atoms which have the same electronegativity value.
(D) The presence of polar bonds in a polyatomic molecule suggests that it has zero dipole moment

Q.22 Rotation around the bond (between the underlined atoms) is restricted in :
(A) $\underline{C}_2H_4$ (B) $H_2\underline{O}_2$ (C) $\underline{Al}_2Cl_6$ (D) $\underline{C}_2H_6$

Q.23 The octet rule is not obeyed in :
(A) CO_2 (B) BCl_3 (C) PCl_5 (D) SiF_4

Q.24 Which of the following two substances are expected to be more covalent :
(A) $BeCl_2$ (B) $SnCl_4$ (C) ZnS (D) $ZnCl_2$

Q.25 To which of the following species octet rule is not applicable :
(A) BrF_5 (B) SF_6 (C) IF_7 (D) CO

Q.26 Which of the following species are hypervalent?
1. ClO_4^-, 2. BF_3, 3. SO_4^{2-}, 4. CO_3^{2-}
(A) 1, 2, 3 (B) 1, 3 (C) 3, 4 (D) 1, 2

Q.27 $AgNO_3$ gives a white precipitate with $NaCl$ but not with CCl_4. Why ?

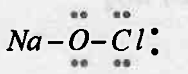
CO-ORDINATE BOND

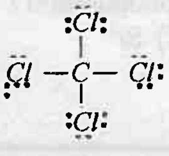
Q.28 NH_3 and BF_3 combine readily because of the formation of :
(A) a covalent bond (B) a hydrogen bond (C) a coordinate bond (D) an ionic bond

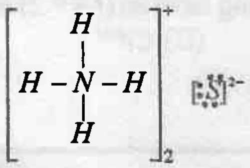
Q.29 Which of the following species contain covalent coordinate bond :
(A) $AlCl_3$ (B) CO (C) $[Fe(CN)_6]^{4-}$ (D) N_3^-

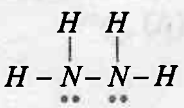
LEWIS STRUCTURE

Q.30 Which of the following Lewis diagrams is(are) incorrect ?

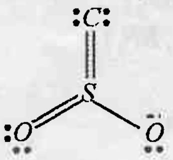
(A) 

(B) 

(C) 

(D) 

Q.31 The possible structure(s) of monothiocarbonate ion is :

(A)

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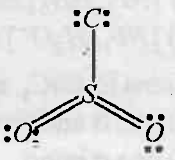
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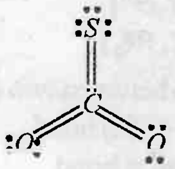
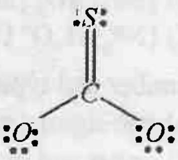

(D)


Q.32 The valency of sulphur in sulphuric acid is :
(A) 2 (B) 8 (C) 4 (D) 6

Q.33 The total number of valence electrons in 4.2g of N_3^- ion are :
(A) 2.2 N (B) 4.2 N (C) 1.6 N (D) 3.2 N

Q.34 No $X-X$ bond exists in which of the following compounds having general form of X_2H_6 ?
(A) B_2H_6 (B) C_2H_6 (C) Al_2H_6 (D) Si_2H_6

Q.35 Pick out among the following species isoelectronic with CO_2 :
(A) N_3^- (B) $(CNO)^-$ (C) $(NCN)^{2-}$ (D) NO_2^-

Q.36 Which of the following have a three dimensional network structure ?
(A) SiO_2 (B) $(BN)_x$ (C) P_4(white) (D) CCl_4

Q.37 Which of the following oxyacids of sulphur contain $S-S$ bonds ?
(A) $H_2S_2O_8$ (B) $H_2S_2O_6$ (C) $H_2S_2O_4$ (D) $H_2S_2O_5$

RESONANCE

Q.38 Resonating structures of a molecule should have:
(A) identical bonding (B) identical arrangement of atoms
(C) nearly the same energy content (D) the same number of paired electrons

Q.39 Which of the following conditions apply to resonating structures ?
(A) The contributing structures should have similar energies
(B) The contributing structures should be represented such that unlike formal charges reside on atoms that are far apart
(C) The more electropositive element should preferably have positive formal charge and the more electronegative element have negative formal charge
(D) The contributing structures must have the same number of unpaired electrons

Q.40 N_2O has a linear, unsymmetrical structure that may be thought of as a hybrid of two resonance forms. If a resonance form must have a satisfactory Lewis structure, which of the five structures shown below are the resonance forms of N_2O ?

(A) $:\overset{-}{N}=\overset{+}{N}=\overset{\cdot\cdot}{O}:$ (B) $:\underset{\cdot\cdot}{\overset{-}{N}}=N=\underset{\cdot\cdot}{\overset{+}{O}}:$ (C) $:\overset{\cdot\cdot}{N}-N\equiv O:$ (D) $:\overset{\cdot\cdot}{N}=\overset{\cdot\cdot}{N}-\overset{\cdot\cdot}{O}:$ (E) $:N\equiv\overset{+}{N}-\underset{\cdot\cdot}{\overset{\cdot\cdot\,-}{O}}:$

Q.41 Resonance occurs due to the
(A) delocalization of a lone pair of electrons (B) delocalization of sigma electrons
(C) delocalization of pi electrons (D) migration of protons

V.B.T. & HYBRIDISATION

Q.42 The strength of bonds by $s-s, p-p, s-p$ overlap is in the order :
(A) $s-s<s-p<p-p$ (B) $s-s<p-p<s-p$
(C) $s-p<s-s<p-p$ (D) $p-p<s-s<s-p$

Q.43 In the following compound $\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H_2-C\equiv CH$, the C_2-C_3 bond is of the type :
(A) $sp-sp^2$ (B) sp^3-sp^3 (C) $sp-sp^3$ (D) sp^2-sp^3

Q.44 Which of the following has a geometry different from the other three species (having the same geometry)?
(A) BF_4^- (B) SO_4^{2-} (C) XeF_4 (D) PH_4^+

Q.45 Maximum bond energy is in :
(A) F_2 (B) N_2 (C) O_2 (D) equal

Q.46 Among the following species, identify the isostructural pairs : $NF_3, NO_3^-, BF_3, H_3O^+, HN_3$
(A) $[NF_3, NO_3^-]$ and $[BF_3, H_3O^+]$ (B) $[NF_3, HN_3]$ and $[NO_3^-, BF_3]$
(C) $[NF_3, H_3O^+]$ *and* $[NO_3^-, BF_3]$ (D) $[NF_3, H_3O^+]$ and $[HN_3, BF_3]$

Q.47 Number and type of bonds between two carbon atoms in CaC_2 are :
(A) one sigma (σ) and one pi (π) bond (B) one σ and two π bonds
(C) one σ and one and a half π bond (D) one σ bond

Q.48 In $C-C$ bond is C_2H_6 undergoes heterolytic fission, the hybridisation of two resulting carbon atoms is/are
(A) sp^2 both (B) sp^3 both (C) sp^2, sp^3 (D) sp, sp^2

Q.49 The hybridisation and geometry of BrF_3 molecules are :
(A) sp^3d and T shaped (B) sp^2d^2 and tetragonal
(C) sp^3d and bent (D) none of these

Q.50 The shape of methyl cation (CH_3^+) is likely to be:
(A) linear (B) pyramidal (C) planar (D) spherical

Q.51 The structure of XeF_2 involves hybridization of the type :
(A) sp^3 (B) dsp^2 (C) sp^3d (D) sp^3d^2

Q.52 In the XeF_4 molecule, the Xe atom is in the
(A) sp^2-hybridized state (B) sp^3-hybridised state (C) sp^2d-hybridized state (D) sp^3d^2-hybridized state

Q.53 How many σ- and π- bonds are there in salicyclic acid?
(A) 10σ, 4π (B) 16σ, 4π (C) 18σ, 2π (D) 16σ, 2π

Q.54 Which of the following statements are not correct?
(A) Hybridization is the mixing of atomic orbitals of large energy difference.
(B) sp^2 – hybrid orbitals are formed from two p - atomic orbitals and one s- atomic orbitals
(C) dsp^2 – hybrid orbitals are all at 90° to one another
(D) d^2sp^3 – hybrid orbitals are directed towards the corners of a regular octahedron

Q.55 Which of the following has been arranged in increasing order of size of the hybrid orbitals ?
(A) $sp < sp^2 < sp^3$ (B) $sp^3 < sp^2 < sp$ (C) $sp^2 < sp^3 < sp$ (D) $sp^2 < sp < sp^3$

Q.56 In the context of carbon, which of the following is arranged in the correct order of electronegativity :
(A) $sp > sp^2 > sp^3$ (B) $sp^3 > sp^2 > sp$ (C) $sp^2 > sp > sp^3$ (D) $sp^3 > sp > sp^2$

Q.57 When $2s-2s, 2p-2p$ and $2p-2s$ orbitals overlap, the bond strength decreases in the order :
(A) $p-p > s-s > p-s$ (B) $p-p > p-s > s-s$ (C) $s-s > p-p > p-s$ (D) $s-s > p-s > p-p$

Q.58 The shapes of IF_5 and IF_7 are respectively :
(A) square pyramidal and pentagonal bipyramidal (B) octahedral and pyramidal
(C) trigonal bipyramidal and square antiprismatic (D) distorted square planar and distorted octahedral

Q.59 Carbon atoms in $C_2(CN)_4$ are :
(A) sp-hybridized (B) sp^2 -hybridized
(C) sp- and sp^2 hybridized (D) sp, sp^2 and sp^3 - hybridized

Q.60 CO_2 has the same geometry as :
(I) $HgCl_2$ (II) NO_2 (III) $SnCl_4$ (IV) C_2H_2
(A) I and III (B) II and IV (C) I and IV (D) III and IV

Q.61 Strongest bond is formed by the head on overlapping of :
(A) $2s$- and $2p$- orbitals (B) $2p$- and $2p$- orbitals
(C) $2s$- and $2s$- orbitals (D) All

Q.62 The ratio of σ and π bonds in benzene is :
(A) 2 (B) 6 (C) 4 (D) 8

Q.63 The bond angle and hybridization in ether (CH_3OCH_3) is :
(A) 106°51′, sp^3 (B) 104°31′, sp^3 (C) 109° 28′ sp^3 (D) None of these

Q.64 The enolic form of acetone contains :
(A) 9 sigma, 1 pi bond and 2 lone pairs (B) 8 sigma, 2 pi bond and 2 lone pairs
(C) 10 sigma, 1 pi bond and 1 lone pairs (D) 9 sigma, 2 pi bond and 1 lone pairs

Q.65 The shape of a molecule which has 3 bond pairs and one lone pair is :
(A) Octahedral (B) Pyramidal (C) Triangular planar (D) Tetrahedral

Q.66 Which molecule is *T* shaped :
(A) BeF_2 (B) BCl_3 (C) NH_3 (D) ClF_3

Q.67 Maximum s-character is in bonds formed by (*) atom:
(A) $\overset{*}{C}H_4$ (B) $\overset{*}{Xe}O_3$ (C) XeO_6^{4-} (D) SF_4

Q.68 Which of the following species is (are) isostructural with XeF_4 ?
(A) ICl_4^- (B) I_5^- (C) BrF_4^- (D) XeO_4

Q.69 A hydrazine molecule is split in NH_2^+ and NH_2^- ions. Which of the following statements is/are correct ?
(A) NH_2^+ shows sp^2 – hybridisation whereas NH_2^- shows sp^3 – hybridisation
(B) $Al(OH)_4^-$ has a regular tetrahedral geometry
(C) sp^2 – hybridized orbitals have equal *s*- and *p*- character
(D) Hybridized orbitals always form σ - bonds

Q.70 There is change in the type of hybridisation when:
(A) NH_3 combines with H^+ (B) AlH_3 combines with H^-
(C) NH_3 forms NH_2^- (D) SiF_4 forms SiF_6^{2-}

Q.71 Which of the following statement is/are correct
(A) Hybridisation is the mixing of atomic orbitals prior to their combining into molecular orbitals :
(B) sp^3d^2 – hybrid orbitals are at 90° to one another
(C) sp^3d – hybrid orbitals are directed towards the corners of a regular tetrahedron
(D) sp^3d^2 – hybrid orbitals are directed towards the corners of a regular octahedron

Q.72 A σ-bond may between two p_x orbitals containing one unpaired electron each when they approach each other appropriately along :
(A) *x* - axis (B) *y* - axis (C) *z* - axis (D) any direction

Q.73 Indicate the wrong statement :
(A) A sigma bond has no free rotation around its axis
(B) *p*-orbitals always have only sideways overlap
(C) *s*-orbitals never form π - bonds
(D) There can be more than one sigma bond between two atoms

Q.74 sp^3 hybridisation is in :
(A) AlH_4^- (B) CH_3^- (C) ClO_2^- (D) NH_2^-

Q.75 Which of the following pairs is (are) isostructural?
(A) SF_4 and SiF_4 (B) SF_6 and SiF_6^{2-} (C) SiF_6^{2-} and SeF_6^{2-} (D) XeO_6^{4-} and TeF_6^{2-}

Q.76 Which of the following has (have) octahedral geometry :
(A) $SbCl_6^-$ (B) $SnCl_6^{2-}$ (C) XeF_6 (D) IO_6^{5-}

Q.77 Shape of NH_3 is very similar to :
(A) SeO_3^{2-} (B) CH_3^- (C) BH_3 (D) CH_3^+

Q.78 Which of the following have same shape as NH_2^- ?
(A) CO_2 (B) $SnCl_2$ (C) SO_2 (D) $BeCl_2$

Q.79 Which of the following is (are) linear ?
(A) I_3^- (B) I_3^+ (C) $PbCl_2$ (D) XeF_2

Q.80 Which of the following species are linear ?
(A) ICl^{2-} (B) I^{3-} (C) N_3^- (D) ClO_2

Q.81 The structure of XeF_6 is :
(A) pentagonal bipyramidal (B) distorted octahedral (C) capped octahedral (D) square pyramidal

Q.82 Using *VSEPR* theory identify the type of hybridisation and draw the structure of OF_2.

Q.83 What should be the structure of the following as per *VSEPR* theory ?
(a) XeF_2 (b) XeF_4 (c) PBr_5 (d) OF_2 (e) I_3^- and (f) I_3^+

M.O.T

Q.84 Arrange the following in order of decreasing $N-O$ bond length : NO_2^+, NO_2^-, NO_3^-
(A) $NO_3^- > NO_2^+ > NO_2^-$ (B) $NO_3^- > NO_2^- > NO_2^+$
(C) $NO_2^+ > NO_3^- > NO_2^-$ (D) $NO_2^- > NO_3^- > NO_2^+$

Q.85 Number of non bonding electrons in N_2 is :
(A) 4 (B) 10 (C) 12 (D) 14

Q.86 Pick out the incorrect statement?
(A) N_2 has greater dissociation energy than N_2^+ (B) O_2 has lower dissociation energy than O_2^+
(C) Bond length in N_2^+ is less than N_2 (D) Bond length in NO^+ is less than in NO.

Q.87 A simplified application of *MO* theory to the hypothetical 'molecule' *OF* would give its bond order as :
(A) 2 (B) 1.5 (C) 1.0 (D) 0.5

Q.88 Which of the following species is paramagnetic ?
(A) NO^- (B) O_2^{2-} (C) CN^- (D) CO

Q.89 Bond order of Be_2 is :
(A) 1 (B) 2 (C) 3 (D) 0

Q.90 The bond order depends on the number of electrons in the bonding and non bonding orbitals. Which of the following statements is /are correct about bond order?
(A) Bond order cannot have a negative value.
(B) It always has an integral value.
(C) It is a nonzero quantity.
(D) It can assume any value-positive or negative, integral or fractional, including zero.

Q.91 In the formation of N_2^+ from N_2, the electron is removed from :
(A) σ orbital (B) π orbital (C) σ^* orbital (D) π^* orbital

Q.92 During the formation of a molecular orbital from atomic orbitals of the same atom, probability of electron density is:
(A) minimum in the nodal plane (B) maximum in the nodal plane
(C) zero in the nodal plane (D) zero on the surface of the lobe

Q.93 Which of the following has fractional bond order :
(A) O_2^{2+} (B) O_2^{2-} (C) F_2^{2-} (D) H_2^-

Q.94 How many unpaired electrons are present in N_2^+ :
(A) 1 (B) 2 (C) 3 (D) 4

Q.95 Which have odd-order bond?
(A) O_2^+ (B) O_2^- (C) NO (D) H_2^+

Q.96 Which of the following have identical bond order?
(A) O_2^{2+} (B) NO^+ (C) CN^- (D) CN^+

Q.97 Which of the following statement is/are correct
(A) The peroxide ion has a bond order of 1 while the oxygen molecule has a bond order of 2
(B) The peroxide ion has a weaker bond than the dioxygen molecule has.
(C) The peroxide ion as well as the dioxygen molecules are paramagnetic
(D) The bond length of the peroxide ion is greater than that of the dioxygen molecule

Q.98 Given the species : N_2, CO, CN^- and NO^+. Which of the following statements are true for these
(A) All species are paramagnetic
(B) The species are isoelectronic
(C) All the species have dipole moment
(D) All the species are linear

Q.99 Which of the following have unpaired electron(s)
(A) O_2^+
(B) O_2^-
(C) NO
(D) H_2^+

Q.100 Which of the following are diamagnetic ?
(A) C_2
(B) O_2^{2-}
(C) Li_2
(D) N_2^+

Q.101 Which of the following are paramagnetic ?
(A) B_2
(B) O_2
(C) N_2
(D) He_2

Q.102 Which of the following species have a bond order of 3 ?
(A) CO
(B) CN^-
(C) NO^+
(D) O_2^+

Q.103 Among the following, the species with one unpaired electron are :
(A) O_2^+
(B) NO
(C) O_2^-
(D) B_2

Q.104 Which of the following pairs have identical values of bond order ?
(A) N_2^+ and O_2^-
(B) F_2 and Ne_2
(C) O_2 and B_2
(D) C_2 and N_2

Q.105 Which of the following is correct ?
(A) During N_2^+ formation, one electron each is removed from the bonding molecular orbitals
(B) During O_2^- formation, one electron each is removed from the antibonding molecular orbitals
(C) During O_2^- formation, one electron each is added to the bonding molecular orbitals
(D) During CN^- formation, one electron each is added to the bonding molecular orbitals

Q.106 Find out the bond order of :
(a) H_2
(b) H_2^+
(c) He_2
(d) Li_2
(e) Be_2
(f) B_2

Q.107 Identify the molecules or atoms or ions from the following molecular orbital energy level formulations. The species should be selected from (B_2, C_2, O_2^{2+}, O_2, F_2, N_2)

(a) $KK\,\sigma(2s)^2\,\sigma^*(2s)^2\,\pi(2p_x)^1\,\pi(2p_y)^1$

(b) $KK\,\sigma(2s)^2\,\sigma^*(2s)^2\,\pi(2p_x)^2\,\pi(2p_y)^2$

(c) $KK\,\sigma(2s)^2\,\sigma^*(2s)^2\,\sigma(2p_z)^2\,\pi(2p_x)^2\,\pi(2p_y)^2$

(d) $KK\,\sigma(2s)^2\,\sigma^*(2s)\,\sigma(2p_z)^2\,\pi(2p_x)^2\,\pi(2p_y)^2\,\pi(2p_x)^1\,\pi^*(2p_y)^1$

(e) $KK\,\sigma(2s)^2\,\sigma^*(2s)^2\,\sigma(2p_z)^2\,\pi(2p_x)^2\,\pi(2p_y)^2\,\pi(2p_x)^2\,\pi^*(2p_y)^2$

(f) $KK\,\sigma(2s)^2\,\sigma^*(2s)^2\,\pi(2p_y)^2\,\pi(2p_x)^2\,\sigma(2p_z)^2$

Q.108 Why does He_2^+ exist whereas He_2 does not ?

Q.109 Of the species O_2^+, O_2^-, O_2 and O_2^{2-} which would have the maximum bond strength ?

Q.110 Based upon *M.O.* theory state reason for the paramagnetic character of *CN*, the diamagnetic character of CN^-, the stability of CN^- and calculate their respective bond orders.

Q.111 Write the electronic structures of :
(a) CO (b) NO (c) HF (d) HCl, based upon Molecular orbital (*MO*) diagram

OTHER FORCES

Q.112 Which of the following models best describes the bonding within a layer of the graphite structure ?
(A) metallic bonding
(B) ionic bonding
(C) non-metallic covalent bonding
(D) van der Waals forces

Q.113 The critical temperature of water is higher than that of O_2 because the H_2O molecule has :
(A) fewer electrons than O_2 (B) two covalent bonds
(C) V - shape (D) dipole moment

Q.114 Ethanol has a higher boiling point than dimethyl ether though they have the same molecular weight. This is due to :
(A) resonance (B) coordinate bonding (C) hydrogen bonding (D) ionic bonding

Q.115 Arrange the following in order of decreasing boiling point :
(I) *n*-Butane (II) *n*-Butanol (III) *n*-Butyl chloride (IV) Isobutane
(A) $IV > III > II > I$ (B) $IV > II > III > I$ (C) $I > II > III > IV$ (D) $II > III > I > IV$

Q.116 Which of the following compounds would have significant intermolecular hydrogen bonding ?
HF, CH_3OH, N_2O_4, CH_4
(A) HF, N_2O_4 (B) HF, CH_4, CH_3OH (C) HF, CH_3OH (D) CH_3OH, CH_4

Q.117 For H_2O_2, H_2S, H_2O and HF, the correct order of increasing extent of hydrogen bonding is :
(A) $H_2O > HF > H_2O_2 > H_2S$ (B) $H_2O > HF > H_2S > H_2O_2$
(C) $HF > H_2O > H_2O_2 > H_2S$ (D) $H_2O_2 > H_2O > HF > H_2S$

Q.118 Iron is harder than sodium because
(A) iron atoms are smaller (B) iron atoms are more closely packed
(C) metallic bonds are stronger in sodium (D) metallic bonds are stronger in iron

Q.119 Which one of the following does not have intermolecular H-bonding?
(A) H_2O (B) *o*-nitro phenol (C) HF (D) CH_3COOH

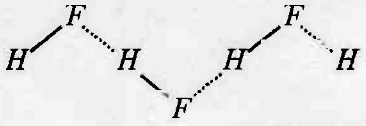
Q.120 The order of strength of hydrogen bonds is:
(A) $ClH...Cl > NH...N > OH...O > FH...F$ (B) $ClH...Cl < NH...N < OH...O < FH...F$
(C) $ClH...Cl < NH...N > OH...O > FH...F$ (D) $ClH...Cl < NH...N < OH...O > FH...F$

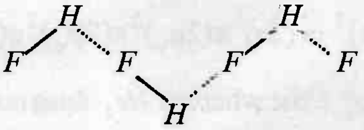
Q.121 Which of the following exhibit/s H-bonding?
(A) CH_4 (B) H_2Se (C) N_2H_4 (D) H_2S

Q.122 Among the following, van der Waals forces are maximum in
(A) HBr (B) LiBr (C) LiCl (D) AgBr

Q.123 The H bond in solid HF can be best represented as:
(A) $H-F....H-F....H-F$

(B) 

(C) 

(D) 

Q.124 The volatility of HF is low because of :
(A) its low polarizability (B) the weak dispersion interaction between the molecules
(C) its small molecular mass (D) its strong hydrogen bonding

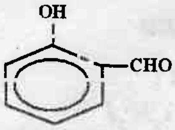
Q.125 The melting point of AlF_3 is 104° C and that of SiF_4 is - 77° C (it sublimes) because :
(A) there is a very large difference in the ionic character of the $Al-F$ and $Si-F$ bonds
(B) in AlF_3, Al^{3+} interacts very strongly with the neighbouring F^- ions to give a three dimensional structure but in SiF_4 no interaction is possible
(C) the silicon ion in the tetrahedral SiF_4 molecule is not shielded effectively from the fluoride ions whereas in AlF_3, the Al^{3+} ion is shielded on all sides
(D) the attractive forces between the SiF_4 molecules are strong whereas those between the AlF_3 molecules are weak

Q.126 Two ice cubes are pressed over each other and unite to form one cube. Which force is responsible for holding them together :
(A) van der Waal's forces (B) Covalent attraction
(C) Hydrogen bond formation (D) Dipole-dipole attraction

Q.127 Intramolecular hydrogen bonding is found in :
(A) Salicylaldehyde (B) Water (C) Acetaldehyde (D) Phenol

Q.128 The pairs of bases in DNA are held together by :
(A) Hydrogen bonds (B) Ionic bonds (C) Phosphate groups (D) Deoxyribose groups

Q.129 In dry ice there are :
(A) Ionic bond (B) Covalent bond (C) Hydrogen bond (D) None of these

Q.130


(A) has intermolecular H - bonding (B) has intramolecular H- bonding
(C) has low boiling point (D) is steam-volatile

Q.131 Which of the following bonds/forces is/are weakest?
(A) covalent bond (B) vander Waals force (C) hydrogen bond (D) london force

Q.132 Compare O–O bond energy among O_2, H_2O_2 and O_3 with reasons.

Q.133 Which of the following is/are observed in metallic bonds ?
(A) Mobile valence electrons (B) Overlapping valence orbitals
(C) Highly directed bond (D) Delocalized electrons

Q.134 Which of the following factors are responsible for van der Waals forces ?
(A) Instantaneous dipole-induced dipole interaction
(B) Dipole-induced dipole interaction and ion-induced dipole interaction
(C) Dipole-dipole interaction and ion-induced dipole interaction
(D) Small size of molecule

Q.135 Which of the following are true ?
(A) Van der Waals forces are responsible for the formation of molecular crystals
(B) Branching lowers the boiling points of isomeric organic compounds due to van der Waals forces of attraction
(C) In graphite, van der Waals forces act between the carbon layers
(D) In diamond, van der Waals forces act between the carbon layers

Q.136 Intermolecular hydrogen bonding increases the enthalpy of vapourization of a liquid due to the:
(A) decrease in the attraction between molecules
(B) increase in the attraction between molecules
(C) decrease in the molar mass of unassociated liquid molecules
(D) increase in the effective molar mass of hydrogen - bonded molecules

Q.137 Which of the following molecules have intermolecular hydrogen bonds ?
(A) KH_2PO_4 (B) H_3BO_3 (C) $C_6H_5CO_2H$ (D) CH_3OH

Q.138 Which of the following have dipole moment ?
(A) nitrobenzene (B) *p*-chloronitrobenzene
(C) *m*-dichlorobenzene (D) *o*-dichlorobenzene

MISCELLEANEOUS

Q.139 Among KO_2, AlO_2^-, BaO_2 and NO_2^+ unpaired electron is present in :
(A) KO_2 only (B) NO_2^+ and BaO_2 (C) KO_2 and AlO_2^- (D) BaO_2 only

Q.140 Cyanogen, $(CN)_2$, has a ____ shape/structure :
(A) Linear (B) Zig-zag (C) Square (D) Cyclic

Q.141 Which of the following contains (electrovalent) and non-polar (covalent) bonds ?
(A) CH_4 (B) H_2O_2 (C) NH_4Cl (D) HCN

Q.142 The types of bond present in N_2O_5 are
(A) only covalent (B) only ionic
(C) ionic and covalent (D) covalent & coordinate

Q.143 The types of bonds present in $CuSO_4 \cdot 5H_2O$ are
(A) electrovalent and covalent (B) electrovalent and coordinate covalent
(C) covalent and coordinate covalent (D) electrovalent, covalent and coordinate covalent

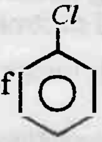
Q.144 For which of the following crystalline substances does the solubility in water increase upto 32° C and then decrease rapidly ?
(A) $CaCl_2.2H_2O$ (B) $Na_2SO_4.10H_2O$ (C) $FeSO_4.7H_2O$ (D) Alums

Q.145 Which of the following has been arranged in order of decreasing dipole moment ?
(A) $CH_3Cl > CH_3F > CH_3Br > CH_3I$ (B) $CH_3F > CH_3Cl > CH_3Br > CH_3I$
(C) $CH_3Cl > CH_3Br > CH_3I > CH_3F$ (D) $CH_3F > CH_3Cl > CH_3I > CH_3Br$

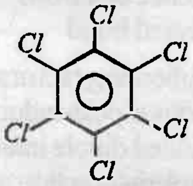
Q.146 Which of the following has the least dipole moment
(A) NF_3 (B) CO_2 (C) SO_2 (D) NH_3

Q.147 The experimental value of the dipole moment of HCl is 1.03 D. The length of the $H-Cl$ bond is 1.275 $\mathring{A}$. The percentage of ionic character in HCl is :
(A) 43 (B) 21 (C) 17 (D) 7

Q.148 The dipole moment of



is 1.5 D. The dipole moment of



is :

(A) 0 D (B) 1.5 D (C) 2.86 D (D) 2.25 D

Q.149 $SnCl_4$ is a covalent liquid because :
(A) electron clouds of the Cl^- ions are weakly polarized to envelop the cation
(B) electron clouds of the Cl^- ions are strongly polarized to envelop the cation
(C) its molecules are attracted to one another by strong van der Waals forces
(D) Sn shows inert pair effect

Q.150 In the cyanide ion the formal negative charge is on
(A) C (B) N
(C) Both C and N (D) Resonate between C and N

Q.151 Which has (have) zero value of dipole moment?
(A) $[Ni(CN)_4]^{2-}$ square planner (B) $CHCl_3$
(C) CO_2 (D)

Q.152 Which of the following compounds possesses zero dipole moment?
(A) Water (B) Benzene (C) Carbon tetrachloride (D) Boron trifluoride

Q.153 Three centre - two electron bonds exist in :
(A) B_2H_6 (B) $Al_2(CH_3)_6$ (C) $BeH_2(s)$ (D) $BeCl_2(s)$

Q.154 $p\pi - d\pi$ back bonding occurs between oxygen and
(A) phosphorus in P_4O_{10} (B) chlorine in $HClO_4$ (C) nitrogen in N_2O_5 (D) carbon in CO_2

Q.155 Hypervalent compound is (are) :
(A) SO_3^{2-} (B) PO_4^{3-} (C) SO_4^{2-} (D) ClO_4^-

Q.156 Which of the following statements are correct?

(A) The crystal lattice of ice is mostly formed by covalent as well as hydrogen bonds

(B) The density of water increases when heated from 0° C to 4° C due to the change in the structure of the cluster of water molecules

(C) Above 4° C the thermal agitation of water molecules increases. Therefore, intermolecular distance increases and water starts expanding

(D) The density of water increases from 0° C to a maximum at 4° C because the entropy of the system increases

Q.157 State whether each statement is true or false. If false, write the correct statement.

(i) The polarising power of a cation is directly proportional to its charge.
(ii) The polarising power of a cation is directly proportional to its size.
(iii) The polarisability of an anion is directly proportional to its charge.
(iv) The polarisability of an anion is directly proportional to its size.
(v) For a given anion, greater the polarising power of the cation, more the ionic character.
(vi) For a given cation, greater the polarisability of the anion, more the covalent character.
(vii) An element with low ionization potential is most likely to form a covalent bond with an other element having a high electron affinity.
(viii) Ionic interactions are stronger than covalent bonds.
(ix) Two non-metal atoms are likely to form covalent bonds on combination.
(x) Ionic interactions are directional.

Q.158 State whether each statements is T or F, if F rectify.

(i) All diatomic molecules are non-polar.
(ii) All molecules having polar bonds are polar (i.e., have a net dipole)
(iii) The lone pairs of electrons do not contribute to the net dipole of a molecule.
(iv) The CH_2Cl_2 molecule may be polar or nonpolar depending on its geometry.
(v) The net dipole in the water molecule is the resultant of its bond dipoles.
(vi) SO_2 is polar whereas CO_2 is non-polar.
(vii) NH_3 is less polar than NF_3
(viii) If all bonds in a molecule are polar, the molecule as a whole must be polar.

Q.159 Fill in the blanks.

(i) π–bonds are formed by the lateral overlap of a p-orbital with another ____ orbital.
(ii) Free rotation is possible if two atoms are bonded together only by a _________ bond.
(iii) The maximum number of σ bonds that can be formed between two atoms is _______.
(iv) The repulsion between ___ is greater than the repulsion between two bonded pairs
(v) A lone pair is ___________ polarisable compared to a σ bonded pair which in turn is ___________ polarisable compared to a π- bonded pair.
(vi) In nitro benzene the total number of bonded electrons equals ___________________.

Q.160 The percent ionic character in HCl is 18.08. The observed dipole moment is 1.08 D. Find the inter-nuclear distance in HCl.

Q.161 In trimethylamine, the nitrogen has a pyramidal geometry whereas in trisilylamine $N(SiH_3)_3$ it has a planar geometry. Explain ? Out of trimethylamine and trisilyamine which one is more basic and why ?

Q.162 Assuming that all the four valency of carbon atom in propane pointing towards the corners of a regular tetrahedron. Calculate the distance between the terminal carbon atoms in propane. Given, $C-C$ single bond length is 1.54 Å.

Q.163 The dipole moment of HBr is 7.95 debye and the intermolecular separation is $1.94\times10^{-10}\,m$ Find the % ionic character in HBr molecule.

Q.164 HBr has dipole moment $2.6\times10^{-30}\ cm$. If the ionic character of the bond is 11.5 %. calculate the interatomic spacing.

Q.165 Dipole moment of LiF was experimentally determined and was found to be 6.32 D. Calculate percentage ionic character in LiF molecule $Li-F$ bond length is 0.156 pm.

Q.166 A diatomic molecule has a dipole moment of 1.2 D. If bond length is 1.0 Å, what percentage of an electronic charge exists on each atom.

BONDS ANGLES & BOND LENGTH

Q.167 The correct order of increasing $X-O-X$ bond angle is ($X = H, F$ or Cl) :
(A) $H_2O > Cl_2O > F_2O$ (B) $Cl_2O > H_2O > F_2O$
(C) $F_2O > Cl_2O > H_2O$ (D) $F_2O > H_2O > Cl_2O$

Q.168 Which of the following is true ?
(A) Bond order $\propto \frac{1}{\text{bond length}} \propto$ bond energy (B) Bond order $\propto$ bond length $\propto \frac{1}{\text{bond energy}}$
(C) Bond order $\propto \frac{1}{\text{bond length}} \propto \frac{1}{\text{bond energy}}$ (D) Bond order $\propto$ bond length $\propto$ bond energy

Q.169 Which of the following has been arranged in order of decreasing bond length ?
(A) $P-O > Cl-O > S-O$ (B) $P-O > S-O > Cl-O$
(C) $S-O > Cl-O > P-O$ (D) $Cl-O > S-O > P-O$

Q.170 If a molecule MX_3 has zero dipole moment, the sigma bonding orbitals used by M (atm. no. < 21) are :
(A) pure p (B) sp hybrid (C) sp^2 hybrid (D) sp^3 hybrid

Q.171 How many sigma and pi bonds are present in tetracyanoethylene ?
(A) Nine σ and nine π (B) Five π and nine σ (C) Nine σ and seven π (D) Eight σ and eight π

Q.172 Among the following species, which has the minimum bond length ?
(A) B_2 (B) C_2 (C) F_2 (D) O_2^-

Q.173 Which has higher bond energy :
(A) F_2 (B) Cl_2 (C) Br_2 (D) I_2

Q.174 The bond angle in PH_3 is :
(A) Much lesser than NH_3 (B) Equal to that in NH_3
(C) Much greater than in NH_3 (D) Slightly more than in NH_3

Q.175 $H-B-H$ bond angle in BH_4^- is :
(A) 180° (B) 120° (C) 109° (D) 90°

Q.176 In the series ethane, ethylene and acetylene, the $C-H$ bond energy is :
(A) The same in all the three compounds (B) Greatest in ethane
(C) Greatest in ethylene (D) Greatest in acetylene

Q.177 Which one of the following compounds has bond angle as nearly 90° ?
(A) NH_3 (B) H_2S (C) H_2O (D) SF_6

Q.178 Of the following species which has the shortest bond length NO, NO^+, NO_2^{2+} and NO^- ?

Q.179 Arrange the following species in decreasing order of bond angle.
NO_2^+, NO_2, NO_2^-

Q.180 In the hydrides of group VI elements the central atoms involve sp^3 hybridisation but the bond angles decrease in the order, H_2O, H_2S, H_2Si, H_2Te . How would you account for this ?

EXERCISE - II

Choose the correct alternative (only one correct answer). [2 × 45 = 90]

Q.1 The bond between carbon atom (1) & carbon atom (2) in compound $N \equiv \underset{1}{C} - \underset{2}{C}H = CH_2$ involves the hybrids as : **[JEE '87]**
(A) sp^2 & sp^2 (B) sp^3 & sp (C) sp & sp^2 (D) sp & sp

Q.2 Amongst the trihalides of nitrogen, which one is least basic? **[JEE '87]**
(A) NF_3 (B) NCl_3 (C) NBr_3 (D) NI_3

Q.3 Hydrogen bonding is maximum in **[JEE '87]**
(A) Ethanol (B) Diethylether (C) Ethyl chloride (D) Triethylamine

Q.4 The species which the central atom uses sp^2 hybrid orbitals in its bonding is **[JEE '88]**
(A) PH_3 (B) NH_3 (C) CH_3^+ (D) SbH_3

Q.5 The molecule that has linear stucture is **[JEE '88]**
(A) CO_2 (B) NO_2 (C) SO_2 (D) SiO_2

Q.6 The compound which has zero dipole moment is **[JEE '89]**
(A) CH_2Cl_2 (B) BF_3 (C) NF_3 (D) ClO_2

Q.7 Which of the following is paramagnetic **[JEE '89]**
(A) O_2^- (B) CN^- (C) CO (D) NO^+

Q.8 The molecule which has pyramidal shape is **[JEE '89]**
(A) PCl_3 (B) SO_3 (C) CO_3^{2-} (D) NO_3^-

Q.9 The compound in which C uses its sp^3 hybrid orbitals for bond formation is : **[JEE '89]**
(A) $H\overset{*}{C}OOH$ (B) $(H_2N)\overset{*}{C}O$ (C) $(CH_3)_3\overset{*}{C}OH$ (D) $CH_3\overset{*}{C}HO$

Q.10 The C - H bond distance is the longest in **[JEE '89]**
(A) C_2H_2 (B) C_2H_4 (C) C_2H_6 (D) $C_2H_2Br_2$

Q.11 Which one of the following is the smallest in size **[JEE '89]**
(A) N^{3-} (B) O^{2-} (C) F^- (D) Na^+

Q.12 The number of sigma and pi bonds in 1-butene-3-yne are **[JEE '89]**
(A) 5 sigma 5 pi (B) 7 sigma 3 pi (C) 8 sigma 2 pi (D) 6 sigma 4 pi

Q.13 Amongst the following the one having highest I.E. is **[JEE '90]**
(A) $[Ne]\,3s^2\,3p^1$ (B) $[Ne]\,3s^2\,3p^3$ (C) $[Ne]\,3s^2\,3p^2$ (D) $[Ar]\,3d^{\circ}\,4s^2\,4p^3$

Q.14 The hybridisation of C atoms in C - C single bond of $HC \equiv C - CH = CH_2$ is **[JEE '91]**
(A) $sp^3 - sp^3$ (B) $sp^2 - sp^3$ (C) $sp - sp^2$ (D) sp^3 - sp

Q.15 The type of hybrid orbitals used by the chlorine atom in ClO_2^- is **[JEE '92]**
(A) sp^3 (B) sp^2 (C) sp (D) none

Q.16 The CN^- & N_2 are isoelectronic. But in contrast to CN^-, N_2 is chemically inert because of **[JEE '92]**
(A) Low bond energy
(B) Absence of bond polarity
(C) Unsymmetrical electron distribution
(D) Presence of more number of electron in bonding orbitals.

Q.17 The maximum possible number of hydrogen bonds a water molecule can form is **[JEE '92]**
(A) 2 (B) 4 (C) 3 (D) 1

Q.18 Pick out the isoelectronic structures from the following **[JEE '93]**
I. CH_3^+ II. H_3O^+ III. NH_3 IV. CH_3^-
(A) I and II (B) III and IV (C) I and III (D) II, III and IV

Q.19 Which one of the following oxides is ionic? **[JEE '95]**
(A) P_2O_5 (B) CrO_3 (C) MnO (D) Mn_2O_7

Q.20 The number of electrons that are paired in oxygen molecule is **[JEE '95]**
(A) 7 (B) 8 (C) 16 (D) 14

Q.21 Allyl isocyanide has **[JEE '95]**
(A) 9s, 4p bonds (B) 9s, 3p bonds and 2 non-bonding electrons
(C) 8s, 5p bonds (D) 8s, 3p bonds and 4 non- bonding electrons

Q.22 The order of increasing thermal stabilities of K_2CO_3(I), $MgCO_3$(II), $CaCO_3$(III), $BaCO_3$(IV) is **[JEE '96]**
(A) II < III < IV < I (B) IV < II < III < I (C) IV < II < I < III (D) II < IV < III < I

Q.23 Identify isostructural pairs from NF_3(I), NO_3^-(II), BF_3(III), H_3O^+(IV), HN_3(V) **[JEE '96]**
(A) I & II, III & IV (B) I & V, II & III (C) I & IV, II & III (D) I & IV, III & V

Q.24 (i)The number and type of bonds between two C - atom in CaC_2 are **[JEE '96]**
(A) 1 sigma 1 pi (B) 1 sigma 2 pi (C) 1 sigma , ½ pi (D) 1 sigma

Q.25 Which is correct for $CsBr_3$? **[JEE '96]**
(A) it is a covalent compound (B) it contains Cs^{3+} & Br^- ions
(C) it contains Cs^+ & Br_3^- ions (D) it contains Cs^+, Br^- & lattice Br_2 molecule

Q.26 Among KO_2, AlO_2^-, BaO_2 & NO_2^+ unpaired electron is present in **[JEE '97]**
(A) NO_2^+ & BaO_2 (B) KO_2 & AlO_2^- (C) KO_2 only (D) BaO_2 only

Q.27 Which of the following has maximum number of unpaired electrons? **[JEE '96]**
(A) Mg^{2+} (B) Ti^{3+} (C) V^{3+} (D) Fe^{2+}

Q.28 KF combines with HF to form KHF_2. The compound contains the species **[JEE '97]**
(A) K^+, F^- and H^+ (B) K^+, F^- and HF (C) K^+ and $[HF_2]^-$ (D) $[KHF]^+$ and F^-

Q.29 Among the following compounds the one that is polar and has the central atom with sp^2 hybridisation is **[JEE '97]**
(A) H_2CO_3 (B) SiF_4 (C) BF_3 (D) $HClO_2$

Q.30 Which contains both polar & non polar covalent bonds **[JEE '97]**
(A) NH_4Cl (B) HCN (C) H_2O_2 (D) CH_4

Q.31 The type of hybrid orbitals used by the chlorine atom in ClO_3^- is **[JEE '97]**
(A) sp^3 (B) sp^3d (C) sp^3d^2 (D) sp^2

Q.32 Which are isoelectronic among the following? **[JEE '97]**
(i) $(CH_3)_3C^+$ (ii) $(CH_3)_3Si^+$ (iii) Ph_3C^+ (iv) S_2
(A) (i), (ii), (iii) (B) (ii), (iii) (C) (i), (iii) (D) (i), (iv)

Q.33 Hybridisation seen in cation of solid PCl_5 **[JEE '97]**
(A) sp^3d (B) sp^3 (C) sp^3d^2 (D) sp

Q.34 What type of hybridisation and how many lone pair of electrons are present in the species I_3^- on the central atom. **[JEE '97]**
(A) sp^2 one lone pair (B) sp^3d three lone pair (C) sp three lone pair (D) sp no lone pair

Q.35 In which of the following the central atom does not use sp^3 hybrid orbitals in its bonding?
(A) BeF_3^- (B) OH_3^+ (C) NH_2^- (D) NF_3 **[JEE '97]**

Q.36 Which of the following ions is expected to be colourless
(A) Cu^{2+} (B) Ti^{4+} (C) V^{3+} (D) Fe^{2+}

Q.37 The structure of IBr_2^- involves hybridisation of the type.
(A) sp^3d (B) sp^3d^2 (C) dsp^3 (D) d^2sp^3

Q.38 The maximum angle around the central atom H-M-H is present in

(A) AsH_3 (B) PH_3 (C) NH_3 (D) SbH_3

Q.39 Which one of the following molecules is planar : **[JEE '97]**

(A) NF_3 (B) NCl_3 (C) PH_3 (D) BF_3

Q.40 Which one has sp^2 hybridisation **[JEE '97]**

(A) CO_2 (B) SO_2 (C) N_2O (D) CO

Q.41 The geometry & the type of hybrid orbitals present about the central atom in BF_3 is : **[JEE '98]**

(A) linear, sp (B) trigonal planar, sp^2 (C) tetrahedra sp^3 (D) pyramidal, sp^3

Q.42 The correct order of increasing C - O bond length of, CO, CO_3^{2-}, CO_2 is **[JEE '99]**

(A) $CO_3^{2-} < CO_2 < CO$ (B) $CO_2 < CO_3^{2-} < CO$

(C) $CO < CO_3^{2-} < CO_2$ (D) $CO < CO_2 < CO_3^{2-}$

Q.43 In the dichromate anion **[JEE '99]**

(A) 4 Cr - O bonds are equivalent (B) 6 Cr - O bonds are equivalent

(C) all Cr - O bonds are equivalent (D) all Cr - O bonds are non equivalent

Q.44 The geometry of H_2S and its dipole moment are **[JEE '99]**

(A) angular & non zero (B) angular & zero

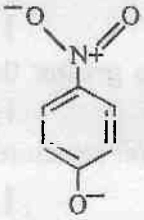
(C) linear & non zero (D) linear & zero

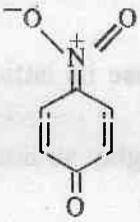
Q.45 In compounds type E Cl_3, where E = B, P, As or Bi, the angles Cl - E - Cl for different E are in the order

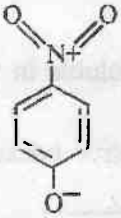
(A) B > P = As = Bi (B) B > P > As > Bi (C) B < P = As = Bi (D) B < P < As < Bi

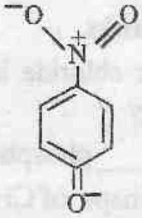
[JEE '99]

Q.46 The most unlikely representation of resonance structure of p–nitrophenoxide is:

(A) 

(B) 

(C) 

(D) 

Q.47 Amongst H_2O, H_2S, H_2Se and H_2Te, the one with the highest boiling point is **[JEE 2000]**

(A) H_2O because of hydrogen bonding (B) H_2Te because of higher molecular weight

(C) H_2S because of hydrogen bonding (D) H_2Se because of lower molecular weight

Q.48 The hybridization of atomic orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ are **[JEE 2000]**

(A) sp^2, sp^3 and sp^2 respectively (B) sp, sp^2 and sp^3 respectively

(C) sp^2, sp and sp^3 respectively (D) sp^2, sp^3 and sp respectively

Q.49 The correct order of hybridization of the central atom in the following species NH_3, $PtCl_4^{-2}$, PCl_5 and BCl_3 is **[JEE 2001]**

(A) dsp^2, sp^3d, sp^2 and sp^3 (B) sp^3, dsp^2, sp^3d, sp^2

(C) dsp^2, sp^2, sp^3, sp^3d (D) dsp^2, sp^3, sp^2, sp^3d

Q.50 The common features among the species CN^-, CO and NO^+ are **[JEE 2001]**

(A) Bond order three and isoelectronic (B) Bond other three and weak field ligands

(C) Bond order two and π – acceptors (D) Isoelectronic and weak field ligands

Q.51 Specify the coordination geometry around and hybridization of N and B atoms in a 1 : 1 complex of BF_3 and NH_3 **[JEE 2002]**
(A) N : tetrahedral, sp^3 ; B : tetrahedral, sp^3 (B) N : pyramidal, sp^3; B : pyramidal, sp^3
(C) N : pyramidal, sp^3 ; B : planar, sp^2 (D) N : pyramidal, sp^3; B : tetrahedral, sp^3

Q.52 The nodal plane in the π-bond of ethene is located in **[JEE 2002]**
(A) the molecular plane
(B) a plane parallel to the molecular plane
(C) a plane perpendicular to the molecular plane which bisects, the carbon-carbon σ bond at right angle.
(D) a plane perpendicular to the molecular plane which contains, the carbon-carbon bond.

Q.53 Which of the following molecular species has unpaired electron(s)? **[JEE 2002]**
(A) N_2 (B) F_2 (C) O_2^- (D) O_2^{2-}

Q.54 Which of the following are isoelectronic and isostructural ? NO_3^-, CO_3^{2-}, ClO_3^-, SO_3 **[JEE 2003]**
(A) NO_3^-, CO_3^{2-} (B) SO_3, NO_3^- (C) ClO_3^-, CO_3^{2-} (D) CO_3^{2-}, SO_3

Q.55 According to molecular orbital theory which of the following statement about the magnetic character and bond order is correct regarding O_2^+ **[JEE 2004]**
(A) Paramagnetic and Bond order < O_2 (B) Paramagnetic and Bond order > O_2
(C) Diamagnetic and Bond order < O_2 (D) Diamagnetic and Bond order > O_2

Q.56 Which species has the maximum number of lone pair of electrons on the central atom? **[JEE 2005]**
(A) ClO_3^- (B) XeF_4 (C) SF_4 (D) I_3^-

Fill in the blanks. **[12 × 2 = 24]**

Q.1 Silver chloride is sparingly soluble in water because its lattice energy is greater than ________ energy. **[JEE '87]**

Q.2 ________ phosphorous is reactive because of its highly strained tetrahedral structure. **[JEE '87]**

Q.3 The shape of CH_3^+ is ____________. **[JEE '90]**

Q.4 The valence atomic orbitals on C in silver acetylide is ________ hybridised. **[JEE '90]**

Q.5 Amongst the three isomers of nitrophenol, the one that is least soluble in water is ______. **[JEE '94]**

Q.6 The kind of delocalization involving sigma bond orbitals are called ______. **[JEE '94]**

Q.7 The two types of bonds present in B_2H_6 are covalent & ________. **[JEE '94]**

Q.8 When N_2 goes to N_2^+, the N - N distance ________ & when O_2 goes to O_2^+, the O - O bond distance ________. **[JEE '96]**

Q.9 Among N_2O, SO_2, I_3^+ & I_3^-, the linear species are ______ & ______. **[JEE '97]**

Q.10 Among PCl_3, CH_3^+, NH_2^- & NF_3, ________ is least relative towards water. **[JEE '97]**

Q.11 The P - P - P angle in P_4 molecule is ________. **[JEE '97]**

Q.12 Compounds that formally contain Pb^{4+} are easily reduced to Pb^{2+}. The stability of lower oxidation state is due to ________. **[JEE '97]**

State whether true or false. [16 × 2 = 32]

Q.1 In benzene carbon uses all the three p-orbitals for hybridisation. [JEE '87]

Q.2 sp^2 hybrid orbitals have equal S & P character. [JEE '87]

Q.3 In group I A of alkali metals, the ionisation potential decreases down the group. Therefore lithium is a poor reducing agent. [JEE '87]

Q.4 All the Al - Cl bond in Al_2Cl_6 are equivalent. [JEE '88]

Q.5 Both potassium ferrocyanide & potassium ferricyanide are diamagnetic. [JEE '88]

Q.6 The presence of polar bonds in a polyatomic molecule suggests that the molecule has non-zero dipole moment. [JEE '90]

Q.7 Nitric oxide, though an odd electron molecule, is diamagnetic in liquid state. [JEE '91]

Q.8 The decreasing order of E A of F, Cl, Br is F > Cl > Br. [JEE '93]

Q.9 Diamond is harder than graphite. [JEE '93]

Q.10 The basic nature of hydroxides of group 13 (III B) decreases progressively down the group. [JEE '93]

Q.11 The tendency for catenation is much higher for C than Si. [JEE '93]

Q.12 The dipolemoment of CH_3F is greater than CH_3Cl. [JEE '93]

Q.13 HBr is stronger acid than HI because of H-bonding. [JEE '97]

Q.14 F atom has less negative E A than Cl atom. [JEE '97]

Q.15 LiCl is predominantly a covalent compound. [JEE '97]

Q.16 $Al(OH)_3$ is amphoteric in nature. [JEE '97]

Explain the following. [11 × 3 = 33]

Q.1 Explain the molecule of magnesium chloride is linear whereas that of stannous chloride is angular. [JEE '87]

Q.2 Give reason carbon oxygen bond lengths in formic acid are 1.23 A° & 1.36 A° and both the carbon oxygen bonds in sodium formate have the same value i.e. 1.27 A°. [JEE '88]

Q.3 Give reason that valency of oxygen is generally two whereas sulphur shows of 2, 4, & 6. [JEE '88]

Q.4 Explain the first I.E. of carbon atom is greater than that of boron atom whereas the reverse is true for the second I.E. [JEE '89]

Q.5 Explain why the dipolemoment of NH_3 is more than that of NF_3. [JEE '95]

Q.6 The experimentally determined N - F bond length in NF_3 is greater than the sum of single bond covalent radii of N & F. Explain. [JEE '95]

Q.7 Explain the difference in the nature of bonding in LiF & LiI. [JEE '96]

Q.8 Compare qualitatively the 1st & 2nd IP of Cu & Zn. Explain the observation. [JEE '96]

Q.9 Explain PCl_5 is formed but NCl_5 cannot. [JEE '97]

Q.10 Give reasons for the following in one or two sentences only. [JEE '99]

(a) $BeCl_2$ can be easily hydrolyed (b) CrO_3 is an acid anhydride.

Q.11 Explain why o-hydroxybenzaldehyde is a liquid at room temperature, while p-hydroxybenzaldehyde is a high melting solid. [JEE '99]

Arrange as directed. [11 × 2 = 22]

Q.1 N_2, O_2, F_2, Cl_2 in increasing order of bond dissociation energy. [JEE '88]

Q.2 $CO_2, N_2O_5, SiO_2, SO_3$ is the increasing order of acidic character. [JEE '88]

Q.3 HOCl, $HOClO_2$, $HOClO_3$, HOClO in increasing order of thermal stability. [JEE '88]

Q.4 Increasing order of ionic size : $N^{3-}, Na^+, F^-, O^{2-}, Mg^{2+}$

Q.5 Increasing order of basic character : MgO . SrO , K_2O , NiO , Cs_2O

Q.6 Increasing strength of H - bonding . (X .... H - X) O , S , F , Cl , N .

Q.7 Increasing order of extent of hydrolysis $CCl_4, MgCl_2, AlCl_3, PCl_5, SiCl_4$

Q.8 Arrange in increasing order of dipole moment. [JEE '96]
Toluene , m - dichcorobenzene , O - dichlorobenzene , P - dichlorobenzene .

Q.9 The decreasing order of acid strength of ClOH, BrOH, IOH. [JEE '97]

Q.10 Arrange in order of increasing radii, $Li^+, Mg^{2+}, K^+, Al^{3+}$. [JEE '97]

Q.11 Arrange $BeSO_4$, $MgSO_4$, $CaSO_4$, $SrSO_4$ in order of decreasing thermal stability. [JEE '97]

Q.12 Decreasing order of the O–O bond length present in them
O_2, KO_2 and O_2 $[AsF_4]$ [JEE 2004]

Miscellaneous.

Q.1 Write the two resonance structures of N_2O that satisfy the octet rule. [JEE '90]

Q.2 Write two resonance structures of ozone which satisfy the octet rule. [JEE '91]

Q.3 Using VSEPR theory, identify the type of hybridisation & draw the structure of OF_2. What are oxidation states of O & F. [JEE '94]

Q.4 What are the types of bond present in B_2H_6? [IIT 1994]

Q.5 Arrange toluene, m–dichlorobenzene, o–dicholorobenzene and p–dichlorobenzene in order of increasing dipole moment. [IIT 1996]

Q.6 Draw the structures of [JEE '97]
(i) XeF_2 (ii) XeO_3 (iii) XeF_4 (iv) BrF_5 (v) SO_3^{2-}

Q.7 Interpret the non-linear shape of H_2S molecule & non planar shape of PCl_3 using VSEPR theory. [JEE '98]

Q.8 Discuss the hybridisation of C - atoms in allene (C_3H_4) and show the π – orbital overlaps. [JEE '99]

Q.9 Write the MO electron distribution of O_2. Specify its bond order and magnetic property [IIT 2000]

Q.10 Using VSEPR theory, draw the shape of PCl_5 and BrF_5. [JEE 2003]

Q.11 Draw the structure of XeF_4 and OSF_4 according to VSEPR theory, clearly indicating the state of hybridisation of the central atom and lone pair of electrons (if any) on the central atom. [JEE 2004]

ANSWER KEY
EXERCISE - I

Q.1	B	Q.2	A	Q.3	C	Q.4	D
Q.5	C	Q.6	D	Q.7	A, B, C, D	Q.8	A, B, C, D
Q.9	A, B, D	Q.10	B, C	Q.11	A, C	Q.12	No
Q.13	B, C, D	Q.14	A, B, C	Q.15	A, C	Q.16	D
Q.17	D	Q.18	B	Q.19	A	Q.20	D
Q.21	A, B	Q.22	A, C	Q.23	B, C	Q.24	A, B
Q.25	A, B, C	Q.26	B	Q.28	C	Q.29	B, C, D
Q.30	A	Q.31	D	Q.32	D	Q.33	C
Q.34	A, C	Q.35	A, B, C	Q.36	A, B	Q.37	B, C, D
Q.38	B, C, D	Q.39	A,B,C,D	Q.40	A, E	Q.41	A, C
Q.42	A	Q.43	D	Q.44	C	Q.45	B
Q.46	C	Q.47	B	Q.48	C	Q.49	A
Q.50	C	Q.51	C	Q.52	D	Q.53	B
Q.54	A	Q.55	A	Q.56	A	Q.57	B
Q.58	A	Q.59	C	Q.60	C	Q.61	B
Q.62	C	Q.63	C	Q.64	A	Q.65	B
Q.66	D	Q.67	A	Q.68	A, C, B	Q.69	A, B, D
Q.70	B, D	Q.71	A, B	Q.72	A	Q.73	A, B
Q.74	A, B, C, D	Q.75	B	Q.76	A, B, D	Q.77	A, B
Q.78	B, C	Q.79	A, D	Q.80	A, B, C	Q.81	C
Q.83	(a) Linear, (b) square planar, (c) T.B.P. (d) bent, (e) linear, (f) bent						
Q.84	B	Q.85	A	Q.86	C	Q.87	B
Q.88	A	Q.89	D	Q.90	A	Q.91	A
Q.92	C	Q.93	D	Q.94	A	Q.95	A, B, C, D
Q.96	A, B, C	Q.97	A, B, D	Q.98	B, D	Q.99	A, B, C, D
Q.100	A, B, C	Q.101	A, B	Q.102	A, B, C	Q.103	A, B, C
Q.104	A	Q.105	A, B, D	Q.106	(a) 1, (b) 1/2, (c) zero, (d) 1, (e) zero, (f) 1		
Q.107	(a) B_2. (b) C_2, (c) O_2^{2+}, (d) O_2, (e) F_2, (f) N_2					Q.109	$O_2^+ > O_2 > O_2^- > O_2^{2-}$
Q.112	C	Q.113	D	Q.114	C	Q.115	D
Q.116	C	Q.117	C	Q.118	D	Q.119	B
Q.120	B	Q.121	C	Q.122	D	Q.123	C
Q.124	D	Q.125	B	Q.126	C	Q.127	A
Q.128	A	Q.129	B	Q.130	B, C, D	Q.131	B, D
Q.132	$O_2>O_3>H_2O_2$	Q.133	A, D	Q.134	A, B, C	Q.135	A, B
Q.136	B	Q.137	A, B, C, D	Q.138	A, B, C, D	Q.139	A
Q.140	A	Q.141	C	Q.142	D	Q.143	D
Q.144	B	Q.145	A	Q.146	B	Q.147	C
Q.148	A	Q.149	B	Q.150	D	Q.151	A, C, D
Q.152	B, C, D	Q.153	A, B	Q.154	A, B	Q.155	B, C, D
Q.156	A, B, C, D	Q.157	T, F, T, T, F, F, F, T, T, F			Q.158	F, F, F, F, T, T, F, F
Q.159	(i) p-orbital, (ii) σ–bond, (iii) 1 , (iv) LP–LP & LP–BP, (v) more, less, (vi) 36						
Q.160	1.2Å	Q.161	$(CH_3)_3N$	Q.162	2.33 Å	Q.163	85%
Q.164	1.4 Å	Q.165	84.5%	Q.166	25%	Q.167	B
Q.168	A	Q.169	B	Q.170	C	Q.171	A
Q.172	B	Q.173	B	Q.174	A	Q.175	C
Q.176	D	Q.177	B, D	Q.178	NO^+	Q.179	$\overset{+}{N}O_2 > NO_2 > NO_2^-$

EXERCISE-II

01.C	02.A	03.A	04.C	05.A	06.B	07.A	08.A	09.C	10.C
11.D	12.B	13.B	14.C	15.A	16.B	17.B	18.D	19.C	20.D
21.B	22.A	23.C	24.B	25.C	26.C	27.D	28.C	29.A	30.A
31.A	32.D	33.B	34.B	35.A	36.B	37.A	38.C	39.D	40.B
41.B	42.D	43.B	44.A	45.B	46.C	47.A	48.B	49.B	50.A
51. A	52.A	53.C	54.A	55.B	56.D				

Fill in the blanks

Q.1	hydration	Q.2	white	Q.3	trigonal planar	Q.4	sp
Q.5	ortho	Q.7	banana	Q.8	increases, decreases		
Q.9	N_2O, I_3^-	Q.10	NH_2^-	Q.11	60°	Q.12	inert pair effect

True/False

Q.1	F	Q.2	F	Q.3	F	Q.4	F	Q.5	F	Q.6	F	Q.7	T
Q.8	F	Q.9	T	Q.10	F	Q.11	T	Q.12	F	Q.13	F	Q.14	T
Q.15	T	Q.16	T										

Explain

Q.1	Lone pair	Q.2	Resonance	Q.3	expansion of octet
Q.5	Lone pair contribution	Q.7	LiF → Ionic charge, LiI → covalent charge		
Q.9	d-orbitals	Q.11	Intra-H-bonding in o-hydroxybenzaldehyde		

Arrange as directed :

Q.1 $F_2 < Cl_2 < O_2 < N_2$

Q.2 $SiO_2 < CO_2 < SO_3 < N_2O_5$

Q.3 $HClO < HClO_2 < HClO_3 < HClO_4$

Q.4 $Mg^{2+} < Na^+ < F^- < O^{2-} < N^{-3}$

Q.5 $Na_2O < MgO < SrO < K_2O < Cs_2O$

Q.6 $S < Cl < N < O < F$

Q.7 $CCl_4 < SiCl_4 < PCl_5 < AlCl_3 < MgCl_2$

Q.8 P - dichlorobenzene < Toluene < m-dichcorobenzene < O-dichlorobenzene

Q.9 ClOH < BrOH < IOH

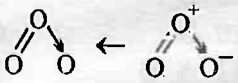
Q.10 $LI^+ < Al^{3+} < Mg^{2+} < K^+$

Q.11 $BeSO_4 < MgSO_4 < CaSO_4 < SrSO_4$

Miscellaneous.

Q.1 $N = N \rightarrow O \rightleftharpoons N \rightleftharpoons N = O$

Q.2



Q.6 (i) Linear, (ii) Pyramidal, (iii) Square planar, (iv) Square pyramidal, (v) pyramidal

Q.8 $\underset{\underset{sp^2}{\downarrow}}{CH_3} = \underset{\underset{sp}{\downarrow}}{C} = \underset{\underset{sp^2}{\downarrow}}{CH_3}$

BANSAL CLASSES

CHEMISTRY

TARGET IIT JEE 2007
XI (P, Q, R, S & J)

REDOX & EQUIVALENT CONCEPTS
(STOCHIOMETRY -II)

CONTENTS

EXERCISE–I (A)
EXERCISE–I (B)
EXERCISE–II
EXERCISE–III
EXERCISE–IV
ANSWER KEY

OXIDATION & REDUCTION

Molecular Equations:

$BaCl_2 + Na_2SO_4 \longrightarrow BaSO_4 \downarrow + 2\,NaCl$.

Ionic Equations :

$Ba^{2+} + SO_4^{2-} \longrightarrow BaSO_4 \downarrow$.

Spectator Ions :

Ions which do not undergo change during a reaction, they are not included in the final balanced equation.

Rules For Writing Ionic Equations :

(i) All soluble electrolytes involved in a chemical change are expresses in ionic symbols and covalent substances are written in molecular form.

(ii) The electrolyte which is highly insoluble, is expressed in molecular form.

(iii) The ions which are common and equal in number on both sides (spectator ions) are cancelled.

(iv) Besides the atoms, the ionic charges must also balance on both the sides.

Oxidation State Of The Elements :

Valency of an element is defined as the number of hydrogen atoms that combine with or are displaced by one atom of the element. Cl, monovalent, O, divalent, N, trivalent, tetravalent C, variable valency P (3, 5). It is never a useful concept despite of physical reality, so more common & artificial concept of oxidation state (oxidation number).

Oxidation Number :

It is the charge (real or imaginary) which an atom appears to have when it is in combination. It may be a whole no. or fractional. For an element may have different values. It depends on nature of compound in which it is present. There are some operational rules to determine oxidation number.

Stock's Notation :

Generally used for naming compounds of metals, some non-metals also. eg. Cr_2O_3 Chromium (iii) oxide and P_2O_5 Phosphorous (v) oxide.

Oxidation :

Addition of oxygen, removal of hydrogen, addition of electro – negative element, removal of electro-positive element, loss of electrons, increase in oxidation number (de–electronation).

Reduction :

Removal of oxygen, addition of hydrogen, removal of electronegative element, addition of electro +ve element, gain of electrons, decrease in oxid. no. (electronation).

Redox Reactions :

A reaction in which oxidation & reduction occur simultaneously.

Oxidising Agents :

(oxidants, oxidisors). They oxidise others, themselves are reduced & gain electrons. eg. O_2, O_3, HNO_3, MnO_2, H_2O_2, halogens, $KMnO_4$, $K_2Cr_2O_7$, KIO_3, $Cl(SO_4)_3$, $FeCl_3$, NaOCl, hydrogen ions.
[Atoms present in their higher oxidation state.]

Reducing Agents :

H_2, molecular is weak but Nascent hydrogen is powerful. C, CO, H_2S, SO_2, $SnCl_2$, Sodium thio Sulphate, Al, Na, CaH_2, $NaBH_4$, $LiAlH_4$. They reduce others, themselves get oxidised & lose electrons. Also called reductants or reducers.
[Atoms present in their lower oxidation state.]

Both Oxidising & Reducing Agents :

SO_2, H_2O_2, O_3, NO_2, etc.

Balancing Of Equations :

(i) Ion - electron method

(ii) Oxidation number method

[Concept involved that in any chemical reaction e^- cannot be produced so no. of e^-s in O.H. & R.H. should be same]

Oxidation Half Reaction : $Na \longrightarrow Na^+ + e^-$.

Reduction Half Reaction : $F_2 + 2e^- \longrightarrow 2F^-$.

COMMON OXIDATION AND REDUCTION PARTS

OXIDATION PARTS	REDUCTION PARTS
$Fe^{2+} \longrightarrow Fe^{3+}$	$Fe^{3+} \longrightarrow Fe^{2+}$
$Zn \longrightarrow Zn^{2+}$	
$X^- \longrightarrow X_2$	$X_2 \longrightarrow X^-$
$S^{2-} \longrightarrow S$	$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$
$H_2O_2 \longrightarrow O_2$	$NO_3^- \longrightarrow NO$
$SO_3^{2-} \longrightarrow SO_4^{2-}$	$MnO_4^- \longrightarrow Mn^{2+}$ (neutral med.)
$C_2O_4^{2-} \longrightarrow CO_2$	$MnO_4^- \longrightarrow MnO_2$ (Basic med.)
$S_2O_3^{2-} \longrightarrow S_4O_6^{2-}$	$SO_4^{2-} \longrightarrow SO_2$
$I_2 \longrightarrow IO_3^-$	$MnO_2 \longrightarrow Mn^{2+}$

Types Of Redox Reduction :

Intermolecular redox, disproportion, Intra molecular redox .

Disproportion:

In such reactions the oxidising and reducing agents(atom) are the same .

oxidation

$$H_2O_2 + H_2O_2 \longrightarrow 2H_2O + O_2 .$$

reduction

To identify whether a reaction is redox or not , find change in oxidation number or loss and gain of electrons. If there is no change in oxidation number , the reaction is not a redox reaction .

Auto Oxidation : $MnO_4^- \longrightarrow MnO_4^{2-} + O_2$.

In this Mn in MnO_4^- is reduced. Oxygen in MnO_4^- is oxidised. The same sub. MnO_4^- acts as oxidising & reducing agent. This is called auto oxidation .

NOTE : To predict the product of reaction remember :

(a) Free halogen on reduction gives halide ion ($F_2 \rightarrow F^-$)

(b) Alkali metals on oxidation give metallic ion with + 1 oxidation state.

(c) Conc. HNO_3 on reduction gives NO_2, while dilute HNO_3 can give NO, N_2, NH_4^+ or other products depending on the nature of reducing agent and on dilution.

(d) In acid solution $KMnO_4$ is reduced to Mn^{2+} while in neutral or alkaline , it gives MnO_2 or K_2MnO_4 .

(e) H_2O_2 on reduction gives water and on oxidation gives oxygen.

(f) Dichromate ion in acid solution is reduced to Cr^{3+}.

Nature Of Oxides Based On Oxidation Number :

Lowest oxidation state	$\longrightarrow$	Basic	(MnO)
Intermediate oxidation state	$\longrightarrow$	Amphoteric	(Mn_3O_4, MnO_2)
Highest oxidation state	$\longrightarrow$	Acidic	(Mn_2O_7)

Metathesis Reactions :

Never redox reactions. In these two compounds react to form two new compounds and no change in oxidation number occur. eg.

(i) $Pb(NO_3)_2 + K_2CrO_4 \longrightarrow PbCrO_4 + 2KNO_3$ (ii) $HCl + NaOH \longrightarrow NaCl + H_2O$

Rules For Assigning Oxidation Number :

(i) Oxidation number of free elements or atoms is zero.

(ii) Oxidation number of allotropes is zero.

(iii) Oxidation number of atoms in homo-nuclear molecules is zero.

(iv) Oxidation number of mono-atomic ions is equal to the algebric charge on them.

(v) Oxidation number of F in compounds is - 1.

(vi) Oxidation number of H in its compounds is + 1, except in metalhydrides where it is - 1.

(vii) Oxidation number of O is - 2 in its compounds, but in F_2O it is + 2 and in peroxides it is - 1 and - 0.5 in KO_2.

(viii) Oxidation number of alkali metals in their compounds + 1.

(ix) Oxidation number of alkaline earth metals in their compounds is + 2.

(x) Oxidation number of an ion is equal to its charge.

(xi) Oxidation number of a molecule as a whole is zero.

(xii) The sum of oxidation number of all the atoms in a molecule should be zero and in an ion equal to its charge.

MOST COMMOM OXIDATION STATES OF REPRESENTATIVE ELEMENTS

Group	**Outer shell configuration**	**Common oxid. states except zero in free state**
I A	ns^1	+ 1
II A	ns^2	+ 2
III A	ns^2np^1	+ 3, + 1
IV A	ns^2np^2	+ 4, + 3, + 2, + 1, - 1, - 2, - 3, - 4
V A	ns^2np^3	+ 5, + 3, + 1, - 1, - 3
VI A	ns^2np^4	+ 6, + 4, + 2, - 2
VII A	ns^2np^5	+ 7, + 5, + 3, + 1, - 1

Average Oxidation Number : **Find Oxidation Number of Fe in Fe_3O_4.**

Fe_3O_4 is $FeO \cdot Fe_2O_3$.

O. N. of Fe in FeO is +2 ; O. N. of Fe in Fe_2O_3 is +3.

Therefore average O. N. of three Fe atoms $= \frac{+2+2x(+3)}{3} = +\frac{8}{3}$.

EQUIVALENT CONCEPT

(A) Volumetric analysis :

This mainly involve titrations based chemistry. It can be divided into two major category.

(I) Non-redox system (II) Redox system

(I) Non – redox system

This involve following kind of titrations:

1. Acid-Base titrations
2. Back titration
3. Precipitation titration
4. Double indicator acid base titration

Titrimetric Method of Analysis : A titrimetric method of analysis is based on chemical reaction such as.

$$aA + tT \longrightarrow \text{Product}$$

Where 'a' molecules of "analysis", A, reacts with t molecules of reagent T.
T is called Titrant normally taken in buret in form of solution of known concentration. The solution of titrant is called "standard solution".

The addition of titrant is added till the amount of T, chemically equivalent to that of 'A' has been added. It is said equivalent point of titration has been reached. In order to know when to stop addition of titrant, a chemical substance is used called indicator, which respond to appearance of excess of titrant by changing colour precisely at the equivalence point. The point in the titration where the indicator changes colour is termed the 'end point'. It is possible that end point be as close as possible to the equivalence point.

The term titration refer's to process of measuring the volume of titrant required to reach the end point. For many years the term volumetric analysis was used rather than titrimetric analysis. However from a rigorons stand point the term titrimetric is preferable because volume measurement may not be confirmed to titration. In certain analysis, for example one might measure the volume of a gas.

We can adopt mole method in balanced chemical reactions to relate reactant and products but it is more easier to apply law of equivalents in volumetric calculations because it does not require knowledge of balanced chemical reactions involved in sequence. Law of equivalents refers to that, equivalents of a limiting reactant is equal to equivalent of other reactant reacting in a chemical reaction or equal to equivalents of products formed in reaction.

n-factor in non-redox system

n factor here we mean a conversion factor by which we divide molar mass of substance to get equivalent mass and it depends on nature of substance which vary from one condition to another condition. We can divide n-factor calculations in two category.

(A) when compound is not reacting.

(B) when compound is reacting.

Acid-Base titration

To find out strength or concentration of unknown acid or base it is titrated against base or acid of known strength. At the equivalence point we can know amount of acid or base used and then with the help of law of equivalents we can find strength of unknown.

Meq of acid at equivalence point = Meq of base at equivalence point

Back titration

Back titration is used in volumetric analysis to find out excess of reagent added by titrating it with suitable reagent. It is also used to find out percentage purity of sample. For example in acid-base titration suppose we have added excess base in acid mixture. To find excess base we can titrate the solution with another acid of known strength.

Precipitation titration :

In ionic reaction we can know strength of unknown solution of salt by titrating it against a reagent with which it can form precipitate. For example NaCl strength can be known by titrating it against $AgNO_3$ solution with which it form white ppt. of AgCl.

So meq. of NaCl at equivalence point = meq of $AgNO_3$ used = meq of AgCl formed

Double indicator acid-base titration:

In the acid-base titration the equivalence point is known with the help of indicator which changes its colour at the end point. In the titration of polyacidic base or polybasic acid there are more than one end point for each step neutralization. Sometimes one indicator is not able to give colour change at every end point. So to find out end point we have to use more than one indicator. For example in the titration of Na_2CO_3 against HCl there are two end points.

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$$

$$NaHCO_3 + HCl \longrightarrow H_2CO_3 + NaCl$$

When we use phenophthalein in the above titration it changes its colour at first end point when $NaHCO_3$ is formed and with it we can not know second end point. Similarly with methyl orange it changes its colour at second end point only and we can not know first end point. It is because all indicator changes colour on the basis of pH of medium. So in titration of $NaHCO_3$, $KHCO_3$ against acid phenolphthalein can not be used.

So we can write with phenolpthalein, if total meq of Na_2CO_3 = 1 then

½ meq of Na_2CO_3 = meq of HCl

with methyl orange,

meq of Na_2CO_3 = meq of HCl

Titration	Indicator	pH Range	n factor
Na_2CO_3	Phenolphthalein	8.3 – 10	1
against acid			
K_2CO_3	Methyl orange	3.1 – 4.4	2

Note:

When we carry out dilution of solution, meq eq, milli mole or mole of substance does not change because they represent amount of substance, however molar concentration may change.

Solubilities of some important salt's :

1. **Chloride :**

AgCl – White ppt.
Hg_2Cl_2 – White ppt
$PbCl_2$ – White ppt.
CuCl – Insolution ppt.

BiOCl – White ppt.
SbOCl – White ppt.
Hg_2OCl_2 – White ppt.

All other chlorides are soluble in water.

2. **Bromide :**

$AgBr$ – Pate yellow ppt.
$PbBr_2$ – White ppt. All other bromides are soluble in water
Hg_2Br_2 – White ppt.
$CuBr$ – White ppt.

3. **Iodide :**

AgI – Yellow ppt.
PbI_2 – Yellow ppt.
Hg_2I_2 – Green ppt.
HgI_2 – Red ppt.
CuI – White ppt.
BI_3 – Black ppt.

4. **Some important oxides and hydroxises :**

Ag_2O – Brown ppt.
$Pb(OH)_2$ – White ppt.
$Pb(OH)_4$ – White ppt.
Hg_2O – Black ppt.
HgO – Yellow ppt.
Cu_2O – Red ppt.
CuO – Black ppt.
$Cu(OH)_2$ – Blue ppt.
$Cd(OH)_2$ – White ppt.
$Fe(OH)_2$ – White ppt.
$Fe(OH)_3$ – Red ppt.
$Sn(OH)_2$ – White ppt.
$Sn(OH)_4$ – White ppt.
$Al(OH)_3$ – White gelatenons
$Cr(OH)_3$ – Grey-Green
$Co(OH)_2$ – Pink
$Co(OH)_3$ – Brownish black
$Ni(OH)_2$ – Green
$Ni(OH)_3$ – Black
$Mn(OH)_2$ – White
$MnO(OH)_2$ – Brown
$Zn(OH)_2$ – White
$Mg(OH)_2$ – White

Carbonates :

Except Alkali metals and NH_4^+ all other carbonates are insoluble.

$Ag_2CO_3 \longrightarrow$ White ppt. $\longrightarrow Ag_2O + CO_2$
$3HgO.HgCO_3 \longrightarrow$ basic murcuric carbonate White ppt.
$CuCO_3 \longrightarrow$ Green ppt.
$CaCO_3 \longrightarrow$ White ppt.

Sulphites (SO_3^{2-}) :

Except Alkali metal and Ammonium, all other sulphite are generally insoluble.

Examples : Ag_2SO_3, $PbSO_3$, $BaSO_3$, $CaSO_3$ $\longrightarrow$ White ppt.

Thiosulphates :

Mostly soluble except

$Ag_2S_2O_3 \longrightarrow$ White ppt. $[Ag(S_2O_3)_2]^{3-}$ soluble
$PbS_2O_3 \longrightarrow$ White ppt.
$BaS_2O_3 \longrightarrow$ White ppt.

Thiocyanate (SCN^-) :

$Hg(SCN)_2$ – White ppt. (Pharaoh's serpent)
$Ag(SCN)$ – White ppt.
$Cu(SCN)_2$ – Black ppt.
$Cu(SCN)$ – White ppt.
$Fe(SCN)_3$ – Red complex.
$[Co(SCN)_4]^{2-}$ – Blue complex
$Co[Hg(SCN)_4]$ – Blue ppt.

Cynaides(CN^-) :

Except Alkali metal Alkaline earth metal cyanides are soluble in water.

$Hg(CN)_2$ – soluble in water in undissociated form
$Ag(CN)$ – White ppt. $[Ag(CN)_2]^-$ soluble
$Pb(CN)_2$ – White ppt.
$Fe(CN)_3$ – Brown ppt. $[Fe(CN)_6]^{3-}$ soluble
$Co(CN)_2$ – Brown ppt. $[Co(CN)_6]^{4-}$ soluble
$Ni(CN)_2$ – Green $[Ni(CN)_4]^{2-}$ soluble

Sulphides :

Except Alkali metals and ammonium salt's all other sulphides are insoluble. Son insoluble sulphides with unusual colour are

$CdS \longrightarrow$ Yellow
$MnS \longrightarrow$ Pink
$ZnS \longrightarrow$ White
$SnS \longrightarrow$ Brown
$SnS_2 \longrightarrow$ Yellow
$AS_2S_3 \longrightarrow$ Yellow
$Sb_2S_3 \longrightarrow$ Orange

Chromates :

$Ag_2CrO_4 \longrightarrow$ Red ppt.
$PbCrO_4 \longrightarrow$ Yellow ppt.
$BaCrO_4 \longrightarrow$ Yellow ppt.
$FeCrO_4 \longrightarrow$ Green ppt.
Dichromates are generally soluble.
MnO_4 – Permangnates are generally soluble.

Phosphates :

Are generally insoluble :

$Ag_3PO_4 \longrightarrow$ Yellow ppt.
$FePO_4 \longrightarrow$ Yellow ppt.
$AlPO_4 \longrightarrow$ Yellow ppt.
$ZrO(HPO_4) \longrightarrow$ White ppt.
$Mg(NH_4)PO_4 \longrightarrow$ White ppt.
$(NH_4)_3[P\,Mo_{12}O_{40}] \longrightarrow$ Canary yellow ppt.

Phosphite (HPO_4^{2-}):

Except Alkali metals all other phosphites are insoluble

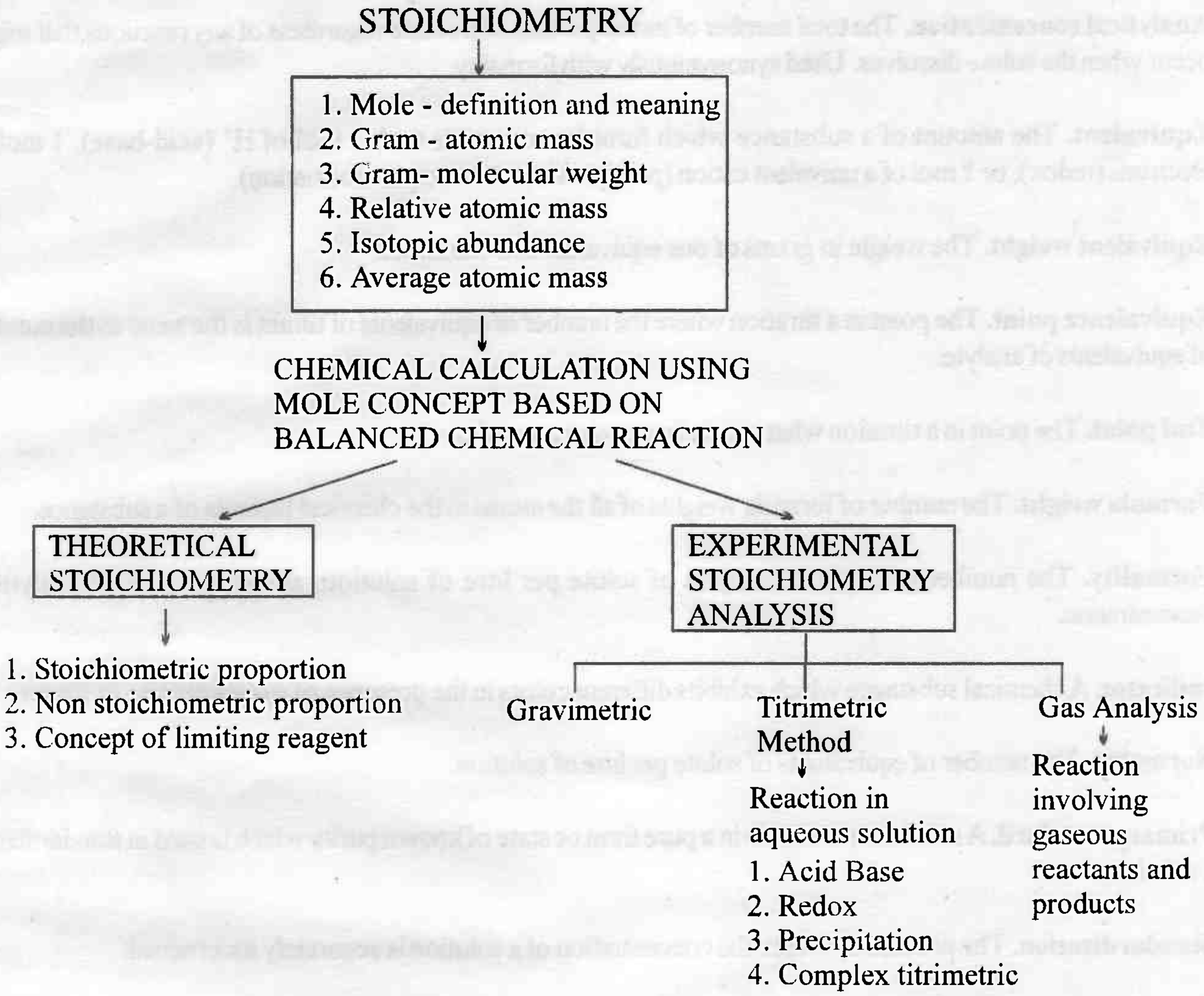
Hypo phosphite:

All hypophosphites are soluble in water.
All Acetate are soluble except $Ag(CH_3COO)$
All formates are soluble except $Ag(HCOO)$
Tatarate, Citrate, Salicylate, Succinate of Silver-are all insoluble white ppt.

Some Important ppt.:

KH (Tartarate) $\longrightarrow$ White ppt.
NH_4H(Tartarate) $\longrightarrow$ White ppt.
$K_2[PtCl_6] \longrightarrow$ White ppt.
$K_3[Co(NO_2)_6] \longrightarrow$ Yellow ppt.
$(NH_4)_3[Co(NO_2)_6] \longrightarrow$ Yellow ppt.
$(NH_4)_2[PtCl_6] \longrightarrow$ Yellow ppt.

THE ATLAS


STOICHIOMETRY
1. Mole - definition and meaning
2. Gram - atomic mass
3. Gram- molecular weight
4. Relative atomic mass
5. Isotopic abundance
6. Average atomic mass
CHEMICAL CALCULATION USING MOLE CONCEPT BASED ON BALANCED CHEMICAL REACTION
THEORETICAL STOICHIOMETRY
1. Stoichiometric proportion
2. Non stoichiometric proportion
3. Concept of limiting reagent
EXPERIMENTAL STOICHIOMETRY ANALYSIS
Gravimetric
Titrimetric Method
Reaction in aqueous solution
1. Acid Base
2. Redox
3. Precipitation
4. Complex titrimetric
Gas Analysis
Reaction involving gaseous reactants and products

GLOSSARY

Aliquot. A portion of the whole, usually a simple fraction. A portion of a sample withdraw from a volumetric flask with a pipet is called an aliquot.

Analytical concentration. The total number of moles per litre of a solute regardless of any reactions that might occur when the solute dissolves. Used synonymously with formality.

Equivalent. The amount of a substance which furnishes or reacts with 1 mol of H^+ (acid-base), 1 mol of electrons (redox), or 1 mol of a univalent cation (precipitation and complex formation).

Equivalent weight. The weight in grams of one equivalent of a substance.

Equivalence point. The point in a titration where the number of equivalents of titrant is the same as the number of equivalents of analyte.

End point. The point in a titration where an indicator changes color.

Formula weight. The number of formula weights of all the atoms in the chemical formula of a substance.

Formality. The number of formula weights of solute per litre of solution; synonymous with analytical concentration.

Indicator. A chemical substance which exhibits different colors in the presence of excess analyte or titrant.

Normality. The number of equivalents of solute per litre of solution.

Primary standard. A substance available in a pure form or state of known purity which is used in standardizing a solution.

Standardization. The process by which the concentration of a solution is accurately ascertained.

Standard solution. A solution whose concentration has been accurately determined.

Titrant. The reagent (a standard solution) which is added from a buret to react with the analyte.

EXERCISE I (A) (Mole & Equivalent Concept)

Q.1 ***Fill in the blanks with appropriate items :***

1. The number of water molecules in 0.5 mol of barium chloride dihydrate is ______.
2. 20ml of 0.1 M $H_2C_2O_4 \cdot 2H_2O$ (oxalic acid) solution contains oxalic acid equal to ______ moles.
3. The volume of 1.204×10^{24} molecules of water at 4°C is ______.
4. 0.2 mol of ozone (O_3) at N.T.P. will occupy volume ______ L.
5. The balancing of chemical equation is based upon ______.
6. 2 gm of hydrogen will have same number of H atoms as are there in ______ g hydrazine (NH_2–NH_2).
7. The mass of x atoms of element = $\frac{\dots\dots x}{N_A}$.
8. The moles of x atoms of a triatomic gas = $\frac{x}{N_A} \times$ ______.
9. The amount of Na_2SO_4 which gives 9.6 gm of SO_4^{2-} is ______.
10. The 44 mg of certain substance contain 6.02×10^{20} molecules. The molecular mass of the substance is ______.
11. The mass of 1×10^{22} molecules of $CuSO_4 . 5H_2O$ is ______.
12. The atomic mass of iron is 56. The equivalent mass of the metal in $FeCl_2$ is ______ and that in $FeCl_3$ is ______.
13. The sulphate of a metal M contains 9.87% of M. The sulphate is isomorphous with $ZnSO_4.7H_2O$. The atomic mass of M is ______.
14. A binary compound contains 50% of A (at. mass = 16) & 50% B (at. mass = 32). The empirical formula of the compound is ______.
15. 10.6 g of Na_2CO_3 react with 9.8 g of H_2SO_4 to form 16 g of Na_2SO_4 & 4.4 g CO_2. This is in accordance with the law of ______.
16. 3 g of a salt (m. wt. 30) are dissolved in 250 ml of water. The molarity of solution is ______.
17. 0.5 mole of $BaCl_2$ are mixed with 0.2 mole of Na_3PO_4 the maximum number of mole of $Ba_3(PO_4)_2$ formed are ______.
18. The Eq. weight of Na_2HPO_4 when it reacts with excess of HCl is ______.
19. The mole fraction of solute in 20% (by weight) aqueous H_2O_2 solution is ______.
20. A metallic oxide contains 60% of the metal. The Eq. weight of the metal is ______.
21. The number of gm of anhydrous Na_2CO_3 present in 250 ml of 0.25 N solution is ______.
22. ______ ml of 0.1 M H_2SO_4 is required to neutralize 50 ml of 0.2 M NaOH solution.
23. The number of mole of water present in 90 g H_2O are ______.
24. The concentration of K^+ ion in 0.2 M $K_2Cr_2O_7$ solution would be ______.
25. 280 ml of sulphur vapour at NTP weight 3.2 g . The Mol. formula of the sulphur vapour is ______.

Q.2 ***True or False Statements :***

1. Equal volumes of helium and nitrogen under similar conditions have equal number of atoms.
2. The smallest particle is a substance which is capable in independent existence is called an atom.
3. The number of formula units in 0.5 mole of KCl is 6.02×10^{23}.
4. 22.4 L of ethane gas at S.T.P. contains H atoms as are present in 3 gram molecules of dihydrogen.
5. Molarity of pure water is 55.5.
6. A 20% solution of KOH (density = 1.02 g/ml) has molarity = 3.64.
7. In a mixture of 1 g C_6H_6 & 1 g C_7H_8, the mole fraction of both are same.
8. 1 mole of $C_{12}H_{22}O_{11}$ contains 22 hydrogen atoms.
9. $KClO_4$ & $KMnO_4$ are isomorphous in nature.
10. Mass of 3.01×10^{23} molecules of of methane is 8 gm.
11. A hydrocarbon contains 86% C. 448 ml of the hydrocarbon weighs 1.68 g at STP. Then the hydrocarbon is an alkene.
12. 6.023×10^{54} e^{-s} weigh one kg.
13. An oxide of metal M has 40% by mass of oxygen. Metal M has relative atomic mass of 24. The empirical formula of the oxide is MO.
14. 5 g of a crystalline salt when rendered anhydrous lost 1.8 g of water. The formula weight of the anhydrous salt is 160. The number of molecules of water of crystallisation in the salt is 5.
15. Number of valence e^{-s} in 4.2 g of N^{3-} is 24 N_A.
16. The equivalent mass of $KMnO_4$ in alkaline medium is molar mass divided by five.
17. The equivalent mass of $Na_2S_2O_3$ in its reaction with I_2 is molar mass divided by two.
18. In a reaction, H_2MoO_4 is changed to MoO_2^+. In this case, H_2MoO_4 acts as an oxidising agent.
19. $KBrO_3$ acts as a strong oxidising agent. It accepts 6 electrons to give KBr.
20. 0.1 M sulphuric acid has normality of 0.05 N.
21. The reaction, $2H_2O_2 \longrightarrow 2H_2O + O_2$ is not an example of a redox reaction.
22. The disproportionation reaction,
$$2Mn^{3+} + 2H_2O \longrightarrow MnO_2 + Mn^{+2} + 4H^+$$
is an example of a redox reaction.
23. The oxidation number of hydrogen is always taken as + 1 in its all compounds.
24. The increase in oxidation number of an element implies that the element has undergone reduction.
25. The oxidation state of oxygen atom in potassium super oxide is $-\frac{1}{2}$.

EXERCISE I (B)

Acid Base Titration

Q.1 A solution containing 4.2 g of KOH and $Ca(OH)_2$ is neutralized by an acid. It consumes 0.1 equivalent of acid, calculate the percentage composition of the sample.

Q.2 How many ml of 0.1 N HCl are required to react completely with 1 g mixture of Na_2CO_3 and $NaHCO_3$ containing equimolar amounts of two?

Q.3 0.5 g of fuming H_2SO_4 (oleum) is diluted with water. The solution requires 26.7 ml of 0.4 N NaOH for complete neutralization. Find the % of free SO_3 in the sample of oleum.

Q.4 10 g $CaCO_3$ were dissolved in 250 ml of M HCl and the solution was boiled. What volume of 2 M KOH would be required to equivalence point after boiling? Assume no change in volume during boiling.

Q.5 H_3PO_4 is a tri basic acid and one of its salt is NaH_2PO_4. What volume of 1 M NaOH solution should be added to 12 g of NaH_2PO_4 to convert it into Na_3PO_4?

Q.6 1.64 g of a mixture of $CaCO_3$ and $MgCO_3$ was dissolved in 50 mL of 0.8 M HCl. The excess of acid required 16 mL of 0.25 M NaOH for neutralization. Calculate the percentage of $CaCO_3$ and $MgCO_3$ in the sample.

Q.7 1.5 g of chalk were treated with 10 ml of 4N – HCl. The chalk was dissolved and the solution made to 100 ml 25 ml of this solution required 18.75 ml of 0.2 N – NaOH solution for complete neutralisation. Calculate the percentage of pure $CaCO_3$ in the sample of chalk?

Double titration

Q.8 A solution contains Na_2CO_3 and $NaHCO_3$. 20ml of this solution required 4ml of 1N – HCl for titration with Ph indicator. The titration was repeated with the same volume of the solution but with MeOH. 10.5 ml of 1 – N HCl was required this time. Calculate the amount of Na_2Co_3 & $NaHCO_3$.

Q.9 A solution contains a mix of Na_2CO_3 and NaOH. Using Ph as indicator 25ml of mix required 19.5 ml of 0.995 N HCl for the end point. With MeOH, 25 ml of the solution required 25ml of the same HCl for the end point. Calculate gms/L of each substance in the mix.

Q.10 200ml of a solution of mixture of NaOH and Na_2CO_3 was first titrated with Ph and $\frac{N}{10}$ HCl. 17.5 ml of HCl was required for end point. After this MeOH was added and 2.5 ml of some HCl was again required for next end point. Find out amounts of NaOH and Na_2CO_3 in the mix.

Q.11 A solution contains Na_2CO_3 and $NaHCO_3$. 10ml of this requires 2ml of 0.1M H_2SO_4 for neutralisation using Ph indicator. MeOH is then added when a further 2.5 ml of 0.2 M H_2SO_4 was needed. Calculate strength of Na_2CO_3 and $NaHCO_3$.

Q.12 A sample containing Na_2CO_3 & NaOH is dissolved in 100ml solution. 10ml of this solution requires 25ml of 0.1N HCl when Ph is used as indicator. If MeOH is used as indicator 10ml of same solution requires 30ml of same HCl. Calculate % of Na_2CO_3 and NaOH in the sample.

Redox Titration

Q.13 It requires 40.05 ml of 1M Ce^{4+} to titrate 20ml of 1M Sn^{2+} to Sn^{4+}. What is the oxidation state of the cerium in the product.

Q.14 A volume of 12.53 ml of 0.05093 M SeO_2 reacted with exactly 25.52 ml of 0.1M $CrSO_4$. In the reaction, Cr^{2+} was oxidized to Cr^{3+}. To what oxidation state was selenium converted by the reaction.

Q.15 Potassium acid oxalate $K_2C_2O_4 \cdot 3HC_2O_4 \cdot 4H_2O$ can be oxidized by MnO_4^- in acid medium. Calculate the volume of 0.1M $KMnO_4$ reacting in acid solution with one gram of the acid oxalate.

Q.16 A 1.0g sample of H_2O_2 solution containing x % H_2O_2 by mass requires x cm^3 of a $KMnO_4$ solution for complete oxidation under acidic conditions. Calculate the normality of $KMnO_4$ solution.

Q.17 Metallic tin in the presence of HCl is oxidized by $K_2Cr_2O_7$ to stannic chloride, $SnCl_4$. What volume of deci-normal dichromate solution would be reduced by 1g of tin.

Q.18 5g sample of brass was dissolved in one litre dil. H_2SO_4. 20 ml of this solution were mixed with KI, liberating I_2 and Cu^+ and the I_2 required 20 ml of 0.0327 N hypo solution for complete titration. Calculate the percentage of Cu in the alloy.

Q.19 A 1.0 g sample of Fe_2O_3 solid of 55.2% purity is dissolved in acid and reduced by heating the solution with zinc dust. The resultant solution is cooled and made upto 100.0 mL. An aliquot of 25.0 mL of this solution requires 17.0 mL of 0.0167 M solution of an oxidant for titration. Calculate the number of moles of electrons taken up by the oxidant in the reaction of the above titration.

Q.20 0.84 g iron ore containing x percent of iron was taken in a solution containing all the iron in ferrous condition. The solution required x ml of a dichromatic solution for oxidizing the iron content to ferric state. Calculate the strength of dichromatic solution.

Q.21 The neutralization of a solution of 1.2 g of a substance containing a mixture of $H_2C_2O_4 \cdot 2H_2O$, $KHC_2O_4 \cdot H_2O$ and different impurities of a neutral salt consumed 18.9 ml of 0.5 N NaOH solution. On titration with $KMnO_4$ solution, 0.4 g of the same substance needed 21.55 ml of 0.25 N $KMnO_4$. Calculate the % composition of the substance.

Back Titration

Q.22 50gm of a sample of $Ca(OH)_2$ is dissolved in 50ml of 0.5N HCl solution. The excess of HCl was titrated with 0.3N – NaOH. The volume of NaOH used was 20cc. Calculate % purity of $Ca(OH)_2$.

Q.23 One gm of impure sodium carbonate is dissolved in water and the solution is made up to 250ml. To 50ml of this made up solution, 50ml of 0.1N – HCl is added and the mix after shaking well required 10ml of 0.16N – NaOH solution for complete titration. Calculate the % purity of the sample.

Q.24 A sample of Mg was burnt in air to give a mix of MgO and Mg_3N_2. The ash was dissolved in 60meq HCl and the resulting solution was back titrated with NaOH. 12 meq of NaOH were required to reach end point. An excess of NaOH was then added and the solution distilled. The NH_3 released was then trapped in 10 meq of second acid solution. Back titration of this solution required 6 meq of the base. Calculate the % of Mg burnt to the nitride.

Q.25 What amount of substance containing 60% NaCl, 37% KCl should be weighed out for analysis so that after the action of 25 ml of 0.1N $AgNO_3$ solution, excess of Ag^+ is back titrated with 5 ml of NH_4SCN solution? Given that 1 ml of NH_4SCN = 1.1 ml of $AgNO_3$.

Q.26 1.64 g of a mixture of $CaCO_3$ and $MgCO_3$ was dissolved in 50 mL of 0.8 M HCl. The excess of acid required 16 mL of 0.25 M NaOH for neutralization. Calculate the percentage of $CaCO_3$ and $MgCO_3$ in the sample.

Q.27 5g of pyrolusite (impure MnO_2) were heated with conc. HCl and Cl_2 evolved was passed through excess of KI solution. The iodine liberated required 40 mL of $\frac{N}{10}$ hypo solution. Find the % of MnO_2 in the pyrolusite.

EXERCISE II

Q.1 A sample of calcium carbonate contains impurities which do not react with a mineral acid. When 2 grams of the sample were reacted with the mineral acid, 375 ml of carbon dioxide were obtained at 27°C and 760 mm pressure. Calculate the % purity of the sample of $CaCO_3$?

Q.2 One gram of an alloy of aluminium and magnesium when heated with excess of dil. HCl forms magnesium chloride, aluminium chloride and hydrogen. The evolved hydrogen collected over mercury at 0°C has a volume of 1.2 litres at 0.92 atm pressure. Calculate the composition of the alloy.

Q.3 10 gm of a mixture of anhydrous nitrates of two metal A & B were heated to a constant weight & gave 5.531 gm of a mixture of the corresponding oxides. The equivalent weights of A & B are 103.6 & 31.8 respectively. What was the percentage of A in the mixture.

Q.4 Sulfur dioxide is an atmospheric pollutant that is converted to sulfuric acid when it reacts with water vapour. This is one source of acid rain, one of our most pressing environmental problems. The sulfur dioxide content of an air sample can be determined as follows. A sample of air is bubbled through an aqueous solution of hydrogen peroxide to convert all of the SO_2 to H_2SO_4

$$H_2O_2 + SO_2 \longrightarrow H_2SO_4$$

Titration of the resulting solution completes the analysis. In one such case, analysis of 1550 L of Los Angeles air gave a solution that required 5.70 ml of 5.96×10^{-3}M NaOH to complete the titration. Determine the number of grams of SO_2 present in the air sample.

Q.5 A mixture of FeO and Fe_2O_3 is reacted with acidified $KMnO_4$ solution having a concentration of 0.2278 M, 100 ml of which was used. The solution was then titrated with Zn dust which converted Fe^{3+} of the solution to Fe^{2+}. The Fe^{2+} required 1000 ml of 0.13 M $K_2Cr_2O_7$ solution. Find the % of FeO & Fe_2O_3.

Q.6 50ml of a solution, containing 0.01 mole each Na_2CO_3, $NaHCO_3$ and NaOH was titrated with N-HCl. What will be the titre readings if
(a) only Ph is used as indicator.
(b) only MeOH is used as indicator from the beginning
(c) MeOH is added after the first end point with Ph.

Q.7 A 0.517g sample containing $Ba(SCN)_2$ was dissolved in a bicarbonate solution. 50.0 mL of 0.107 N iodine was added, and the mixture was allowed to stand for five minutes. The solution was then acidified, and the excess I_2 was titrated with 16.3 mL of 0.0965 M sodium thiosulphate. Write a balanced equation for the oxidation of SCN^- into SO_4^{2-} and HCN. Calculate the percent $Ba(SCN)_2$ in the sample.

Q.8 An acid solution of a $KReO_4$ sample containing 26.83 mg of combined rhenium was reduced by passage through a column of granulated zinc. The effluent solution, including the washings from the column, was then titrated with 0.10 N $KMnO_4$. 11.45 mL of the standard permanganate was required for the re-oxidation of all the rhenium to the perrhenate ion, ReO_4^-. Assuming that rhenium was only element reduced. What is the oxidation state to which rhenium was reduced by the Zn column.
(Atomic mass of Re = 186.2)

Q.9 The element Se, dispersed in a 5.0 ml sample of detergent for dandruff control, was determined by suspending the sample in warm, ammonical solution that contain 45.0 ml of 0.020 M $AgNO_3$.

$$6Ag^+ + 3Se(s) + 6NH_3 + 3H_2O \longrightarrow 2Ag_2Se(s) + Ag_2SeO_3(s) + 6NH_4^+$$

The mixture was next treated with excess nitric acid which dissolves the Ag_2SeO_3 but not the Ag_2Se. The Ag^+ from the Ag_2SeO_3 and excess $AgNO_3$ consumed 16.74 ml of 0.0137 N KSCN in a Volhard titration. How many milligrams of Se were contained per millilitre of sample.

Q.10 Chrome alum $K_2SO_4 . Cr_2(SO_4)_3 . 24\,H_2O$ is prepared by passing SO_2 gas through an aqueous solution of $K_2Cr_2O_7$ acidified with dilute sulphuric acid till the reduction is complete. The alum is crystallized followed by filtration/centrifugation. If only 90% of the alum can be recovered from the above process, how much alum can be prepared from 10kg of $K_2Cr_2O_7$? Give the number of moles of electrons supplied by SO_2 for reducing one mole of $K_2Cr_2O_7$.

Q.11 A substance of crude copper is boiled in H_2SO_4 till all the copper has reacted. The impurities are inert to the acid. The SO_2 liberated in the reaction is passed into 100 mL of 0.4 M acidified $KMnO_4$. The solution of $KMnO_4$ after passage of SO_2 is allowed to react with oxalic acid and requires 23.6 mL of 1.2 M oxalic acid. If the purity of copper is 91%, what was the weight of the sample.

Q.12 A 1.87gm. sample of chromite ore($FeO.Cr_2O_3$) was completely oxidized by the fusion of peroxide. The fused mass was treated with water and boiled to destroy the excess of peroxide. After acidification the sample was treated with 50ml. of 0.16M Fe^{2+}. In back titration 2.97 ml of 0.005 M barium dichromate was required to oxidize the excess iron (II). What is the percentage of chromite in the sample?

Q.13 25 mL of a solution containing HCl was treated with excess of M/5 KIO_3 and KI solution of unknown concentration where I_2 liberated is titrated against a standard solution of 0.021M $Na_2S_2O_3$ solution whose 24 mL were used up. Find the strength of HCl and volume of KIO_3 solution consumed.

Q.14 A 10g sample of only CuS and Cu_2S was treated with 100 mL of 1.25 M $K_2Cr_2O_7$. The products obtained were Cr^{3+}, Cu^{2+} and SO_2. The excess oxidant was reacted with 50 mL of Fe^{2+} solution. 25 ml of the same Fe^{2+} solution required 0.875M acidic $KMnO_4$ the volume of which used was 20 mL. Find the % of CuS and Cu_2S in the sample.

Q.15 H_2O_2 is reduced rapidly by Sn^{2+}, the products being Sn^{4+} & water. H_2O_2 decomposes slowly at room temperature to yield O_2 & water. Calculate the volume of O_2 produced at 20°C & 1.00 atm when 200g of 10.0 % by mass H_2O_2 in water is treated with 100.0 ml of 2.00 M Sn^{2+} & then the mixture is allowed to stand until no further reaction occurs.

Q.16 0.6213 g of sample contains an unknown amount of As_2O_3. The sample was treated with HCl resulting in formation of $AsCl_3(g)$ which was distilled into a beaker of water. The hydrolysis reaction is as follows

$$AsCl_3 + 2H_2O \rightarrow HAsO_2 + 3H^+ + 3Cl^-.$$

The amount of $HAsO_2$ was determined by titration with 0.04134 M I_2, requiring 23.04 mL to reach the equivalence point. The redox products in the titration were H_3AsO_4 and I^-. Find the amount of $KMnO_4$ needed to oxidize As in As_2O_3 to its maximum possible oxidation state in acidic medium.

Q.17 A sample of steel weighing 0.6 gm and containing S as an impurity was burnt in a stream of O_2, when S was converted to its oxide SO_2. SO_2 was then oxidized to SO_4^{--} by using H_2O_2 solution containing 30ml of 0.04 M NaOH. 22.48 ml of 0.024 M HCl was required to neutralize the base remaining after oxidation. Calculate the % of S in the sample.

Q.18 3.6 g of Mg is burnt in limited supply of oxygen. The residue was treated with 100 mL of H_2SO_4 (35% by mass, 1.26 g mL^{-1} density). When 2.463 L of H_2 at 760 mm Hg at 27°C was evolved. After the reaction, H_2SO_4 was found to have a density of 1.05 g mL^{-1}. Assuming no volume change in H_2SO_4 solution. Find

(i) % by mass of final H_2SO_4

(ii) % by mass of Mg converted to oxide

(iii) mass of oxygen used. (Mg = 24, S= 32) [☺ Metal reacts with acids to displace H_2 gas ☺]

Q.19 A 10gm mixture of Cu_2S and CuS was treated with 200 ml of 0.75 M MnO_4^- in acid solution, producing SO_2, Cu^{2+} & Mn^{2+}. The SO_2 was boiled off and the excess MnO_4^- was titrated with 175 ml of 1M Fe^{2+} solution. Calculate the % CuS in the original mixture.

Q.20 3.3 gm of a sample of Anhydrous $CuSO_4$ was dissolved in water and made to 250ml. 25 ml of this solution after taking usual precautions was treated with a little excess of KI solution. A white ppt. of Cu_2I_2 and iodine was evolved. The iodine so evolved required 24.6 ml of hypo solution containing 20gm of ($Na_2S_2O_3 \cdot 5H_2O$) per litre. What is the purity of $CuSO_4$ solution.

Q.21 A certain sample of coal contained some iron pyrite (FeS_2) – a pollution causing impurity. When the coal was burned iron(II) was oxidised and SO_2 was formed. The SO_2 was reacted with NaOH when sodium sulphite and water was formed. On a particular fay 10^3 kg of coal was burned and it required 4 litres of 5M NaOH for the treatment of SO_2. What was the percentage of pyrite in the coal. What was the percentage of sulphur in the coal.

Q.22 In the presence of fluoride ion, Mn^{2+} can be titrated with MnO_4^-, both reactants being converted to a complex of Mn(III). A 0.545 g sample containing Mn_3O_4 was dissolved and all manganese was converted to Mn^{2+}. Titration in the presence of fluoride ion consumed 31.1 ml of $KMnO_4$ that was 0.117 N against oxalate.

(a) write a balanced chemical equation for the reaction, assuming that the complex is MnF_4^-.

(b) what was the % of Mn_3O_4 in the sample?

Q.23 Calculate the % of MnO_2 in a sample of pyrolusite ore, 1.5 g which was made to react with 10 g. of Mohr's salt ($FeSO_4.(NH_4)_2SO_4.\ 6H_2O$) and dilute H_2SO_4. MnO_2 was converted Mn^{2+}. After the reaction the solution was diluted to 250 ml and 50 ml of this solution, when titrated with 0.1 N $K_2Cr_2O_7$, required 10 ml of the dichromate solution.

Q.24 1.4 g of a complex $[Co(NH_3)_x]\,Cl_3$ was treated with 50 mL of 2N NaOH solution and boiled. Ammonia gas evolved was passed through 50 mL of 1N H_2SO_4. After the reaction was over, excess acid required 37.2 mL of 0.5 N NaOH. Calculate

(i) The percentage of ammonia in the sample. (ii) The value of x in the formula.

EXERCISE III

Q.1 A mixture of two gases, H_2S and SO_2 is passed through three beakers successively. The first beaker contains Pb^{2+} ions, which absorbs S^{2-} forming PbS. The second beaker contains 25 ml of 0.0396 N I_2 to oxidize SO_2 to SO_4^{2-}. The third contains 10 ml of 0.0345 N thiosulphate solution to retain any I_2 carried over from the second absorber. A 25 *l* gas sample was passed through the apparatus followed by an additional amount of N_2 to sweep last traces of SO_2 from first and second absorber. The solution from the first absorber was made acidic and treated with 20ml of 0.0066 M $K_2Cr_2O_7$ which converted S^{2-} to SO_2. The excess dichromate was reacted with solid KI and the liberated iodine required 7.45 ml of 0.0345 N $Na_2S_2O_3$ solution. The solutions in the second and third absorbers were combined and the resultant iodine was titrated with 2.44 ml of the same thiosulphate solution. Calculate the concentrations of SO_2 and H_2S in mg/L of the sample.

Q.2 Chromium exists as $FeCr_2O_4$ in the nature and it contains $Fe_{0.95}O$ & other impurity. To obtain pure chromium from $FeCr_2O_4$, the ore is fused with KOH and oxygen is passed through the mixture when K_2CrO_4 and Fe_2O_3 are produced. 2 g of ore required 270 mL of O_2 at STP for complete oxidation of ore. K_2CrO_4 is then precipitated as $BaCrO_4$ after addition of a Barium salt. To remaining solution 10 mL of 1 M $K_4Fe(CN)_6$ is added when Fe^{3+} ions react with it to form $KFe[Fe(CN)_6]$, often called 'Prussian Blue'. To determine excess of $K_4Fe(CN)_6$ in solution 7mL of 0.2 N of Fe^{2+} is added when all the $K_4Fe(CN)_6$ is precipitated as $K_2Fe[Fe(CN)_6]$. Calculate the percentage of $Fe_{0.95}O$.

Q.3 2g of chromite ore sample was mixed with enough potassium carbonate and potassium chlorate and fused. The reaction that occurred was:

$$6FeCr_2O_4 + 12K_2CO_3 + 7KClO_3 \rightarrow 3Fe_2O_3 + 12\ K_2CrO_4 + 7KCl + 12CO_2$$

The fused mass was cooled and extracted with 2N sulphuric acid. This was filtered and thoroughly washed. The filterate and washings were collected in a 500 ml. Volumetric flask. When all the soluble portion of the fused mass was extracted, 100 ml of 1M solution of ferrous ammonium sulphate were added and the solution made to 500ml. An aliquot of 25ml was titrated with potassium dichromate solution, prepared by dissolving 0.98 g of dried potassium dichromate in distilled water in a 250ml volumetric flask. The titration required 32.5 ml of this solution. Calculate the percentage of chromium in the sample of the ore.

Q.4 One gram of a moist sample of a mixture of $KClO_3$ and KCl was dissolved in water and made upto 250 mL. 25 ml of this solution was treated with SO_2 to reduce chlorate into chloride and the excess SO_2 was boiled off. When the total chloride was precipitated, 0.1435 g of AgCl was obtained. In another experiment 25mL of the original solution was treated with 30 mL of 0.2N solution of $FeSO_4$ and unreacted $FeSO_4$ required 37.5 mL of 0.08 N solution of an oxidizing agent for complete oxidation. Calculate the molar ratio of chlorate and chloride in the given mixture. Fe^{2+} reacts with ClO_3^- according to the equation.

$$ClO_3^- + 6Fe^{2+} + 6H^+ \rightarrow Cl^- + 6Fe^{3+} + 3H_2O$$

Also calculate the mass per cent of moisture present in the moist sample.

Q.5 A steel sample is to be analysed for Cr and Mn simultaneously. By suitable treatment the Cr is oxidized to $Cr_2O_7^{2-}$ and the Mn to MnO_4^-. A 10.00g sample of steel is used to produce 250.0 mL of a solution containing $Cr_2O_7^{2-}$ and MnO_4^-. A 10.00 mL portion of this solution is added to a $BaCl_2$ solution and by proper adjustment of the acidity, the chromium is completely precipitated as $BaCrO_4$; 0.0549 g is obtained. A second 10.00 mL portion of this solution requires exactly 15.95 mL of 0.0750M standard Fe^{2+} solution for its titration (in acid solution). Calculate the % of Mn and % of Cr in the steel sample.

Q.6 25 ml from a stock solution containing $NaHCO_3$ and Na_2CO_3 was diluted to 250 ml with CO_2 free distilled water. 25 ml of the diluted solution when titrated with 0.12 MHCl required 8 ml., when phenolphthalein was used as an indicator. When 20 ml of diluted solution was titrated with same acid it required 18 ml when methly orange was used as an indicator. Calculate concentration of $NaHCO_3$ in the stock solution in gm/litre and in mole / litre. To 100 ml of the stock solution how much NaOH should be added so that all bicarbonate will be converted into carbonate?

Q.7 1.16 g $CH_3(CH_2)_n$ COOH was burnt in excess air and the resultant gases (CO_2 and H_2O) were passed through excess NaOH solution. The resulting solution was divided in two equl parts. One part requires 50 mL of 1 N HCl for neutralization using phenolphthalein as indicator. Another part required 80 mL of 1N HCl for neutralization using methyl orange as indicator. Find the value of n and the amount of excess NaOH solution taken initially

Q.8 A 2.50g sample containing As_2O_5 and Na_2HAsO_3, and inert material is dissolved and the pH is adjusted to neutral with excess $NaHCO_3$. The As(III) is titrated with 0.150 M I_2 solution, requiring 11.3 mL to just reach the end point. Then, the solution (all the arsenic in the +5 state now) is acidified with HCl, excess KI is added, and the liberated I_2 is titrated with 0.120 M $Na_2S_2O_3$, requiring 41.2 mL. Calculate the per cent As_2O_5 and Na_2HAsO_3 in the sample?

Q.9 A 0.141g sample of a phosphorus containing compound was digested in a mixture of HNO_3 and H_2SO_4 which resulted in formation of CO_2, H_2O and H_3PO_4. Addition of ammonium molybdate yielded a solid having the composition $(NH_4)_3\ PO_4.\ 12\ MoO_3$. The precipitate was filtered , washed and dissolved in 50.0 mL of 0.20 M NaOH :

$$(NH_4)_3PO_4\ .\ 12\ MoO_3\ (s)\ +26OH^- \rightarrow HPO_4^{2-} + 12MoO_4^{2-} + 14H_2O + 3NH_3(g)$$

After boiling the solution to remove the NH_3, the excess NaOH was titrated with 14.1 mL of 0.174M HCl. Calculate the percent of phosphorus in the sample.

Q.10 An accurately weighed 3.15 gm of $H_2C_2O_4 \cdot 2H_2O$ was dissolved in water to make 500 ml solution. A warmed 20ml of this solution acidified with H_2SO_4 required 18ml of a $KMnO_4$ solution for complete oxidation. Then 10ml solution containing 1g ion / litre of Fe^{2+} & Fe^{3+} together free from Cl^- ions or other ions which interfere in $KMnO_4$ titration, was diluted 10 fold with water. 20 ml of this diluted solution required 9.5 ml of the above $KMnO_4$ solution for complete oxidation in H_2SO_4 medium. Determine the amount of Fe^{3+} ion in gm/litre of original solution.

Q.11 A 1.65 gm sample of FeS_2 was oxidized by excess oxygen & the products were SO_2 and Fe^{2+}. The SO_2 gas produced was passed through an acidified solution of 40ml $Ba(MnO_4)_2$ produced SO_4^{--} & Mn^{2+}. The excess permagnate was diluted to 100 ml & 10 ml of it was treated with excess KI & iodine produced req. 0.05 M 5 ml hypo solution producing $S_4O_6^{2-}$. In a separate titration the 25 ml of same solution of permagnate under alkaline condition when treated with KI produced I_2 that required 20 ml of 0.05 M hypo solution producing $S_4O_6^{2-}$ & Mn^{6+}. Calculate the % of FeS_2 in the sample.

Q.12 30cc of a solution containing 9.15gm of a salt $K_XH_Y(C_2O_4)_Z \cdot nH_2O$ per litre required 27cc of 0.12 N NaOH for neutralization. The same quantity of solution was also found to require 36cc of 0.12 N $KMnO_4$ solution for complete oxidation. Calculate X, Y, Z and n.

Q.13 Reducing sugars are sometimes characterized by a number R_{Cu}, which is defined as the number of mg of copper reduced by 1 gm of sugar, in which half reaction for the copper is

$$Cu^{2+} + OH^{-} \longrightarrow Cu_2O + H_2O$$

It is sometimes more convenient to determine the reducing power of a carbohydrate by an indirect method. In this method 43.2 mg of the carbohydrate was oxidized by an excess of $K_3(Fe(CN)_6)$. The $Fe(CN)_6^{4-}$ formed in this reaction required 5.29 ml of 0.0345 N $Ce(SO_4)_2$ for reoxidation to $Fe(CN)_6^{3-}$. Determine the R_{Cu} value for the sample.

Q.14 12.0 g of an impure sample of arsenious oxide (acting as acidic oxide) was dissolved in water containing 7.5g of sodium bicarbonate and resulting solution was diluted to 250 ml. 25 ml of this solution was completely oxidized by 22.4 ml of a solution of iodine. 25ml of this iodine solution reacted with same volume of a solution containing 24.8g of hydrated sodium thiosulphate ($Na_2S_2O_3 \cdot 5H_2O$) in one litre. Calculate the percentage of arsenious oxide in the sample. Also report the % purity of $NaHCO_3$.

EXERCISE IV

Q.1 A 5.0 cm^3 solution of H_2O_2 liberates 0.508g of iodine from an acidified KI solution. Calculate the strength of H_2O_2 solution in terms of volume strength at STP. **[JEE' 1995]**

Q.2 A 3.00g sample containing Fe_3O_4, Fe_2O_3 and an inert impure substance, is treated with excess of KI solution in presence of dilute H_2SO_4. The entire iron is converted into Fe^{2+} along with the liberation of iodine. The resulting solution is diluted to 100 ml. A 20 ml of the diluted solution require 11.0 ml of 0.5 M $Na_2S_2O_3$ solution to reduce the iodine present. A 50 ml of the diluted solution, after complete extraction of the iodine requires 12.80 ml of 0.25 M $KMnO_4$ solution in dilute H_2SO_4 medium for the oxidation of Fe^{2+}. Calculate the percentages of Fe_2O_3 and Fe_3O_4 in the original sample. **[JEE'96, 5]**

Q.3 The number of moles of $KMnO_4$ that will be needed to react completely with one mole of ferrous oxalate in acid solution is **[JEE 1996]**

(A) 3/5 (B) 2/5 (C) 4/5 (D) 1

Q.4 The number of moles of $KMnO_4$ that will be needed to react with one mole of sulphite ions in acidic solution is **[JEE 1997]**

(A) 2/5 (B) 3/5 (C) 4/5 (D) 1

Q.5 One litre of a mixture of O_2 and O_3 at NTP was allowed to react with an excess of acidified solution of KI. The iodine liberated required 40 ml of M/10 sodium thiosulphate solution for titration. What is the percent of ozone in the mixture? Ultraviolet radiation of wavelength 300 nm can decompose ozone. Assuming that one photon can decompose one ozone molecule, how many photons would have been required for the complete decomposition of ozone in the original mixture? **[JEE'97, 5]**

Q.6 A sample of hard water contains 96 ppm of SO_4^{2-} and 183 ppm of HCO_3^-, with Ca^{2+} as the only cation. How many moles of CaO will be required to remove HCO_3^- from 1000 kg of this water? If 1000 kg of this water is treated with the amount of CaO calculate above, what will be the conentration (in ppm) of residual Ca^{2+} ions (Assume $CaCO_3$ to be completely insoluble in water)? If the Ca^{2+} ions in one litre of the treated water are completely exchanged with hydrogen ions, what will be its pH (one ppm means one part of the substance in one million part of water, weight/ weights)? **[JEE' 1997]**

Q.7 An aqueous solution containing 0.10g KIO_3 (formula wt. = 214.0) was treated with an excess of KI solution. The solution was acidified with HCl. The liberated I_2 consumed 45.0 ml of thiosulphate solution to decolourise the blue starch – iodine complex. Calculate the molarity of the sodium thiosulphate solution. **[JEE' 1998]**

Q.8 How many millilitre of 0.5 M H_2SO_4 are needed to dissolve 0.5 gm of copper II carbonate? **[JEE' 1999]**

Q.9 The normality of 0.3 M phosphorus acid (H_3PO_3) is **[JEE 1999]**

(A) 0.1 (B) 0.9 (C) 0.3 (D) 0.6

Q.10 One mole of calciums phosphide on reaction with excess of water gives **[JEE 1999]**

(A) one mole of phosphine (B) Two moles of phsophoric acid

(C) Two moles of phosphine (D) One mole of phosphorus pentoxide

Q.11 An aqueous solution of 6.3 gm of oxalic acid dihydrate is made upto 250 ml. The volume of 0.1 N NaOH required to completely neutralize 10 ml of this solution is **[JEE 2001]**

(A) 40 ml (B) 20 ml (C) 10 ml (D) 4 ml

Q.12 In the standarization of $Na_2S_2O_3$ using $K_2Cr_2O_7$ by iodometry the equivalent mass of $K_2Cr_2O_7$ is

(A) $\frac{\text{M. Mass}}{2}$ (B) $\frac{\text{M. Mass}}{6}$ (C) $\frac{\text{M. Mass}}{3}$ (D) Same as M. Mass.

[JEE 2001]

Q.13 Hydrogen peroxide solution (20 mL) reacts quantitatively with a solution of $KMnO_4$ (20 mL) acidified with dilute H_2SO_4. The same volume of the $KMnO_4$ solution is just decolorized by 10mL of $MnSO_4$ in neutral medium simultaneously forming a dark brown precipitate of hydrated MnO_2. The brown precipitate is dissolved in 10mL of 0.2M sodium oxalate under boiling condition in the presence of dilute H_2SO_4. Write the balanced equations involved in the reactions and calculate the molarity of H_2O_2.

[JEE' 2001]

ANSWER KEY

EXERCISE I (A)

Q.1

1.	6.02×10^{23}	2.	2×10^{-3} mol	3.	36 ml	4.	4.48 L
5.	Laws of conservation of mass			6.	16 gm	7.	GAM
8.	1/3	9.	14.2 gm	10.	44 g mol^{-1}	11.	4.13 g
12.	44.8 L	13.	24.3	14.	A_2B	15.	Conservation of mass
16.	0.4	17.	0.1	18.	M/2	19.	0.1168
20.	12	21.	3.3125 g	22.	50	23.	5
24.	0.4 M	25.	S_8				

Q.2

1.	False	2.	False	3.	False	4.	True
5.	True	6.	True	7.	False	8.	False
9.	True	10.	True	11.	True	12.	False
13.	True	14.	True	15.	False	16.	False
17.	False	18.	True	19.	True	20.	False
21.	False	22.	True	23.	False	24.	False
25.	True						

EXERCISE I (B)

Acid Base Titration

Q.1	KOH = 35%, $Ca(OH)_2$ = 65%			Q.2	V = 157.8 ml	Q.3	20.72 %
Q.4	V = 25 mL	Q.5	200 mL	Q.6	$MgCO_3$ = 52.02%, $CaCO_3$ = 47.98 %		
Q.7	83.33						

Double titration

Q.8	0.424 gm; 0.21gm	Q.9	23.2 gm, 22.28gm			Q.10	0.06gm; .0265gm
Q.11	4.24 g/L; 5.04 g/L	Q.12	39.85%; 60.15%				

Redox Titration

Q.13	+ 3	Q.14	zero	Q.15	V = 31.68 ml	Q.16	0.588 N
Q.17	337 mL	Q.18	41.53%	Q.19	6.07 ≈ 6	Q.20	0.15 N
Q.21	$H_2C_2O_4 . 2H_2O$ = 14.35%, $KHC_2O_4 . H_2O$ = 81.71%						

Back Titration

Q.22	1.406%	Q.23	90.1%	Q.24	27.27%	Q.25	0.1281 g
Q.26	$MgCO_3$= 52.02% , $CaCO_3$= 47.98%			Q.27	0.174g; 3.48%		

EXERCISE II

Q.1 76.15% Q.2 Al = 0.546 g; Mg = 0.454 g Q.3 51.64%

Q.4 1.09×10^{-3} gm Q.5 FeO = 13.34%; Fe_2O_3 = 86.66% Q.6 20 ml; 40 ml; 20 ml

Q.7 $SCN^- + 3I_2 + 4H_2O \rightleftharpoons SO_4^{2-} + HCN + 7H^+ + 6I^-$, 15.4%

Q.8 –1 Q.9 7.93 mg/ml Q.10 30.55kg, 6 electrons

Q.11 5g Q.12 15.68% chromite

Q.13 $V_{KIO_3} = 0.42$ mL, [HCl] = 0.02N Q.14 57.4% CuS, 42.6% Cu_2S

Q.15 4.67L Q.16 0.06 g Q.17 1.75%

Q.18 (i) 33.33%, (ii) 33.33%, (iii) 0.8g Q.19 CuS = 57.3 % Q.20 42.6 %

Q.21 pyrite : 0.06 %; S = 0.032% Q.22 40.77% Q.23 59.16%

Q.24 (i) 38.13% , (ii) 6

EXERCISE III

Q.1 0.12 mg H_2S/L, 0.718×10^{-3} mg SO_2/L Q.2 10.1% Q.3 41.6%

Q.4 ClO_3^-/Cl^- = 1, 1.5% moisture by mass Q.5 Cr = 2.821%, Mn = 1.498%

Q.6 26.2 g / lit , 0.312 M , 1.248 g Q.7 n = 4, NaOH = 6.4 g

Q.8 3.57 mass% As_2O_5 and 11.52 mass% Na_2HAsO_3

Q.9 6.38% Q.10 26.474 gm Q.11 10%

Q.12 X = 1, Y = 3, Z = 2, n = 2 Q.13 $R_{Cu} = 269$

Q.14 As_2O_3 = 9.24%; $NaHCO_3$ = 37.63 %

EXERCISE IV

Q.1 4.48 % Q.2 Fe_2O_3 = 49.33%, Fe_3O_4 = 34.8% Q.3 A

Q.4 A Q.5 6.57% O_3(by weight), 1.2×10^{21} photons

Q.6 1.5, 40 ppm, pH = 2.6989 Q.7 0.0623M Q.8 8.097 ml

Q.9 D Q.10 C Q.11 A Q.12 B

Q.13 0.1M

BANSAL CLASSES

PHYSICS

TARGET IIT JEE 2007
XI (PQRS)

CALORIMETRY & HEAT TRANSFER

CONTENTS

THERMAL EXPANSION

Definition of Heat :

Heat is a form of energy which is transferred between a system and its surrounding as a result of temperature difference only.

Thermal Expansion : Expansion due to increase in temperature.

1. Type of thermal expansion

	Coefficient of expansion	For temperature change Δt change in
(i) Linear	$\alpha = \lim_{\Delta t \to 0} \frac{1}{l_0}\frac{\Delta l}{\Delta t}$	length $\Delta l = l_0 \alpha \Delta t$
(ii) Superficial	$\beta = \lim_{\Delta t \to 0} \frac{1}{A_0}\frac{\Delta A}{\Delta t}$	Area $\Delta A = A_0 \beta \Delta t$
(iii) Volume	$\gamma = \lim_{\Delta t \to 0} \frac{1}{V_0}\frac{\Delta V}{\Delta t}$	volume $\Delta V = V_0 \gamma \Delta t$

(a) For isotropic solids $\alpha_1 = \alpha_2 = \alpha_3 = \alpha$ (let)
so $\beta = 2\alpha$ and $\gamma = 3\alpha$

(b) For anisotropic solids $\beta = \alpha_1 + \alpha_2$ and $\gamma = \alpha_1 + \alpha_2 + \alpha_3$
Here α_1, α_2 and α_3 are coefficient of linear expansion in X, Y and Z directions.

2. ***Variation in density :*** With increase of temperature volume increases so density decreases and vice-versa.

$$d = \frac{d_0}{(1 + \gamma \Delta t)}$$

For solids values of γ are generally small so we can write $d = d_0(1 - \gamma \Delta t)$ (using bimomial expansion)

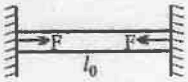
Note :

(i) γ for liquids are in order of 10^{-3}

(ii) For water density increases from 0 to 4°C so γ is –ve (0 to 4° C) and for 4° C to higher temperature γ is +ve. At 4° C density is maximum.

3. ***Thermal Stress :*** A rod of length l_0 is clamped between two fixed walls with distance l_0. If temperature is changed by amount Δt then

stress $= \frac{F}{A}$ (area assumed to be constant)



strain $= \frac{\Delta l}{l_0}$

so, $$Y = \frac{F/A}{\Delta l/l_0} = \frac{F l_0}{A \Delta l} = \frac{F}{A \alpha \Delta t}$$

or $$F = Y A \alpha \Delta t$$

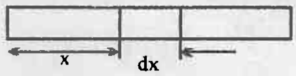
4. ***If α is not constant***

(i) (α varies with distance) Let $\alpha = ax+b$

Total expansion = $\int$ *expansion of length dx* $= \int_0^l (ax+b)dx\,\Delta t$

(ii) (α varies with tempearture)

Let $\alpha = f(T)$



$$\Delta l = \int_{T_1}^{T_2} \alpha\, l_0\, dT$$

Caution : If α is in °C then put T_1 and T_2 in °C.
similarly if α is in K then put T_1 and T_2 in K.

CALORIMETRY

Quantity of heat transfered and specific heat

The amount of heat needed to incerase the temperature of 1 gm of water from 14.5° C to 15.5°C at STP is 1 calorie

$dQ = mcdT$

$Q = m\int_{T_1}^{T_2} C\,dT$ (be careful about unit of temperature, use units according to the given units of C)

Heat transfer in phase change

$Q = mL$ L = latent heat of substance in cal/ gm/ °C or in Kcal/ kg/ °C

L_{ice} = 80 cal/ gm for ice

L_{steam} = 540 cal/ gm

HEAT - TRANSFER

(A) ***Conduction :*** Due to vibration and collision of medium particles.

(i) ***Steady State :*** In this state heat absorption stops and temperature gradient throughout the rod becomes constant i.e. $\frac{dT}{dx}$ = constant.

(ii) ***Before steady state :*** Temp of rod at any point changes

Note : If specific heat of any substance is zero, it can be considered always in steady state.

1. ***Ohm's law for Thermal Conduction in Steady State :***

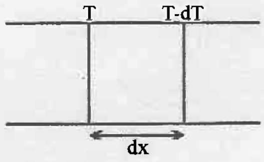
Let the two ends of rod of length l is maintained at temp T_1 and T_2($T_1 > T_2$)

Thermal current $\frac{dQ}{dT} = \frac{T_1 - T_2}{R_{Th}}$

Where thermal resistance $R_{Th} = \frac{l\;l}{K\,A}$

2. ***Differential form of Ohm's Law***

$\frac{dQ}{dT} = KA\frac{dT}{dx}$ $\frac{dT}{dx}$ = temperature gradient



(B) ***Convection :*** Heat transfer due to movement of medium particles.

(C) ***Radiation:*** Every body radiates electromagnetic radiation of all possible wavelength at all temp>0 K.

1. ***Stefan's Law :*** Rate of heat emitted by a body at temp T K from per unit area $E = \sigma T^4$ J/sec/m^2

Radiation power $\quad \dfrac{dQ}{dT} = P = \sigma A T^4$ watt

If a body is placed in a surrounding of temperature T_S

$$\frac{dQ}{dT} = \sigma A (T^4 - T_s^{\,4})$$

valid only for black body

Emissivity or emmisive power $\quad e = \dfrac{\text{heat from general body}}{\text{heat from black body}}$

If temp of body falls by dT in time dt

$$\frac{dT}{dt} = \frac{eA\sigma}{mS}(T^4 - T_s^4) \qquad \text{(dT/dt = rate of cooling)}$$

2. ***Newton's law of cooling***

If temp difference of body with surrounding is small i.e. $T = T_s$

then, $\quad \dfrac{dT}{dt} = \dfrac{4eA\sigma}{mS} T_s^3 (T - T_s)$

so $\quad \dfrac{dT}{dt} \;\alpha\; (T - T_s)$

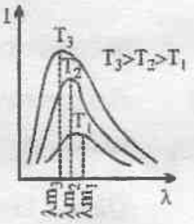
3. ***Average form of Newtons law of cooling***

If a body cools from T_1 to T_2 in time δt

$$\frac{T_1 - T_2}{\delta t} = \frac{K}{mS}\left(\frac{T_1 + T_2}{2} - T_s\right) \qquad \text{(used generally in objective questions)}$$

$$\frac{dT}{dt} = \frac{K}{mS}(T - T_s) \qquad \text{(for better results use this generally in subjective)}$$

4. ***Wein's black body radiation***



At every temperature (>0K) a body radiates energy radiations of all wavelengths. According to Wein's displacement law if the wavelength corresponding to maximum energy is λ_m.

then $\lambda_m T = b$ where b = is a constant (Wein's constant)

T = temperature of body

EXERCISE – I

Q.1 An aluminium container of mass 100 gm contains 200 gm of ice at – 20°C. Heat is added to the system at the rate of 100 cal/s. Find the temperature of the system after 4 minutes (specific heat of ice = 0.5 and L = 80 cal/gm, specific heat of A*l* = 0.2 cal/gm/°C)

Q.2 A U-tube filled with a liquid of volumetric coefficient of 10^{-5}/°C lies in a vertical plane. The height of liquid column in the left vertical limb is 100 cm. The liquid in the left vertical limb is maintained at a temperature = 0°C while the liquid in the right limb is maintained at a temperature = 100°C. Find the difference in levels in the two limbs.

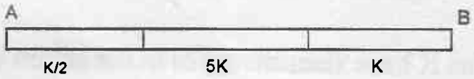
Q.3 A thin walled metal tank of surface area $5m^2$ is filled with water tank and contains an immersion heater dissipating 1 kW. The tank is covered with 4 cm thick layer of insulation whose thermal conductivity is 0.2 W/m/K. The outer face of the insulation is 25°C. Find the temperature of the tank in the steady state

Q.4 A glass flask contains some mercury at room temperature. It is found that at different temperatures the volume of air inside the flask remains the same. If the volume of mercury in the flask is 300 cm^3, then find volume of the flask (given that coefficient of volume expansion of mercury and coefficient of linear expansion of glass are $1.8 \times 10^{-4}\,(°C)^{-1}$ and $9 \times 10^{-6}\,(°C)^{-1}$ respectively)

Q.5 A clock pendulum made of invar has a period of 0.5 sec at 20°C. If the clock is used in a climate where average temperature is 30°C, aporoximately. How much fast or slow will the clock run in 10^6 sec. ($\alpha_{invar} = 1 \times 10^{-6}/°C$)

Q.6 A pan filled with hot food cools from 50.1 °C to 49.9 °C in 5 sec. How long will it take to cool from 40.1 °C to 39.9°C if room temperature is 30°C?

Q.7 A composite rod made of three rods of equal length and cross-section as shown in the fig. The thermal conductivities of the materials of the rods are K/2, 5K and K respectively. The end A and end B are at constant temperatures. All heat entering the face A goes out of the end B there being no loss of heat from the sides of the bar. Find the effective thermal conductivity of the bar

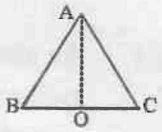


Q.8 An iron bar (Young's modulus = 10^{11} N/m^2 , $\alpha = 10^{-6}$ /°C) 1 m long and 10^{-3} m^2 in area is heated from 0°C to 100°C without being allowed to bend or expand. Find the compressive force developed inside the bar.

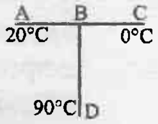
Q.9 A solid copper cube and sphere, both of same mass & emissivity are heated to same initial temperature and kept under identical conditions. What is the ratio of their initial rate of fall of temperature?

Q.10 A cylindrical rod with one end in a stream chamber and other end in ice cause melting of 0.1 gm of ice/sec. If the rod is replaced with another rod of half the length and double the radius of first and thermal conductivity of second rod is 1/4 that of first, find the rate of ice melting in gm/sec

Q.11 Three aluminium rods of equal length form an equilateral triangle ABC. Taking O (mid point of rod BC) as the origin. Find the increase in Y-coordinate per unit change in temperature of the centre of mass of the system. Assume the length of the each rod is 2m, and $\alpha_{al} = 4\sqrt{3}\times10^{-6}$ /°C



Q.12 Three conducting rods of same material and cross-section are shown in figure. Temperature of A, D and C are maintained at 20°C, 90°C and 0°C. Find the ratio of length BD and BC if there is no heat flow in AB

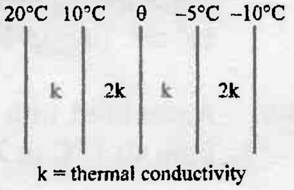


Q.13 If two rods of layer L and 2 L having coefficients of linear expansion α and 2α respectively are connected so that total length becomes 3 L, determine the average coefficient of linear expansion of the composite rod.

Q.14 A volume of 120 ml of drink (half alcohol + half water by mass) originally at a temperature of 25°C is cooled by adding 20 gm ice at 0°C. If all the ice melts, find the final temperature of the drink. (density of drink = 0.833 gm/cc, specific heat of alcohol = 0.6 cal/gm/°C)

Q.15 A solid receives heat by radiation over its surface at the rate of 4 kW. The heat convection rate from the surface of solid to the surrounding is 5.2 kW, and heat is generated at a rate of 1.7 kW over the volume of the solid. The rate of change of the average temperature of the solid is 0.5°Cs^{-1}. Find the heat capacity of the solid.

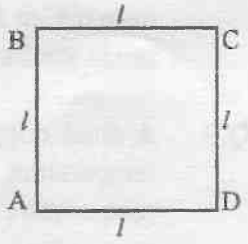
Q.16 The figure shows the face and interface temperature of a composite slab containing of four layers of two materials having identical thickness. Under steady state condition, find the value of temperature θ.



Q.17 Two identical calorimeter A and B contain equal quantity of water at 20°C. A 5 gm piece of metal X of specific heat 0.2 cal g^{-1} (C°)$^{-1}$ is dropped into A and a 5 gm piece of metal Y into B. The equilibrium temperature in A is 22°C and in B 23°C. The initial temperature of both the metals is 40°C. Find the specific heat of metal Y in cal g^{-1} (C°)$^{-1}$.

Q.18 Two spheres of same radius R have their densities in the ration 8 : 1 and the ratio of their specific heats are 1 : 4. If by radiation their rates of fall of temperature are same, then find the ratio of their rates of losing heat.

Q.19 In the square frame of side *l* of metallic rods, the corners A and C are maintained at T_1 and T_2 respectively. The rate of heat flow from A to C is ω. If A and D are instead maintained T_1 & T_2 respectivley find, find the total rate of heat flow.



Q.20 A hot liquid contained in a container of negligible heat capacity loses temperature at rate 3 K/min, just before it begins to solidify. The temperature remains constant for 30 min. Find the ratio of specific heat capacity of liquid to specific latent heat of fusion is in K^{-1} (given that rate of losing heat is constant).

Q.21 A thermostatted chamber at small height h above earth's surface maintained at 30°C has a clock fitted in it with an uncompensated pendulum. The clock designer correctly designs it for height h, but for temperature of 20°C. If this chamber is taken to earth's surface, the clock in it would click correct time. Find the coefficient of linear expansion of material of pendulum. (earth's radius is R)

Q.22 The coefficient of volume expansion of mercury is 20 times the coefficient of linear expansion of glass. Find the volume of mercury that must be poured into a glass vessel of volume V so that the volume above mercury may remain constant at all temperature.

Q.23 Two 50 gm ice cubes are dropped into 250 gm of water ion a glass. If the water was initially at a temperature of 25°C and the temperature of ice –15°C. Find the final temperature of water. (specific heat of ice = 0.5 cal/gm/°C and L = 80 cal/gm)

Q.24 Water is heated from 10°C to 90°C in a residential hot water heater at a rate of 70 litre per minute. Natural gas with a density of 1.2 kg/m³ is used in the heater, which has a transfer efficiency of 32%. Find the gas consumption rate in cubic meters per hour. (heat combustion for natural gas is 8400 kcal/kg)

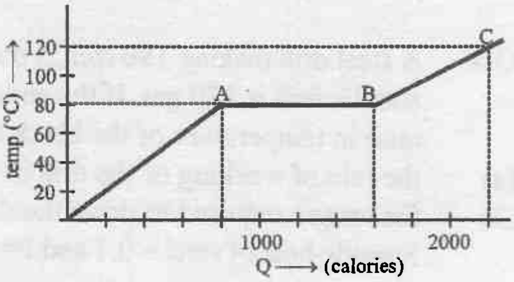
Q.25 A metal rod A of 25cm lengths expands by 0.050cm. When its temperature is raised from 0°C to 100°C. Another rod B of a different metal of length 40cm expands by 0.040 cm for the same rise in temperature. A third rod C of 50cm length is made up of pieces of rods A and B placed end to end expands by 0.03 cm on heating from 0°C to 50°C. Find the lengths of each portion of the composite rod.

Q.26 A substance is in the solid form at 0°C. The amount of heat added to this substance and its temperature are plotted in the following graph. If the relative specific heat capacity of the solid substance is 0.5, find from the graph

(i) the mass of the substance ;

(ii) the specific latent heat of the melting process, and

(iii) the specific heat of the substance in the liquid state.



Q.27 One end of copper rod of uniform cross-section and of length 1.5 meters is in contact with melting ice and the other end with boiling water. At what point along its length should a temperature of 200°C be maintained, so that in steady state, the mass of ice melting is equal to that of steam produced in the same interval of time? Assume that the whole system is insulated from the surroundings.

Q.28 Two solids spheres are heated to the same temperature and allowed to cool under identical conditions. Compare: (i) initial rates of fall of temperature, and (ii) initial rates of loss of heat. Assume that all the surfaces have the same emissivity and ratios of their radii of, specific heats and densities are respectively 1 : α, 1 : β, 1 : γ.

Q.29 A vessel containing 100 gm water at 0°C is suspended in the middle of a room. In 15 minutes the temperature of the water rises by 2°C. When an equal amount of ice is placed in the vessel, it melts in 10 hours. Calculate the specific heat of fusion of ice.

Q.30 The maximum in the energy distribution spectrum of the sun is at 4753 Å and its temperature is 6050K. What will be the temperature of the star whose energy distribution shows a maximum at 9506 Å.

EXERCISE – II

Q.1 A copper calorimeter of mass 100 gm contains 200 gm of a mixture of ice and water. Steam at 100°C under normal pressure is passed into the calorimeter and the temperature of the mixture is allowed to rise to 50°C. If the mass of the calorimeter and its contents is now 330 gm, what was the ratio of ice and water in the beginning? Neglect heat losses.
Given : Specific heat capacity of copper = 0.42×10^3 J kg^{-1}K^{-1},
Specific heat capacity of water = 4.2×10^3 J kg^{-1}K^{-1},
Specific heat of fusion of ice = 3.36×10^5 J kg^{-1}
Latent heat of condensation of steam = 22.5×10^5 Jkg^{-1}

Q.2 An isosceles triangle is formed with a rod of length l_1 and coefficient of linear expansion α_1 for the base and two thin rods each of length l_2 and coefficient of linear expansion α_2 for the two pieces, if the distance between the apex and the midpoint of the base remain unchanged as the temperatures varied show that $\frac{l_1}{l_2} = 2\sqrt{\frac{\alpha_2}{\alpha_1}}$.

Q.3 A solid substance of mass 10 gm at – 10°C was heated to – 2°C (still in the solid state). The heat required was 64 calories. Another 880 calories was required to raise the temperature of the substance (now in the liquid state) to 1°C, while 900 calories was required to raise the temperature from –2°C to 3°C. Calculate the specific heat capacities of the substances in the solid and liquid state in calories per kilogram per kelvin. Show that the latent heat of fusion L is related to the melting point temperature t_m by $L = 85400 + 200\, t_m$.

Q.4 A steel drill making 180 rpm is used to drill a hole in a block of steel. The mass of the steel block and the drill is 180 gm. If the entire mechanical work is used up in producing heat and the rate of raise in temperature of the block and the drill is 0.5 °C/s. Find
(a) the rate of working of the drill in watts, and
(b) the torque required to drive the drill.
Specific heat of steel = 0.1 and J = 4.2 J/cal. Use : $P = \tau\omega$

Q.5 A brass rod of mass m = 4.25 kg and a cross sectional area 5 cm^2 increases its length by 0.3 mm upon heating from 0°C. What amount of heat is spent for heating the rod? The coefficient of linear expansion for brass is 2×10^{-5}/K, its specific heat is 0.39 kJ/kg.K and the density of brass is 8.5×10^3 kg/m^3.

Q.6 A submarine made of steel weighing 10^9 g has to take 10^8 g of water in order to submerge when the temperature of the sea is 10°C. How much less water it will have to take in when the sea is at 15°C? (Coefficient of cubic expansion of sea water = 2×10^{-4}/°C, coefficient of linear expansion of steel = 1.2×10^{-5}/°C)

Q.7 A flow calorimeter is used to measure the specific heat of a liquid. Heat is added at a known rate to a stream of the liquid as it passes through the calorimeter at a known rate. Then a measurement of the resulting temperature difference between the inflow and the outflow points of the liquid stream enables us to compute the specific heat of the liquid. A liquid of density 0.2 g/cm^3 flows through a calorimeter at the rate of 10 cm^3/s. Heat is added by means of a 250-W electric heating coil, and a temperature difference of 25°C is established in steady-state conditions between the inflow and the outflow points. Find the specific heat of the liquid.

Q.8 Toluene liquid of volume 300 cm^3 at 0°C is contained in a beaker an another quantity of toluene of volume 110 cm^3 at 100°C is in another beaker. (The combined volume is 410 cm^3). Determine the total volume of the mixture of the toluene liquids when they are mixed together. Given the coefficient of volume expansion $\gamma = 0.001/C$ and all forms of heat losses can be ignored. Also find the final temperature of the mixture.

Q.9 Ice at -20°C is filled upto height $h = 10$ cm in a uniform cylindrical vessel. Water at temperature θ°C is filled in another identical vessel upto the same height $h = 10$ cm. Now, water from second vessel is poured into first vessel and it is found that level of upper surface falls through $\Delta h = 0.5$ cm when thermal equilibrium is reached. Neglecting thermal capacity of vessels, change in density of water due to change in temperature and loss of heat due to radiation, calculate initial temperature θ of water.

Given,	Density of water,	$\rho_w = 1$ gm cm^{-3}
	Density of ice,	$\rho_i = 0.9$ gm/cm^3
	Specific heat of water,	$s_w = 1$ cal/gm °C
	Specific heat of ice,	$s_i = 0.5$ cal/gm°C
	Specific latent heat of ice,	$L = 80$ cal/gm

Q.10 A composite body consists of two rectangular plates of the same dimensions but different thermal conductivities K_A and K_B. This body is used to transfer heat between two objects maintained at different temperatures. The composite body can be placed such that flow of heat takes place either parallel to the interface or perpendicular to it. Calculate the effective thermal conductivities $K_{||}$ and $K_{\perp}$ of the composite body for the parallel and perpendicular orientations. Which orientation will have more thermal conductivity?

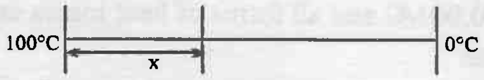
Q.11 Two identical thermally insulated vessels, each containing n mole of an ideal monatomic gas, are interconnected by a rod of length l and cross-sectional area A. Material of the rod has thermal conductivity K and its lateral surface is thermally insulated. If, at initial moment ($t = 0$), temperature of gas in two vessels is T_1 and T_2 ($< T_1$), neglecting thermal capacity of the rod, calculate difference between temperature of gas in two vessels as a function of time.

Q.12 A highly conducting solid cylinder of radius a and length l is surrounded by a co-axial layer of a material having thermal conductivity K and negligible heat capacity. Temperature of surrounding space (out side the layer) is T_0, which is higher than temperature of the cylinder. If heat capacity per unit volume of cylinder material is s and outer radius of the layer is b, calculate time required to increase temperature of the cylinder from T_1 to T_2. Assume end faces to be thermally insulated.

Q.13 A vertical brick duct(tube) is filled with cast iron. The lower end of the duct is maintained at a temperature T_1 which is greater than the melting point T_m of cast iron and the upper end at a temperature T_2 which is less than the temperature of the melting point of cast iron. It is given that the conductivity of liquid cast iron is equal to k times the conductivity of solid cast iron. Determine the fraction of the duct filled with molten metal.

Q.14 Water is filled in a non-conducting cylindrical vessel of uniform cross-sectional area. Height of water column is h_0 and temperature is 0°C. If the vessel is exposed to an atmosphere having constant temperature of $-\theta$°C ($<$ 0°C) at $t = 0$, calculate total height h of the column at time t. Assume thermal conductivity of ice to be equal to K. Density of water is ρ_ω and that of ice is ρ. Latent heat of fusion of ice is L.

Q.15 A lagged stick of cross section area 1 cm^2 and length 1 m is initially at a temperature of 0°C. It is then kept between 2 reservoirs of tempeature 100°C and 0°C. Specific heat capacity is 10 J/kg°C and linear mass density is 2 kg/m. Find



(a) temperature gradient along the rod in steady state.
(b) total heat absorbed by the rod to reach steady state.

Q.16 A cylindrical block of length 0.4 m an area of cross-section $0.04 m^2$ is placed coaxially on a thin metal disc of mass 0.4 kg and of the same cross-section. The upper face of the cylinder is maintained at a constant temperature of 400K and the initial temperature of the disc is 300K. If the thermal conductivity of the material of the cylinder is 10 watt/m-K and the specific heat of the material of the disc in 600 J/kg-K, how long will it take for the temperature of the disc to increase to 350K? Assume, for purposes of calculation, the thermal conductivity of the disc to be very high and the system to be thermally insulated except for the upper face of the cylinder.

Q.17 A copper calorimeter of negligible thermal capacity is filled with a liquid. The mass of the liquid equals 250 gm. A heating element of negligible thermal capacity is immersed in the liquid. It is found that the temperature of the calorimeter and its contents rises from 25°C to 30°C in 5 minutes when a current of 20.5 ampere is passed through it at potential difference of 5 volts. The liquid is thrown off and the heater is again switched on. It is now found that the temperature of the calorimeter alone is constantly maintained at 32°C when the current through the heater is 7A at the potential difference 6 volts. Calculate the specific heat capacity of the liquid. The temperature of the surroundings is 25°C.

Q.18 A solid copper sphere cools at the rate of 2.8°C per minute, when its temperature is 127°C. Find the rate at which another solid copper sphere of twice the radius lose its temperature at 327°C, if in both the cases, the room temperature is maintained at 27°C.

Q.19 A calorimeter contains 100 cm^3 of a liquid of density 0.88 g/cm^3 in which are immersed a thermometer and a small heating coil. The effective water equivalent of calorimeter, thermometer and heater may be taken to be 13 gm. Current of 2 A is passed through the coil. The potential difference across the coil is 6.3 V and the ultimate steady state temperature is 55°C. The current is increased so that the temperature rises slightly above 55°C, and then it is switched off. The calorimeter and the content are found to cool at the rate of 3.6°C/min.
(a) Find the specific heat of the liquid.
(b) The room temperature during the experiment was 10°C. If the room temperature rises to 26°C, find the current required to keep the liquid at 55°C. You may assume that Newton's law is obeyed and the resistance of the heater remains constant.

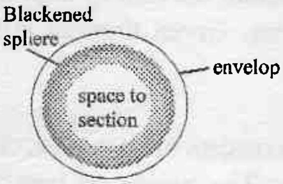
Q.20 End A of a rod AB of length L = 0.5 m and of uniform cross-sectional area is maintained at some constant temperature. The heat conductivity of the rod is k = 17 J/s-m°K. The other end B of this rod is radiating energy into vacuum and the wavelength with maximum energy density emitted from this end is $\lambda_0 = 75000$ Å. If the emissivity of the end B is e = 1, determine the temperature of the end A. Assuming that except the ends, the rod is thermally insulated.

Q.21 A wire of length 1.0 m and radius 10^{-3} m is carrying a heavy current and is assumed to radiate as a blackbody. At equilibrium temperature of wire is 900 K while that of the surroundings is 300 K. The resistivity of the material of the wire at 300 K is $\pi^2 \times 10^{-8}$ Ω-m and its temperature coefficient of resistance is 7.8×10^{-3} /°C. Find the current in the wire. [$\sigma \simeq 5.68 \times 10^{-8}$ w/m^2K^4].

Q.22 The temperature distribution of solar radiation is more or less same as that of a black body whose maximum emission corresponds to the wavelength 0.483 μm. Find the rate of change of mass due to radiation. [Radius of Sun = 7.0 × 10^8 m]

Q.23 A black plane surface at a constant high temperature T_h, is parallel to another black plane surface at constant lower temperature T_l. Between the plates is vacuum. In order to reduce the heat flow due to radiation, a heat shield consisting of two thin black plates, thermally isolated from each other, it placed between the warm and the cold surfaces and parallel to these. After some time stationary conditions are obtained. By what factor η is the stationary heat flow reduced due to the presence of the heat shield? Neglect end effects due to the finite size of the surfaces.

Q.24 The shell of a space station is a blackened sphere in which a temperature T = 500K is maintained due to operation of appliances of the station. Find the temperature of the shell if the station is enveloped by a thin spherical black screen of nearly the same radius as the radius of the shell.



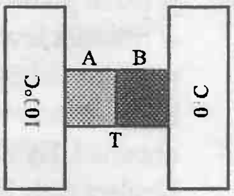
Q.25 A liquid takes 5 minutes to cool from 80°C to 50°C. How much time will it take to cool from 60°C to 30°C ? The temperature of surrounding is 20°C. Use exact method.

Q.26 Find the temperature of equilibrium of a perfectly black disc exposed normally to the Sun's ray on the surface of Earth. Imagine that it has a nonconducting backing so that it can radiate only to hemisphere of space. Assume temperature of surface of Sun = 6200 K, radius of sun = 6.9 × 10^8 m, distance between the Sun and the Earth = 1.5 × 10^{11} m. Stefan's constant = 5.7 × 10^{-8} W/m^2.K^4. What will be the temperature if both sides of the disc are radiate?

EXERCISE – III

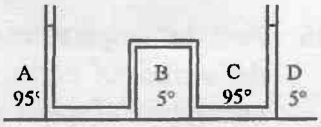
Q.1 The temperature of 100 gm of water is to be raised from 24° C to 90° C by adding steam to it. Calculate the mass of the steam required for this purpose. [JEE '96]

Q.2 Two metal cubes A & B of same size are arranged as shown in figure. The extreme ends of the combination are maintained at the indicated temperatures. The arrangement is thermally insulated. The coefficients of thermal conductivity of A & B are 300 W/m° C and 200 W/m° C respectively. After steady state is reached the temperature T of the interface will be ______. [JEE' 96]



Q.3 A double pane window used for insulating a room thermally from outside consists of two glass sheets each of area 1 m^2 and thickness 0.01 m separated by a 0.05m thick stagnant air space. In the steady state, the room glass interface and the glass outdoor interface are at constant temperatures of 27^0C and 0^0C respectively. Calculate the rate of heat flow through the window pane. Also find the temperatures of other interfaces. Given thermal conductivities of glass and air as 0.8 and 0.08 W $m^{-1}K^{-1}$ respectively. [JEE'97]

Q.4 The apparatus shown in the figure consists of four glass columns connected by horizontal sections. The height of two central columns B & C are 49 cm each. The two outer columns A & D are open to the atmosphere. A & C are maintained at a temperature of 95° C while the columns B & D are maintained at 5° C. The height of the liquid in A & D measured from the base line are 52.8 cm & 51 cm respectively. Determine the coefficient of thermal expansion of the liquid. [JEE '97]



Q.5 A spherical black body with a radius of 12 cm radiates 450 W power at 500 K. If the radius were halved and the temperature doubled, the power radiated in watt would be :
(A) 225 (B) 450 (C) 900 (D) 1800

Q.6 Earth receives 1400 W/m^2 of solar power. If all the solar energy falling on a lens of area 0.2 m^2 is focussed on to a block of ice of mass 280 grams, the time taken to melt the ice will be ______ minutes. (Latent heat of fusion of ice = 3.3 x 10^5 J/kg) [JEE '97]

Q.7 A solid body X of heat capacity C is kept in an atmosphere whose temperature is T_A = 300K. At time t = 0, the temperature of X is T_0 = 400K. It cools according to Newton's law of cooling. At time t_1 its temperature is found to be 350K. At this time t_1, the body X is connected to a larger body Y at atmospheric temperature T_A, through a conducting rod of length L, cross-sectional area A and thermal conductivity K. The heat capacity of Y is so large that any variation in its temperature may be neglected. The cross-sectional area A of the connecting rod is small compared to the surface area of X. Find the temperature of X at time t = $3t_1$. [JEE' 98]

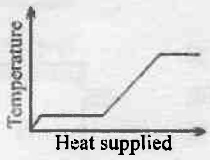
Q.8 A black body is at a temperature of 2880 K. The energy of radiation emitted by this object with wavelength between 499 nm and 500 nm is U_1, between 999 nm and 1000 nm is U_2 and between 1499 nm and 1500 nm is U_3. The Wien constant b = 2.88 × 10^6 nm K. Then [JEE' 98]
(A) $U_1 = 0$ (B) $U_3 = 0$ (C) $U_1 > U_2$ (D) $U_2 > U_1$

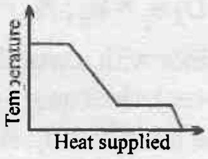
Q.9 A bimetallic strip is formed out of two identical strips one of copper and the other of brass. The coefficient of linear expansion of the two metals are α_C and α_B. On heating, the temperature of the strip goes up by ΔT and the strip bends to form an arc of radius of curvature R. Then R is :

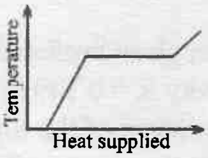
(A) proportional at ΔT (B) inversely proportional to ΔT [JEE' 99]

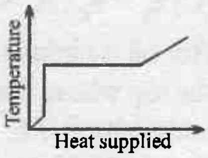
(C) proportional to $|\alpha_B - \alpha_C|$ (D) inversely proportional to $|\alpha_B - \alpha_C|$

Q.10 A block of ice at – 10°C is slowly heated and converted to steam at 100°C. Which of the following curves represents the phenomenon qualitatively? [JEE (Scr) 2000]

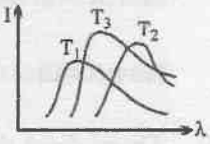
(A) 

(B) 

(C) 

(D) 

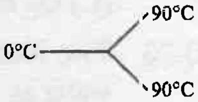
Q.11 The plots of intensity versus wavelength for three black bodies at temperature T_1, T_2 and T_3 respectively are as shown. Their temperatures are such that [JEE (Scr) 2000]



(A) $T_1 > T_2 > T_3$ (B) $T_1 > T_3 > T_2$

(C) $T_2 > T_3 > T_1$ (C) $T_3 > T_2 > T_1$

Q.12 Three rods made of the same material and having the same cross-section have been joined as shown in the figure. Each rod is of the same length. The left and right ends are kept at 0°C and 90°C respectively. The temperature of the junction of the three rods will be [JEE(Scr)2001]



(A) 45°C (B) 60°C (C) 30°C (D) 20°C

Q.13 An ideal black body at room temperature is thrown into a furnace. It is observed that

(A) initially it is the darkest body and at later times the brightest.

(B) it the darkest body at all times

(C) it cannot be distinguished at all times.

(D) initially it is the darkest body and at later times it cannot be distinguished. [JEE(Scr)2002]

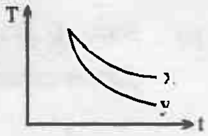
Q.14 An ice cube of mass 0.1 kg at 0°C is placed in an isolated container which is at 227°C. The specific heat S of the container varies with temperature T according the empirical relations = A + BT, where A = 100 cal/kg-K and B = 2×10^{-2} cal/kg-K^2. If the final temperature of the container is 27°C, determine the mass of the container. (Latent heat of fusion for water = 8×10^4 cal/kg. Specific heat of water = 10^3 cal/kg-K) [JEE' 2001]

Q.15 Two rods one of aluminium of length l_1 having coefficient of linear expansion α_a, and other steel of length l_2 having coefficient of linear expansion α_s are joined end to end. The expansion in both the rods is same on variation of temperature. Then the value of $\frac{l_1}{l_1 + l_2}$ is [JEE' (Scr) 2003]

(A) $\frac{\alpha_s}{\alpha_a + \alpha_s}$ (B) $\frac{\alpha_s}{\alpha_a - \alpha_s}$ (C) $\frac{\alpha_a + \alpha_s}{\alpha_s}$ (D) None of these

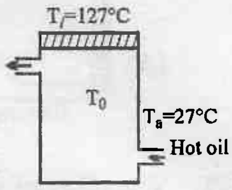
Q.16 2 kg ice at – 20°C is mixed with 5 kg water at 20°C. Then final amount of water in the mixture would be; Given specific heat of ice = 0.5cal/g°C, specific heat of water = 1 cal/g°C, Latent heat of fusion of ice = 80 cal/g. [JEE' (Scr) 2003]
(A) 6 kg (B) 5 kg (C) 4 kg (D) 2 kg

Q.17 If emissivity of bodies X and Y are e_x and e_y and absorptive power are A_x and A_y then [JEE' (Scr) 2003]



(A) $e_y > e_x$; $A_y > A_x$ (B) $e_y < e_x$; $A_y < A_x$
(C) $e_y > e_x$; $A_y < A_x$ (D) $e_y = e_x$; $A_y = A_x$

Q.18 Hot oil is circulated through an insulated container with a wooden lid at the top whose conductivity K = 0.149 J/(m-°C-sec), thickness t = 5 mm, emissivity = 0.6. Temperature of the top of the lid in steady state is at T_l = 127°. If the ambient temperature T_a = 27°C. Calculate



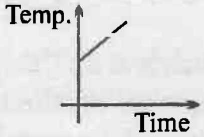
(a) rate of heat loss per unit area due to radiation from the lid.

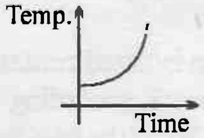
(b) temperature of the oil. (Given $\sigma = \frac{17}{3} \times 10^{-8}$) [JEE' 2003]

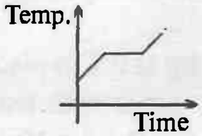
Q.19 Three discs A, B, and C having radii 2 m, 4 m and 6 m respectively are coated with carbon black on their outer surfaces. The wavelengths corresponding to maximum intensity are 300 nm, 400 nm and 500 nm respectively. The power radiated by them are Q_A, Q_B and Q_C respectively.
(a) Q_A is maximum (B) Q_B is maximum [JEE' 2004 (Scr.)]
(C) Q_C is maximum (D) $Q_A = Q_B = Q_C$

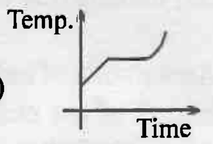
Q.20 Two identical conducting rods are first connected independently to two vessels, one containing water at 100°C and the other containing ice at 0° C. In the second case, the rods are joined end to end and connected to the same vessels. Let q_1 and q_2 g/s be the rate of melting of ice in the two cases respectively. The ratio q_2/q_1 is
(A) 1/2 (B) 2/1 (C) 4/1 (D) 1/4 [JEE' 2004 (Scr.)]

Q.21 Liquid oxygen at 50 K is heated to 300 K at constant pressure of 1 atm. The rate of heating is constant. Which of the following graphs represents the variation of temperature with time?

(A)


(B)


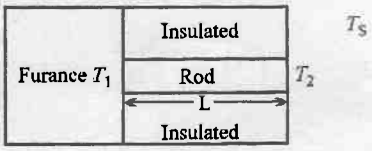
(C)


(D)


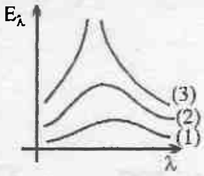
[JEE' 2004 (Scr.)]

Q.22 A cube of coefficient of linear expansion α_s is floating in a bath containing a liquid of coefficient of volume expansion γ_l. When the temperature is raised by ΔT, the depth upto which the cube is submerged in the liquid remains the same. Find the relation between α_s and γ_l, showing all the steps. [JEE 2004]

Q.23 One end of a rod of length L and cross-sectional area A is kept in a furnace of temperature T_1. The other end of the rod is kept at a temperature T_2. The thermal conductivity of the material of the rod is K and emissivity of the rod is e. It is given that $T_2 = T_S + \Delta T$ where $\Delta T << T_S$, T_S being the temperature of the surroundings. If $\Delta T \propto (T_1 - T_S)$, find the proportionality constant. Consider that heat is lost only by radiation at the end where the temperature of the rod is T_2. [JEE 2004]



Q.24 Three graphs marked as 1, 2, 3 representing the variation of maximum emissive power and wavelength of radiation of the sun, a welding arc and a tungsten filament. Which of the following combination is correct



(A) 1-bulb, 2 → welding arc, 3 → sun
(B) 2-bulb, 3 → welding arc, 1 → sun
(C) 3-bulb, 1 → welding arc, 2 → sun
(D) 2-bulb, 1 → welding arc, 3 → sun

[JEE' 2005 (Scr)]

Q.25 In which of the following phenomenon heat convection does not take place
(A) land and sea breeze
(B) boiling of water
(C) heating of glass surface due to filament of the bulb
(D) air around the furance

[JEE' 2005 (Scr)]

Q.26 2 litre water at 27°C is heated by a 1 kW heater in an open container. On an average heat is lost to surroundings at the rate 160 J/s. The time required for the temperature to reach 77°C is
(A) 8 min 20 sec (B) 10 min (C) 7 min (D) 14 min

[JEE' 2005 (Scr)]

Q.27 A spherical body of area A, and emissivity e = 0.6 is kept inside a black body. What is the rate at which energy is radiated per second at temperature T
(A) $0.6\,\sigma AT^4$ (B) $0.4\,\sigma AT^4$ (C) $0.8\,\sigma AT^4$ (D) $1.0\,\sigma AT^4$

[JEE' 2005 (Scr)]

Q.28 1 calorie is the heat required to increased the temperature of 1 gm of water by 1°C from
(A) 13.5°C to 14.5°C at 76 mm of Hg (B) 14.5°C to 15.5°C at 760 mm of Hg
(C) 0°C to 1°C at 760 mm of Hg (D) 3°C to 4°C to 760 mm of Hg

[JEE' 2005 (Scr)]

ANSWER KEY

EXERCISE –I

Q.1 25.5°C   Q.2 0.1 cm   Q.3 65°C   Q.4 2000 cm^3

Q.5 5 sec slow   Q.6 10 sec   Q.7 15K/16   Q.8 10, 000 N

Q.9 $\left(\frac{6}{\pi}\right)^{1/3}$ Q.10 0.2   Q.11 4×10^{-6} m/°C

Q.12 7/2   Q.13 $5\alpha/3$ Q.14 4°C   Q.15 1000 J $(C°)^{-1}$

Q.16 5°C   Q.17 27/85   Q.18 2 : 1   Q.19 (4/3) ω

Q.20 1/90   Q.21 h/5R   Q.22 3V / 20   Q.23 0 °C

Q.24 104.2   Q.25 10cm , 40cm   Q.26 (i)0.02kg,(ii) 40,000calkg^{-1},(iii)750cal$kg^{-1}K^{-1}$

Q.27 10.34 cm   Q.28 $\alpha\beta\gamma : 1 ; 1 : \alpha^2$ Q.29 80 k cal/kg   Q.30 3025 K

EXERCISE – II

Q.1 1 : 1.26   Q.3 800 cal kg^{-1} K^{-1}, 1000 cal kg^{-1} K^{-1}

Q.4 (a) 37.8 J/s (Watts), (b) 2.005 N-m   Q.5 25 kJ   Q.6 9.02×10^5 gm

Q.7 5000 J/°C kg   Q.8 decrease by 0.75 cm^3, 25°C   Q.9 45°C

Q.10 $K_{11} > K_{\perp}$, $K_{\parallel} = \frac{K_A + K_B}{2}$, $K_{\perp} = \frac{2K_AK_B}{K_A + K_B}$ Q.11 $(T_1 - T_2)e^{-\left(\frac{4KAt}{3nR\ell}\right)}$

Q.12 $\frac{a^2 s}{2K}\log_e\left(\frac{b}{a}\right)\log_e\left(\frac{T_0 - T_1}{T_0 - T_2}\right)$ Q.13 $\frac{l_1}{l} = \frac{k(T_1 - T_m)}{k(T_1 - T_m) + (T_m - T_2)}$

Q.14 $h_0 + \left(1 - \frac{\rho_i}{\rho_w}\right)\sqrt{\frac{2k_i\theta t}{\rho_i L_f}}$ Q.15 (a) 100 °C/m, (b) 1000 J   Q.16 166.3 sec

Q.17 21000 $Jkg^{-1}K^{-1}$ Q.18 9.72°C/min   Q.19 (a)0.42 cal/gm°C, (b) 1.6A

Q.20 $T_A = 423$ K   Q.21 36 A   Q.22 $\frac{dm}{dt} = 5.06 \times 10^9$ kg/s

Q.23 $\eta = 3$ Q.24 $T'' = \sqrt[4]{2} \times 500 = 600$ K

Q.25 10 minutes   Q.26 $T_0 = 420$ K, $T_0 = 353.6$ K

EXERCISE – III

Q.1 12 gm   Q.2 60° C   Q.3 41.53 Watt; 26.48 °C ; 0.55°C

Q.4 2×10^{-4} C   Q.5 D   Q.6 5.5 min

Q.7 $k = \frac{\log_e 2}{t_1}$; $T = 300 + 50 \exp.\left[-\left\{\frac{KA}{LC} + \frac{\log_e 2}{t_1}\right\}2t_1\right]$

Q.8 D   Q.9 B, D   Q.10 A   Q.11 B   Q.12 B   Q.13 D   Q.14 0.5 kg

Q.15 A   Q.16 A   Q.17 A   Q.18 (a) 595 watt/m^2, (b) $T_0 \approx 420$ K   Q.19 B

Q.20 D   Q.21 C   Q.22 $\gamma_l = 2\alpha_s$ Q.23 $\frac{K}{4e\sigma L T_S^3 + K}$ Q.24 A

Q.25 C   Q.26 A   Q.27 A   Q.28 B

BANSAL CLASSES

PHYSICS

TARGET IIT JEE 2007
XI (PQRS)

QUESTION BANK ON

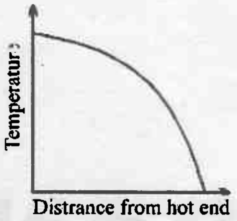
CALORIMETRY & HEAT TRANSFER

Time Limit : 2 Sitting Each of 90 minutes. duration approx.

Objective Question Bank On Heat

There are 58 questions in this question bank.

Q.1 The ends of a long bar are maintained at different temperatures and there is no loss of heat from the sides of the bar due to conduction or radiation. The graph of temperature against distance of the bar when it has attained steady state is shown here. The graph shows



(A) the temperature gradient is not constant
(B) the bar has uniform cross–sectional area
(C) the cross–sectional area of the bar increases as the distance from the hot end increases
(D) the cross–sectional area of the bar decreases as the distance from the hot end increases.

Q.2 One end of a 2.35m long and 2.0cm radius aluminium rod ($K = 235\ W.m^{-1}K^{-1}$) is held at 20°C. The other end of the rod is in contact with a block of ice at its melting point. The rate in $kg.s^{-1}$ at which ice melts is
(A) $48\pi \times 10^{-6}$ (B) $24\pi \times 10^{-6}$ (C) $2.4\pi \times 10^{-6}$ (D) $4.8\pi \times 10^{-6}$

[Take latent heat of fusion for ice as $\frac{10}{3} \times 10^5 J.kg^{-1}$]

Q.3 The power radiated by a black body is P and it radiates maximum energy around the wavelength λ_0. If the temperature of the black body is now changed so that it radiates maximum energy around wavelength $3/4\lambda_0$, the power radiated by it will increase by a factor of
(A) 4/3 (B) 16/9 (C) 64/27 (D) 256/81

Q.4 A rod of length L with sides fully insulated is of a material whose thermal conductivity varies with temperature as $K = \frac{\alpha}{T}$, where α is a constant. The ends of the rod are kept at temperature T_1 and T_2. The temperature T at x, where x is the distance from the end whose temperature is T_1 is
(A) $T_1\left(\frac{T_2}{T_1}\right)^{\frac{x}{L}}$ (B) $\frac{x}{L} ln \frac{T_2}{T_1}$ (C) $T_1 e^{\frac{T_2 x}{T_1 L}}$ (D) $T_1 + \frac{T_2 - T_1}{L} x$

Q.5 Equal masses of three liquids A, B and C have temperatures 10°C, 25°C and 40°C respectively. If A and B are mixed, the mixture has a temperature of 15°C. If B and C are mixed, the mixture has a temperature of 30°C,. If A and C are mixed the mixture will have a temperature of
(A) 16°C (B) 20°C (C) 25°C (D) 29°C

Q.6 A volume of 120 ml of drink (half alcohol + half water by mass) originally at a temperature of 25°C is cooled by adding 20 gm ice at 0°C. If all the ice melts, the final temperature of the drink is : (density of drink = 0.833 gm/cc, specific heat of alcohol = 0.6 cal/gm/°C)
(A) 4°C (B) 5°C (C) 0°C (D) 6°C

Q.7 A clock pendulum made of invar has a period of 0.5 sec at 20°C. If the clock is used in a climate where average temperature is 30°C, approximately how much fast or slow will the clock run in 10^6 sec. [$\alpha_{invar} = 1 \times 10^{-6}/°C$]
(A) 5 sec fast (B) 10 sec fast (C) 10 sec slow (D) 5 sec slow

Q.8 An aluminium container of mass 100 gm contains 200 gm of ice at – 20°C. Heat is added to the system at the rate of 100 cal/s. The temperature of the system after 4 minutes will be (specific heat of ice = 0.5 and L = 80 cal/gm, specific heat of Al = 0.2 cal/gm/°C)
(A) 40.5°C (B) 25.5°C (C) 30.3°C (D) 35.0°C

Q.9 A black metal foil is warmed by radiation from a small sphere at temperature 'T' and at a distance 'd'. It is found that the power received by the foil is P. If both the temperature and distance are doubled, the power received by the foil will be :
(A) 16 P (B) 4 P (C) 2 P (D) P

Q.10 A steel tape gives correct measurement at 20°C. A piece of wood is being measured with the steel tape at 0°C. The reading is 25 cm on the tape, the real length of the given piece of wood must be:
(A) 25 cm (B) <25 cm (C) >25 cm (D) can not say

Q.11 A rod of length 20 cm is made of metal. It expands by 0.075 cm when its temperature is raised from 0°C to 100°C. Another rod of a different metal B having the same length expands by 0.045 cm for the same change in temperature, a third rod of the same length is composed of two parts one of metal A and the other of metal B. Thus rod expand by 0.06 cm.for the same change in temperature. The portion made of metal A has the length :
(A) 20 cm (B) 10 cm (C) 15 cm (D) 18 cm

Q.12 A crystal has a coefficient of expansion 13×10^{-9} in one direction and 231×10^{-9} in every direction at right angles to it. Then the cubical coefficient of expansion is :
(A) 4.62×10^{-7} (B) 2.44×10^{-7} (C) 4.75×10^{-7} (D) 2.57×10^{-7}s

Q.13 Star S_1 emits maximum radiation of wavelength 420 nm and the star S_2 emits maximum radiation of wavelength 560 nm, what is the ratio of the temperature of S_1 and S_2 :
(A) 4/3 (B) $(4/3)^{1/4}$ (C) 3/4 (D) $(3/4)^{1/2}$

Q.14 If 1 gm water requires x heat to boil to steam at 100°C, and 1 gm water requires y heat to evaporate completely at 0°C, then
(A) $x > y$ (B) $x = y$ (C) $x < y$ (D) $y = 0$

Q.15 A container is filled with water at 4°C. At one time the temperature is increased by few degrees above 4°C and at another time it is decreased by few degrees below 4°C. One shall observe that:
(A) the level remains constant in each case
(B) water overflows in both the cases
(C) water overflows in the latter case, while come down in the previous case
(D) in previous case water overflows while in later case its levels comes down

Q.16 Spheres P and Q are uniformly constructed from the same material which is a good conductor of heat and the radius of Q is thrice the radius of P. The rate of fall of temperature of P is x times that of Q when both are at the same surface temperature. The value of x is :
(A) 1/4 (B) 1/3 (C) 3 (D) 4

Q.17 A sphere of diameter 7 cm and mass 266.5 gm floats in a bath of a liquid. As the temperature is raised, the sphere just begins to sink at a temperature 35°C. If the density of a liquid at 0°C is 1.527 gm/cc, then neglecting the expansion of the sphere, the coefficient of cubical expansion of the liquid is f :
(A) 8.486×10^{-4} per °C (B) 8.486×10^{-5} per °C
(C) 8.486×10^{-6} per °C (D) 8.486×10^{-3} per °C

Q.18 The volume of the bulb of a mercury thermometer at 0°C is V_0 and cross section of the capillary is A_0. The coefficient of linear expansion of glass is as per °C and the cubical expansion of mercury γ_m per °C. If the mercury just fills the bulb at 0°C, what is the length of mercury column in capillary at T°C.
(A) $\frac{V_0T(\gamma_m+3a_g)}{A_0(1+2a_gT)}$ (B) $\frac{V_0T(\gamma_m-3a_g)}{A_0(1+2a_gT)}$ (C) $\frac{V_0T(\gamma_m+2a_g)}{A_0(1+3a_gT)}$ (D) $\frac{V_0T(\gamma_m-2a_g)}{A_0(1+3a_gT)}$

Q.19 A thermally insulated vessel contains some water at 0°C. The vessel is connected to a vacuum pump to pump out water vapour. This results in some water getting frozen. It is given Latent heat of vaporization of water at 0°C = 21×10^5 J/kg and latent heat of freezing of water = 3.36×10^5 J/kg. The maximum percentage amount of water that will be solidified in this manner will be
(A) 86.2% (B) 33.6% (C) 21% (D) 24.36%

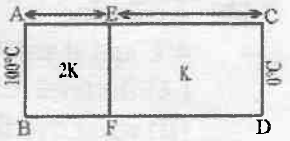
Q.20 A metallic rod 1 cm long with a square cross-section is heated through 1°C. If Young's modulus of elasticity of the metal is E and the mean coefficient of linear expansion is α per degree Celsius, then the compressional force required to prevent the rod from expanding along its length is :
(A) $EA\alpha t$ (B) $EA\alpha t/(1+\alpha t)$ (C) $EA\alpha t/(1-\alpha t)$ (D) $E/\alpha t$

Q.21 Four rods of same material with different radii r and length l are used to connect two reservoirs of heat at different temperatures. Which one will conduct most heat ?
(A) r = 2cm, l = 0.5m (B) r = 2cm, l = 2m (C) r = 0.5cm, l = 0.5m (D) r = 1 cm, l = 1 m

Q.22 A cylinder of radius R made of a material of thermal conductivity k_1 is surrounded by a cylindrical shell of inner radius R and outer radius 2R made of a material of thermal conductivity k_2. The two ends of the combined system are maintained at different temperatures. There is no loss of heat from the cylindrical surface and the system is in steady state. The effective thermal conductivity of the system is
(A) $k_1 + k_2$ (B) $\frac{k_1k_2}{k_1+k_2}$ (C) $\frac{1}{4}(k_1+3k_2)$ (D) $\frac{1}{4}(3k+k_2)$

Q.23 The loss in weight of a solid when immersed in a liquid at 0°C is W_0 and at t°C is W. If cubical coefficient of expansion of the solid and the liquid by γ_s and γ_1 respectively, then W is equal to :
(A) $W_0[1+(\gamma_s-\gamma_l)t]$ (B) $W_0[1-(\gamma_s-\gamma_l)t]$
(C) $W_0[(\gamma_s-\gamma_l)t]$ (D) $W_0t/(\gamma_s-\gamma_l)$

Q.24 Heat is conducted across a composite block of two slabs of thickness d and 2d. Their thermal conductivities are 2k and k respectively. All the heat entering the face AB leaves from the face CD. The temperature in °C of the junction EF of the two slabs is :
(A) 20 (B) 50 (C) 60 (D)80



Q.25 A thin walled cylindrical metal vessel of linear coefficient of expansion 10^{-3} °C^{-1} contains benzenr of volume expansion coefficient 10^{-3}°C^{-1}. If the vessel and its contents are now heated by 10°C, the pressure due to the liquid at the bottom.
(A) increases by 2% (B) decreases by 1% (C) decreases by 2% (D) remains unchanged

Q.26 A rod of length 2m at 0°C and having expansion coefficient $\alpha = (3x+2)\times10^{-6}$°C^{-1} where x is the distance (in cm) from one end of rod. The length of rod at 20°C is :
(A) 2.124 m (B) 3.24 m (C) 2.0124 m (D) 3.124 m

Q.27 A copper ring has a diameter of exactly 25 mm at its temperature of 0°C. An aluminium sphere has diameter of exactly 25.05 mm at its temperature of 100°C. The sphere is placed on top of the ring ar two are allowed to come to thermal equilibrium, no heat being lost to the surrounding. The sphere just passes through the ring at the equilibrium temperature. The ratio of the mass of the sphere & ring is :
(given : $\alpha_{Cu} = 17\times10^{-6}$/°C, $\alpha_{Al} = 2.3\times10^{-5}$/°C, specific heat of Cu = 0.0923 Cal/g°C and specific heat of Al = 0.215 cal/g°C)
(A) 1/5 (B) 23/108 (C) 23/54 (D) 216/23

Q.28 A black body radiates radiation at temperature 727°C the maximum density of energy radiation E_m. Another identical body radiates at temperature 1727°C & the maximum density of rod is E_{2m} then E_m/E_{2m} is
(A) 1/8 (B) 1/16 (C) 1/32 (D) 1/64

Q.29 An ice cube at temperature – 20°C is kept in a room at temperature 20°C. The variation of temperature of the body with time is given by

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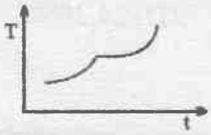

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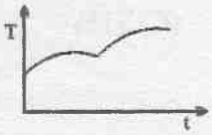

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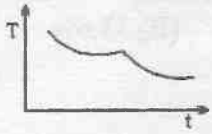

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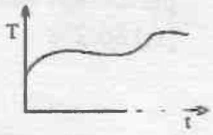
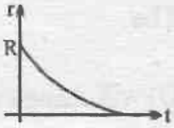


Q.30 A sphere of ice at 0°C having initial radius R is placed in an environment having ambient temperature > 0°C. The ice melts uniformly, such that shape remains spherical. After a time 't' the radius of the sphere has reduced to r. Assuming the rate of energy of outside heat is proportional to the surface area of the sphere at any moment, which graph best depicts r (t).

(A)


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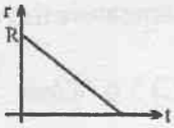
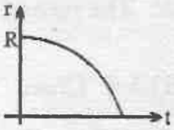


(C)


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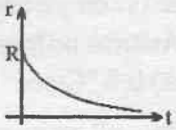
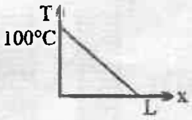
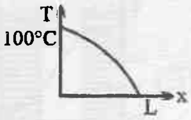


Q.31 A rod of length L and uniform cross-sectional area has varying thermal conductivity which changes linearly from 2K at end A to K at the other end B. The ends A and B of the rod are maintained at constant temperature 100°C and 0°C, respectively. At steady state, the graph of temperature : T = T(x) where x = distance from end A will be

(A)


(B)


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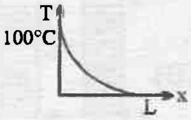
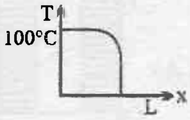
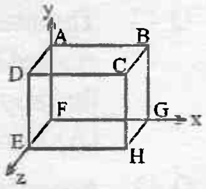


(D)


Q.32 A cuboid ABCDEFGH is anisotropic with $\alpha_x = 1 \times 10^{-5}$ /°C, $\alpha_y = 2 \times 10^{-5}$ /°C, $\alpha_z = 3 \times 10^{-5}$ /°C. Coefficient of superficial expansion of faces can be



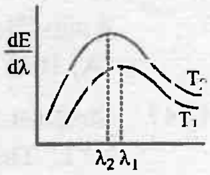
(A) $\beta_{ABCD} = 5 \times 10^{-5}$ /°C
(B) $\beta_{BCGH} = 4 \times 10^{-5}$ /°C
(C) $\beta_{CDEH} = 3 \times 10^{-5}$ /°C
(D) $\beta_{EFGH} = 2 \times 10^{-5}$ /°C

Q.33 An open vessel is filled completely with oil which has same coefficient of volume expansion as that of the vessel. On heating both oil and vessel,
(A) the vessel can contain more volume and more mass of oil
(B) the vessel can contain same volume and same mass of oil
(C) the vessel can contain same volume but more mass of oil
(D) the vessel can contain more volume but same mass of oil

Q.34 A vessel containing a liquid is heated with its contents. The pressure at the bottom of vessel due to the liquid should. (no evaporation take place)
(A) increase
(B) decrease
(C) increases if $\gamma_{liq} > 3\ \alpha_{vessel}$
(D) decreases if $\gamma_{liq} > 3\ \alpha_{vessel}$

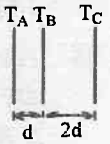
Q.35 A block of mass 2.5 kg is heated to temperature of 500°C and placed on a large ice block. What is the maximum amount of ice that can melt (approx.). Specific heat for the body = 0.1 Cal/gm°C.
(A) 1 kg
(B) 1.5 kg
(C) 2 kg
(D) 2.5 kg

Q.36 The spectral emissive power E_λ for a body at temperature T_1 is plotted against the wavelength and area under the curve is found to be A. At a different temperature T_2 the area is found to be 9A. Then λ_1/λ_2 =



(A) 3
(B) 1/3
(C) $1/\sqrt{3}$
(D) $\sqrt{3}$

Q.37 Two sheets of thickness d and 2 d and same area are touching each other on their face. Temperature T_A, T_B, T_C shown are in geometric progression with common ratio r = 2. Then ratio of thermal conductivity of thinner and thicker sheet are



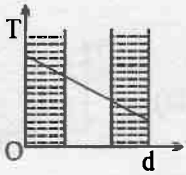
(A) 1
(B) 2
(C) 3
(D) 4

Q.38 The ratio of densities of 2 bodies is 3 : 4 and ratio of their specific heats is 4 : 3. Then ratio of their heat capacity per unit volume is
(A) 1 : 1
(B) 3 : 4
(C) 9 : 16
(D) 16 : 9

Q.39 10 gm of ice at 0°C is kept in a calorimeter of water equivalent 10 gm. How much heat should be supplied to the apparatus to evaporate the water thus formed? (Neglect loss of heat)
(A) 6200 cal (B) 7200 cal (C) 13600 cal (D) 8200 cal

Q.40 Heat is being supplied at a constant rate to a sphere of ice which is melting at the rate of 0.1 gm/sec. It melts completely in 100 sec. The rate of rise of temperature thereafter will be
(Assume no loss of heat.)
(A) 0.8 °C/sec (B) 5.4 °C/sec (C) 3.6 °C/sec (D) will change with time

Q.41 The wall with a cavity consists of two layers of brick separated by a layer of air. All three layers have the same thickness and the thermal conductivity of the brick is much greater than that of air. The left layer is at a higher temperature than the right layer and steady state condition exists. Which of the following graphs predicts correctly the variation of temperature T with distance d inside the cavity?

(A)


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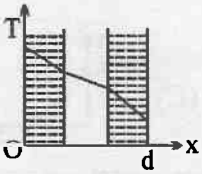
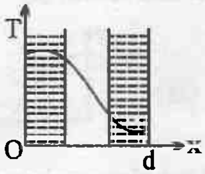
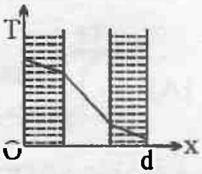


(C)


(D)


Q.42 The intensity of radiation emitted by the Sun has its maximum value at a wavelength of 510 nm and that emitted by the North Star has the maximum value at 350 nm. If these stars behave like black bodies then the ratio of the surface temperature of the Sun and the North Star is
(A) 1.46 (B) 0.69 (C) 1.21 (D) 0.83

Q.43 A metal ball immersed in Alcohol weights W_1 at 0°C and W_2 at 50°C. The coefficient of cubical expansion of the metal $(\gamma)_m$ is less than that of alcohol $(\gamma)_{Al}$. Assuming that density of metal is large compared to that of alcohol, it can be shown that
(A) $W_1 > W_2$ (B) $W_1 = W_2$ (C) $W_1 < W_2$ (D) any of (A), (B) or (C)

Q.44 Two bodies P and Q have thermal emissivities of ε_P and ε_Q respectively. Surface areas of these bodies are same and the total radiant power is also emitted at the same rate. If temperature of P is θ_P kelvin then temperature of Q i.e. θ_Q is
(A) $\left(\frac{\varepsilon_Q}{\varepsilon_P}\right)^{1/4}\theta_P$ (B) $\left(\frac{\varepsilon_P}{\varepsilon_Q}\right)^{1/4}\theta_P$ (C) $\left(\frac{\varepsilon_Q}{\varepsilon_P}\right)^{1/4}\times\frac{1}{\theta_P}$ (D) $\left(\frac{\varepsilon_Q}{\varepsilon_P}\right)^{4}\theta_P$

Q.45 1 kg of ice at – 10°C is mixed with 4.4 kg of water at 30°C. The final temperature of mixture is :
(specific heat of ice is 2100 J/kg/k)
(A) 2.3°C (B) 4.4°C (C) 5.3°C (D) 8.7°C

Q.46 A black body calorimeter filled with hot water cools from 60°C to 80°C in 4 min and 40°C to 30°C in 8 min. The approximate temperature of surrounding is :
(A) 10°C (B) 15°C (C) 20°C (D) 25°C

Q.47 Steam at 100°C is added slowly to 1400 gm of water at 16°C until the temperature of water is raised to 80°C. The mass of steam required to do this is (L_V = 540 cal/gm) :
(A) 160 gm (B) 125 mg (C) 250 gm (D) 320 gm

Q.48 A solid ball is completely immersed in a liquid. The coefficients of volume expansion of the ball and liquid are 3×10^{-6} and 8×10^{-6} per °C respectively. The percentage change in upthrust when the temperature is increased by 100 °C is
(A) 0.5 % (B) 0.11 % (C) 1.1 % (D) 0.05 %

Q.49 A wall has two layer A and B each made of different material, both the layers have the same thickness. The thermal conductivity of the material A is twice that of B. Under thermal equilibrium the temperature difference across the wall B is 36°C. The temperature difference across the wall A is
(A) 6°C (B) 12°C (C) 18°C (D) 72°C

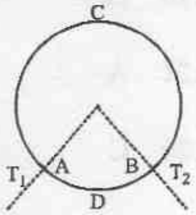
Q.50 The rate of emission of radiation of a black body at 273°C is E, then the rate of emission of radiation of this body at 0°C will be

(A) $\frac{E}{16}$ (B) $\frac{E}{4}$ (C) $\frac{E}{8}$ (D) 0

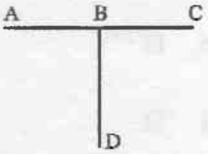
Q.51 A thin copper wire of length L increase in length by 1% when heated from temperature T_1 to T_2. What is the percentage change in area when a thin copper plate having dimensions 2L × L is heated from T_1 to T_2?
(A) 1% (B) 2% (C) 3% (D) 4%

Q.52 A ring consisting of two parts ADB and ACB of same conductivity k carries an amount of heat H. The ADB part is now replaced with another metal keeping the temperatures T_1 and T_2 constant. The heat carried increases to 2H. What should be the conductivity of the new ADB part? Given $\frac{ACB}{ADB} = 3$:

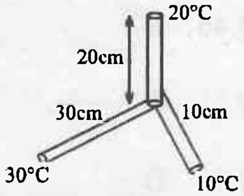
(A) $\frac{7}{3}$k (B) 2 k (C) $\frac{5}{2}$ k (D) 3 k



Q.53 Three conducting rods of same material and cross-section are shown in figure. Temperatures of A, D and C are maintained at 20°C, 90°C and 0°C. The ratio of lengths of BD and BC if there is no heat flow in AB is:
(A) 2 / 7 (B) 7 / 2 (C) 9 / 2 (D) 2 / 9



Q.54 Three rods made of the same material and having same cross-sectional area but different lengths 10cm, 20 cm and 30 cm are joined as shown. The temperature of the joint is:
(A) 20°C (B) 23.7°C (C) 16.4°C (D) 18.2°C

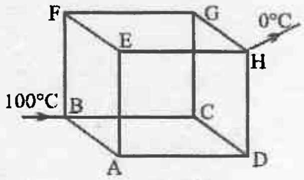


Q.55 If two rods of length L and 2L having coefficients of linear expansion α and 2α respectively are connected so that total length becomes 3L, the average coefficient of linear expansion of the composition rod equals:

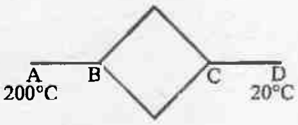
(A) $\frac{3}{2}\alpha$ (B) $\frac{5}{2}\alpha$ (C) $\frac{5}{3}\alpha$ (D) none of these

Q.56 One end of a conducting rod is maintained at temperature 50°C and at the other end, ice is melting at 0°C. The rate of melting of ice is doubled if:
(A) the temperature is made 200°C and the area of cross-section of the rod is doubled
(B) the temperature is made 100°C and length of rod is made four times
(C) area of cross-section of rod is halved and length is doubled
(D) the temperature is made 100°C and the area of cross-section of rod and length both are doubled.

Q.57 Twelve conducting rods form the riders of a uniform cube of side 'l'. If in steady state, B and H ends of the rod are at 100°C and 0°C. Find the temperature of the junction 'A'.
(A) 80°C (B) 60°C (C) 40°C (D) 70°C



Q.58 Six identical conducting rods are joined as shown in figure. Points A and D are maintained at temperature of 200°C and 20°C respectively. The temperature of junction B will be:
(A) 120°C (B) 100°C (C) 140°C (D) 80°C



ANSWER KEY

Q.1	A, D	Q.2	C	Q.3	D	Q.4	A	Q.5	A
Q.6	A	Q.7	D	Q.8	B	Q.9	B	Q.10	B
Q.11	D	Q.12	C	Q.13	A	Q.14	B	Q.15	B
Q.16	C	Q.17	A	Q.18	B	Q.19	A	Q.20	B
Q.21	A	Q.22	C	Q.23	A	Q.24	D	Q.25	C
Q.26	C	Q.27	C	Q.28	C	Q.29	B	Q.30	B
Q.31	B	Q.32	C	Q.33	D	Q.34	B	Q.35	B
Q.36	D	Q.37	A	Q.38	A	Q.39	D	Q.40	A
Q.41	D	Q.42	B	Q.43	C	Q.44	B	Q.45	D
Q.46	B	Q.47	A	Q.48	D	Q.49	C	Q.50	A
Q.51	B	Q.52	A	Q.53	B	Q.54	C	Q.55	C
Q.56	D	Q.57	B	Q.58	C				

BANSAL CLASSES

CHEMISTRY

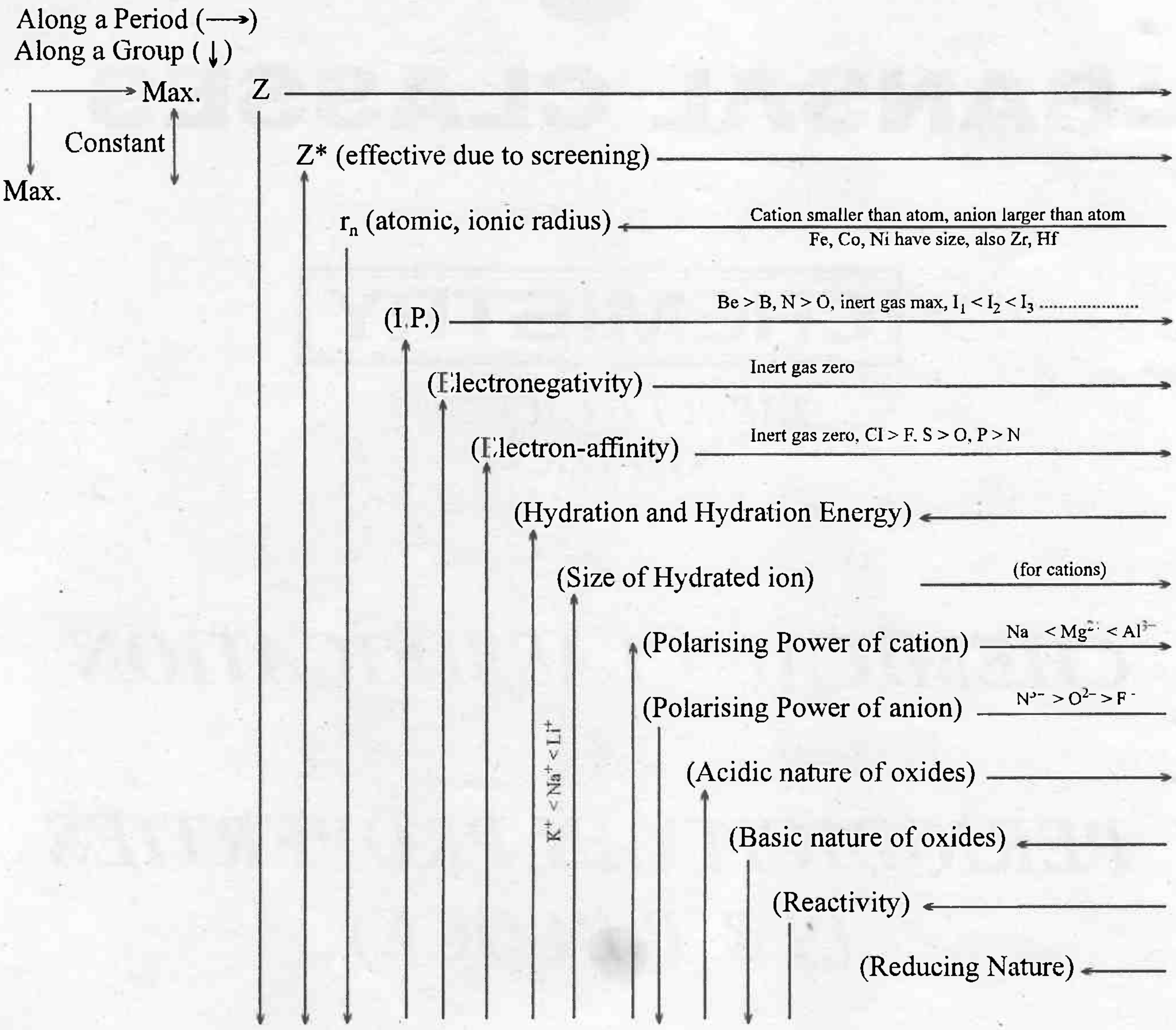
TARGET IIT JEE 2007
XI (P,Q,R,S)

CHEMICAL CLASSIFICATION & PERIODICITY IN PROPERTIES (S & P BLOCK)

Knowledge when not " Classified " or assorted properly is as useless as a book not placed according to the order in a Huge library.

CONTENTS

PERIODICITY



- Isoelectric ions have different size.
- Inert pair effect is in p-block. Stability of higher state decreases and that of lower state increases going along a group. $Ge^{2+} < Sn^{2+} < Pb^{2+}$
- Reducing nature of hydride increases in a group and decreases in a period.

Part–A (Periodic Table)

INTRODUCTION :

Many attempts were made to classify the known elements from time to time . These are :

(i) Proust Hypothesis (ii) Doberniers Triad law (iii) Newlands Octave law
(iv) Lother Meyer's curve (v) Mendeleev Periodic law (vi) Modern periodic law

PERIODIC LAW (1869) :

The physical and chemical properties of elements are periodic functions of their **atomic weight**.

MODERN PERIODIC LAW :

The physical and chemical properties of elements are periodic functions of their **atomic number**.

LONG FORM OF PERIODIC TABLE : [BOHR'S TABLE]

based on modern periodic law and Bohr Burry Scheme of E.C.

CLASSIFICATION OF ELEMENT INTO GROUPS AND PERIODS :

Group A : s and p block elements, representative elements. IA to VII A and O group.
Group B : d and f block elements, transition and inner transition elements IB to VII B and VIII groups.
Total 16 Groups
Period 1 to 7 classified as short, shortest, long, longest and incomplete period.

CLASSIFICATION OF ELEMENTS INTO s , p , d & f BLOCK ELEMENTS :

s – block :

(i) configuration ns^{1-2} **(ii)** last e^- enters in s orbital
(iii) two groups I A or 1 ; II A or 2

p – block :

(i) configuration $ns^2\ np^{1-6}$ **(ii)** last e^- enters in p orbital
(iii) six groups III A, IV A, V A, VI A, VII A, zero or 13, 14, 15, 16, 17, 18

d – block : [Transition Elements]

(i) configuration $ns^{1-2}\ (n-1)\ d^{1-10}$ **(ii)** last e^- enters in d orbital
(iii) their two outermost shell are incomplete
(iv) 10 groups III B , IV B , V B , VI B , VII B , VIII (Triad) , I B , II B or 3 , 4 , 5 , 6 , 7 , (8 , 9 , 10), 11 , 12 .
(v) four series 3 d , 4 d , 5 d , 6 d .

f – block : [Inner Transition]

(i) configuration $ns^2\ (n-1)\ d^{0-1}\ (n-2)\ f^{1-14}$
(ii) last e^- enters in f orbital
(iii) two series 4 f Lanthanides & 5 f Actinides

ESTIMATING POSITION OF AN ELEMENT FROM ITS ELECTRONIC CONFIGURATION:

The last electron enters which subshell gives idea of its block.

[☺ ***Think*** : $1s^1$ and $1s^2$ belongs to which block]

Period no. is equal to the valence shell present in the configuration. Also for s and p block elements.
Period no. = valence shell, for ‘d’ block = shell + 1, for f block = shell + 2 and so on.
Group no. for s and p block = valence shell electron (A)
for d block = d^1 to d^5 [no. of (s + d) electron (B)]
d^6, d^7, d^8 (VIII)
$s^1\ d^9$, d^{10} (IB, IIB)

[☺ **Use these carefully while locating the position.]**

COMMONLY ASKED PROPERTIES :

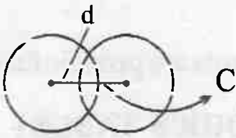
1. *Atomic Volume* : Volume occupied by one gm atom of an element .

$$\text{Atomic volume} = \frac{\text{Atomic weight}}{\text{density}}$$

Lower atomic volume leads to higher density , increased hardness higher melting point, boiling point, less malleability & ductility.

2. *Atomic Radius :* Problem in calculating actual size of atom and hence distance between nuclei is calculated giving rise to three type of radii for atoms.

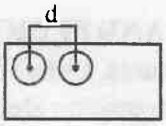
(a) ***Covalent radius :***



$C_r = \frac{d}{2}$ $C_r <$ actual atom size [Slight difference]

[Used for H_2, Cl_2 and such molecules]

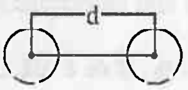
(b) ***Metallic Radius :***



$M_r = \frac{d}{2}$ $M_r >$ actual size [Slight difference]

[Used for metals]

(c) ***Vanderwaal radius :***



$V_r = \frac{d}{2}$ $V_r >>$ actual size [very large difference]

In general $V_R > M_r > C_R$

(d) ***Ionic Radius :*** A cation is smaller than parent atom . An anion is larger than parent atom.

FACTORS AFFECTING ATOMIC SIZE :

(a) 'n' increase size increases

(b) Z_{eff} increase size decrease [$Z_{eff} - Z - \sigma$]

(c) Type of measurement of radii.

Calculation of Z_{eff}

$$Z_{eff} = \sqrt{\frac{En^2}{1312}}$$ where E is I.E. in kJ/mole ; $$Z_{eff} = \sqrt{\frac{E \times n^2}{13.6}}$$ E is I.E. in eV per atom.

or Calculated by *Slaters rule*.

SLATER'S RULE :

(a) For calculating σ on a (s or p) block (other than on 1s)

Rule-1 : Each (ns, nP) electron contribute to a screening factor of 0.35.

Rule-2 : Each $(n-1)^{th}$ shell electron contribute to a screening factor of 0.85.

Rule-3 : Each $(n-2)^{nd}$ and deeper shell electron contribute to a screening factor of 1.

[* On 1s, the screening factor due to other electron is taken as 0.3]

(b) For calculating σ on (d or f) block.

Rule-1 : Each screening causing electron (d and f only) of same shell has factor of 0.35.

Rule-2 : Each electron other than *Rule*-1 have screening factor of 1.

General Trend :

Along a period, size decrease ['n' constant, $Z_{eff} \uparrow$]

Along a group, size increase ['n' increasing, Z_{eff} constant]

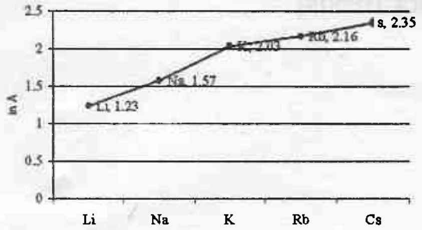
Exceptions :

(1) Noble gases have largest atomic sizes [Vander waal radii]. However, their covalent radii are smaller *e.g.* Xe.

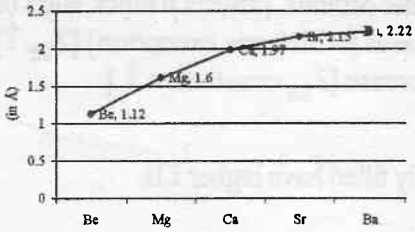
(2) Size of Ga and Al are same, [Z_{eff} increasing]

ATOMIC RADIUS

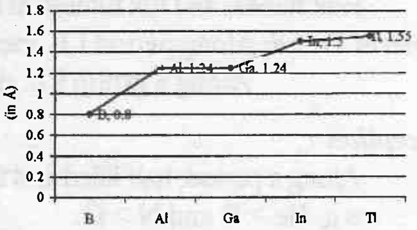
ALKALI METALS



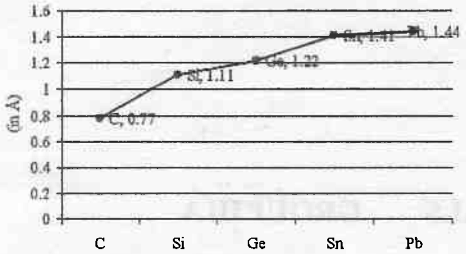
ALKALINE EARTH METALS



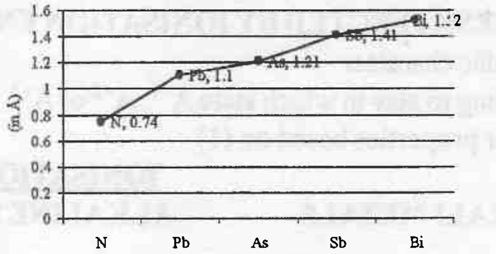
GROUP III-A



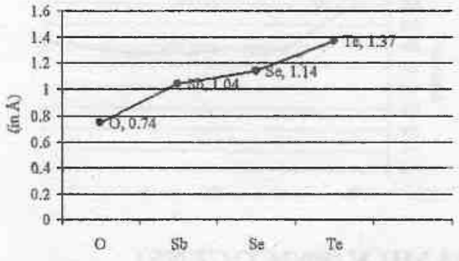
CARBON FAMILY



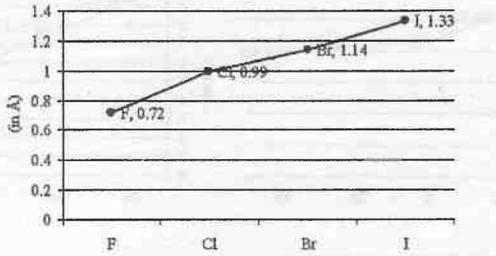
NITROGEN FAMILY (PNICOGENS)



CHALCOGENS



HALOGENS



[☺ what can you predict or say about the increment in size along a group and decrement along a period]

ISOELECTRONIC SPECIES [Size depends upon Z, more Z less size]:

(i) S^{2-}, Cl^-, K^+, Ca^{2+}, Sc^{2+} **(ii)** SO_3, NO_3^-, CO_3^{2-}, $COCl_2$
(iii) N_2, CO, CN^- **(iv)** NH_3, H_3O^+
(v) H^-, He, Li^+ **(vi)** CH_4, NH_4^+
(vii) NCS^-, CS_2 **(viii)** $\dfrac{\text{radius of cation}}{\text{radius of anion}} = \dfrac{Z_{eff}\text{ of Anion}}{Z_{eff}\text{ of Cation}}$

[☺ Check out for size for an isoelectronic noble gas.]

IONISATION ENERGY :

Amount of energy required to remove the most loosely bounded electron from an isolated gaseous atom.
Units : kJ mol^{-1}, k cal mol^{-1}, eV per atom.
Ionisation is endothermic (endoergic) i.e. requires energy hence
ΔH is +ve

$$M + \text{Energy } (IE_1) \longrightarrow M^+ + e^-$$
$$M \longrightarrow M^+ + e^- \qquad \Delta H = IE_1$$
$$M^+ \longrightarrow M^{+2} + e^- \qquad \Delta H = IE_2$$
$$M^{+2} \longrightarrow M^{+3} + e^- \qquad \Delta H = IE_3$$

$IE_3 > IE_2 > IE_1$ always

FACTORS AFFECTING IONISATION ENERGY :

(1) Atomic size : Varies inversely
(2) Screening effect : varies inversely
(3) Nuclear charge : varies directly

(4) Sp Elect. config of outermost electron (half filled / fully filled)

(5) Type of orbital involved in Ionisation : s > p > d > f.

Half fillness and full fillness of inner orbitals. [affects d block and f block trends]

General Trend: Along period I.E. increases [with some exception] [$Z_{eff}\uparrow$]

Along a group I.E. decrease [Z_{eff} constant, n $\uparrow$]

Exception :

(1) Along a period, half filled and fully filled have higher I.E.
e.g. Be > B and N > O.

(2) along a group, Ga > Al

PROPERTIES AFFECTED BY IONISATION ENERGY:

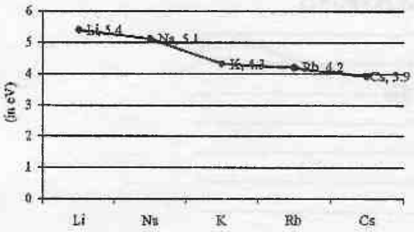
(1) Metallic character

(2) Tending to stay in which state A^{+1}. A^{+2} or A^{+3}

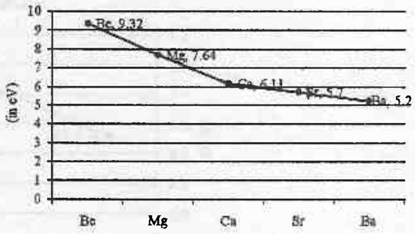
(3) Other properties based on (1)

IONISATION ENERGY

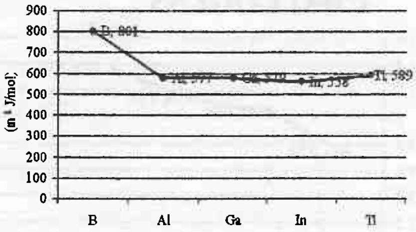
ALKALI METALS



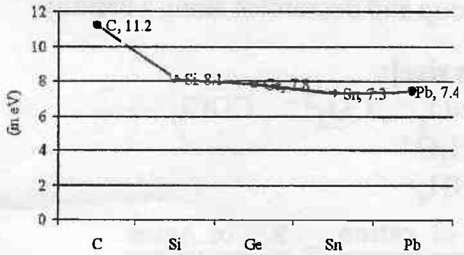
ALKALINE EARTH METALS



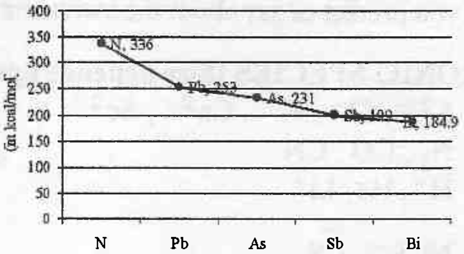
GROUP III A



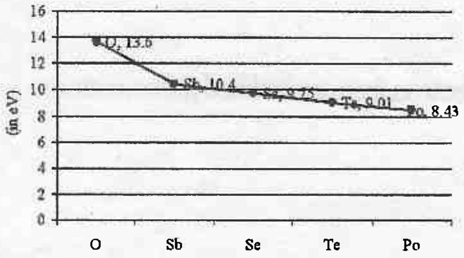
CARBON FAMILY



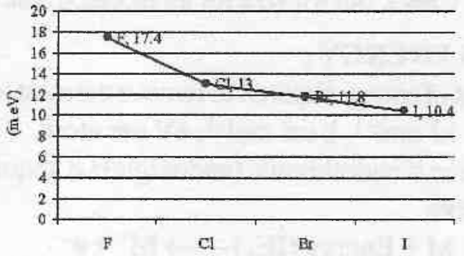
NITROGEN FAMILY (PNICOGENS)



CHALCOGENS



HALOGENS



ELECTRON AFFINITY :

Amount of energy released when an electron is added to an isolated gaseous atom.

Units : k J mol $^{-1}$, k Cal mol $^{-1}$ and eV per atom.

Exothermic (exoergic) . EA_1 is always released .

2nd E. A. is always energy required. The sum of EA_1 & EA_2 is energy required.

$$E A \propto \frac{1}{\text{atomic size}} \propto Z_{eff}$$. Cl has the highest E.A.

ELECTRON GAIN ENTHALPY :

When expressed in terms of enthalpy change (ΔH) then it is termed as E.G.E. Remember that $\Delta H = -$ ve for exothermic change.

For EA_1, energy is released ∴ $\Delta H_{EA1} = -$ ve
For EA_2, onwards is required ∴ $\Delta H_{EA2} = +$ ve
$EA_1 + EA_2$, energy is always required.

FACTORS AFFECTING ELECTRON AFFINITY :

(1) ***Atomic size :*** varies inversely
(2) ***Nuclear change :*** varies directly
(3) Sp E.C. of half filled and fully filled shells.

General Trend : Along a period, electron affinity increases [with exception] as $Z_{eff}\uparrow$.

Along a group, electron affinity decreases after 3rd period. Between 2nd and 3rd period in p block electron affinity of 2nd period is lowering to high electron density.

Exception :

(1) A fully filled and half filled which have low values or even sometimes energy is required rather than getting released.
(2) 2nd period has lower value than 3rd owing to repulsion between electrons.

E. A. VALUES FOR s AND p BLOCK

IA							**0**
H							**He**
– 72	II A	III A	IV A	V A	VI A	VII A	$+20^a$
Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
– 60	$+240^a$	– 23	– 123	0	– 141	– 322	+30
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
– 53	$+230^a$	– 44	– 139	– 74	– 201	– 348	$+35^a$
K	**Ca**	**Ga**	**Ge**	**As**	**Sc**	**Br**	**Kr**
– 48	$+150^a$	-40^a	– 116	– 77	– 195	– 324	$+40^a$
Rb	**Sr**	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**
– 46	$+160^a$	-40^a	– 121	– 101	– 190	– 295	$+40^a$
Cs	**Ba**	**Tl**	**Pb**	**Bi**	**Po**	**At**	**Rn**
– 45	$+50^a$	– 50	– 101	– 101	-170^a	-270^a	$+40^a$

ELECTRO NEGATIVITY : [Properties of an atom in a molecule]

F has highest. Decreasing order → F > O > Cl = N > Br > S = C > I > H.

Pauling Scale: $X_A - X_B = 0.208\sqrt{\Delta}$ E in kcal/mol

$$\Delta = E_{A-B} - (E_{A-A} \text{ x } E_{B-B})^{1/2}$$

Mulliken's Scale : $X_A = \dfrac{I_p + E_A}{2}$ (ev) .

Mulliken's values of E N are about 2.8 times as large as Pauling .

Allred–Rochows : $X_A = \dfrac{0.359\ Z_{eff}}{r^2} + 0.744$

Sanderson : $X_A = 0.21\ X_A + 0.77$

Pauling Sanderson
Anion is less electronegative than parent atom.

FACTOR AFFECTING ELECTRO NEGATIVITY :

(1) ***Nuclear attraction :*** varies directly
(2) ***Atomic radius :*** varies inversely
(3) ***Change on ions :*** More positive charge more electronegativity and more –ve change less electronegativity.
(4) ***Hybridisation :*** to be discussed later in bonding.

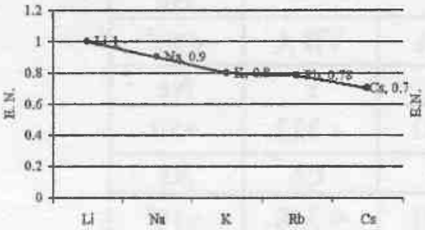
General Trends : Along a period, electronegativity increases
Along a group, electronegativity decreases
Exceptions : None noteworthy.

FACTORS DEPENDENT ON ELECTRO NEGATIVITY :

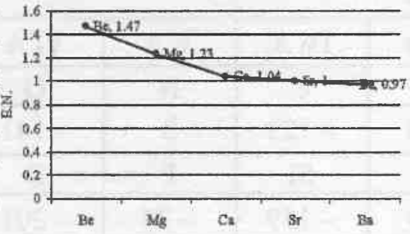
(1) % ionic character varies directly.
(2) Strength of bond varies directly.
(3) B.L. : varies inversely.
(4) Nature of hydrides
(5) Nature of hydroxide.

ELECTRONEGATIVITY

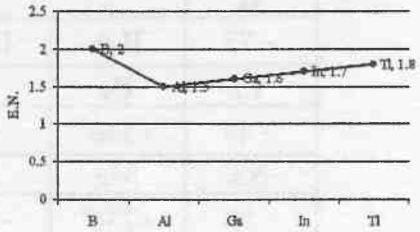
ALKALI METALS



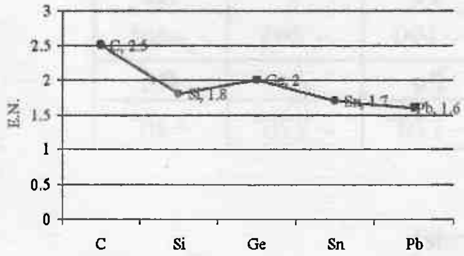
ALKALINE EARTH METALS



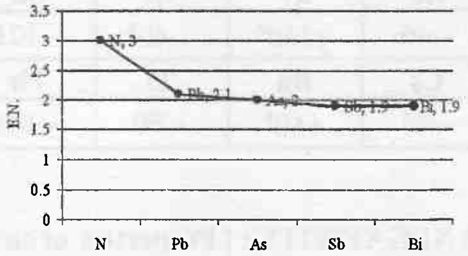
GROUP HI A



CARBON FAMILY

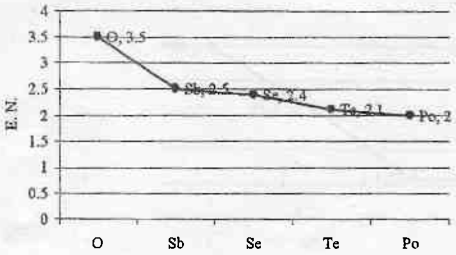


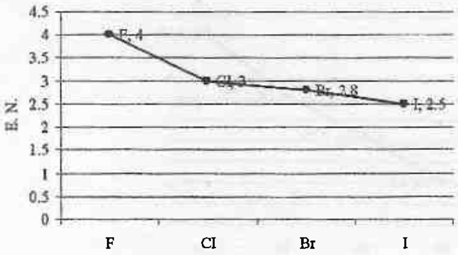
NITROGEN FAMILY (PNICOGENS)



CHALCOGENS

HALOGENS





MISCELLANEOUS CHEMICAL PROPERTIES :

1. *Periodicity of hydra acids :*

(a) Acidic character of hydra acid increases from left to right in a period.

(b) Acidic character of hydra acid increases from top to bottom in a group.

2. *Periodicity of oxy acids :*

(a) Acidic character of oxy acid increases from left in a period.

(b) Acidic character of oxy acid decreases from top to bottom in a group.

3. *Periodicity of nature of oxide :*

(a) On moving from left to right in a period acidic nature of oxide generally increases.
e.g. $CO_2 < P_2O_3 < SO_2 < ClO_2$

(b) On moving from top to bottom in a group acidic nature of oxide generally decreases.

4. *Solubility of salt in water :*

(a) ***Hydration energy*** decreases along a group.

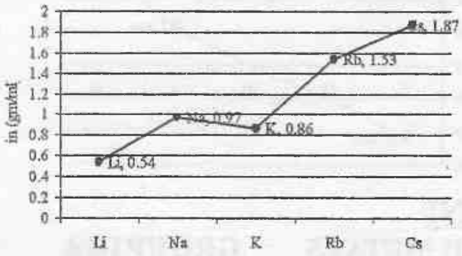
(b) ***Lattice energy*** decreases along a group.

TRENDS IN PHYSICAL PROPERTIES :

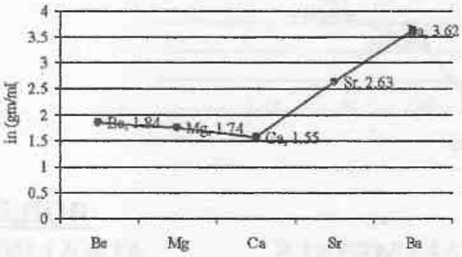
Physical properties are mostly dependent on. Atomic weight and so not regular trend. Mark out exception in the graph and think out of the reasons?

DENSITY

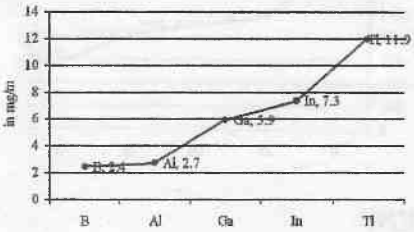
ALKALI METALS



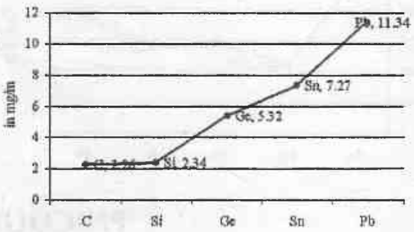
ALKALINE EARTH METALS



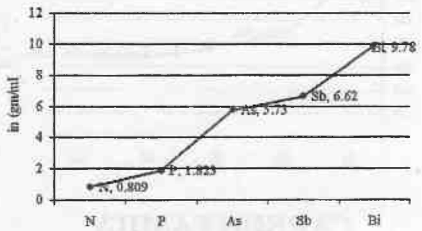
GROUP IIIA



CARBON FAMILY

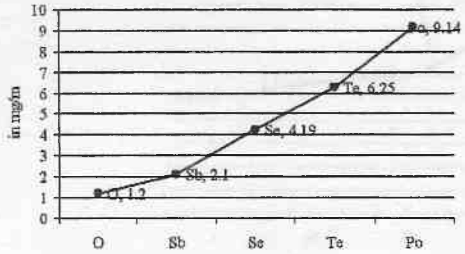


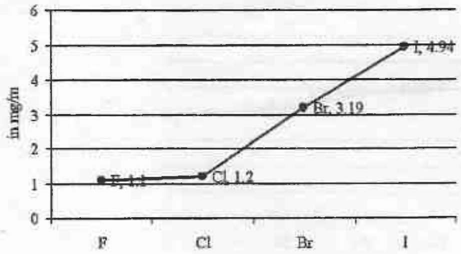
(PNICOGENS)



CHALCOGENS

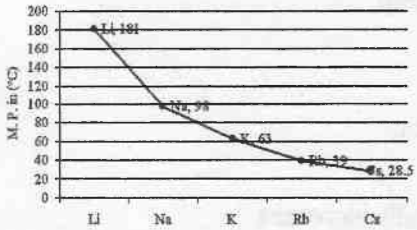
HALOGENS

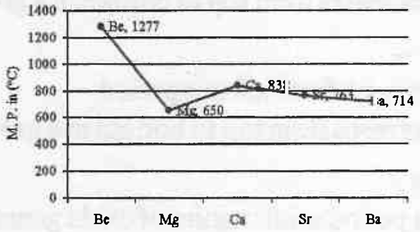


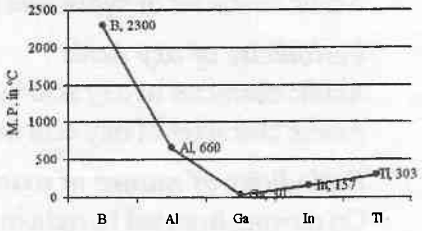


MELTING POINT

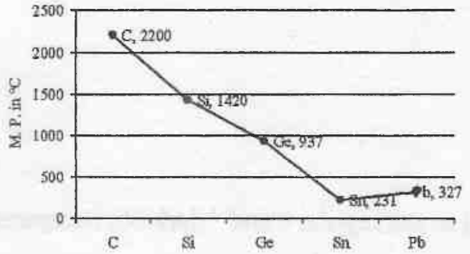
ALKALI METALS **ALKALINE EARTH METALS** **GROUP III A**

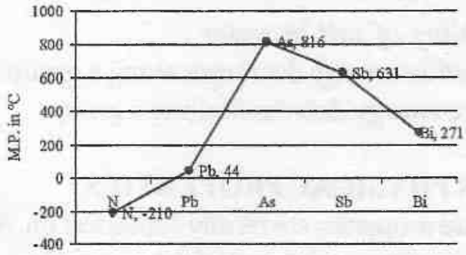




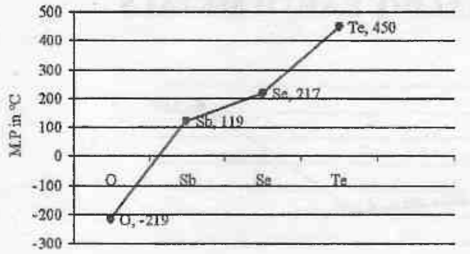


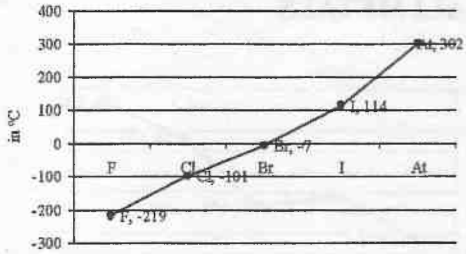
CARBON FAMILY **PNICOGENS**





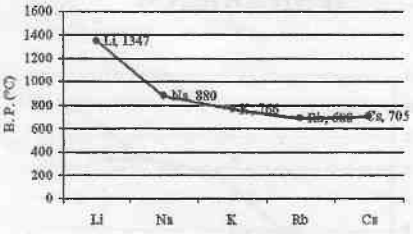
CHALCOGENS **HALOGENS**

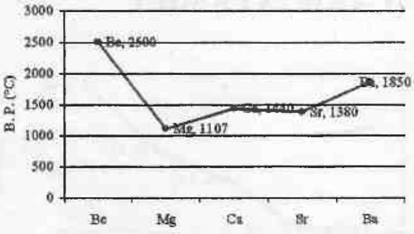


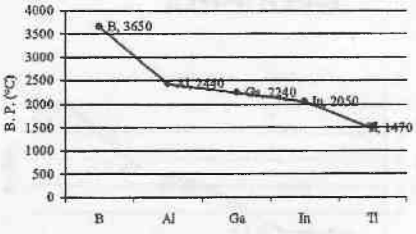


BOILING POINT

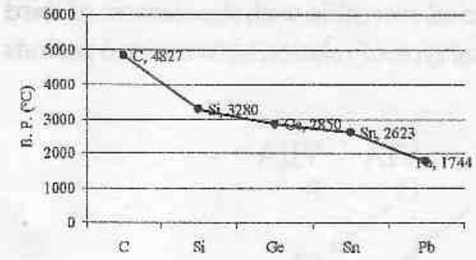
ALKALI METALS **ALKALINE EARTH METALS** **GROUP III A**

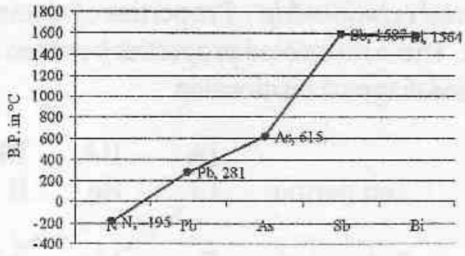


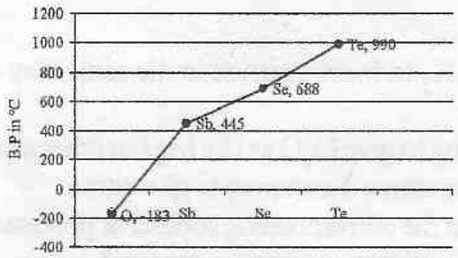


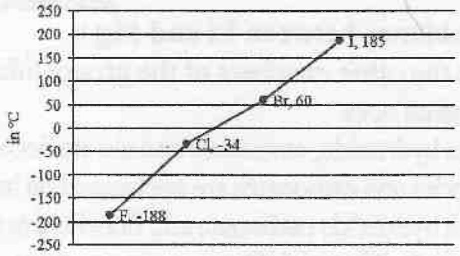


CARBON FAMILY **PNICOGENS**






CHALCOGENS


HALOGENS

SOME POINTS TO REMEMBER :

1. Second most electronegative element–Oxygen
2. Hydrogen is the lightest element and Lithium is lightest metal.
3. Helium has the highest value of I.P.
4. Fr has minimum value of electronegativity and ionisation potential.
5. In periodic table metalloids are only in p-block.
6. According to CAS system (chemical abstract system) total no. of groups are 16.
7. Total gaseous elements are 11 (He, Ne, Ar, Kr, Xe, Rn, H_2, N_2, O_2, Cl_2, F_2)
8. Liquid metal is – Hg.
9. Diamond is hardest natural substance.
10. Francium has the highest atomic volume.
11. Halogens have highest electron affinity and in that to Cl has the highest amongst them.
12. The largest cation of the periodic table = Cs^+.
13. The smallest cation of the periodic table = H^+.
14. The largest anion of the periodic table = I^-.
15. The smallest anion of the periodic table = H^-.
16. The biggest element of periodic table = Fr.
17. The smallest element of periodic table = H.
18. Br liquid non-metal.
19. Osmium heaviest element known.
20. Flourine is the most electronegative element.

SOME COMMONLY USED TERMS :

1. ***Noble Gases :*** Element of group 18 are called noble gases. These are also called as inert gases because their outermost ns and np orbitals are completely filled (except He and $1s^2$) and these gaseous are non-reactive in nature under ordinary conditions.
2. ***Representative elements :*** All the s and p block elements are known as representative elements except zero group.
3. ***Transition elements :*** All the d-block elements (except IIB group) are called transition element. It comprises into 4th, 5th, 6th and 7th period. They lie between s and p block elements.
4. ***Inner transition elements :*** All the f-block elements or 4f and 5f block elements are called inner transition element. Total number of these elements is 28. They lie in IIIB and placed at the bottom of periodic table.

5. *Typical elements :* Elements second and third period are known as typical elements.
6. *Diagonal relationship :* Properties of elements of second period resemble with the element of third period. These resembled properties between two periods or this type of relation between two periods are called diagonal relationship.

$$\begin{tikzcd}
 & \text{IA} & \text{IIA} & \text{IIIA} & \text{IVA} & \text{VA} & \text{VIA} & \text{VIIA} \\
\text{2nd period} & \text{Li} \arrow[dr] & \text{Be} \arrow[dr] & \text{B} \arrow[dr] & \text{C} \arrow[dr] & \text{N} \arrow[dr] & \text{O} \arrow[dr] & \text{F} \\
\text{3rd period} & \text{Ba} & \text{Mg} & \text{Al} & \text{Si} & \text{P} & \text{S} & \text{Cl}
\end{tikzcd}$$

Increase your I bank

(i) Resemblance between Li and Mg :

(a) Unlike the other members of the group, lithium reacts with N_2 to form a nitride in the same way as magnesium does.

(b) Lithium hydroxide, carbonate and nitrate decomposes on heating to give Li_2O as like Mg but other alkali hydroxides and carbonates are unchanged on heating where as the nitrate decompose to give nitrite.

(c) Lithium hydroxide carbonate and fluoride are much soluble than the corresponding sodium or potassium compounds. The solubilities are comparable to those of corresponding magnesium compound.

(ii) Resemblance between Be and Al :

(a) The ionic radius of Be^{2+} is nearly same as that for the Al^{3+}.

(b) Like aluminium, beryllium is not readily attacked by acids because of the pressure of an oxide film.

(c) Beryllium dissolved in alkali to give the beryllate ion $[B(OH)_4]^{2-}$ just as aluminium does to give $(Al(OH)_6)^{3-}$.

(d) The oxides BeO and Al_2O_3 are hard high melting insoluble solids. The oxides as well as their hydroxides amphoteric and dissolve in sodium hydroxide solution.

(e) Beryllium and aluminium from fluoro complex anion, BeF_4^{2-} and AlF_6^{3-} in solution, the other group II metals do not form stable fluoro complexes in solution.

(f) Beryllium chloride ($BeCl_2$) is essentially covalent and has a bridged polymeric structure just as aluminium trichloride is covalent forming a bridged dimer, Al_2Cl_6. Both the chlorides are soluble in organic solvent and are strong Lewis acid.

(iii) Resemblance between B and Si :

(a) Boron and silicon form numerous hydride which spontaneously catch fire on exposure to air and are easily hydrolysed.

(b) Boron halide like silicon halides hydrolysed by water. Aluminium halides are only partially hydrolysed by water.

(c) Boron forms binary compounds with several metals known as borides just as silicon forms metal silicides some of the borides and silicides under go hydrolysis to yield boron and silicon respectively.

(d) B_2O_3 and SiO_2 are acidic in nature, Borates and silicates have tetrahedral BO_4 and SiO_4 structural units respectively. Boro silicates are known in which form can replace silicon in three dimensional lattice. However boron can also form planer BO_3 unit.

(e) Both B and Al are semiconductors.

Bridge Elements : Typical elements of III period.

NOMENCLATURE OF THE ELEMENT :

The names are derived by using roots for the three digits in the atomic number of the element and adding the ending –ium. The roots for the number are

EXERCISE # I

General Info about periodic table

Q.1 Which of the following does not reflect the periodicity of element
(A) Bonding behaviour (B) Electronegativity (C) Ionisation potential (D) Neutron/ Proton ratio

Q.2 Choose the s-block element in the following:
(A) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^1$ (B) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^1$
(C) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$ (D) all of the above

Q.3 False statement for periodic classification of elements is
(A) The properties of the elements are periodic function of their atomic numbers.
(B) No. of non-metallic elements is less than the no. of metallic elements.
(C) First ionization energy of elements is not change continuously with increasing of atomic no. in a period.
(D) d-subshell is filled by final electron with increasing atomic no. of inner transition elements.

Q.4 Pick out the isoelectronic structure from the following:
I. $^+CH_3$ II. H_3O^+ III. NH_3 IV. CH_3^-
(A) I and II (B) III and IV (C) I and III (D) II, III and IV

Q.5 Based on location in P.T., which of the following would you expect to be acidic & which basic.
(a) CsOH (b) IOH (c) $Sr(OH)_2$ (d) $SeO_3(OH)_2$ (e) FrOH (f) BrOH

Q.6 Which of the ions are paramagnetic
$Sr^{2+}, Fe^{3+}, Co^{2+}, S^{2-}, Pb^{2+}$

Q.7 If there were 10 periods in the periodic table then how many elements would this period can maximum comprise of.

Q.8 If (n + *l*) for energy rule is not followed, what are the blocks of the following elements.
(a) K(19) (b) Fe(26) (c) Ga(31) (d) Sn(50)

Q.9 Use the following system of naming elements in which first alphabets of the digits are written collectively,

0	1	2	3	4	5	6	7	8	9
nil	uni	bi	tri	quad	pent	hex	sept	oct	enn

to write three-letter symbols for the elements with atomic number 101 to 109.
[Example : 101 is Unu....]

Q.10 A student is given samples of three elements, X, Y and Z, which could be an alkali metal, a member of group IV A, and a member of group VA. She makes the following observations:
Element X has a metallic lusture and conducts electricity. It reacts slowly with aq HCl to produce H_2. Element Yis a light-yellow solid and does not conduct electricity Element Z has a metallic lusture and conducts electricity. When exposed to air, it forms a white powder aqueous solution of which is basic. What can you conclude about the elements from these observations?

Properties and Periodic trends

Q.11 The size of the following species increases in the order:
(A) $Mg^{2+} < Na^+ < F^- < Al$ (B) $F^- < Al < Na^+ < Mg^{2+}$
(C) $Al < Mg < F^- < Na^+$ (D) $Na^+ < Al < F^- < Mg^{2+}$

Q.12 Element in which maximum ionization energy of following electronic configuration would be
(A) $[Ne]\ 3s^2\ 3p^1$ (B) $[Ne]\ 3s^2\ 3p^2$ (C) $[Ne]\ 3s^2\ 3p^3$ (D) $[Ar]\ 3d^{10}\ 4s^2\ 4p^3$

Q.13 The outermost electronic configuration of most electronegative element is:
(A) $ns^2\ np$ (B) $ns^2\ np^4$ (C) $ns^2\ np^5$ (D) $ns^2\ np^5$

Q.14 The electron affinity of the members of oxygen of the periodic table, follows the sequence
(A) O > S > Se (B) S > O > Se (C) S > Se > O (D) Se > O > S

Q.15 The process of requiring absorption of energy is
(A) $F \rightarrow F^-$ (B) $Cl \rightarrow Cl^-$ (C) $O^- \rightarrow O^{2-}$ (D) $H \rightarrow H^-$

Q.16 In the following which configuration of element has maximum electronegativity.
(A) $1s^2, 2s^2 2p^5$ (B) $1s^2, 2s^2 2p^6$ (C) $1s^2, 2s^2 2p^4$ (D) $1s^2, 2s^2 2p^6, 3s^2 3p^3$

Q.17 Highest size will be of
(A) Br^- (B) I (C) I^- (D) I^+

Q.18 Atomic radii of flourine and neon in Å units are respectively given by
(A) 0.72, 1.60 (B) 1.60, 1.60 (C) 0.72, 0.72 (D) none of these

Q.19 The correct order of second ionisation potential of C, N, O and F is:
(A) C > N > O > F (B) O > N > F > C (C) O > F > N > C (D) F > O > N > C

Q.20 Decreasing ionization potential for K, Ca & Ba is
(A) Ba > K > Ca (B) Ca > Ba > K (C) K > Ba > Ca (D) K > Ca > Ba

Q.21 Element Hg has two oxidation states Hg^{+1} & Hg^{+2}. the right order of radii of these ions.
(A) $Hg^{+1} > Hg^{+2}$ (B) $Hg^{+2} > Hg^{+1}$ (C) $Hg^{+1} = Hg^{+2}$ (D) $Hg^{+2} \geq Hg^{+1}$

Q.22 The ionization energy will be maximum for the process.
(A) $Ba \rightarrow Ba^{++}$ (B) $Be \rightarrow Be^{++}$ (C) $Cs \rightarrow Cs^+$ (D) $Li \rightarrow Li^+$

Q.23 Why the first ionisation energy of carbon atom is greater than that of boron atom whereas, the reverse is true for the second ionisation energy.

Q.24 On the Pauling's electronegativity scale, which element is next to F.

Q.25 Mg^{2+}, O^{2-}, Na^+, F^-, N^{3-} (Arrange in decreasing order of ionic size)

Q.26 Why Ca^{2+} has a smaller ionic radius than K^+.

Q.27 Calculate E.N. of flourine if $(r_F)_{covalent} = 0.72$ Å.

Q.28 Calculate E.N. of chlorine atom on Mulliken's scale if I.E. of Cl^- is 4eV & of E.A. of Cl^+ is + 13.0 eV.

Q.29 Calculate the electronegativity of fluorine from the following data :
$E_{H-H} = 104.2$ kcal mol^{-1} $E_{F-F} = 36.2$ kcal mol^{-1}
$E_{H-F} = 134.6$ kcal mol^{-1} $X_H = 2.1$

Q.30 Calculate the E.N. of Cl from the bond energy of ClF (61 KCal/mol). Given that bond energies of F_2 and Cl_2 are 38 and 58 KCal/mol respectively.

Q.31 Calculate the radii of Na^+ & F^- if interionic distance between Na^+ & F^- ions is 2.31 Å.

Q.32 Arrange H_2, O_2, F_2, N_2 in the increasing order of bond length.

Q.33 Why do alkaline earth metals always form dipositive ions.

Q.34 State giving reasons which one have higher value :
(a) IE_1 of F or Cl (b) E A of O or O^-
(c) ionic radius of K^+ or Cl^-

Q.35 Explain why a few elements such as Be (+0.6), N(+0.3) & He(+0.6) have positive electron affinities while majority of elements do have negative values.

Q.36 From among the elements, choose the following: Cl, Br, F, Al, C, Li, Cs & Xe.
(i) The element with highest electron affinity. (ii) The element with lowest ionisation potential.
(iii) The element whose oxide is amphoteric. (iv) The element which has smallest radii.
(v) The element whose atom has 8 electrons in the outermost shell.

Q.37 Which property will increase and which will decrease for IA group as we go down the group.

(a) Atomic size
(b) Ionic radii
(c) I E
(d) Density
(e) Melting point
(f) Boiling point
(g) E N
(h) At. mass
(i) Valance e^-
(j) Metallic ch
(k) Chemical reactivity
(l) Power as red. agent

Q.38 The IE do not follow a regular trend in II & III periods with increasing atomic number. Why?

Q.39 Arrange in decreasing order of atomic size : Na, Cs, Mg, Si, Cl.

Q.40 In the ionic compound KF, the K^+ and F^- ions are found to have practically radii, about 1.34 Å each. What do you predict about the relative covalent radii of K and F?

Q.41 The IE values of $Al_{(g)} = Al^+ + e$ is 577.5 kJ mol^{-1} and ΔH for $Al_{(g)} = Al^{3+} + 3e$ is 5140 kJ mol^{-1}. If second and third IE values are in the ratio 2 : 3. Calculate IE_2 and IE_3.

Q.42 How many chlorine atoms will be ionised $Cl \longrightarrow Cl^+ + e^{-1}$ by the energy released from the process $Cl + e^{-1} \longrightarrow Cl^-$ for 6.02×10^{23} atoms (I.P. for Cl = 1250 kJ mol^{-1} and E.A. = 350 kJ $mole^{-1}$)

Q.43 For the gaseous reaction,
$K + F \longrightarrow K^+ F^-$, ΔH was calculated to be 19 kcal under conditions where the cations and anions were prevented by electrostatic separation from combining with each other. The ionisation potential of K is 4.3 eV. What is the electron affinity of F?

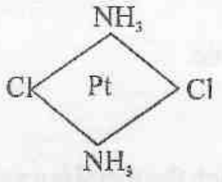
Q.44 The ionisation potentials of atoms A and B are 400 and 300 kcal mol^{-1} respectively. The electron affinities of these atoms are 80.0 and 85.0 k cal mol^{-1} respectively. Prove that which of the atoms has higher electronegativity.

Q.45 The As-Cl bond distance in $AsCl_3$ is 2.20 Å. Estimate the SBCR (single bond covalent radius) of As. (Assume EN of both to be same and radius of Cl = 0.99 Å.)

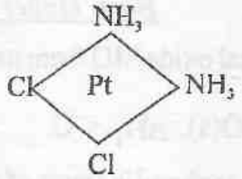
Q.46 Does Na_2(g) molecule exhibit metallic properties.

Q.47 The Pt-Cl distance has been found to be 2.32 Å in several crystalline compounds. If this value applies to both of the compounds shown in figure. What is Cl - Cl distance in (a) and (b)

(a)



(b)



Q.48 Which will have a higher boiling point, Br_2 or ICl, & why?

Q.49 Why the elements of S block impart colour to the flame?

Q.50 Which bond in each pair is more polar
(a) P – Cl or P – Br (b) S – Cl or S – O (c) N – O or N – F

Q.51 Arrange noble gases, in the increasing order of b.p.

Q.52 A mixture contains F and Cl atoms. the removal of an electron from each atom of the sample requires 284 kJ while the addition of an electron to each atom of the mixture releases 68.8 kJ. Determine the % composition of the mixture.

	(IE) per atom	**(EA) per atom**
F	27.91×10^{-22} kJ	-5.53×10^{-22} kJ
Cl	20.77×10^{-22} kJ	-5.78×10^{-22} kJ

Effective nuclear charge and screening

Q.53 Calculate the screening constant of Ca. (atomic number 20)

Q.54 Calculate the effective nuclear charge on–
(i) 4s valency e^- in Bromine atom. and (ii) 3d electron in Bromine atom.

Q.55 Complete the E.C. $Is^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^7$ & calculate.
(a) Z (b) σ (c) Zeff (d) Zeff for 4f (e) from (c) & (d) judge whether it would be easier to remove valence e^- or from the highest energy level (4f).

Q.56 I.P. of Be^{+x} is found to be 217.6 electron volt. What is the value of x.

Q.57 For K, calculate Zeff from slater's rule & from Bohr's model. Take I.E. of K from graph.

Miscellaneous Properties

Q.58 Arrange the following ions Na^+, Mg^{2+}, Al^{3+} in increasing
(a) extent of hydration (b) hydration energy (c) size of hydrations
(d) Ionic mobility (e) size of gaseous ions.

Q.59 LiCl is hydrated but NaCl is always anhydrous. Explain.

Q.60 Arrange following oxides in increasing acidic nature
Li_2O, BeO, B_2O_3

Q.61 Which oxide is more basic, MgO or BaO? Why?

Q.62 The heats of formation ($\Delta H_f^{'}$) of the oxides of the third period, sodium to chlorine, are in kJ mol^{-1}

Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
–416	–602	–1676	–911	–2984	–395	+250

Divide these values by the number of oxygen atoms in the formula of the oxide. The resulting figure is a measure of the strength of the oxide. What is the link between the figures and the structures of the oxides?

Q.63 The basic nature of hydroxides of group 13 (III-A) decreases progressively down the group. Comment.

Born Haber Cycle

Q.64 The formation of a typical metal oxide MO from its elements is exothermic:

$$M(s) + \frac{1}{2}O_2(g) = MO(s),\ \Delta H_f^{\circ} < O.$$

Show that this reaction can be analysed in terms of a series of steps in which the metal is a vaporized, the oxygen dissociated, the gaseous atoms converted to ions, and the ions converted to a solid. Discuss how the ΔH_f° of the oxide is affected by (a) the strength of the bonding in the metallic crystal, (b) the ionization energy of the metal atom, and (c) the size of the metallic ion.

Q.65 Calculate the lattice energy of NaCl crystal from the following date by the use of Born-Haber cycle. Sublimation energy of Na = 26 kcal/g. atom, dissociation energy of Cl_2 = 54 kcal/mole, ionisation energy for Na(s) = 117 kcal/ mol, electron affinity for Cl(g) = 84 kcal/g atom, heat of formation of NaCl = –99 kcal/mole.

Q.66 Calculate the electron affinity of iodine with the help of the following data (given in Kcal/mole).

$$(\Delta H_{fir})_{NaI} = -68.8,\ (\Delta H_{sub})_{Na} = 25.9,\ \frac{1}{2}(\Delta H_{diss})_{I_2} = 25.5,\ (IP)_{Na} = 118.4,\ (U)_{NaI} = -165.4$$

EXERCISE # II

Q.1 Moving from right to left in a periodic table, the atomic size is: **[JEE 1995]**
(A) increased (B) decreased (C) remains constant (D) none of these

Q.2 The increasing order of electronegativity in the following elements: **[JEE 1995]**
(A) C, N, Si, P (B) N, Si, C, P (C) Si, P, C, N (D) P, Si, N, C

Q.3 One element has atomic weight 39. Its electronic configuration is $1s^2, 2s^2 2p^6, 3s^2 3p^6 4s^1$. The true statement for that element is:
(A) More (IE) (B) Transition element
(C) Isotone with $_{18}Ar^{38}$ (D) Stable oxide M_2O **[JEE 1995]**

Q.4 The number of paired electrons in oxygen is: **[JEE 1995]**
(A) 6 (B) 16 (C) 8 (D) 32

Q.5 The decreasing size of K^+, Ca^{2+}, Cl^- & S^{2-} follows the order: **[REE 1995]**
(A) $K^+ > Ca^{+2} > S^{-2} > Cl^-$ (B) $K^+ > Ca^{+2} > Cl^- > S^{-2}$
(C) $Ca^{+2} > K^+ > Cl^- > S^{-2}$ (D) $S^{-2} > Cl^- > K^+ > Ca^{+2}$

Q.6 Fluorine is the most reactive among all the halogens, because of its: **[REE 1995]**
(A) small size (B) low dissociation energy of F – F bond
(C) large size (D) high dissociation energy of F – F bond

Q.7 The experimentally determined N – F bond length in NF_3 is greater than the sum of single bond covalent radii of N & F. Explain. **[JEE 1995]**

Q.8 Which of the following oxide is neutral? **[JEE 1996]**
(A) CO (B) SnO_2 (C) ZnO (D) SiO_2

Q.9 Which of the following has the maximum number of unpaired electrons **[JEE 1996]**
(A) Mg^{2+} (B) Ti^{3+} (C) V^{3+} (D) Fe^{2+}

Q.10 The following acids have been arranged in the order of decreasing acid strength. Identify the correct order **[JEE 1996]**
ClOH(I) BrOH(II) IOH(III)
(A) I > II > III (B) II > I > III (C) III > II > I (D) I > III > II

Q.11 The incorrect statement among the following is: **[JEE 1997]**
(A) the first ionisation potential of Al is less that the first ionisation potential of Mg
(B) the second ionisation potential of Mg is greater that the second ionisation potential of Na
(C) the first ionisation potential of Na is less than the first ionisation potential of Mg
(D) the third ionisation potential of Mg is greater than the third ionisation potential of Al

Q.12 Which of the following are amphoteric? **[REE 1997]**
(A) $Be(OH)_2$ (B) $Sr(OH)_2$ (C) $Ca(OH)_2$ (D) $Al(OH)_2$

Q.13 Which one of the following halogens has the highest bond energy? **[REE 1997]**
(A) F_2 (B) Cl_2 (C) Br_2 (D) I_2

Q.14 Li^+, Mg^{2+}, K^+, Al^{3+} (Arrange in increasing order of radii) **[JEE 1997]**

Q.15 The incorrect statement among the following is
(A) the IE_1 of Al is less than IE_1 of Mg (B) the IE_2 of Mg is greater than IE_2 of Na
(C) the IE_1 of Na is less than IE_1 of Mg (D) the IE_3 of Mg is greater than IE_3 of Al
[JEE 1997]

Q.16 Property of the alkaline earth metals that increases with their atomic number is
(A) IE (B) solubility of their hydroxides
(C) solubility of their sulphates (D) electronegativity **[JEE 1997]**

Q.17 Anhydrous $AlCl_3$ is covalent. From the data given below predict whether it would remain covalent or become ionic in aqueous solution. [IE for Al = 5137 kJ/mol]
ΔH hydration for $Al^{3+} = -4665$ kJ/mol; ΔH_{hydra} for $Cl^- = -381$ kJ/mol. **[JEE 1997]**

Q.18 Which one of the following statement (s) is (are) correct? **[JEE 1998]**
(A) The electronic configuration of Cr is [Ar] $3d^5\ 4s^1$.(Atomic No. of Cr = 24)
(B) The magnetic quantum number may have a negative value
(C) In silver atom, 23 electrons have a spin of one type and 24 of the opposite type. (Atomic No. of Ag = 47)
(D) The oxidation state of nitrogen in HN_3 is –3.

Q.19 Ionic radii of: **[JEE 1999]**
(A) $Ti^{4+} < Mn^{7+}$ (B) $^{35}Cl^- > {}^{37}Cl^-$ (C) $K^+ > Cl^-$ (D) $P^{3+} > P^{5+}$

Directions: The questions below to consist of an 'assertion in column-1 and the 'reason' in column-2. Against the specific question number, write in the appropriate space.
(A) If both assertion and reason are CORRECT, and reason is the CORRECT explanation of the assertion. (B) If both assertion and reason are CORRECT, but reason is not the CORRECT explanation of the assertion. (C) If assertion if CORRECT but reason is INCORRECT (D) If assertion is INCORRECT reason in CORRECT.

Q.20 **Assertion**: F atom has a less negative electron gain enthalpy than Cl atom. **[JEE 2000]**
Reason: Additional electron is repelled more efficiently by 3p electron in Cl atom than by 2p electron in F atom.

Q.21 **Assertion**: $Al(OH)_3$ is amphoteric in nature. **[JEE 2000]**
Reason: Al –O and O – H bonds can be broken with equal case in $Al(OH)_3$.

Q.22 **Assertion**: The first ionization energy of Be is greater than that of B. **[JEE 2000]**
Reason: 2p orbital is lower in energy than 2s.

Q.23 The correct order of radii is: **[JEE 2000]**
(A) N < Be < B (B) $F^- < O^{2-} < N^{3-}$ (C) Na < Li < K (D) $Fe^{3+} < Fe^{2+} < Fe^{4+}$

Q.24 The correct order of acidic strength is: **[JEE 2000]**
(A) $Cl_2O_7 > SO_2 > P_4O_{10}$ (B) $CO_2 > N_2O_5 > SO_3$
(C) $Na_2O > MgO > Al_2O_3$ (D) $K_2O > CaO > MgO$

Q.25 The IE_1 of Be is greater than that of B. [T/F] **[JEE 2001]**

Q.26 The set representing correct order of IP_1 is **[JEE 2001]**
(A) K > Na > Li (B) Be > Mg > Ca (C) B > C > N (D) Fe > Si > C

Q.27 Identify the least stable ion amongst the following: **[JEE 2002]**
(A) Li^- (B) Be^- (C) B^- (D) C^-

Q.28 Identify the correct order of acidic strengths of CO_2, CO, CuO, CaO, H_2O: **[JEE 2002]**
(A) $CaO < CuO < H_2O < CO_2$ (B) $H_2O < CuO < CaO < CO_2$
(C) $CaO < H_2O < CuO < CO_2$ (D) $H_2O < CO_2 < CaO < CuO$

ANSWER KEY

EXERCISE # I

Q.1 D Q.2 C Q.3 D Q.4 D

Q.5 (a) basic (b) acidic (c) basic (d) acidic (e) basic (f) acidic

Q.6 Fe^{3+} , CO^{2+} Q.7 72

Q.8 (a) d block, (b) d block, (c) p block, (e) f block

Q.9 101 102 103 104 105 106 107 108 109
Unu nb Unt Unq Unp Unh Uns Uno Une

Q.10 X: Sn or Pb, Y : P, Z: alkali metal

Q.11 A Q.12 C Q.13 C, D Q.14 B

Q.15 C Q.16 A Q.17 C Q.18 A

Q.19 C Q.20 B Q.21 A Q.22 B

Q.23 Zeff & half filled config. Q.24 O Q.25 $N^{3-} > O^{2-} > F^- > Na^+ > Mg^{2+}$

Q.26 Isolelectronic Ca^{+2}(higher) Q.27 4 Q.28 3.03 (P)

Q.29 3.8752 Q.30 3.2 Q.31 0.95Å, 1.36Å Q.32 $H_2 < N_2 < 0_2 < F_2$

Q.33 difference in $1E_1$ & $1E_2$ is less than 10ev. Q.34 (a) F (b) O (c) Cl^-

Q.35 half filled and fully filled orbitals Q.36 (i) Cl (ii) Cs (iii) Al (iv) F (v) Xe

Q.37 Increases → a , b , d, h , j , k , Decrease → c , e , f , g , Same → i

Q.38 half filled & fully filled orbitals Q.39 Cs > Na > Mg > Si > Cl

Q.40 $r_k = 1.34Å > f_F$ Q.41 $IE_2 = 1825$ kJ/mole, $IE_3 = 2737.5$ kJ/mol

Q.42 1.686×10^{23} atom Q.43 3.476 eV Q.44 $EN_1 > EN_2$

Q.45 1.21 Å Q.46 No Q.47 4.64 Å ; b = 3.28 Å

Q.48 ICl Q.49 low IE Q.50 (a) P–Cl (b) S–O, (C) N–F

Q.51 He < Ne < Ar < Kr < Xe < Rn Q.52 Fe = 37.81%, Cl = 62.19%

Q.53 17.15 Q.54 (i) 9.4 (ii) 13.85

Q.55 (a) 63, (b) 60.15, (c) 2.85, (d) 20.4. (e) valance electron

Q.56 Be^{+3}

Q.57 2.2, (Slater's rule) 2.25 (Bohr's model)

Q.58 (a) $Al^{+3} > Mg^{+2} > Na^+$, (b) $Al^{+3} > Mg^{+2} > Na^+$, (c) $Al^{+3} > Mg^{+2} > Na^+$, (d) $Na^+ > Mg^{+2} > Al^{+3}$, (e) $Na^{+2} > Mg^{+2} > Al^{+3}$

Q.59 Size of Li^+ is very small & hence attracts H_2O. (electron rich species)more strongly.

Q.60 Li_2O < BeO < B_2O_3
basic amphoteric acidic

Q.61 BaO Q.62 $Cl_2O_7 < SO_3 < P_4O_{10} < Na_2O < SiO_2 < Al_2O_3 < MgO$

Q.63 False

Q.64 (a) SE, (b) IE $\propto 1/\Delta H_f$, (c) LE Q.65 –185 kcal/mole Q.66 –73.2 kcal/mole

EXERCISE # II

Q.1 A Q.2 C Q.3 C Q.4 A

Q.5 D Q.6 A, B Q.7 small size (repulsion)

Q.8 A Q.9 D Q.10 A Q.11 B

Q.12 A, D Q.13 B Q.14 $Li^+ < Al^{+3} < Mg^{2+} < K^+$

Q.15 B Q.16 B Q.17 Ionic

Q.18 A, B, C Q.19 D Q.20 C Q.21 C

Q.22 C Q.23 B Q.24 A Q.25 True

Q.26 B Q.27 B Q.28 A

BANSALCLASSES

TARGET IIT JEE 2007

PHYSICAL CHEMISTRY

XII (ALL)

CHEMICAL EQUILIBRIUM

" A SPECIALLY DESIGNED KIT FOR LEARNING."

CONTENTS

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THE KEY

CHEMICAL EQUILIBRIUM

Most of the chemical reaction do not go to completion in a closed system and attain a state of equilibrium. Equilibrium is said to have reached in a physical or chemical system when rate of forward and reverse processes are equal. At equilibrium macroscopic properties of the system like concentration. Pressure ect. become constant at constant temperature.

State of chemical equilibrium is characterised by equilibrium constant. Equilibrium constant have constant value at a given temperature.

UNDERSTANDING EQUILIBRIUM

There are two approaches to understand nature of equilibrium. One stems from kinetics as developed by Gulberg and Wagge (1863). The other approach comes from thermodynaics. Equilibrium criteria is explained on the basis of thermodynamic function like ΔH (change in enthalpy), ΔS (change in entropy) and ΔG (change in Gibb's function).

According to kinetic approaches -The state of equilibrium is characterised by equal rate of forward and backward process.
At equilibrium

$$\boxed{\text{Rate of forward reaction} = \text{Rate of backward reaction.}}$$

Example : Physical equilibria. Solid liquid equilibria
Solid $\rightleftharpoons$ liquid
Example: $H_2O\,(s) \rightleftharpoons H_2O(l)$: 273 K ; 1 atm P.

Solid ice and liquid can coexist at 273 K and 1 atm. Solid form is said to be in equilibrium with liquid form. At equilibrium, if heat exchanged from surrounding is zero, amount of solid ice and liquid water will remain unchanged. However it must be noted that, the process of conversion of ice into water and vica-versa-never ceases. At equilibrium

$$\boxed{\text{Net rate of conversion of ice into water} = \text{Net rate of conversion of water into ice.}}$$

OTHER EXAMPLES OF PHYSICAL EQUILIBRIA

The liquid vapour equilibria :

(i) Example : $H_2O\,(l) \rightleftharpoons H_2O\,(g)$ 373 K ; 1 atm pressure.
Equilibrium is characterized by constant value of vapour pressure of $H_2O\,(l)$ at 373 K (= 1 atm)

Net rate of condensation of H_2O (g) = net rate of evaporation of H_2O (l)

(ii) Sugar (s) $\rightleftharpoons$ sugar (aq)
This is example of dissolution equilibria Equilibrium is characterised by constant molar concentration of sugar at specified temperature. At equilibrium, the solution of sugar in aqueous solution is called saturated solution.

(iii) The dissolution of gas in liquid.
Example $CO_2\,(g) + H_2O \rightleftharpoons CO_2(aq)$
The concentration of gas in liquid is proportional to the pressure of gas over the liquid.

Process	*Characteristic constant*
$H_2O\ (l) \rightleftharpoons H_2O\ (g)$	P_{H_2O} constant at given temperature
$H_2O\ (s) \rightleftharpoons H_2O\ (l)$	P_{H_2O} constant at given temperature
solute (s) $\rightleftharpoons$ solute (solⁿ)	concentration of solute is constant at given temperature
gas (g) $\rightleftharpoons$ gas (aq)	[Gas(aq)]/[Gas(g)] = constant at given temperature

IMPORTANT CHARACTERISTIC OF EQUILIBRIUM

(i) Equilibrium is possible only in closed system.
(ii) The rate of forward process at equilibrium is equal to rate of backward process.
(iii) All measurable properties of system remain constant over time.
(iv) When equilibriums is attained for a physical process, it is characterised by constant value of one of its parameter
(v) The constant value of these parameters indicate extent to which equilibria is shifted in forward direction.
(vi) Both, *Kinetic* and *Thermodynamics* theories can be invoked to understand the extent to which a reaction proceed to forward direction. *e.g.* If extent of reaction is too large for forward direction (equilibrium is tilted heavily to forward direction) than
  (a) Specific rate of forward reaction >>> specific rate of backward reaction
  (b) Product is thermodynamically very stable as compared to reactant.
  (c) Gibb's function of product is vary small as compared to Gibb's function of reactant.

EQUILIBRIUM IN CHEMICAL PROCESS

A general equation for a reversible reaction may be written

$$mA + nB + \ldots\ldots \rightleftharpoons xC + yD + \ldots\ldots$$

we can write the reaction quotient, Q for this equation as

$$Q = \frac{[C]^x[D]^y\ldots\ldots}{[A]^m[B]^n\ldots\ldots}$$

where we use bracket to indicate "molar concentration of." The reaction quotient is a ratio of the molar concentrations of the product of the chemical equation (multiplied together) and of the reactants (also multiplied together), each raised to a power equal to the coefficient preceding that substance in the balanced chemical equation. The reaction quotient for the reversible reaction.

$$2NO_2\ (g) \rightleftharpoons N_2O_4\ (g)$$

is given by the expression $Q = \dfrac{[N_2O_4]}{[NO_2]^2}$

The numerical value of Q for a given reaction varies ; it depends on the concentration of products and reactants present at the time when Q is determined.

When a mixture of reactants and products of a reaction reaches equilibrium at a given temperature, its reaction quotient always has the same value. This value is called the equilibrium constant, K, of the reaction at that temperature. When a reaction is at equilibrium at a given temperature, the concentration of reactants and products is such that the value of reaction quotient, Q is always equal to the equilibrium constant, K, for that reaction at that temperature.

The mathematical expression that indicates that a reaction quotient always assumes the same value at equilibriums

$$Q = K = \frac{[C]^x[D]^y\ldots\ldots}{[A]^m[B]^n\ldots\ldots}$$

is a mathematical statement of the *law of mass action*. When a reaction has attained equilibrium at a given temperature, the reaction quotient for the reaction always has the same value.

The magnitude of an equilibrium constant is a measure of the yield of a reaction when it reaches equilibrium.

A large value for K indicates that equilibrium is attained only after the reactants have been largely converted into products. A small value of K-much less than 1-indicates the equilibrium is attained when only a small proportion of the reactants have been converted into products.

Regardless of the initial mixture of reactants and products in a reversible reaction, the composition of a system will always adjust itself to a condition of equilibrium for which the value of the reaction quotient is equal to the equilibrium constant for the system, provided that the temperature does not change.

An equilibrium can be established either starting from reactants or starting from products. In fact, one technique that is used to determine whether a reaction it truly at equilibrium is to approach equilibrium starting with reactants in one experiment and starting with products in another. If the same value of the reaction quotient is observed when the concentrations stop changing in both experiments, then we may be certain that the system has reached equilibrium.

We should calculate the value of Q or K from the activities of the reactants and products rather than from their concentrations. However, the activity of a dilute solute is usefully approximated by its molar concentration; so we will use concentrations as approximated by its pressure (in atmospheres), so we use pressures for gases. However, we also can use molar concentrations of gases in our equilibrium calculations, because the molar concentration of a gas is directly proportional to its pressure. The activity of a pure solid or pure liquid is 1, and the activity of a solvent in a dilute solution is close to 1. Thus these species (solids, liquids, and solvents) are omitted from reactions quotients and equilibrium calculations.

Using concentrations and pressure instead of activities means that we calculate approximate values for reaction quotients and equilibrium constants. However, these approximations hold well for dilute solutions and for gases with pressures less than about 2 atmospheres.

CONCENTRATION VERSES TIME GRAPH FOR HABER PROCESS

$$3H_2(g) + N_2(g) \longrightarrow 2NH_3(g)$$

Starting with pure H_2 and N_2 as reaction proceeds in forward direction. Ammonia is formed. At initially conc. of H_2 and N_2 drops and attain a steady value at equilibrium. On the others hand conc. of NH_3 increases and at equilibrium attains a constant value.

Concentration time graphs for $N_2 + 3H_2 \rightleftharpoons 2NH_3$

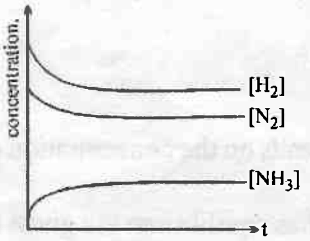


fig (1)

Concentration time graph for $H_2 + I_2 \rightleftharpoons 2HI$

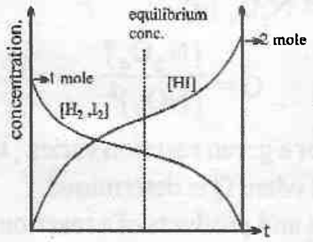


fig (2)

This graph shows how equilibrium state can be achieved from both direction.

HOMOGENEOUS CHEMICAL EQUILIBRIA

A homogeneous equilibrium is equilibrium with in a single phase i.e. when physical state of all the reactants and product are same.

LIQUID PHASE HOMOGENEOUS EQUILIBRIUM

Example : (i) $I_2\,(aq) + I^-\,(aq) \rightleftharpoons I_3^-\,(aq)$

(ii) $Hg_2^{2+}\,(aq) + NO_3^-(aq) + 3H_3O^+(aq) \rightleftharpoons 2Hg^{2+}\,(aq) + HNO_2(aq) + 4H_2O(l)$

(iii) $NH_3(aq) + H_2O\,(l) \rightleftharpoons NH_4^+(aq) + OH^-\,(aq)$

Eq. constants for

(i) $K = \dfrac{[I_3^-(aq)]}{[I_2(aq)][I^-(aq)]}$

(ii) $K = \dfrac{[Hg^{2+}]^2[HNO_2]}{[Hg_2^{2+}][NO_3^-][H_3O^+]^3}$

(iii) $K = \dfrac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]}$

The equilibrium constant in all theses cases can be called K_C. The subscrit 'C' denoting active masses of solute expressed in terms of molar concentration.

HOMOGENEOUS EQUILIBRIA IN GASES

Example : (i) $C_2H_6(g) \rightleftharpoons C_2H_4() + H_2(g)$

(ii) $3O_2(g) \rightleftharpoons 2O_3(g)$

(iii) $C_3H_8(g) + 5O_2(g) \rightleftharpoons 3CO_2(g) + 4H_2O(g)$

Equilibrium constant expression for then are

(i) $K_C = \dfrac{[C_2H_4O)][H_2]}{[C_2H_6(g)]}$ $K_P = \dfrac{[P_{C_2H_4}][P_{H_2}]}{[P_{C_2H_6}]}$

[ ] represents concentration in mol/ litre at equilibrium

$P_{C_2H_4}$ & other are partial pressure at equilibrium

(ii) $K_C = \dfrac{[O_3]^2}{[O_2]^3}$ $K_P = \dfrac{P_{O_3}^2}{P_{O2}^3}$

(iii) $K_C = \dfrac{[CO_2]^2[H_2O]^4}{[C_3H_8][O_2]^5}$ $K_P = \dfrac{P_{CO_2}^3 \cdot P_{H_2O}^4}{P_{C_3H_8} \cdot P_{O_2}^5}$

Note : Equilibrium constant for gaseous homogeneous equilibrium can be expressed in two ways Vi2; K_P and K_C. This means value of equilibrium constant depends upon choice of standard state in which concentration of reactant's and product are expressed.

HETROGENEOUS EQUILIBRIA

If reactants and product are found in two or more phases, the equilibria describing them is called hetrogeneous equilibrium.

Example: (i) $PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-\,(aq)$

(ii) $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$

(iii) $Br_2\,(l) \rightleftharpoons Br_2(g)$

Equilibrium expression for them can be written as

(i) $K = [Pb^{2+}(aq)][Cl^-(aq)]^2$

(ii) $K_P = \dfrac{1}{P_{CO_2}}$ $K_C = \dfrac{1}{[CO_2(g)]}$

(iii) $K_P = P_{Br_2}$ $K_C = [Br_2(g)]$

Note : Active masses of pure solid and liquid are taken as T. It is because as pure solids and liquid took part in reaction, their concentration (or density) remain constant. In thermodynamic sense. We can say this is because Gibb's functions for pure solid and liquid is defined at stipulated pressure of 1.00 bar and as pressure of system changes, Gibb's function for pure solid and liquid remain constant and equal to their value at 1 bar.

UNIT OF EQUILIBRIUM CONSTANT

We have already noted that the value of an equilibrium constant has meaning only when we give the corresponding balanced chemical equation. Its value changes for the new equation obtained by multiplying or dividing the original equation by a number. The value for equilibrium constant, K_C is calculate substituting the concentration in mol/L and for K_P by substituting partial pressure in Pa, kPa, etc. in atm. Thus, units of equilibrium constant will turn out to be units based on molarity or pressure, unless the sum of the exponents in the numerator is equal to the sum of the exponents in the denominator. Thus for the reaction:

$H_2(g) + I_2(g) \rightleftharpoons 2HI$, K_C and K_P do not have any unit

$N_2(g) + 3H_2(g) \rightleftharpoons 2\,NH_3$, K_C has unit $(mol/L)^{-2}$ and K_P has unit bar^{-2} or

$N_2O_4\,(g) \rightleftharpoons 2NO_2$, K_C has unit mol / L and K_P has unit bar

However, these days we express equilibrium constants in dimensionless quantities by specifying the standard state of the reactants and the products. The standard state for pure gas is 1 bar and now the partial pressure are measured with respect to this standard. Thus a pressure of 2 bar in term of this standard state is equal to 2 bar / 1 bar = 2, a dimensionless number. Similarly for a solute the standard state; c_0, is 1 molar solution and all concentrations are measured with respect to it. The numerical value of equilibrium constant depends on the standard state chosen.

FACTOR'S AFFECTING EQUILIBRIA

Effect of change in concentration on equilibrium. A chemical system at equilibrium can be shifted out of equilibrium by adding or removing one more of reactants or products. Shifting out of equilibrium doesn't mean that value of equilibrium constant change. Any alteration of concentration of reactant or product will disturb the equilibrium and concentration of reactant and product one readjust to one again attain equilibrium concentration.

In other word, as we add or remove reactant (or product) the ratio of equilibrium concentration become 'Q' (reaction quotient) and depending upon.

Q < K : equilibrium will shift in forward direction.

Q >K : equilibrium will shift in backward direction.

Example: $Fe^{3+}\,(a) + SCN^-\,(aq) \rightleftharpoons Fe\,(SCN)^{2+}(aq)$

(i) adding Fe^3 or SCN^- will more $\dfrac{[Fe(SCN)^{2+}]}{[Fe^{3+}][SCN^-]}$ = Q less then K_C and equilibria will shift in forward direction.

(ii) Removing $Fe(SCN)^{2+}$ will have same effect

(iii) Adding $Fe(SCN)^{2+}$ from outside source in equilibrium mixture will have effect of increasing 'Q' hence reaction shift in backward direction.

EFFECT OF CHANGE IN PRESSURE

Sometimes we can change the position of equilibrium by changing the pressure on a system. However, changes in pressure have a measurable effect only in system where gases are involved – and then only when the chemical reaction produces a change in the total number of gas molecules in the system.

As we increase the pressure of a gaseous system at equilibrium, either by decreasing the volume of the system or by adding more of the equilibrium mixture, we introduce a stress by increasing the number of molecules per unit of volume. In accordance with Le Chatelier's principle, a chemical reaction that reduces the total number of molecules per unit of volume will be favored because this relieves the stress. The reverse reaction would be favoured by a decrease in pressure.

Consider what happens when we increase the pressure on a system in which NO, O_2 and NO_2 are in equilibrium

Example : $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

The formation of additional amounts of NO_2 decreases the total number of molecules in the system, because each time two molecules of NO_2 form, a total of three molecules of NO and O_2 react. This reduces the total pressure exerted by the system and reduces, but does not completely relieve, the stress of the increased pressure. On the other hand, a decrease in the pressure on the system favors decomposition of NO_2 into NO and O_2 which tends to restore the pressure.

Let us now consider the reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

Because there is no change in the total number of molecules in the system during reaction, a change in pressure does not favor either formation or decomposition of gaseous nitric oxide.

EFFECT OF CHANGE IN TEMPERATURE ON EQUILIBRIUM

Changing concentration or pressure upsets an equilibrium because the reaction quotient is shifted away from the equilibrium value. Changing the temperature of a system at equilibrium has a different effect: A change in temperature changes the value of the equilibrium constant. However, we can predict the effect of the temperature change by treating it as a stress on the system and applying Le Chatelier's principle. When hydrogen reacts with gaseous iodine, energy is released as heat is evolved.

$$H_2(g) + I_2(g) \rightleftharpoons 2I(g) \quad \Delta H = -9.4 \text{ kJ (exothermic)}$$

Because this reaction is exothermic, we can write it with heat as a product.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) + 9.4 \text{ kJ}$$

Increasing the temperature of the reaction increases the amount of energy present. Thus, increasing the temperature has the effect of increasing the amount of one of the products of this reaction. The reaction shifts to the left to relieve the stress, and there is an increase in the concentration of H_2 and I_2 and a reduction in the concentration of HI. When we change the temperature of a system at equilibrium, the equilibrium constant for the reaction changes. Lowering the temperature in the HI system increases the equilibrium constant from 50.0 at 400°C to 67.5 at 357°C. At equilibrium at the lower temperature, the concentration of HI has increased and the concentrations of H_2 and I_2 have decreased. Raising the temperature decreases the value of the equilibrium constant from 67.5 at 357°C to 50.0 at 400°C.

EFFECT OF TEMPERATURE : VAN'T HOFF EQUATION

(a) $\dfrac{d(\ell nK)}{dT} = \dfrac{\Delta H^\circ}{RT^2}$ (b) $\dfrac{d(\ell nK)}{d(\frac{1}{T})} = -\dfrac{\Delta H^\circ}{R}$. **Integrated form** $ln\left(\dfrac{K_2}{K_1}\right) = -\dfrac{\Delta H^\circ}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$

A THERMODYNAMIC RELATIONSHIP :

$$\Delta G^\circ = -RT\,lnK\ .$$

EFFECT OF CATALYST ON EQUILIBRIUM

A catalyst has no effect on the value of an equilibrium constant or on equilibrium concentrations. The catalyst merely increase the rates of both the forward and the reverse reactions to the same extent so that equilibrium is reached more rapidly.

All of these effects change in concentration or pressure, change in temperature, and the effect of a catalyst on a chemical equilibrium play a role in the industrial synthesis of ammonia from nitrogen and hydrogen according to the equation.

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

One way to increase the yield of ammonia is to increase the pressure on the system in which N_2, H_2 and NH_3 are in equilibrium or are coming to equilibrium.

$N_2(g)\ 3H_2(g) \rightleftharpoons 2NH_3(g)$

The formation of additional amounts of ammonia reduces the total pressure exerted by the system and somewhat reduces the stress of the increased pressure.

Although increasing the pressure of a mixture of N_2, H_2 and NH_3 increase the yield ammonia, at low temperatures the rate of formation of ammonia is slow. At room temperature, for example, the reaction is so slow that if we prepared a mixture of N_2 and H_2, no detectable amount of ammonia would form during our lifetime. Attempts to increase the rate of the reaction by increasing the temperature are counterproductive. The formation of ammonia from hydrogen and nitrogen is an exothermic process:

$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) \qquad \Delta H = -92.2\text{ kJ}$

Thus increasing the temperature to increase the rate lowers the yield. If we lower the temperature to shift the equilibrium to the right to favor the formation of more ammonia, equilibrium is reached more slowly because of the large decrease of reaction rate with decreasing temperature.

Part of the rate of formation lost by operating at lower temperatures can be recovered by using a catalyst to increase the reaction rate. Iron powder is one catalyst used. However, as we have seen, a catalyst serves equally well to increase the rate of a reverse reaction in this case, the decomposition of ammonia into its constituent elements. Thus the net effect of the iron catalyst on the reaction is to cause equilibrium to be reached more rapidly.

In the commercial production of ammonia, conditions of about 500°C and 150–900 atmosphere are selected to give the best compromise among rate, yield and the cost of the equipment necessary to produce and contain gases at high pressure and high temperatures.

APPLICATION OF EQUILIBRIUM CONSTANT

Before we consider the applications of equilibrium constants, let us consider its important features:

(i) the expression for equilibrium constant, K is applicable only when concentrations of the reactants and products have attained their equilibrium values and do not change with time.

(ii) The value of equilibrium constant is independent of initial concentration of the reactants and product. Equilibrium constant has one unique value for a particular reaction represented by a balanced equation at a given temperature.

(iii) The equilibrium constant for the reverse reaction is equal constant for the forward reaction.

(iv) The equilibrium constant, K for a reaction is related to the equilibrium constant of the corresponding reaction whose equation is obtained by multiplying or dividing the equation for the original reaction by a small integer.

Now we will consider some applications of equilibrium constant and use it to answer question like:

(i) predicting the extent of a reaction on the basis of its magnitude.

(ii) predicting the direction of the reaction, and

(iii) calculating equilibrium concentration.

Predicting the extent of a reaction

The magnitude of equilibrium constant is very useful especially in reactions of industrial importance. An equilibrium constant tells us whether we can expect a reaction mixture to contain a high or low concentration of product(s) at equilibrium. (It is important to note that an equilibrium constant tells us nothing about the rate at which equilibrium is reached). In the expression of K_C or K_P, product of the concentrations of products is written in numerator and the product of the concentrations of reactants is written in denominator. High value of equilibrium constant indicates that product(s) concentration is high and its low value indicates that concentration of the product(s) in equilibrium mixture is low.

For reaction, H_2 (g) + Br_2(g) $\rightleftharpoons$ 2HBr(g), the value of

$$K_P = \frac{(P_{HBr})^2}{(P_{H_2})(P_{Br_2})} = 5.4 \times 10^{18}$$

The large value of equilibrium constant indicates that concentration of the product, HBr is very high and reaction goes nearly to completion.

Similarly, equilibrium constant for the reaction H_2(g) + Cl_2(g) $\rightleftharpoons$ 2HCl(g) aty 300 K is very high and reaction goes virtually to completion.

$$K_C = \frac{[HCl]^2}{[H_2][Cl_2]} = 4.0 \times 10^{31}$$

Thus, large value of K_P or K_C (larger than about 10^3), favour the products strongly. For intermediate values of K (approximately in the range of 10^{-3} to 10^3), the concentrations of reactants and products are comparable. Small values of equilibrium constant (smaller than 10^{-3}), favour the reactants strongly.

At 298 K for reaction, N_2(g) + O_2(g) $\rightleftharpoons$ 2NO(g)

$$K_C = \frac{[NO]^2}{[N_2][O_2]} - 4.8 \times 10^{-31}$$

The very small value of K_C implies that reactants N_2 and O_2 will be the predominant species in the reaction mixture at equilibrium.

Predicting the direction of the reaction.

The equilibrium constant is also used to find in which direction an rabidity reaction mixture of reactants and products will proceed. For this purpose, we calculate the reaction quotient, Q. The reaction quotient is defined in the same way as the equilibrium constant (with molar concentrations to give Q_C, or with partial pressure to give Q_P) at any stage of reaction. For a general reaction:

$$aA + bB \rightleftharpoons cC + dD$$

$$Q_C - \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Then, if $Q_C > K_c$, the reaction will proceed in the direction of reactants (reverse reaction).
if $Q_C < K_c$, the reaction will move in the direction of the products
if $Q_C = K_c$, the reaction mixture is already at equilibrium.

In the reaction, H_2(g) + I_2(g) $\rightleftharpoons$ 2HI(g), if the molar concentrations of H_2, I_2 and HI are 0.1 mol L^{-1} respectively at 783 K, then reaction quotient at this stage of the reaction is

$$Q_C = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.4)^2}{(0.1)(0.2)} = 8$$

K_C for this reaction at 783 K is 46 and we find that $Q_C < K_C$. The reaction, therefore, will move to right i.e. more H_2(g) and I_2(g) will react to form more HI (g) and their concentration will decrease till $Q_C = K_C$.

THE ATLAS

EQUILIBRIUM

Type of equilibria

Physical Equilibrium

1. Solid - Liquid
2. Liquid - gas
3. Solid- Liquid - gas
4. Solubility of Solute in solution
5. Solubility of gas in solution

Chemical Equilibrium

(1) Reaction quotient:
(2) Significance of equilibrium constant
(3) Law of mass action:
(4) Homogeneous equilibria
(a) degree of dissociation from vapour density measurement
(b) relation between K_P and K_C
(5) Equilibrium constant K_P and K_C
(6) Hetreogeneous equilibrium
(7) Temperature dependent of equilibrium constant
(8) Kinetics & equilibrium constant

Application of equilibrium constant

(i) Pridicting extent of reaction
(ii) Pridicting direction of change
(iii) Calculation of equilibrium concentration

Le Chatleir's principle

Effect of following factor's on equlibrium	Once pressure temperature catalyst inert gas

Temperature dependence- Von't Hoff's equation

Understanding equilibrium
(i) From kinetic's approach (Gulber & Wagge approach)
(ii) From thermodynamics approach – Criteria for equilibrium in terms of Gibb's function

EXERCISE I

Reaction quotient and equilibrium constant

Q.1 The initial concentrations or pressure of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the directions in which each system will shift to reach equilibrium.

(a) $2NH_3\,(g) \rightleftharpoons N_2\,(g) + 3H_2\,(g)$ $K = 17$
$[NH_3] = 0.20$ M ; $[N_2] = 1.00$ M ; $[H_2] = 1.00$ M

(b) $2NH_3\,(g) \rightleftharpoons N_2\,(g) + 3H_2\,(g)$ $K_p = 6.8 \times 10^4\ \text{atm}^2$
Initial pressure : $NH_3 = 3.0$ atm ; $N_2 = 2.0$ atm ; $H_2 = 1.0$ atm

(c) $2SO_3(g) \rightleftharpoons 2SO_2\,(g) + O_2\,(g)$ $K = 0.230$ atm
$[SO_3] = 0.00$ M ; $[SO_2] = 1.00$ M ; $[O_2] = 1.00$ M

(d) $2SO_3(g) \rightleftharpoons 2SO_2\,(g) + O_2\,(g)$ $K_p = 16.5$ atm
Initial pressure : $SO_3 = 1.0$ atm ; $SO_2 = 1.0$ atm ; $O_2 = 1.0$ atm

(d) $2NO(g) + Cl_2\,(g) \rightleftharpoons 2NOCl\,(g)$ $K = 4.6 \times 10^4$
$[NO] = 1.00$ M ; $[Cl_2] = 1.00$ M ; $[NOCl] = 0$ M

(f) $N_2\,(g) + O_2\,(g) \rightleftharpoons 2NO\,(g)$ $K_p = 0.050$
Initial pressure : NO = 10.0 atm ; $N_2 = O_2 = 5$ atm

Q.2 Among the solubility rules is the statement that all chlorides are soluble except Hg_2Cl_2, AgCl, $PbCl_2$, and CuCl.

(a) Write the expression for the equilibrium constant for the reaction represented by the equation.
$AgCl\,(s) \rightleftharpoons Ag^+(aq) + Cl^-\,(aq)$
Is K greater than 1, less than 1, or about equal to 1? Explain your answer

(b) Write the expression for the equilibrium constant for the reaction represented by the equation
$Pb^{2+}\,(aq) + 2Cl^-\,(aq) \rightleftharpoons PbCl_2\,(s)$
Is K greater than 1, less than 1, or about equal to 1? Explain your answer.

Q.3 Among the solubility rules is the statement that carbonates, phosphates, borates, arsenates, and arsenites, except those of the ammonium ion and the alkali metals are insoluble.

(a) Write the expression for the equilibrium constant for the reaction represented by the equation
$CaCO_3\,(s) \rightleftharpoons Ca^{2+}\,(aq) + CO_3^{2-}\,(aq)$
Is K greater than 1, less than 1, or about equal to 1? Explain your answer

(b) Write the expression for the equilibrium constant for the reaction represented by the equation.
$3Ba^{2+}\,(aq) + 2PO_4^{3-}\,(aq) \rightleftharpoons Ba_3(PO_4)_2\,(s)$
Is K greater than 1, less than 1, or about equal to 1? Explain your answer.

Q.4 Benzene is one of the compounds used as octane enhancers in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene.
$3C_2H_2 \longrightarrow C_6H_6$
Would this reaction be most useful commercially if K were about 0.01, about 1, or about 10? Explain your answer.

Q.5 Show the complete chemical equation and the net ionic equation for the reaction represented by the equation
$KI\,(aq) + I_2\,(aq) \rightleftharpoons KI_3\,(aq)$
give the same expression for the reaction quotient. KI_3 is composed of the ions K^+ and I_3^-.

Pentagonal bipyramidal?

} I_3^- has 10e⁻ on central Iodine.

Using the equilibrium constant

Q.6 Which of the following reactions goes almost all the way to completion, and which proceeds hardly at all?

(a) $N_2(g) + O_2(g) \rightleftharpoons 2NO\ (g)$; $K_c = 2.7 \times 10^{-18}$

(b) $2NO(g) + O_2(g) \rightleftharpoons 2NO_2\ (g)$; $K_c = 6.0 \times 10^{13}$

Q.7 For which of the following reactions will the equilibrium mixture contain an appreciable concentration of both reactants and products?

(a) $Cl_2(g) \rightleftharpoons 2Cl\ (g)$; $K_c = 6.4 \times 10^{-39}$

(b) $Cl_2(g) + 2NO\ (g) \rightleftharpoons 2NOCl\ (g)$; $K_c = 3.7 \times 10^{8}$

(c) $Cl_2(g) + 2NO_2\ (g) \rightleftharpoons 2NO_2Cl\ (g)$; $K_c = 1.8$

Q.8 The value of K_c for the reaction $3O_2\ (g) \rightleftharpoons 2O_3\ (g)$ is 1.7×10^{-56} at 25°C. Do you expect pure air at 25°C to contain much O_3 (ozone) when O_2 and O_3 are in equilibrium? If the equilibrium concentration of O_2 in air at 25°C is 8×10^{-3} M, what is the equilibrium concentration of O_3?

Q.9 At 1400 K, $K_c = 2.5 \times 10^{-3}$ for the reaction $CH_4\ (g) + 2H_2S \rightleftharpoons CS_2(g) + 4H_2(g)$. A 10.0 L reaction vessel at 1400 K contains 2.0 mol of CH_4, 3.0 mol of CS_2, 3.0 mol of H_2 and 4.0 mol of H_2S. Is the reaction mixture at equilibrium? If not, in which direction does the reaction proceed to reach equilibrium?

Q.10 The first step in the industrial synthesis of hydrogen is the reaction of steam and methane to give water gas, a mixture of carbon monoxide and hydrogen.

$$H_2O\ (g) + CH_4(g) \rightleftharpoons CO\ (g) + 3H_2(g)\quad K_c = 4.7 \text{ at } 1400\text{ K}$$

A mixture of reactants and product at 1400 K contains 0.035 M H_2O, 0.050M CH_4, 0.15 M CO, and 0.20 M H_2. In which direction does the reaction proceed to reach equilibrium?

Q.11 An equilibrium mixture of N_2, H_2, and NH_3 at 700 K contains 0.036 M N_2 and 0.15 M H_2. At this temperature, K_c for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is 0.29. What is the concentration of NH_3?

Q.12 The air pollutant NO is produced in automobile engines from the high temperature reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO\ (g)$; $K_c = 1.7 \times 10^{-3}$ at 2300 K. If the initial concentrations of N_2 and O_2 at 2300 K are both 1.40 M, what are the concentrations of NO, N_2, and O_2 when the reaction mixture reaches equilibrium?

Q.13 At a certain temperature, the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ has an equilibrium constant $K_c = 5.8 \times 10^{-2}$. Calculate the equilibrium concentrations of PCl_5, PCl_3 and Cl_2 if only PCl_5 is present initially, at a concentration of 0.160 M.

Q.14 At 700 K, $K_p = 0.140$ for the reaction $ClF_3\ (g) \rightleftharpoons ClF\ (g) + F_2(g)$. Calculate the equilibrium partial pressure of ClF_3, ClF, and F_2 if only ClF_3 is present initially, at a partial pressure of 1.47 atm.

Homogeneous equilibria degree of dissociation, vapour density and equilibrium constant

Q.15 The degree of dissociation of N_2O_4 into NO_2 at 1.5 atmosphere and 40°C is 0.25. Calculate its K_p at 40°C. Also report degree of dissociation at 10 atmospheric pressure at same temperature.

Q.16 At 46°C, K_p for the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is 0.667 atm. Compute the percent dissociation of N_2O_4 at 46° C at a total pressure of 380 Torr.

Q.17 When 36.8g $N_2O_4(g)$ is introduced into a 1.0-litre flask at 27°C. The following equilibrium reaction occurs : $N_2O_4(g) \rightleftharpoons 2NO_2(g)$; $K_p = 0.1642$ atm.

(a) Calculate K_c of the equilibrium reaction.

(b) What are the number of moles of N_2O_4 and NO_2 at equilibrium?

(c) What is the total gas pressure in the flask at equilibrium?

(d) What is the percent dissociation of N_2O_4?

Q.18 At some temperature and under a pressure of 4 atm, PCl_5 is 10% dissociated. Calculate the pressure at which PCl_5 will be 20% dissociated, temperature remaining same.

Q.19 In a mixture of N_2 and H_2 in the ratio of 1:3 at 64 atmospheric pressure and 300°C, the percentage of ammonia under equlibrium is 33.33 by volume. Calculate the equilibrium constant of the reaction using the equation. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$.

Q.20 The system $N_2O_4 \rightleftharpoons 2NO_2$ maintained in a closed vessel at 60°C & a pressure of 5 atm has an average (i.e. observed) molecular weight of 69, calculate K_p. At what pressure at the same temperature would the observed molecular weight be (230/3)?

Q.21 The vapour density of N_2O_4 at a certain temperature is 30. Calculate the percentage dissociation of N_2O_4 at this temperature. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$.

Q.22 In the esterfication $C_2H_5OH\ (l) + CH_3COOH\ (l) \rightleftharpoons CH_3COOC_2H_5\ (l) + H_2O\ (l)$ an equimolar mixture of alcohol and acid taken initially yields under equilibrium, the water with mole fraction = 0.333. Calculate the equilibrium constant.

Hetrogeneous equilibrium

Q.23 Solid Ammonium carbamate dissociates as: $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$. In a closed vessel solid ammonium carbamate is in equilibrium with its dissociation products. At equilibrium, ammonia is added such that the partial pressure of NH_3 at new equilibrium now equals the original total pressure. Calculate the ratio of total pressure at new equilibrium to that of original total pressure.

Q.24 A sample of $CaCO_3(s)$ is introduced into a sealed container of volume 0.821 litre & heated to 1000K until equilibrium is reached. The equilibrium constant for the reaction $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ is 4×10^{-2} atm at this temperature. Calculate the mass of CaO present at equilibrium.

Q.25 Anhydrous calcium chloride is often used as a dessicant. In the presence of excess of $CaCl_2$, the amount of the water taken up is governed by $K_p = 6.4 \times 10^{85}$ for the following reaction at room temperature, $CaCl_2(s) + 6H_2O(g) \rightleftharpoons CaCl_2.6H_2O(s)$. What is the equilibrium vapour pressure of water in a closed vessel that contains $CaCl_2(s)$?

Q.26 20.0 grams of $CaCO_3(s)$ were placed in a closed vessel, heated & maintained at 727° C under equilibrium $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ and it is found that 75 % of $CaCO_3$ was decomposed. What is the value of K_p? The volume of the container was 15 litres.

Changes in concentration at equilibrium Le Chatelier's principle

Q.27 Suggest four ways in which the concentration of hydrazine, N_2H_4, could be increased in an equilibrium described by the equation

$$N_2(g) + 2H_2(g) \rightleftharpoons N_2H_4(g) \qquad \Delta H = 95\ kJ$$

Q.28 How will an increase in temperature affect each of the following equilibria? An increase in pressure?

(a) $2NH_3\,(g) \rightleftharpoons N_2\,(g) + 3H_2\,(g)$ $\quad \Delta H = 92$ kJ

(b) $N_2\,(g) + O_2\,(g) \rightleftharpoons 2NO\,(g)$ $\quad \Delta H = 181$ kJ

(c) $2O_3\,(g) \rightleftharpoons 3O_2\,(g)$ $\quad \Delta H = -285$ kJ

(d) $CaO\,(s) + CO_2\,(g) \rightleftharpoons CaCO_3\,(s)$ $\quad \Delta H = -176$ kJ

Q.29(a) Methanol, a liquid fuel that could possibly replace gasoline, can be prepared from water gas and additional hydrogen at high temperature and pressure in the presence of a suitable catalyst. Write the expression for the equilibrium constant for the reversible reaction.

$$2H_2\,(g) + CO\,(g) \rightleftharpoons CH_3OH\,(g) \qquad \Delta H = -90.2\ \text{kJ}$$

(b) Assume that equilibrium has been established and predict how the concentration of H_2, CO and CH_3OH will differ at a new equilibrium if (1) more H_2 is added. (2) CO is removed. (3) CH_3OH is added. (4) the pressure on the system is increased. (5) the temperature of the system is increased. (6) more catalyst is added.

Q.30(a) Water gas, a mixture of H_2 and CO, is an important industrial fuel produced by the reaction of steam with red-hot coke, essentially pure carbon. Write the expression for the equilibrium constant for the reversible reaction.

$$C(s) + H_2O\,(g) \rightleftharpoons CO\,(g) + H_2\,(g) \qquad \Delta H = 131.30\ \text{kJ}$$

(b) Assume that equilibrium has been established and predict how the concentration of each reactant and product will differ at a new equilibrium if (1) more C is added. (2) H_2O is removed. (3) CO is added. (4) the pressure on the system is increased. (5) the temperature of the system is increased.

Q.31 Ammonia is a weak base that reacts with water according to the equation

$$NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+ + OH^-\,(aq)$$

Will any of the following increase the percent of ammonia that is converted to the ammonium ion in water? (a) Addition of NaOH. (b) Addition of HCl. (c) Addition of NH_4Cl.

Q.32 Suggest two ways in which the equilibrium concentration of Ag^+ can be reduced in a solution of Na^+, Cl^-, Ag^+ and NO_3^-, in contact with solid AgCl.

$$Na^+\,(aq) + Cl^-\,(aq) + Ag^+\,(aq) + NO_3^-\,(aq) \rightleftharpoons AgCl\,(s) + Na^+\,(aq) + NO_3^-\,(aq) \quad \Delta H = -65.9\ \text{kJ}$$

Q.33 Additional solid silver sulfate, a slightly soluble solid, is added to a solution of silver ion and sulfate ion in equilibrium with solid silver sulfate. Which of the following will occur? (a) The Ag^+ and SO_4^{2-} concentration will not change. (b) The added silver sulfate will dissolve. (c) Additional silver sulfate will form and precipitate from solution as Ag^+ ions and SO_4^{2-} ions combine. (d) The Ag^+ ion concentration will increase and the SO_4^{2-} ion concentration will decrease.

Kinetics and equilibrium constant

Q.34 Consider a general, single-step reaction of the type $A + B \rightleftharpoons C$. Show that the equilibrium constant is equal to the ratio of the rate constant for the forward and reverse reaction, $K_c = k_f/k_r$.

Q.35 Which of the following relative values of k_f and k_r results in an equilibrium mixture that contains large amounts of reactants and small amounts of product?

(a) $k_f > k_r$ (b) $k_f = k_r$ (c) $k_f < k_r$

Q.36 Consider the gas-phase hydration of hexafluoroacetone, $(CF_3)_2CO$:

$$(CF_3)_2CO\,(g) + H_2O\,(g) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} (CF_3)_2C(OH)_2\,(g)$$

At 76°C, the forward and reverse rate constants are $k_f = 0.13\ M^{-1}s^{-1}$ and $k_r = 6.02 \times 10^{-4} s^{-1}$. What is the value of the equilibrium constant K_c?

Q.37 Consider the reaction of chloromethane with OH^- in aqueous solution

$$CH_3Cl\,(aq) + OH^-\,(aq) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} CH_3OH\,(aq) + Cl^-\,(aq)$$

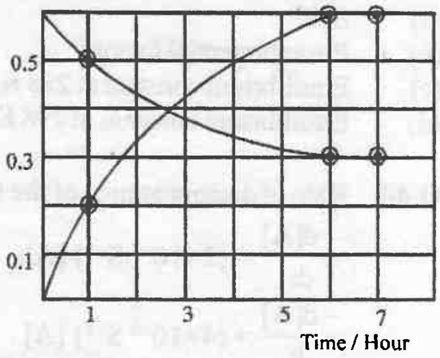
At 25°C, the rate constant for the forward reaction is $6 \times 10^{-6}\ M^{-1}s^{-1}$, and the equilibrium constant K_c is 1×10^{16}. Calculate the rate constant for the reverse reaction at 25°C.

Q.38 The progress of the reaction $A \rightleftharpoons nB$ with time, is presented in figure. Determine

(i) the value of n.

(ii) the equilibrium constant k.

(iii) the initial rate of conversion of A.



Temperature dependence of equilibrium constant

Q.39 Listed in the table are forward and reverse rate constants for the reaction $2NO\,(g) \rightleftharpoons N_2(g) + O_2(g)$

Temperature (K)	**k_f ($M^{-1}s^{-1}$)**	**k_r ($M^{-1}s^{-1}$)**
1400	0.29	1.1×10^{-6}
1500	1.3	1.4×10^{-5}

Is the reaction endothermic or exothermic? Explain in terms of kinetics.

Q.40 Forward and reverse rate constant for the reaction $CO_2(g) + N_2(g) \rightleftharpoons CO(g) + N_2O\,(g)$ exhibit the following temperature dependence.

Temperature (K)	**k_f ($M^{-1}s^{-1}$)**	**k_r ($M^{-1}s^{-1}$)**
1200	9.1×10^{-11}	1.5×10^{5}
1500	2.7×10^{-9}	2.6×10^{5}

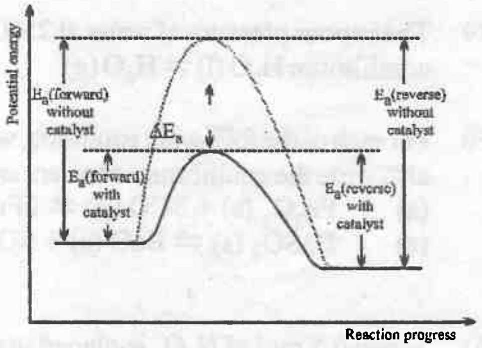
Is the reaction endothermic or exothermic? Explain in terms of kinetics.

Q.41 The equilibrium constant K_p for the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ is 3.81×10^2 at 600 K and 2.69×10^3 at 700 K. Calculate $\Delta_r H$.

Q.42 As shown in figure a catalyst lowers the activation energy for the forward and reverse reactions by the same amount, ΔE_a.

(a) Apply the Arrhenius equation, $K = Ae^{-E_a/RT}$ to the forward and reverse reactions, and show that a catalyst increases the rates of both reactions by the same factor.

(b) Use the relation between the equilibrium constant and the forward and reverse rate constants, $K_c = k_f/k_r$, to show that a catalyst does not affect the value of the equilibrium constant.



Temperature dependence of equilibrium constant

Q.43 Variation of equilibrium constant 'K' with temperature 'T' is given by equation

$$\log K = \log A - \frac{\Delta H^\circ}{2.303\,RT}$$

A graph between log K and 1/T was a straight line with –ve slope of 0.5 and intercept 10. Calculate

(a) ΔH°
(b) Pre exponential factor
(c) Equilibrium constant at 298 K
(d) Equilibrium constant at 798 K assuming ΔH° to be independent of temperature.

Q.44 Rate of disappearance of the reactant A at two different temperature is given by $A \rightleftharpoons B$

$$\frac{-d[A]}{dt} = (2\times10^{-2}\,S^{-1})\,[A] \quad - 4 \times 10^{-3}\,S^{-1}[B]\ ;\ 300K$$

$$\frac{-d[A]}{dt} = (4\times10^{-2}\,S^{-1})\,[A] \quad -16 \times 10^{-4}\,[B]\ ;\ 400K$$

Calculate heat of reaction in the given temperature range. When equilibrium is set up.

Q.45 The K_P for reaction $A + B \rightleftharpoons C + D$ is 1.34 at 60°C and 6.64 at 100°C. Determine the free energy change of this reaction at each temperature and ΔH° for the reaction over this range of temperature?

Equilibrium expressions and equilibrium constants

Q.46 If $K_c = 7.5 \times 10^{-9}$ at 1000 K for the reaction $N_2\,(g) + O_2\,(g) \rightleftharpoons 2NO\,(g)$, what is K_c at 1000 K for the reaction $2NO\,(g) \rightleftharpoons N_2\,(g) + O_2\,(g)$?

Q.47 An equilibrium mixture of PCl_5, PCl_3 and Cl_2 at a certain temperature contains 8.3×10^{-3} M PCl_5, 1.5×10^{-2} M PCl_3, and 3.2×10^{-2} M Cl_2. Calculate the equilibrium constant K_c for the reaction $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$.

Q.48 A sample of HI (9.30×10^{-3} mol) was placed in an empty 2.00 L container at 1000 K. After equilibrium was reached, the concentration of I_2 was 6.29×10^{-4} M. Calculate the value of K_c at 1000 K for the reaction $H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$.

Q.49 The vapour pressure of water at 25°C is 0.0313 atm. Calculate the values of K_p and K_c at 25°C for the equilibrium $H_2O\,(l) \rightleftharpoons H_2O\,(g)$.

Q.50 For each of the following equilibria, write the equilibrium constant expression for K_c. Where appropriate, also write the equilibrium constant expression for K_p.

(a) $Fe_2O_3\,(s) + 3CO\,(g) \rightleftharpoons 2Fe\,(l) + 3CO_2\,(g)$ (b) $4Fe\,(s) + 3O_2\,(g) \rightleftharpoons 2Fe_2O_3\,(s)$
(c) $BaSO_4\,(s) \rightleftharpoons BaO\,(s) + SO_3\,(g)$ (d) $BaSO_4\,(s) \rightleftharpoons Ba^{2+}\,(aq) + SO_4^{2-}\,(aq)$

General problems

Q.51 When 0.5 mol of N_2O_4 is placed in a 4.00 L reaction vessel and heated at 400 K, 79.3% of the N_2O_4 decomposes to NO_2.
Calculate K_c and K_p at 400 K for the reaction $N_2O_4\,(g) \rightleftharpoons 2NO_2(g)$

Q.52 What concentration of NH_3 is in equilibrium with 1.0×10^{-3} M N_2 and 2.0×10^{-3} M H_2 at 700K? At this temperature $K_c = 0.291$ for the reaction $N_2(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$.

Q.53 At 100 K, the value of K_c for the reaction $C\,(s) + H_2O\,(g) \rightleftharpoons CO\,(g) + H_2\,(g)$ is 3.0×10^{-2}. Calculate the equilibrium concentrations of H_2O, CO_2, and H_2 in the reaction mixture obtained by heating 6.0 mol of steam and an excess of solid carbon in a 5.0 L container. What is the molar composition of the equilibrium mixture?

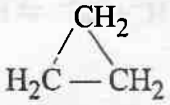
Q.54 When 1.0 mol of PCl_5 is introduced into a 5.0 L container at 500 K, 78.5 % of the PCl_5 dissociates to give an equilibrium mixture of PCl_5, PCl_3, and Cl_2.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

(a) Calculate the values of K_c and K_p.

(b) If the initial concentrations in a particular mixture of reactants and products are $[PCl_5] = 0.5$ M, $[PCl_3] = 0.15$ M, and $[Cl_2] = 0.6$ M, in which direction does the reaction proceed to reach equilibrium? What are the concentrations when the mixture reaches equilibrium?

Q.55 The equilibrium constant K_c for the gas-phase thermal decomposition of cyclopropane to propene is 1.0×10^5 at 500 K.



$\rightleftharpoons CH_3{-}CH{=}CH_2$ $\qquad K_c = 1.0 \times 10^5$

cyclopropane Propene

(a) What is the value of K_p at 500 K?

(b) What is the equilibrium partial pressure of cyclopropane at 500 K when the partial pressure of propene is 5.0 atm?

(c) Can you alter the ratio of the two concentrations at equilibrium by adding cyclopropane or by decreasing the volume of the container? Explain.

(d) Which has the larger rate constant, the forward reaction or the reverse reaction?

(e) Why is cyclopropane so reactive?

Thermodynamic and equilibrium constant

Q.56 α-D-Glucose undergoes mutarotation to β-D-Glucose in aqueous solution. If at 298 K there is 60% conversion. Calculate ΔG° of the reaction.

$$\alpha\text{-D-Glucose} \rightleftharpoons \beta\text{-D-Glucose}$$

Q.57 For the reaction at 298 K

$$A(g) + B(g) \rightleftharpoons C(g) + D(g)$$

$\Delta H° = -29.8$ kcal ; $\Delta S° = -0.1$ kcal / K

Calculate ΔG° and K.

Q.58 The equilibrium constant of the reaction $2C_3H_6(g) \rightleftharpoons C_2H_4(g) + C_4H_8(g)$ is found to fit the expression

$$\ln K = -1.04 - \frac{1088K}{T}$$

Calculate the standard reaction enthalpy and entropy at 400 K.

PROFICIENCY TEST

1. K for the reaction $2A + B \rightleftharpoons 2C$ is 1.5×10^{12}. This indicates that at equilibrium the concentration of ______ would be maximum.

2. The reaction $N_2 + O_2 \rightleftharpoons 2NO$ – Heat, would be favoured by ________ temperature.

3. K for the reaction $X_2 + Y_2 \rightleftharpoons 2XY$ is 100 K. For reaction $XY \rightleftharpoons \frac{1}{2}X_2 + \frac{1}{2}Y_2$ would be ________.

4. Compared to K for the dissociation, $2H_2S \rightleftharpoons 2H^+ + 2HS^-$, then K' for the $H^+ + HS^- \rightleftharpoons H_2S$ would have ________.

5. The equilibrium constant for a reaction decreases with increase in temperature, the reaction must be ______.

6. For the reaction, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, K_P and K_C are related as ______.

7. For the reactions, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, at equilibrium, increase in pressure shifts the equilibrium in _______ direction.

8. $\Delta G°$ is related to K by the relation ________.

9. Vant Hoff's equation is ________.

10. When the reaction is at equilibrium, the value of ΔG is ________.

11. Dimensions of equilibrium constant for the reaction $2NH_3 \rightleftharpoons N_2 + 3H_2$, are ________.

12. The value of K for a reaction can be changed by changing ________.

13. The law of mass action was proposed by ________.

14. The degree of dissociation of PCl_5 [$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$], ________ with increase in pressure at equilibrium.

15. If concentration quotient, Q is greater than K_C, the net reaction in taking place in _____ direction.

16. The reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$ would be favoured by ____ pressure.

17. K_P is related to K_C as ________.

18. Solubility of a gas in water ___ with increase in temperature.

19. Introduction of inert gas at constant volume to a gaseous reaction at equilibrium results in formation of ______ product.

20. The product is more stable than reactants in reaction having ______ K.

21. Van't Hoff's equation gives the quantitative relation between change in value of K with change in temperature.

22. The larger value of K indicates that the product is more stable relative to reactants.

23. The value of equilibrium constant changes with change in the initial concentration of the reactants.

24. Extent of a reaction can always be increased by increasing the temperature.

25. K_P is related to K_C as $K_P = K_C\,(RT)^{\Delta n}$.

26. Introduction of inert gas at a gaseous reaction at equilibrium keeping pressure constant has no effect on equilibrium state.

27. For the reaction, $N_2O_4\,(g) \rightleftharpoons 2NO_2(g)$, $K_P = K_C\,(RT)$.

28. For a reaction the value of Q greater than K indicates that the net reaction is proceeding in backward direction.

29. Solubilities of all solids in water increase with increase in temperature.

30. Dissolution of all gases in water is accompanied by evolution of heat.

31. For the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$, the equilibrium expression may be written as $K = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$.

32. For the reaction, $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, $K_P = p_{CO_2}$.

33. A catalyst increases the value of the equilibrium constant for a reaction.

34. If concentration quotient of reaction is less than K, the net reaction is proceeding in the backward direction.

35. In case of endothermic reactions, the equilibrium shifts in backward direction on increasing the temperature.

36. The value of K increases with increase in pressure.

37. For the reaction, $H_2 + I_2 \rightleftharpoons 2HI$, the equilibrium constant, K is dimensionless.

38. The reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, $\Delta H = -X$ kJ, is favoured by high pressure and high temperature.

39. A very high value of K indicates that at equilibrium most of the reactants are converted into products.

40. The value of K for the reaction, $N_2 + 2H_2 \rightleftharpoons 2NH_3$, can be increased by applying high pressure or by using a catalyst.

EXERCISE II

Q.1 At high temperatures phosgene, $COCl_2$ decompose to give CO & Cl_2. In a typical experiment 9.9×10^{-4} kg of $COCl_2$ is injected into a flask of volume 0.4105 dm^3 at 1000 K. When equilibrium is established it is found that the total pressure in the flask is 3.039×10^5 pascals. Calculate the equilibrium constant (K_p) for this reaction at 1000 K.

Q.2 2 moles of A & 3 moles of B are mixed in 1 litre vessel and the reaction is carried at 400°C according to the equation; $A + B \rightleftharpoons 2C$. The equilibrium constant of the reaction is 4. Find the number of moles of C at equilibrium.

Q.3 $2\,NOBr(g) \rightleftharpoons 2\,NO(g) + Br_2(g)$. If nitrosyl bromide (NOBr) is 33.33% dissociated at 25° C & a total pressure of 0.28 atm. Calculate K_p for the dissociation at this temperature.

Q.4 At 90°C, the following equilibrium is established :
$H_2(g) + S(s) \rightleftharpoons H_2S(g) \quad K_p = 6.8 \times 10^{-2}$
If 0.2 mol of hydrogen and 1.0 mol of sulphur are heated to 90°C in a 1.0 litre vessel, what will be the partial pressure of H_2S at equilibrium?

Q.5 The equilibrium constant for the reaction is 9.40 at 900°C $S_2(g) + C(s) \rightleftharpoons CS_2(g)$. Calculate the pressure of two gases at equilibrium, when 1.42 atm of S_2 and excess of C(s) come to equilibrium.

Q.6 A mixture of 2 moles of CH_4 & 34 gms of H_2S was placed in an evacuated container, which was then heated to & maintained at 727° C. When equilibrium was established in the gaseous reaction $CH_4 + 2\,H_2S \rightleftharpoons CS_2 + 4\,H_2$ the total pressure in the container was 0.92 atm & the partial pressure of hydrogen was 0.2 atm. What was the volume of the container ?

Q.7 At 817° C, K_p for the reaction between pure CO_2 and excess hot graphite to form 2CO(g) is 10 atm.

(a) What is the analysis of the gases at equilibrium at 817°C & a total pressure of 4.0 atm ? What is the partial pressure of CO_2 at equilibrium ?

(b) At what total pressure will the gas mixture analyze 6%, CO_2 by volume ?

Q.8 The equilibrium mixture $SO_2 + NO_2 \rightleftharpoons SO_3 + NO$ was found to contain 0.6 mol of SO_3, 0.40 mol of NO, 0.8 mol of SO_2 & 0.1 mol of NO_2 in a 1L vessel. One mole of NO was then forced into the reaction vessel with V & T constant Calculate the amounts of each gas in the new equilibrium mixture.

Q.9 For the reaction $N_2O_4 \rightleftharpoons 2NO_2$, equilibrium mixture contains NO_2 at P = 1.1 atm & N_2O_4 at P = 0.28 atm at 350 K. The volume of the container is doubled. Calculate the equilibrium pressures of the two gases when the system reaches new equilibrium.

Q.10 In the preceding problem, calculate the degree of dissociation, α at both pressures corresponding to mean molar masses of 65 & 76.667. Use data from the preceding problem.

Q.11 PCl_5 dissociates according to the reaction $PCl_5 \rightleftharpoons PCl_3(g) + Cl_2(g)$. At 523 K, K_p = 1.78 atm. Find the density of the equilibrium mixture at a total pressure of 1 atm.

Q.12 The reaction $3/2H_2(g) + 1/2\,N_2(g) \rightleftharpoons NH_3(g)$ was carried out at T = 620 K & P = 10 atm with an initial mixture of $H_2 : N_2 = 3 : 1$, the mixture at equilibrium contained 7.35 % NH_3. Find K_p and K_c.

Q.13 For the reaction $SO_2(g) + 1/2\ O_2(g) \rightleftharpoons SO_3(g)$ $\Delta H°_{298} = -98.32$ kJ/mole, $\Delta S°_{298} = -95.0$ J/K/mole. Find the K_p for this reaction at 298 K.

Q.14 The following data for the equilibrium composition of the reaction

$$2Na(g) \rightleftharpoons Na_2(g)$$

at 1.013 MPa pressure and 1482.53 K have been obtained.

mass % Na (monomer gas) = 71.3
mass % Na_2 (dimer gas) = 28.7

Calculate the equilirium constant K_p.

Q.15 The degree of dissociation of HI at a particular temperature is 0.8. Find the volume of 1.5M sodium thiosulphate solution required to react completely with the iodine present at equilibrium in acidic conditions, when 0.135 mol each of H_2 and I_2 are heated at 440 K in a closed vessel of capacity 2.0 L.

Q.16 A reaction system in equilibrium according to the equation $2SO_2 + O_2 \rightleftharpoons 2SO_3$ in 1 litre reaction vessel at a given temperature was found to contain 0.11 mol of SO_2, 0.12 mol of SO_3 and 0.05 mol of O_2. Another 1 litre reaction vessel contains 64 g of SO_2 at the same temperature. What mass of O_2 must be added to this vessel in order that at equilibrium half of SO_2 is oxidised to SO_3?

Q.17 A mixture of hydrogen & iodine in the mole ratio 1.5 : 1 is maintained at 450° C. After the attainment of equilibrium $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, it is found on analysis that the mole ratio of I_2 to HI is 1 : 18. Calculate the equilibrium constant & the number of moles of each species present under equilibrium, if initially, 127 grams of iodine were taken.

Q.18 In a closed container nitrogen and hydrogen mixture initially in a mole ratio of 1:4 reached equilibrium. It is found that the half hydrogen is converted to ammonia. If the original pressure was 180 atm, what will be the partial pressure of ammonia at equilibrium. (There is no change in temperature)

Q.19 The equilibrium constant for the reaction $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ is 7.3 at 450°C & 1atm pressure. The initial concentration of water gas $[CO + H_2]$ & steam are 2 moles & 5 moles respectively. Find the number of moles of CO, H_2, CO_2 & H_2O (vapour) at equilibrium.

Q.20 At 1200°C, the following equilibrium is established between chlorine atoms & molecule:

$$Cl_2(g) \rightleftharpoons 2Cl\ (g)$$

The composition of the equilibrium mixture may be determined by measuring the rate of effusion of the mixture through a pin hole. It is found that at 1200°C and 1 atm pressure the mixtureeffuses 1.16 times as fast as krypton effuses under the same condition. Calculate the equilibrium constant k_c.

Q.21 Two solids X and Y disssociate into gaseous products at a certain temperature as follows: $X(s) \rightleftharpoons A(g) + C(g)$, and $Y(s) \rightleftharpoons B(g) + C(g)$. At a given temperature, pressure over excess solid X is 40 mm and total pressure over solid Y is 60 mm. Calculate:

(a) the values of K_p for two reactions (in mm)
(b) the ratio of moles of A and B in the vapour state over a mixture of X and Y
(c) the total pressure of gases over a mixture of X and Y

Q.22 SO_3 decomposes at a temperature of 1000 K and at a total pressure of 1.642 atm. At equilibrium, the density of mixture is found to be 1.28 g/l in a vessel of 90 literes. Find the degree of dissociation of SO_3 for $SO_3 \rightleftharpoons SO_2 + 1/2O_2$.

Q.23 Consider the equilibrium: $P(g) + 2Q(g) \rightleftharpoons R(g)$. When the reaction is carried out at a certain temperature, the equilibrium concentration of P and Q are 3M and 4M respectively. When the volume of the vessel is doubled and the equilibrium is allowed to be reestablished, the concentration of Q is found to be 3M. Find (A) K_c (B) concentration of R at two equilibrium stages.

Q.24 When PCl_5 is heated, it dissociates into PCl_3 and Cl_2. The vapor density of the gaseous mixture at 200°C and 250°C is 70.2 and 57.9 respectively. Find the % dissociation of PCl_5 at 200°C and 250°C.

Q.25 The density of an equilibrium mixture of N_2O_4 and NO_2 at 101.32 KP_a is 3.62g dm^{-3} at 288 K and 1.84 g dm^{-3} at 348K. What is the heat of the reaction for $N_2O_4 \rightleftharpoons 2NO_2\,(g)$.

Q.26 Two solid compounds A & C dissociates into gaseous productat temperature as follows

$$A(s) \overset{\Delta}{\rightleftharpoons} B(g) + E\,(g)$$

$$C(s) \overset{\Delta}{\rightleftharpoons} D(g) + E\,(g)$$

At 20° C pressure over excess solid A is 50atm & that over excess solid C is 68atm. Find the total pressure of gases over the solid mixture.

Q.27 The equilibrium constant for the following reaction at 1395 K.

$$2H_2O \rightleftharpoons 2H_2 + O_2 \qquad K_1 = 2.1 \times 10^{-13}$$

$$2CO_2 \rightleftharpoons 2CO + O_2 \qquad K_2 = 1.4 \times 10^{-12}$$

Calculate the value of K for the reaction : $H_2 + CO_2 \rightleftharpoons CO + H_2O$

Q.28 A saturated solution of iodine in water contains 0.33g I_2 / L. More than this can dissolve in a KI solution because of the following equilibrium : $I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$. A 0.10 M KI solution (0.10 M I^-) actually dissolves 12.5 g of iodine/L, most of which is converted to I_3^-. Assuming that the concentration of I_2 in all saturated solutions is the same, calculate the equilibrium constant for the above reaction. What is the effect of adding water to a clear saturated of I_2 in the KI solution ?

Q.29 The equilibrium p–Xyloquinone + methylene white $\rightleftharpoons$ p–Xylohydroquinone + methylene blue may be studied convinently by observing the difference in color methylene white and methylene blue. One mmol of methylene blue was added to 1L of solution that was 0.24 M in p–Xylohydroquinone and 0.012 M in p–Xyloquinone. It was then found that 4% of the added methylene blue was reduced to methylene white. What is the equilibrium constant of the above reaction? The equation is balanced with one mole each of 4 substances.

Q.30 A mixture of N_2 & H_2 are in equilibrium at 600 K at a total pressure of 80 atm. If the initial ratio of N_2 and H_2 are 3:1 and at equilibrium NH_3 is 10% by volume. Calculate K_P of reaction at given temperature.

Q.31 ΔG° (298 K) for the reaction $1/2\,N_2 + 3/2\,H_2 \overset{K_1}{\rightleftharpoons} NH_3$ is $-16.5\ kJ\ mol^{-1}$. Find the equilibrium constant (K_1) at 25°C. What will be the equilibrium constants K_2 and K_3 for the following reactions:

$$N_2 + 3H_2 \overset{K_2}{\rightleftharpoons} 2NH_3$$

$$NH_3 \overset{K_3}{\rightleftharpoons} 1/2\,N_2 + 3/2\,H_2$$

Q.32 A certain gas A polymerizes to a small extent at a given temperature & pressure, $nA \rightleftharpoons A_n$. Show that the gas obeys the approx. equation $\frac{PV}{RT} = \left[1 - \frac{(n-1)K_c}{V^{n-1}}\right]$ where $K_c = \frac{[A_n]}{[A]^n}$ & V is the volume of the conatiner. Assume that initially one mole of A was taken in the container.

Q.33 10^{-3} mol of $CuSO_4.5H_2O$ is introduced in a 1.9 L vessel maintained at a constant temperature of 27°C containing moist air at relative humidity of 12.5%. What is the final molar composition of solid mixture? For $CuSO_4.5H_2O(s) \rightleftharpoons CuSO_4(s) + 5H_2O(g), K_p(atm) = 10^{-10}$. Take vapor pressure of water at 27°C as 28 torrs.

Q.34 When 1 mol of A(g) is introduced in a closed 1 L vessel maintained at constant temperature, the following equilibria are established.

$$A(g) \rightleftharpoons B(g) + 2C(g)\ ; \qquad K_1 = ?$$
$$C(g) \rightleftharpoons 2D(g) + 3B(g)\ ; \qquad K_2 = ?$$

The pressure at equilibrium is $\left(\frac{13}{6}\right)$ times the initial pressure.

Calculate K_{C_1} & K_{C_2} if $\frac{[C]_{eq}}{[A]_{eq}} = \frac{4}{9}$.

Q.35 When NO & NO_2 are mixed, the following equilibria are readily obtained;

$$2NO_2 \rightleftharpoons N_2O_4 \qquad K_p = 6.8\ atm^{-1}$$
$$NO + NO_2 \rightleftharpoons N_2O_3 \qquad K_p = ?$$

In an experiment when NO & NO_2 are mixed in the ratio of 1 : 2, the total final pressure was 5.05 atm & the partial pressure of N_2O_4 was 1.7 atm. Calculate

(a) the equilibrium partial pressure of NO.

(b) K_p for $NO + NO_2 \rightleftharpoons N_2O_3$

Q.36 Solid NH_4I on rapid heating in a closed vessel at 357°C develops a constant pressure of 275 mm Hg owing to partial decomposition of NH_4I into NH_3 and HI but the pressure gradually increases further (when the excess solid residue remains in the vessel) owing to the dissociation of HI. Calculate the final pressure developed at equilibrium.

$$NH_4I\ (s) \rightleftharpoons NH_3(g) + HI(g)$$
$$2HI\ (g) \rightleftharpoons H_2(g) + I_2(g),\ K_c = 0.065 \text{ at } 357°C$$

Q.37 Given are the following standard free energies of formation at 298K.

	CO(g)	$CO_2(g)$	$H_2O(g)$	$H_2O(l)$
$\Delta_fG/kJ\ mol^{-1}$	–137.17	–394.36	–228.57	–237.13

(a) Find $\Delta_rG°$ and the standard equilibrium constant K_u^0 at 298 K for the reaction

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

(b) If CO, CO_2 and H_2 are mixed so that the partial pressure of each is 101.325 kPa and the mixture is brought into contact with excess of liquid water, what will be the partial pressure of each gas when equilibrium is attained at 298K. The volume available to the gases is constant.

Q.38 For the reaction

$$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$$

K_p^0 is 0.05 and $\Delta_rG°$ is 22.384 $kJmol^{-1}$ at 900 K. If an initial mixture comprising 20 mol of C_2H_6 and 80 mol of N_2(inert) is passed over a dehydrogenation catalyst at 900K, what is the equilibrium percentage composition of the effluent gas mixture? The total pressure is kept at 0.5 bar. Given : $\Delta_rS° = 135.143\ J\ K^{-1}\ mol^{-1}$ at 300K. Calculate $\Delta_rG°$ at 300K. (Assume $\Delta_rC_p = 0$)

Q.39(a) The equilibrium $H_2(g) + CO_2(g) \Leftrightarrow H_2O(g) + CO(g)$ is established in an evacuated vessel at 723 K starting with 0.1 mole of H_2 & 0.2 mole of CO_2. If the equilibrium mixture contains 10 mole per cent of water vapour, calculate K_p, given that the equilibrium pressure is 0.5 atm. Calculate the partial pressures of the component species & the volume of the container.

(b) If now, into the flask (mentioned in the preceding problem), solid CoO & solid Co are introduced two new equilibria are established.

$$CoO(s) + H_2(g) \rightleftharpoons Co(s) + H_2O(g) \;;\; CoO(s) + CO(g) \rightleftharpoons Co(s) + CO_2(g)$$

The new equilibrium mixture contains 30 mole precent of water vapour. Calculate the equilibrium constants for the new equilibria.

Q.40 Some iodine is dissolved in an aqueous solution of KI of concentration 0.102 mole/1, and the solution is then shaken with equal volume of CCl_4 until equilibrium is reached (at 15°C). The total amount of iodine (present as I_3^- (aq) or as I_2 (aq)) at equilibrium is found to be 0.048 mol/1 in the aqueous layer and 0.085 mol/1 in the CCl_4 layer. The distribution coefficient of iodine between CCl_4 and water is 85. Calculate the equilibrium constant at 15^0C for the reaction:

$$I_3^- (aq) \rightleftharpoons I_2 (aq) + I^- (aq)$$

EXERCISE III

Q.1 Consider following reactions in equilibrium with equilibrium concentration 0.01 M of every species

(I) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ (II) $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

(III) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Extent of the reactions taking place is:

(A) I > II > III (B) I < II < III (C) II < III < I (D) III < I < II

Q.2 For the reaction $3A(g) + B(g) \rightleftharpoons 2C(g)$ at a given temperature, $K_c = 9.0$. What must be the volume of the flask, if a mixture of 2.0 mol each of A, B and C exist in equilibrium?

(A) 6L (B) 9L (C) 36 L (D) None of these

Q.3 Sulfide ion in alkaline solution reacts with solid sulfur to form polysulfide ions having formulas S_2^{2-}, S_3^{2-}, S_4^{2-} and so on. The equilibrium constant for the formation of S_2^{2-} is 12 (K_1) & for the formation of S_3^{2-} is 132 (K_2), both from S and S^{2-}. What is the equilibrium constant for the formation of S_3^{2-} from S_2^{2-} and S?

(A) 11 (B) 12 (C) 132 (D) None of these

Q.4 For the following gases equilibrium. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

K_p is found to be equal to K_c. This is attained when

(A) 0°C (B) 273 K (C) 1 K (D) 12.19 K

Q.5 1 mole N_2 and 3 mol H_2 are placed in a closed container at a pressure of 4 atm. The pressure falls to 3 atm at the same temperature when the following equilibrium is attained.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. The equilibrium constant K_P for dissociation of NH_3 is:

(A) $\frac{1}{0.5} \times (1.5)^3\ \text{atm}^{-2}$ (B) $0.5 \times (1.5)^3\ \text{atm}^2$ (C) $\frac{0.5 \times (1.5)^3}{3 \times 3}\ \text{atm}^2$ (D) $\frac{3 \times 3}{0.5 \times (1.5)^3}\ \text{atm}^{-2}$

Q.6 One mole of $N_2O_4(g)$ at 300 K is left in a closed container under one atm. It is heated to 600 K when 20 % by mass of $N_2O_4(g)$ decomposes to $NO_2(g)$. The resultant pressure is :

(A) 1.2 atm (B) 2.4 atm (C) 2.0 atm (D) 1.0 atm

Q.7 For the reaction : $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$, the degree of dissociated (α) of HI(g) is related to equilibrium constant K_P by the expression

(A) $\frac{1+2\sqrt{K_p}}{2}$ (B) $\sqrt{\frac{1+2K_p}{2}}$ (C) $\sqrt{\frac{2K_p}{1+2K_p}}$ (D) $\frac{2\sqrt{K_p}}{1+2\sqrt{K_p}}$

Q.8 The vapour density of N_2O_4 at a certain temperature is 30. What is the % dissociation of N_2O_4 at this temperature?

(A) 53.3% (B) 106.6% (C) 26.7% (D) None

Q.9 For the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, the forward reaction at constant temperature is favoured by

(A) introducing an inert gas at constant volume

(B) introducing chlorine gas at constant volume

(C) introducing an inert gas at constant pressure

(D) increasing the volume of the container

(E) introducing PCl_5 at constant volume.

Q.10 When N_2O_5 is heated at temp. T, it dissociates as $N_2O_5 \rightleftharpoons N_2O_3 + O_2$, $K_c = 2.5$. At the same time N_2O_3 also decomposes as : $N_2O_3 \rightleftharpoons N_2O + O_2$. If initially 4.0 moles of N_2O_5 are taken in 1.0 litre flask and allowed to attain equilibrium, concentration of O_2 was formed to be 2.5 M. Equilibrium concentration of N_2O is
(A) 1.0 (B) 1.5 (C) 2.166 (D) 0.334

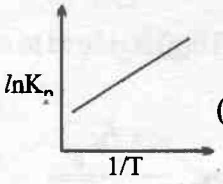
Q.11 Densities of diamond and graphite are 3.5 and 2.3 gm/mL.
C (diamond) $\rightleftharpoons$ C (graphite) $\Delta_r H = -1.9$ kJ/mole
favourable conditions for formation of diamond are
(A) high pressure and low temperature (B) low pressure and high temperature
(C) high pressure and high temperature (D) low pressure and low temperature

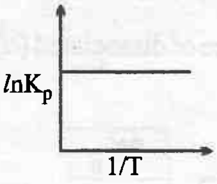
Q.12 When $NaNO_3$ is heated in a closed vessel, oxygen is liberated and $NaNO_2$ is left behind. At equilibrium
(A) addition of $NaNO_2$ favours reverse reaction
(B) addition of $NaNO_3$ favours forward reaction
(C) increasing temperature favours forward reaction
(D) increasing pressure favours reverse reaction

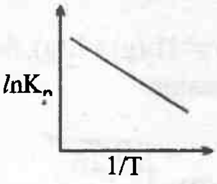
Q.13 The equilibrium $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$ is attained at 25°C in a closed rigid container and an inert gas, helium is introduced. Which of the following statements is/are correct.
(A) concentrations of SO_2, Cl_2 and SO_2Cl_2 do not change
(B) more chlorine is formed
(C) concentration of SO_2 is reduced
(D) more SO_2Cl_2 is formed

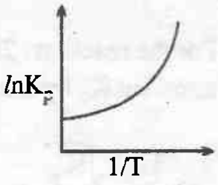
Q.14 For the gas phase reaction, $C_2H_4 + H_2 \rightleftharpoons C_2H_6$ ($\Delta H = -32.7$ kcal), carried out in a closed vessel, the equilibrium concentration of C_2H_4 can be increased by
(A) increasing the temperature (B) decreasing the pressure
(C) removing some H_2 (D) adding some C_2H_6

Q.15 An exothermic reaction is represented by the graph :

(A)


(B)


(C)


(D)


Q.16 The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K is
(A) $-\Delta G^\circ = RT \ln K$ (B) $\Delta G = RT \ln K$ (C) $-\Delta G = RT \ln K$ (D) $\Delta G^\circ = RT \ln K$

Q.17 The value of ΔG_f° of gaseous mercury is 31 K J/mole. At what total external pressure mercury start boiling at 25°C. [R' = 8.3]
(A) $10^{-5.44}$ (B) $10^{-12.5}$ (C) $10^{-6.52}$ (D) $10^{-3.12}$

Q.18 What is $\Delta_r G$ (KJ/mole) for synthesis of ammonia at 298 K at following sets of partial pressure:
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; $\Delta_r G^\circ = -33$ KJ/mole. [Take R = 8.3 J/K mole, log2 = 0.3; log3 = 0.48]

Gas	N_2	H_2	NH_3
Pressure (atm)	1	3	0.02

(A) + 6.5 (B) – 6.5 (C) + 60.5 (D) – 60.5

Q.19 In a 7.0 L evacuated chamber, 0.50 mol H_2 and 0.50 mol I_2 react at 427°C.
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$. At the given temperature, K_C = 49 for the reaction.

(i) What is the value of K_p ?
(A) 7 (B) 49 (C) 24.5 (D) None

(ii) What is the total pressure (atm) in the chamber?
(A) 83.14 (B) 831.4 (C) 8.21 (D) None

(iii) How many moles of the iodine remain unreacted at equilibrium?
(A) 0.388 (B) 0.112 (C) 0.25 (D) 0.125

(iv) What is the partial pressure (atm) of HI in the equilibrium mixture?
(A) 6.385 (B) 12.77 (C) 40.768 (D) 646.58

Q.20 Equilibrium constants are given (in atm) for the following reactions at 0° C:

$SrCl_2 \cdot 6H_2O(s) \rightleftharpoons SrCl_2 \cdot 2H_2O\ (s) + 4H_2O(g)$ $K_p = 5 \times 10^{-12}$

$Na_2HPO_4 \cdot 12\ H_2O(s) \rightleftharpoons Na_2HPO_4 \cdot 7H_2O\ (s) + 5H_2\ O(g)$ $K_p = 2.43 \times 10^{-13}$

$Na_2SO_4 \cdot 10\ H_2O(s) \rightleftharpoons Na_2SO_4\ (s) + 10\ H_2O\ (g)$ $K_p = 1.024 \times 10^{-27}$

The vapor pressure of water at 0°C is 4.56 torr.

(i) Which is the most effective drying agent at 0°C?
(A) $SrCl_2 \cdot 2H_2O$ (B) $Na_2HPO_4 \cdot 7\ H_2O$ (C) Na_2SO_4 (D) all equally

(ii) At what relative humidities will $Na_2SO_4 \cdot 10H_2O$ be efflorescent when exposed to air at 0°C?
(A) above 33.33% (B) below 33.33 % (C) above 66.66% (D) below 66.66%

(iii) At what relative humidities will Na_2SO_4 be deliquescent (i.e. absorb moisture) when exposed to the air at 0°C?
(A) above 33.33% (B) below 33.33 % (C) above 66.66% (D) below 66.66%

EXERCISE IV

Q.1 A sample of air consisting of N_2 and O_2 was heated to 2500K until the equilibrium $N_2(g) + O_2(g) \rightleftharpoons 2NO$ was established with an equilibrium constant $K_c = 2.1 \times 10^{-3}$. At equilibrium, the mol% of NO was 1.8. Estimate the initial composition of air in mol fraction of N_2 and O_2.
[JEE 1997]

Q.2 For the reaction $CO(g) + H_2O \rightleftharpoons CO_2(g) + H_2(g)$ at a given temperature the equilibrium amount of $CO_2(g)$ can be increased by :
(A) adding a suitable catalyst
(B) adding an inert gas
(C) decreasing the volume of the container
(D) increasing the amount of CO(g).
[JEE 1998]

Q.3 The degree of dissociation is 0.4 at 400 K & 1.0 atm for the gaseous reaction, $PCl_5 \rightleftharpoons PCl_3 + Cl_2$. Assuming ideal behaviour of all the gases, calculate the density of equilibrium mixture at 400 K & 1.0 atmosphere. (atomic mass of P = 31.0 & Cl = 35.5) **[JEE 1998]**

Q.4 For the reaction, $N_2O_5(g) = 2NO_2(g) + 0.5\,O_2(g)$, calculate the mole fraction of $N_2O_5(g)$ decomposed at a constant volume & temperature, if the initial pressure is 600 mm Hg & the pressure at any time is 960 mm Hg. Assume ideal gas behaviour. **[JEE 1998]**

Q.5 The degree of dissociation is 0.4 at 400K & 1.0 atm for the gasoeus reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2(g)$. Assuming ideal behaviour of all gases. Calculate the density of equilibrium mixture at 400K & 1.0 atm pressure. **[JEE 1999]**

Q.6 When 3.06g of solid NH_4HS is introduced into a two litre evacuated flask at 27°C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide.
(i) Calculate K_C & K_P for the reaction at 27°C.
(ii) What would happen to the equilibrium when more solid NH_4HS is introduced into the flask?
[JEE 2000]

Q.7 When 1-pentyne (A) is treated with 4N alcoholic KOH at 175°C, it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne (A), 95.2% 2–pentyne (B) & 3.5% of 1, 2,–pentadiene (C). The equilibrium was maintained at 175^0C. Calculate ΔG° for the following equilibria.

$B = A \qquad \Delta G_1^{\,0} = ?$

$B = C \qquad \Delta G_2^{\,0} = ?$

From the calculated value of $\Delta G_1^{\,0}$ & $\Delta G_2^{\,0}$ indicate the order of stability of A, B & C. Write a reasonable reaction mechanism sharing all intermediate leading to A, B & C. **[JEE 2001]**

Q.8 $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
This reaction is carried out at 298 K and 20 bar. 5 mol each of N_2O_4 and NO_2 are taken initially.

$$\text{Given: } \Delta G^{o}_{N_2O_4} = 100\text{ kJ mol}^{-1};\ \Delta G^{o}_{NO_2} = 50\text{ kJ mol}^{-1}$$

(i) Find ΔG for reaction at 298 K under given condition.
(ii) Find the direction in which the reaction proceeds to achieve equilibrium. **[JEE 2004]**

Q.9 $N_2 + 3H_2 \rightleftharpoons 2NH_3$
Which is correct statement if N_2 is added at equilibrium condition?
(A) The equilibrium will shift to forward direction because according to II law of thermodynamics the entropy must increases in the direction of spontaneous reaction.
(B) The condition for equilibrium is $G_{N_2} + 3G_{H_2} = 2G_{NH_3}$ where G is Gibbs free energy per mole of the gaseous species measured at that partial pressure. The condition of equilibrium is unaffected by the use of catalyst, which increases the rate of both the forward and backward reactions to the same extent.
(C) The catalyst will increase the rate of forward reaction by α and that of backward reaction by β.
(D) Catalyst will not alter the rate of either of the reaction. **[JEE 2006]**

ANSWER KEY

EXERCISE I

Q.1 (a) 25, shifts left, (b) 0.22, shifts right, (c) ∞, shifts left, (d) 1, shifts right, (e) 0, shift right, (f) 4, shifts left

Q.2 (a) $K = [Ag^+][Cl^-]$ is less than 1. AgCl is insoluble thus the concentration of ions are much less than 1 M
(b) $K = 1/[Pb^{2+}][Cl^-]^2$ is greater than one because $PbCl_2$ is insoluble and formation of the solid will reduce the concentration of ions to a low level

Q.4 K about 10 Q.6p (a) incomplete (b) almost complete Q.7 c Q.8 $\sim 9 \times 10^{-32}$ mol/L

Q.9 The reaction is not an equilibrium because $Q_c > K_c$. The reaction will proceed from right to left to reach equilibrium

Q.11 5.9×10^{-3} M Q.12 [NO] = 0.056 M, $[N_2] = [O_2] = 1.37$ M

Q.13 $[PCl_3] = [Cl_2] = 0.071$ M, $[PCl_5] = 0.089$

Q.14 $P_{ClF} = P_{F_2} = 0.389$ atm, $P_{ClF_3} = 1.08$ atm

Q.15 $K_p = 0.4$, $a \simeq 0.1$ Q.16 50%

Q.17 (a) 6.667×10^{-3} mol L^{-1}; (b) n (N_2O_4) = 0.374 mol; n (NO_2) = 0.052 mol ; (c) 10.49 atm (d) 6.44 %

Q.18 0.97 atm Q.19 $K_P = 1.3 \times 10^{-3}$ atm^{-2}

Q.20 $K_p = 2.5$ atm, P = 15 atm Q.21 53.33%

Q.22 K = 4 Q.23 31/27 Q.24 22.4 mg

Q.25 $P_{H_2O} = 5 \times 10^{-15}$ atm Q.26 0.821 atm

Q.27 add N_2, add H_2, increase the pressure, heat the reaction

Q.28 (a) shift right, shift left, (b) shift right, no effect, (c) shift left, shift left, (d) shift left, shift right

Q.29 (a) $K = [CH_3OH]/[H_2]^2[CO]$,
(b) 1. $[H_2]$ increase, [CO] decrease, $[CH_3OH]$ increase ; 2. $[H_2]$ increase, [CO] decrease, $[CH_3OH]$ decrease ; 3. $[H_2]$ increase, [CO] increase, $[CH_3OH]$ increase ; 4. $[H_2]$ increase, [CO] increase, $[CH_3OH]$ increase ; 5. $[H_2]$ increase, [CO] increase, $[CH_3OH]$ decrease ; 6. no change

Q.30 (a) $K = [CO][H_2]/[H_2O]$;
(b) in each of the following cases the mass of carbon will change, but its concentration (activity) will not change. 1. $[H_2O]$ no change, [CO] no change, $[H_2]$ no change ; 2. $[H_2O]$ decrease, [CO] decrease, $[H_2]$ decrease ; 3. $[H_2O]$ increase, [CO] increase, $[H_2]$ decrease; 4. $[H_2O]$ increase, [CO] increase, $[H_2]$ increase ; 5. $[H_2O]$ decrease , [CO] increase , $[H_2]$ increase

Q.31 b

Q.32 Add NaCl or some other salt that produces Cl^- in the solution. Cool the solution.

Q.33 a

Q.34 $k_f[A][B] = k_r[C]$; $\frac{k_f}{k_r} = \frac{[C]}{[A][B]} = k_c$ Q.36 216

Q.38 (i) 2; (ii) 1.2 mol/L; (iii) 0.1 moles/hr

Q.39 k_r increase more than k_f, this means that E_a (reverse) is greater than E_a (forward). The reaction is exothermic when E_a (reverse) > E_a (forward).

Q.43 (a) –9.574 J/mol, (b) $A = 10^{10}$, (c) 9.96×10^9, (d) 9.98×10^9

Q.44 16.06 kJ Q.45 –810 J/mol ; – 5872 J/mol and 41.3 kJ / mol

Q.46 1.3×10^8 Q.47 0.058

Q.48 29.0 Q.49 $K_p = 0.0313$ atm, $K_c = 1.28 \times 10^{-3}$

Q.50 (a) $K_c = \frac{[CO_2]^3}{[CO]^3}$, $K_p = \frac{(P_{CO_2})^3}{(P_{CO})^3}$, (b) $K_c = \frac{1}{[O_2]^3}$, $K_p = \frac{1}{(P_{O_2})^3}$, (c) $K_c = [SO_3]$, $K_p = P_{SO_3}$
$K_c = [Ba^{2+}]\,[SO_4^{2-}]$

Q.51 $K_c = 1.51k\ K_p = 49.6$ Q.52 1.5×10^{-6} M
Q.53 $[CO] = [H_2] = 0.18$ M ; $[H_2O] = 1.02$ M
Q.54 (a) $K_c = 0.573$ and $K_p = 23.5$; (b) to the right, $[PCl_5] = 0.365$ M; $[PCl_3] = 0.285$ M, ; $[Cl_2] = 0.735$ M
Q.56 –1.005 kJ/ mol Q.57 $\Delta G° = 0$; $K = 1$
Q.58 $\Delta H° = 9.07$ kJ/mol; $\Delta S° = -8.92$ J/mol^{-1}K^{-1}

PROFICIENCY TEST

1.	C	2.	high	3.	$\frac{1}{10}$	4.	$\frac{1}{\sqrt{K}}$
5.	exothermic	6.	$K_P = K_C(RT)$	7.	backward	8.	$\Delta G° = -RT \ln K$
9.	$\log\frac{K_2}{K_1} = \frac{\Delta H°}{2.303R}\left[\frac{T_2 - T_1}{T_2T_1}\right]$			10.	zero	11.	mol^{2}L^{-2}
12.	temperature	13.	Guldberg and Waage			14.	decreases
15.	backward	16.	high	17.	$K_P = K_C(RT)^{\Delta n}$		
18.	decreases	19.	same amount of			20.	larger value of
21.	T	22.	T	23.	F	24.	F
25.	T	26.	F	27.	T	28.	T
29.	F	30.	T	31.	T	32.	T
33.	F	34.	F	35.	F	36.	F
37.	T	38.	F	39.	T	40.	F

EXERCISE II

Q.1 $K_p(atm) = 1.13$
Q.2 2.4 mole Q.3 $K_p = 0.01$ atm Q.4 0.379 atm
Q.5 $P_{CS_2} = 1.284$ atm, $P_{S2} = 0.1365$ atm
Q.6 300L
Q.7 (i) $x_{co} = 0.765$, $x_{co_2} = 0.235$; $p(CO_2) = 0.938$ atm (ii) $P_{Total} = 0.68$ atm
Q.8 $(K_c = 3)$, $n_{SO_2} = 0.92$, $n_{SO_3} = 0.48$, $n_{NO} = 1.28$, $n_{NO_2} = 0.22$
Q.9 $P_{NO_2} = 0.64$ atm, $P_{N_2O_4} = 0.095$ atm Q.10 $\alpha = 0.415$ and 0.2
Q.11 2.7 g / lit Q.12 $K_c = 1.337$, $K_p = 0.0263$ Q.13 $K_p = 1.862 \times 10^{12}$ atm$^{-1/2}$
Q.14 $p_{Na} = 0.843$ M Pa; $p_{Na_2} = 0.170$ M Pa; $k_p = 0.239$ Q.15 V = 144 mL
Q.16 9.34 g Q.17 $K_c = 54$, $n_{HI} = 0.9$ mol, $n_{I2} = 0.05$ mol, $n_{H2} = 0.3$ mol
Q.18 48 atm Q.19 $n_{CO2} = 0.938$, $n_{H2} = 1.938$, $n_{CO} = 0.062$, $n_{H2Og} = 4.062$
Q.20 6.71×10^{-4} Q.21 (a) 400mm^2, 900mm^2 (b) 4: 9, (c) 72.15 mm Hg
Q.22 $\alpha = 0.5$
Q.23 $K_c = 1/12$, [R] = 4 (initial), = 1.5 (final) Q.24 dissociation = 48.5%, 80.05%
Q.25 $\Delta_rH = 75.5$ kJ mol^{-1} Q.26 $B \rightarrow NH_4NO_2$; Total pressure = 84.34 atm
Q.27 K = 2.58 Q.28 K=707.2, backward reaction is favoured
Q.29 $K_c = 480$ Q.30 1.32×10^{-3}
Q.31 $K_A = 779.4$, $K_B = 6.074 \times 10^5$; $K_c = 1.283 \times 10^{-3}$
Q.32 To be proved Q.33 $CuSO_4.5H_2O = 9.2 \times 10^{-4}$mol, $CuSO_4 = 8 \times 10^{-5}$ moles
Q.34 $k_{C_1} = 0.111$; $k_{C_2} = 0.14$ Q.35 (a) 1.05 atm, (b) 3.43 atm^{-1} Q.36 314.1 atm

Q.37 $p_{CO_2} = 202.65$ kPa; $p_{H_2O} = 3.16$ kPa; $p_{CO} = 0.124$ kPa

Q.38 103.47 kJ/mol

Q.39 (a) $K_p = 7.563 \times 10^{-2}$, v = 35.62, $p(H_2O) = p(CO) = 0.05$atm, $p(H_2) = 0.1167$atm, $p(CO_2) = 0.2833$atm
(b) $K_1 = 9$, $K_2 = 119$

Q.40 $K = 1.17 \times 10^{-3}$

EXERCISE III

Q.1	B	Q.2	A	Q.3	A	Q.4	D
Q.5	B	Q.6	B	Q.7	D	Q.8	A
Q.9	C,D,E	Q.10	D	Q.11	C	Q.12	C,D
Q.13	A	Q.14	A,B,C,D	Q.15	A	Q.16	A
Q.17	A	Q.18	D	Q.19	(i) B, (ii) C, (iii) B, (iv) A		
Q.20	(i) A, (ii) B, (iii) A						

EXERCISE IV

Q.1 $X_{N2} = 0.79$, $X_{O2} = 0.21$ Q.2 D

Q.3 $\rho = 0.454$ g L^{-1} Q.4 Fraction decomposed = 0.4

Q.5 4.54 g dm^{-3} Q.6 (i) $k_c = 8.1 \times 10^{-5}$ $mol^2 L^2$; $k_p = 4.19 \times 10^{-2}$ atm^2 (ii) Noeffect;

Q.7 15991 J mol^{-1}, 12304 J mol^{-1}; B > C > A

Q.8 (i) 5.705×10^3 kJ mol^{-1}
(ii) Since initial Gibbs free energy change of the reaction is positive, so the reverse reaction will take place

Q.9 B

BANSALCLASSES

TARGET IIT JEE 2007

PHYSICAL CHEMISTRY

XII (ALL)

CHEMICAL KINETICS

" A SPECIALLY DESIGNED KIT FOR LEARNING."

CONTENTS

THE KEY	⟶	Basic principles of subjects. An outline of the topics to be discussed in class lectures.
THE ATLAS	⟶	Basic layout of subject. A route map correlating different subtopics in coherent manner.
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EXERCISE I	⟶	Introductory problems to get first hand experience of problem solving.
PROFICIENCY TEST	⟶	To check you newly acquired concepts.
EXERCISE II	⟶	A collection of good problems.
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THE KEY

CHEMICAL KINETICS :

It is a branch of physical chemistry deals with the "Rate of Chemical Reactions" including the effect of temperature, pressure, concentration, etc., on the rates, and the mechanism by which the reaction takes place.

RATE OF CHEMICAL REACTION is defined as the change in concentration of a reactant (or a product) in a particular time interval. Average rate of reaction, Instantaneous rate of reaction.

Units of Reaction Rate are unit of concentration divided by the unit of time (mol $L^{-1}s^{-1}$ or mol $L^{-1}min^{-1}$ or so on).

FACTORS AFFECTING REACTION RATES :

(i) Concentration of reactants and

(ii) Reaction temperature

Besides these, presence of catalyst and surface area (if a reactant or a catalyst is a solid) exposure to radiation also affect the reaction rates.

EXPRESSIONS OR THE RATE :

For a general reaction : $aA + bB \longrightarrow cC + dD$,

The rate of disappearance of A $= -\dfrac{d[A]}{dt}$; Rate of disappearance of B $= -\dfrac{d[B]}{dt}$;

Rate of appearance of C $= \dfrac{d[C]}{dt}$ & Rate of appearance of D $= \dfrac{d[D]}{dt}$.

The positive sign shows that concentrations of C and D increases with time and the negative sign indicating that concentrations of A and B decrease with time. Thus the rate of general reaction.

$$\text{rate} : -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}.$$

RATE EQUATION AND RATE CONSTANT :

An expression which relates the rate of a reaction to the concentration of the reactants is called the ***Rate Equation*** **or** ***Rate Law***. Rate $\propto [A]^a \cdot [B]^b$ or Rate $= k\,[A]^a\,[B]^b$. The constant of proportionality, k is known as the ***Rate Constant*** (specific reaction rate) and may be defined as the rate at unit concentrations of the reactants. k depends on the temperature and is independent of the initial concentrations of the reactants. At a fixed temperature, k is constant characteristic of the reaction. Larger value of k indicates fast reaction and small k indicates slow reactions.

MOLECULARITY :

Molecularity of a reaction is defined as the numbers of particles (atoms, ions, groups or molecules) of reactants actually taking part in a single step chemical reaction.

Molecularity of a reaction is :

(i) Always a whole number (not zero) and never a fraction.

(ii) The value of molecularity of a simple or one step reaction does not exceed 3.

ORDER OF REACTION :

It is defined as the sum of the exponents (powers) of the molar concentrations of the reactants in the experimentally determined rate equations.

If rate of reaction $\alpha\ [A]^p\,[B]^q\,[C]^r$ or Rate of reaction $= k\,[A]^p\,[B]^q\,[C]^r$

order of reaction $= p + q + r$ & the order w.r.t. A, B & C are p, q & r respectively.

For a "Reaction of n^{th} order", the order of the reaction is n and the rate equation (or Rate law) is rate $\propto [A]^n = k\,[A]^n$.

The order of a reaction is obtained from the experimentally determined rate (and not from the stoichiometric equation) and may be zero, an integer or a fraction and never exceeds 3. In a multi-step complex reaction, the order of the reaction depends on the slowest step.

ZERO ORDER REACTION :

A reaction is said to be of zero order if the rate is independent of the concentration of the reactants.

$A \longrightarrow$ products ; Rate α $k\,[A]^\circ = k$ mol L^{-1} s^{-1}

EXAMPLES :

(i) $H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl(g)$ (ii) $N_2O(g) \xrightarrow[\text{Surface}]{\text{hot Pt.}} N_2(g) + \frac{1}{2}O_2(g)$

(iii) $2NH_3(g) \xrightarrow[\text{surface}]{\text{Mo or W}} N_2 + 3H_2$ (iv) $2HI(g) \xrightarrow[\text{surface}]{\text{Au}} H_2(g) + I_2(g)$

CHARACTERISTICS OF ZERO ORDER REACTION :

(1) Concentration of reactant decreases lineraly with time. $[A]_t = [A]_0 - kt$.

(2) Units of k are, mol l^{-1} time^{-1}.

(3) Time required for the completion of reaction $t = \frac{[A]_0}{k}$ & $t_{1/2} = \frac{0.5\,[A]_0}{k}$

FIRST ORDER REACTION :

A reaction is said to be of first order if its rate is proportinal to the concentration of one reactant only.

	$A \longrightarrow$	Products.
at time t = 0	a (or C_0)	0
at time t = t	a – x (or C_t)	x

Rate α $[A] = k_1\,[A]$ or $\frac{dx}{dt} = k_1(a - x)$ (1 st order differtial equation)

Integrated 1 st order rate equation is $k_1 = \frac{2.303}{t}\log\frac{a}{a - x}$.

Exponential form of 1 st order equation is $C_t = C_0 e^{-k_1 t}$

Characteristics Of First Order Reaction :

(1) Unit of rate constant is time^{-1}.

(2) Change in concentration unit will not change the numerical value of k_1.

(3) $t_{1/2} = \frac{0.693}{k_1}$ (Half-life); Average life $= \frac{1}{k}$;

(4) log (a – x) v/s t is a straight line with slope $-\frac{k_1}{2.303}$.

EXAMPLES :

(i) Radioactive disintegration is a first order reaction.

(ii) $C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{Inversion}]{H^+ \text{ catalysed hydrolysis}} C_6H_{12}O_6 + C_6H_{12}O_6$.
(glucose) (fructose)

(iii) Mineral acid catalyzed hydrolysis of esters.

(iv) Decomposition of H_2O_2 in aqueous solution.

SECOND ORDER REACTION :

(i) When two molecules of the same reactant are involved or the concentrations of the both reactants are equal reactions $2A \longrightarrow$ products or $A + B \longrightarrow$ products.

Differential rate equation $\frac{dx}{dt} = k_2(a - x)^2$

Integrated rate equation $k_2 = \frac{1}{t}.\frac{x}{a(a - x)}$ or $k_2 t = \frac{1}{a - x} - \frac{1}{a}$.

(ii) When the initial concentrations of the two reactants are different;

$A + B \longrightarrow$ products

a b

differential rate equation $\frac{dx}{dt} = k_2 (a-x)(b-x)$.

Integrated rate equation $k_2 = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$

CHARACTERISTICS OF SECOND ORDER REACTION :

(i) Unit of rate constant L mol^{-1} time^{-1}.

(ii) Numerical value of k will depend upon unit of concentration.

(iii) $t_{1/2} \propto a^{-1}$ (In general $t_{1/2} \propto a^{(1-n)}$; n = order of reactions).

(iv) 2nd order reaction conforms to first order when one of the reactant in excess.

EXAMPLES :

(i) Saponification (hydrolysis of esters catalysed with alkali).

$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$

(ii) Hydrogenation of ethane $C_2H_4 + H_2 \xrightarrow{100°C} C_2H_6$.

(iii) $2\,O_3 \longrightarrow 3\,O_2$.

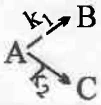
nth ORDER REACTION.

$A \rightarrow$ Product

$$k_n t = \frac{1}{n-1}\left\{\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right\} \qquad [n \neq 1,\ n = \text{order}]$$

$$t_{1/2} = \frac{1}{k_n(n-1)} \cdot \left[\frac{2^{n-1}-1}{a^{n-1}}\right]$$

SIDE OR CONCURENT REACTION :



; $\ln \frac{[A]_0}{[A]_t} = (k_1 + k_2)\,t$; $\frac{[B]}{[C]} = \frac{k_1}{k_2}$

CONSECUTIVE REACTION :

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \ ;\ t_{max} = \frac{1}{(k_1-k_2)} \ln\left(\frac{k_1}{k_2}\right) ;\quad [B]_{max} = [A]_0 \left(\frac{k_2}{k_1}\right)^{\frac{k_2}{k_1-k_2}}$$

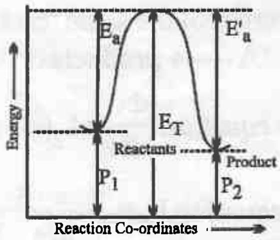
THRESHOLD ENERGY AND ACTIVATION ENERGY :

For a reaction to take place the reacting molecules must colloid together, but only those collisions, in which colliding molecules possess certain minimum energy is called threshold energy (E_T).

ACTIVATION ENERGY (E_a) :

The extra energy needed for the reactant molecules to be able to react chemically is known as Activation energy.

E_T = Threshold energy
E_a = Activation energy of forward reaction
E'_a = activation energy of backward reaction
P_1 = Potential energy of reactants
P_2 = Potential energy of products



INFLUENCE OF TEMPERATURE ON REACTION RATES :

TEMPERATURE COEFFICIENT :

The temperature coefficient of a chemical reaction is defined as the ratio of the reaction rates at two temperatures differing by 10°C. Its value usually lies between 2 & 3.

Temperature coefficient = $\frac{k_{t+10}}{k_t}$.

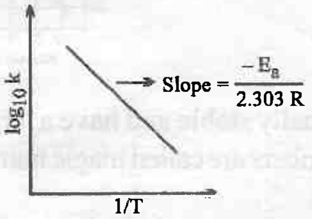
ARRHENIUS EQUATION :

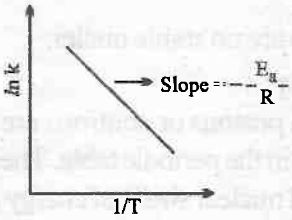
A quantitative relationship was proposed by Arrhenius $k = A.\ e^{-Ea/RT}$ Where,

k = rate constant ; A = frequency factor (or pre – exponential factor);
R = gas constant ; T = Temperature (kelvin) ; E_a = Activation energy.

The Logarithmic expressions are $\log_{10}\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$; Vant Hoff's Isochore $\frac{d}{dt} \ln k = \frac{E_a}{RT^2}$

GRAPHICAL REPRESENTATIONS ARE :





METHODS OF DETERMINATION OF ORDER OF REACTIONS :

A few methods commonly used are given below :

1. **Hit & Trial Method** : It is method of using integrated rate equations, where the experimental values of a, x & t are put into these equations. One which gives a constant value of k for different sets of a, x & t correspond to the order of the reaction.

2. **Graphical Method** :

(i) A plot of log (a – x) versus 't' gives a straight lines for the First order reaction.

(ii) A plot of $(a-x)^{-(n-1)}$ versus 't' gives a straight line any reaction of the order n (except n = 1).

3. **Half Life Method** : The half life of different order of reactions is given by $a_n = \left(\frac{1}{2}\right)^n a_0$.

By experimental observation of the dependence of half life on initial concentration we can determine n, the order of reaction. $n = 1 + \frac{\log t_2 - \log t_1}{\log a_1 - \log a_2}$.

4. **Initial rate method.** Initial rate method is used to determine the order or reaction in cases where more than one reactant is used. It involves the determination of the order of different reactants separately. A series of experiments are performed in which concentration of one particular reactant is varied whereas conc. of other reactants are kept constant. In each experiment the initial rate is determined from the plot of conc. vs. time, e.g., if conc. of A is doubled, and initial rate of reaction is also doubled, order of reaction is 1.

MECHANISM OF REACTIONS :

The path way which reactants are converted into the products is called the reaction mechanism. It should be clear that experimentally determined rate expression cannot be predicted from the stiochiometry of the reaction. For example for the reaction ;

$NO_2(g) + CO\ (g) \longrightarrow CO_2(g) + NO(g)$, the rate expression is ; rate $= -\frac{d}{dt}[NO_2] = k[NO_2]^2$, i.e. the expression has no dependence of CO (g) concentration.

The reason is that the reaction occurs by a series of elementary steps.

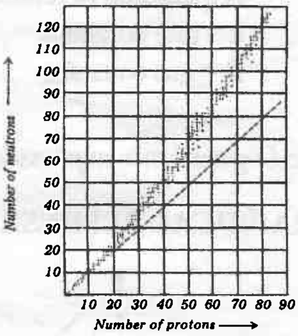
The sequence of elementary processes leading to the overall stiochiometry is known as the "Mechanism of the reaction". A_n in a sequence of reactions leading to the formation of products from reactants, the slowest step is the rate determining step.

The mechanism proposed for the above reaction is a two step one.

$$NO_2 + NO_2 \longrightarrow NO + NO_3 \text{ (step 1 : slow)}$$
$$NO_3 + CO \longrightarrow CO_2 + NO_2 \text{ (step 2 : fast)}$$

The sum of the two gives the stiochiometry & the slow step decided the rate expression.

Nuclear Chemistry



Neutron / proton ratio and stability

- For atomic number < 20, most stable nuclei have n: p ratio nearly 1 : 1 (except H & Ar).
- For n/p ratio > 1.5, nucleus is unstable. Largest stable nucleus is $^{209}_{83}Bi$ for which n/p ratio is 1.52.
- For atomic number > 83, there are no stable nuclei.

Magic numbers and nuclear stability

Nuclei with 2, 8, 20, 28, 50, 82 or 126 protons or neutrons are unusually stable and have a larger number of stable isotopes than neighboring nuclei in the periodic table. These numbers are called magic numbers. They are supposed to represent completely filled nuclear shells of energy levels.

- Nuclei with magic number of protons as well as neutrons have notably high stabilities. [eg. $^{4}_{2}He$, $^{16}_{8}O$, $^{40}_{20}Ca$ and $^{208}_{82}Pb$]. 165 such stable nuclei are known.
- There exist 55 known nuclei with even number of protons and odd number of neutrons, and 50 known stable nuclei with odd number of protons and even number of neutrons. On the other hand, the number of known stable nuclei having odd numbers of both neutrons and protons is only 4.

Expected emissions from unstable nucleus

1. ***n/p ratio above stability belt:*** electron (β^-) or neutron.
2. ***n/p ratio below stability belt:*** positron (β^+) or K capture.
3. ***Atomic number > 83,*** various particles, including α–particles.

Radioactive decay

- Radioactive decay is a first order process. Hence $-\dfrac{dN}{dt} = \lambda N$ or $N = N_0 e^{-\lambda t}$

  where N = number of radioactive nuclei at any time t ; N_0 = number of radioactive nuclei at t = 0 ; λ = decay constant.

- **Activity** activity (a) $= -\dfrac{dN}{dt} = \lambda N$

  S.I. units : disintegration per second (symbol s^{-1} or dps). This unit is also called *becquerel* (symbol Bq)

  Other units: Curie (Ci) 1Ci = 3.7×10^{10}dps.

- **Half life ($t_{½}$)** The time taken by half the nuclei (originally present) to decay. $t_{½} = 0.693/\lambda$

  Note : After *n* half–lives have passed, activity is reduced to $\dfrac{1}{2^n}$ of its initial value.

- **Average life (t_{av})** $t_{av} = 1/\lambda = 1.44\ t_{½}$

  Isotopes : Nuclei with same atomic number but different atomic mass number.

  Isobars : Nuclei with different atomic number but same atomic mass number.

  Isotones : Nuclei with same number of neutrons but different number of protons.

THE ATLAS

Some basic concept

1.Rate of reaction.
2.Rate of reaction in terms of extent of reaction.
3.Average and instantaneous rate of reaction.
4.Dependence of rate of reaction on concentration, pressure, temperature and catalyst.
5.Rate law expression.
6.Order and molecularity of reaction.

CHEMICAL KINETICS

Experimental Aspects

1.Determination of order of reaction.
(a) Graphical Method.
(b) Initial rate method.
(c) Oswald's isolation method.
(d) Half life meyhod.
2. Differential and integerated expressions for
(a) Zero order
(b) First order
(c) nth order reaction
(d) $t_{1/2}$ and $t_{p/q}$ of a reaction.
(e) Rate constant expression in which conc. terms is replaced by other variables litre pressure, volume of reagent, obsorbance etc..
(f) Brancing Decay
(g) Conseqative or sequential Decay
(h) Mechanism of reaction
3. Radioactivity.

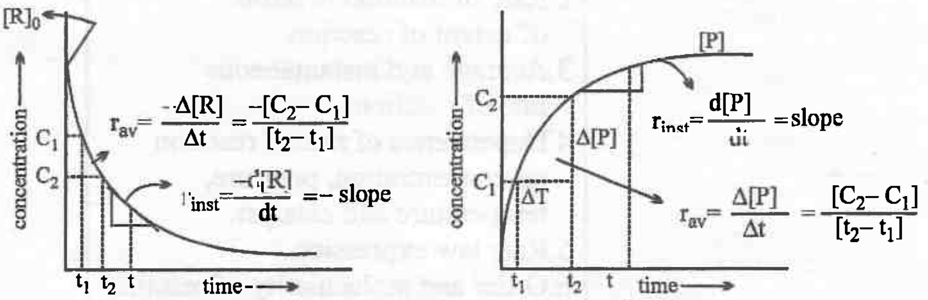
Theoretical Aspects

1.Collision theory of rate of reaction
2. Temperature depedence of rate of reaction
3. Transition state theory for rate of reaction
4. Mechanism of reaction and steady state approximation

GLOSSARY

IMPORTANT TERMS AND DEFINITIONS

1. **Rate of reaction.** It is defined as the change in concentration of reactant (or product) in a particular time interval. Its unit is mol $L^{-1}s^{-1}$. If time is in minutes, then units are mol L^{-1} min^{-1} and so on.
2. **Average rate.** The rate of reaction measured over a long time interval is called average rate of reaction. It is equal to $\Delta x/\Delta t$ as shown in fig.(a) and (b).



(a) (b)

Instantaneous and average rate of reaction

3. **Instantaneous rate.** It is the rate of reaction when the average rate is taken over a very small interval of time. It is equal to dx / dt as shown in fig. (a) and (b).
4. **Rate law or rate equation.** It is the expression which relates the rate of reaction with concentration of the reactants. The constant of proportionality 'k' is known as rate constant.
5. **Rate constant.** When concentration of both reactants are unity, then the rate of reaction is known as rate constant. It is also called specific reaction rate.
6. **Molecularity.** Total number of molecules of the reactants involved in the reaction is termed as its molecularity. It is always in whole number, It is never more than three. It cannot be zero.
7. **Order of a reaction.** The sum of the powers of the concentration of reactants in the rate law is termed as order of the reaction. It can be in fraction. It can be zero also.
8. **Zero order reaction.** The rate of reaction does not change with the concentration of the reactants, i.e., rate = $k[A]^{\circ}$
9. **First order reaction.** The reaction in which the rate of reaction is directly proportional to the concentration of reacting substance. Rate constant of first order reaction is

$$k = \frac{2.303}{t}\log\frac{a}{a-x} \text{ or } k = \frac{2.303}{t}\log\frac{[A_0]}{[A]}$$

where 'a' is initial concentration, (a–x) is the conc. of reactants after time 't'. The unit of 'k' is s^{-1} or min^{-1}. A plot between *l*n [A] vs. t is a straight line with slope equal to –k. [A] is concentration of reactants after time t.

10. **Half–life of a reaction.** The time taken for a reaction when half of the starting material has reacted is called half–life of a reaction. For first order reaction

$$t_{1/2} = \frac{0.693}{k}, \text{ where k is rate constant.}$$

11. **Second order reaction.** The reaction in which sum of powers of concentration terms in rate law or rate equation is equal to 2, e.g.,

$$\frac{dx}{dt} = k[A]^1[B]^1$$

12. **Third order reaction.** The reaction in which sum of powers of concentration terms in rate law or rate equation is equal to 3, e.g.,

$$\frac{dx}{dt} = k[A]^x[B]^y \text{ where } x + y = 3$$

13. **Specific rate constant (k).** It is defined as equal to rate of reaction when molar concentration of reactant is unity.

14. **Activation energy.** It is extra energy which must be possessed by reactant molecules so that collision between reactant molecules is effective and leads to formation of product molecules.

15. **Initial rate.** The rate at the beginning of the reaction when the concentrations have not changed appreciably is called in initial rate of reaction.

16. **Arrhenius equation of reaction rate.** It gives the relation between rate of reaction and temperature.

$$K = Ae^{-E_a/RT}$$

where k = rate constant A = frequency factor, E_a = energy of activation

R = gas constant, T = temperature in kelvin.

$$ln\, k = ln\, A - E_a/RT$$

$$\log k = \log A - \frac{E_a}{2.303\, RT}$$

17. **Photochemical reactions.** Those reactions which take place in the presence of light are called photochemical reactions. Photosynthesis is an example of photochemical reaction.

18. **Photosensitization.** The process in which a molecule that absorbs light transfers its extra energy to another molecule which may undergo a reaction. This process is called photosensitization.

19. **Chain reaction.** The sequence of reactions, where a reactive species produces more reactive species is called chain reaction. It involves free radicals.

20. **Elementary processes.** Some reactions occur by a series of elementary steps and such simple steps are called elementary processes.

21. **Mechanism of reaction.** The sequence of elementary processes leading to the overall stiochiometry of a chemical reaction is known as mechanism of a reaction.

22. **Slow reaction.** Those reactions which take place very slowly are called slow reactions, e.g., rusting of iron and reaction of oxalic acid with acidified $KMnO_4$ at room temperature are slow reactions.

23. **Life time.** The time in which 98% of the reaction is complete is called lifetime.

24. **Threshold energy.** The minimum energy that reacting species must possess in order to undergo effective collision to form product molecules is called threshold energy.

25. **Effective collision (f).** Those collisions which lead to the formation of product molecules are called effective collisions. Rate of reaction = f × z where 'z' is collision frequency and 'f' is fraction of collisions, which are effective.

26. **Collision frequency (z).** It is defined as total number of collisions per unit volume per unit time.

$z = \sqrt{2\pi \bar{v}}\,\sigma^2 n^2$, where $\bar{v}$ is average velocity, σ = molecular diameter in cm, n = no. of molecules per ml.

27. **Activated complex.** It is defined as unstable intermediate formed between reacting molecules which is highly unstable and readily changes into product.

28. **Thermodynamic stability.** A mixture of substances may not undergo reaction although thermodynamic predict the reaction to be spontaneous. Such substances are thermodynamically unstable at ordinary temperature but may not be kinetically unstable.

29. **Kinetic stability.** The reaction occurs only when the reactant crosses energy–barrier. Once it occurs, it becomes kinetically unstable because the reaction is spontaneous. The energy evolved helps the other reactants to cross energy–barrier. Thus, reactants should be thermodynamically as well as kinetically unstable so as to change into products at a particular temperature.

30. **Rate determining step.** The slowest step in the reaction mechanism is called rate determining step.

31. **Temperature coefficient.** It is the ratio of rate constant at temperature 308 K to the rate constant at temperature 298 K.

$$\text{Temperature coefficient} = \frac{\textit{Rate constant}\ \text{'k' at } 308\ \text{K}}{\textit{Rate constant}\ \text{'k' at } 298\ \text{K}}$$

It lies between 2 and 3.

32. **Pseudo first order reaction.** The reaction in which one reacted is in excess so order is one is called Pseudo first order reaction, e.g., acidic hydrolysis of ester.

$$CH_3COOC_2H_5 + H_2O\ (\text{excess}) \overset{H^+}{\rightleftharpoons} CH_3COOH + C_2H_5OH$$

33. **Einstein's law of photochemical equivalence.** Each atom or molecule is activated by 1 photon (quantum of light).
34. **Chain initiation step.** The step in which neutral molecule changes into free radicals by absorbing photons is called chain initiation step.
35. **Chain propagation step.** The step in which free radical reacts with neutral molecule to form a neutral molecule and a free radical is called chain propagation step.
36. **Chain termination step.** The step in which radicals combine to form neutral molecules.
37. **Fast reactions.** Those reactions which occur instantaneously and is complete in fraction of seconds are called fast reactions, e.g., $AgNO_3(aq) + HCl(aq) \longrightarrow AgCl \downarrow + HNO_3$, takes place in 10^{-12} seconds.
38. **Thermochemical reactions.** Those reactions initiated by heat energy are called thermochemical reactions. They can occur in dark. Temperature coefficient is generally high because rate of reaction increases with increase in temperature. ΔG is – ve for such reactions.
39. **Photosensitiser.** The substance which when added to the reaction mixture helps to start the photochemical reaction but does not undergo any chemical change itself is called photosensitiser. It acts as a carrier of energy.

EXERCISE-I

RATE OF REACTION AND STOICHIOMETRIC COEFFICIENT

Q.1 In a catalytic experiment involving the Haber process, $N_2 + 3H_2 \longrightarrow 2NH_3$, the rate of reaction was measured as

$$\text{Rate} = \frac{\Delta[NH_3]}{\Delta t} = 2 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}.$$

If there were no sides reactions, what was the rate of reaction expressed in terms of (a) N_2, (b) H_2?

Q.2 For the reaction $3BrO^- \rightarrow BrO_3^- + 2Br^-$ in an alkaline aquesous solution, the value of the second order (in BrO^-) rate constant at 80°C in the rate law for $-\frac{\Delta[BrO^-]}{\Delta t}$ was found to be $0.056\ \text{L mol}^{-1}\text{s}^{-1}$.

What is the rate of constant when the rate law is written for (a) $\frac{\Delta[BrO_3^-]}{\Delta t}$, (b) $\frac{\Delta[Br^-]}{\Delta t}$?

Q.3 Dinitropentaoxide decomposes as follows :

$$N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$$

Given that $-d\,[N_2O_5] / dt = k_1[N_2O_5]$

$d\,[NO_2] / dt = k_2[N_2O_5]$

$d\,[O_2] / dt = k_3[N_2O_5]$

What is the relation between k_1, k_2 and k_3?

Q.4 The reaction $2A + B + C \rightarrow D + E$ is found to be first order in A second order in B and zero order in C.

(i) Give the rate law for the reaction in the form of differential equation.

(ii) What is the effect in rate of increasing concentrations of A, B, and C two times?

Q.5 For the elementary reaction $2A + B_2 \longrightarrow 2AB$. Calculate how much the rate of reaction will change if the volume of the vessel is reduced to one third of its original volume?

Q.6 Ammonia and oxygen reacts at higher temperatures as

$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$

In an experiment, the concentration of NO increases by 1.08×10^{-2} mol litre^{-1} in 3 seconds. Calculate.

(i) rate of reaction.

(ii) rate of disappearance of ammonia

(iii) rate of formation of water

Q.7 In the following reaction $2H_2O_2 \longrightarrow 2H_2O + O_2$

rate of formation of O_2 is $3.6\ \text{M min}^{-1}$.

(a) What is rate of formation of H_2O?

(b) What is rate of disappearance of H_2O_2?

Q.8 The reaction $A(g) + 2B(g) \longrightarrow C(g) + D(g)$ is an elementary process. In an experiment, the initial partial pressure of A & B are $P_A = 0.6$ and $P_B = 0.8$ atm, if $P_C = 0.2$ atm then calculate the ratio of rate of reaction relative to initial rate.

ZERO ORDER

Q.9 In the following reaction, rate constant is $1.2 \times 10^{-2}\ \text{M s}^{-1}$ $A \longrightarrow B$. What is concentration of B after 10 and 20 min., if we start with 10 M of A.

Q.10 For the following data for the reaction $A \longrightarrow$ products. Calculate the value of k.

Time (min.)	[A]
0.0	0.10 M
1.0	0.09 M
2.0	0.08 M

Q.11 The rate constant for a zero order reaction is 2×10^{-2} mol $L^{-1}sec^{-1}$, if the concentration of the reactant after 25 sec is 0.25 M, calculate the initial concentration.

Q.12 A drop of solution (volume 0.10 ml) contains 6×10^{-6} mole of H^+, if the rate constant of disappearance of H^+ is 1×10^7 mole $litre^{-1}$ sec^{-1}. How long would it take for H^+ in drop to disappear?

Q.13 A certain substance A is mixed with an equimolar quantity of substance B. At the end of an hour A is 75% reacted. Calculate the time when A is 10% unreacted. (Given: order of reaction is zero)

FIRST ORDER

Q.14 A first order reaction is 75% completed in 72 min.. How long time will it take for
(i) 50% completion (ii) 87.5% completion

Q.15 A first order reaction is 20% complete in 10 min. calculate (i) the specific rate constant, (ii) the time taken for the reactions to go to 75% completion.

Q.16 Show that in case of unimolecular reaction, the time required for 99.9% of the reaction to take place in ten times that required for half of the reaction.

Q.17 A first order reaction has a rate constant is 1.5×10^{-3} sec^{-1}. How long will 5.0 g of this reactant take to reduce to 1.25 g.

Q.18 A drug is known to be ineffective after it has decomposed 30%. The original concentration of a sample was 500 units/ml. When analyzed 20 months later, the concentration was found to be 420 units/ml. Assuming that decomposition is of I order, what will be the expiry time of the drug?

Q.19 A viral preparation was inactivated in a chemical bath. The inactivation process was found to be first order in virus concentration. At the beginning of the experiment 2.0 % of the virus was found to be inactivated per minute. Evaluate k for inactivation process.

Q.20 If a reaction A $\longrightarrow$ Products, the concentrations of reactant A are C_0, aC_0, a^2C_0, a^3C_0, ... after time interval 0, t, 2t, 3t, ... where a is a constant. Given $0 < a < 1$. Show that the reaction is of first order. Also calculate the relation in k, a and t.

Q.21 The reaction $SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$ is a first order gas reaction with $k = 2.2 \times 10^{-5}$ sec^{-1} at 320°C. What % of SO_2Cl_2 is decomposed on heating this gas for 90 min.

ORDER OF REACTION & RATE LAW

Q.22 At 800° C the rate of reaction

$$2\,NO + H_2 \longrightarrow N_2 + H_2O$$

Changes with the concentration of NO and H_2 are

	[NO] in M	[H_2] in M	$-\frac{1}{2}\frac{d[NO]}{dt}$ in M sec^{-1}
(i)	1.5×10^{-4}	4×10^{-3}	4.4×10^{-4}
(ii)	1.5×10^{-4}	2×10^{-3}	2.2×10^{-4}
(iii)	3.0×10^{-4}	2×10^{-3}	8.8×10^{-4}

(a) What is the order of this reaction?
(b) What is the rate equation for the reaction?
(c) What is the rate when
$[H_2] = 1.5 \times 10^{-3}$ M and $[NO] = 1.1 \times 10^{-3}$M?

Q.23 The data below are for the reaction if NO and Cl_2 to form NOCl at 295 K

Concentration of Cl_2 [M]	Concentration of NO	Initial Rate ($M\ s^{-1}$)
0.05	0.05	1×10^{-3}
0.15	0.05	3×10^{-3}
0.05	0.15	9×10^{-3}

(a) What is the order w.r.t NO and Cl_2 in the reaction.
(b) Write the rate expression
(c) Calculate the rate constant
(d) Determine the reaction rate when concentration of Cl_2 and NO are 0.2 M & 0.4 M respectively.

Q.24 The catalytic decomposition of N_2O by gold at 900°C and at an initial pressure of 200mm is 50% complete in 53 minutes and 73% complete in 100 minutes.
(i) What is the order of the reaction?
(ii) Calculate the velocity constant.
(iii) How much of N_2O will decompose in 100 min. at the same temperature but at initial pressure of 600 mm?

Q.25 The following data are for the reaction A + B → products:

Conc. A (M)	**Conc. B (M)**	**Initial Rate (mol $L^{-1}\ s^{-1}$)**
0.1	0.1	4.0×10^{-4}
0.2	0.2	1.6×10^{-3}
0.5	0.1	2.0×10^{-3}
0.5	0.5	1.0×10^{-2}

(i) What is the order with respect to A and B for the reaction?
(ii) Calculate the rate constant.
(iii) Determine the reaction rate when the concentrations of A and B are 0.2M and 0.35M, respectively.

Q.26 The pressure of a gas decomposing at the surface of a solid catalyst has been measured at different times and the results are given below

t (sec)	0	100	200	300
Pr. (Pascal)	4×10^3	3.5×10^3	3×10^3	2.5×10^3

Determine the order of reaction, its rate constant.

Q.27 The half life period of decomposition of a compound is 50 minutes. If the initial concentration is halved, the half life period is reduced to 25 minutes. What is the order of reaction?

Q.28 At 600°C, acetone (CH_3COCH_3) decomposes to ketene ($CH_2 = C = O$) and various hydrocarbons. Given the initial rate data in the table:
(a) What is the order?
(b) Write rate law
(c) Calculate rate constant
(d) Calculate the rate of decomposition when the acetone concentartion is 1.8×10^{-3} M

Experiment	Initial [CH_3COCH_3]	Rate $M\ s^{-1}$
1.	6.0×10^{-3} M	5.2×10^{-5}
2.	9.0×10^{-3} M	7.8×10^{-5}
3.	1.8×10^{-3} M	?

HALF LIFE

Q.29 The half life period of a first order reaction is 50 min. In what time will it go to 90% completion?

Q.30 A first order reaction has $k = 1.5 \times 10^{-6}$ per second at 200°C. If the reaction is allowed to run for 10 hrs., what percentage of the initial concentration would have changed into the product? What is the half life of this reaction?

Q.31 Show that in case of a first order reaction, the time required for 93.75% of the reaction to take place is four times that required for half of the reaction.

Q.32 The half time of the first order decomposition of nitramide is 2.1 hour at 15°C.

$$NH_2NO_2\ (aq.) \longrightarrow N_2O\ (g) + H_2O\ (l)$$

If 6.2 g of NH_2NO_2 is allowed to deompose, calculate (i) time taken for NH_2NO_2 to decompose 99%, and (ii) volume of dry N_2O produced at this point, measured at STP.

Q.33 A flask contains a mixture of compounds A and B. Both compounds decompose by first-order kinetics. The half-lives are 54.0 min for A and 18.0 min. for B. If the concentartions of A and B are equal initially, how long will it take for the concentration of A to be four times that of B?

Q.34 Two substances A ($t_{1/2}$= 5 mins) and B ($t_{1/2}$ = 15 mins) follow first order kinetics are taken in such a way that initially [A]= 4[B]. Calculate the time after which the concentration of both the substance will be equal.

CONCENTRATION REPLACED BY OTHER QUANTITIES IN FIRST ORDER INTEGRATED RATE LAW

Q.35 In this case we have

$A \longrightarrow B + C$

Time	t	∞
Total pressure of A + B+C	P_2	P_3

Find k.

Q.36 $A \longrightarrow B + C$

Time	t	∞
Total pressure of (B+C)	P_2	P_3

Find k.

Q.37 $A \longrightarrow B + C$

Time	0	t
Volume of reagent	V_1	V_2

The reagent reacts with A, B and C. Find k.

Q.38 $A \longrightarrow 2B + 3C$

Time	t	∞
Volume of reagent	V_2	V_3

Reagent reacts with all A, B and C. Find k.

Q.39 $S \longrightarrow G + F$

Time	t	∞
Rotation of Glucose & Fructose	r_t	r_∞

Find k.

Q.40 At 27°C it was observed during a reaction of hydrogenation that the pressure of hydrogen gas decreases from 2 atmosphere to 1.1 atmosphere in 75 minutes. Calculate the rate of reaction (in M sec^{-1}) and rate of reaction in terms of pressure.

Q.41 At 100°C the gaseous reaction $A \longrightarrow 2B + C$ was observed to be of first order. On starting with pure A it is found that at the end of 10 minutes the total pressure of system is 176 mm. Hg and after a long time 270 mm Hg. From these data find (a) initial pressure of A (b) the pressure of A at the end of 10 minutes (c) the specific rate of reaction and (d) the half life period of the reaction?

Q.42 The reaction $AsH_3(g) \longrightarrow As(s) + \frac{3}{2} H_2(g)$ was followed at constant volume at 310°C by measuring the gas pressure at intervals Show from the following figures that reaction is of first order.

Time (in hrs)	0	5	7.5	10
Total pressure (in mm)	758	827	856	882

Q.43 The decomposition of N_2O_5 according to the equation $2\,N_2O_5(g) \longrightarrow 4\,NO_2(g) + O_2(g)$ is a first order reaction. After 30 min. from start of decomposition in a closed vessel the total pressure developed is found to be 284.5 mm Hg. On complete decomposition, the total pressure is 584.5 mm Hg. Calculate the rate constant of the reaction.

Q.44 The thermal decomposition of dimethyl ether as measured by finding the increase in pressure of the reaction

$$(CH_3)_2O(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$$

at 500°C is as follows:

Time (sec.)	390	1195	3155	∞
Pressure increase (mm Hg)	96	250	467	619

the initial pressure of ether was 312 mm Hg. Write the rate equation for this reaction and determine the rate constant of reaction.

Q.45 From the following data show that decomposition of H_2O_2 in aqueous solution is first order.

Time (in minutes)	0	10	20
Volume (in c.c. of $KMnO_4$)	22.8	13.3	8.25

Q.46 A definite volume of H_2O_2 under going spontaneous decomposition required 22.8 c.c. of standard permanganate solution for titration. After 10 and 20 minutes respectively the volumes of permanganate required were 13.8 and 8.25 c.c.

(a) Find order of reaction. How may the result be explained?
(b) Calculate the time required for the decomposition to be half completed.
(c) Calculate the fraction of H_2O_2 decomposed after 25 minutes.

Q.47 The following data were obtained in experiment on inversion of cane sugar.

Time (minutes)	0	60	120	180	360	∞
Angle of rotation (degree)	+13.1	+ 11.6	+ 10.2	+9.0	+5.87	–3.8

Show that the reaction is of first order. After what time would you expect a zero reading in polarimeter?

Q.48 In the hydrolysis of propyl acetate in the presence of dilute hydrochloric acid in dilute aqueous solution the following data were recorded :

Time from start in minutes	60	350
Percentage of ester decomposed	18.17	69.12

Calculate the time in which half the ester was decomposed.

Q.49 Hydrogen peroxide solution was stored in a mild steel vessel. It was found, however, that the hydrogen peroxide decomposed on the walls of the vessel (a first order reaction). An experiment with 100 ml of a solution gave 10.31 ml oxygen (corrected to N.T.P.) after 5.1 days under similar storage conditions. Find how long the peroxide can be stored before the loss of 20.00 ml oxygen occurs (per 100 ml solution) if complete decomposition of the sample to H_2O_2 gave 46.34 ml oxygen.

Q.50 The reaction given below, rate constant for disappearance of A is $7.48 \times 10^{-3}\ sec^{-1}$. Calculate the time required for the total pressure in a system containing A at an initial pressure of 0.1 atm to rise to 0.145 atm and also find the total pressure after 100 sec. exactly half

$$2A\,(g) \longrightarrow 4B(g) + C(g)$$

PARALLEL AND SEQUENTIAL REACTION

Q.51 For a reaction $x \begin{array}{l} \xrightarrow{k_1} y \\ \xrightarrow[k_2]{} z \end{array}$, calculate value of ratio, $\dfrac{[x]_t}{[y]+[z]}$ at any given instant t.

Q.52 $$\begin{tikzcd}[row sep=small] & B \\ A \arrow[ur, "k_1"] \arrow[dr, "k_2"'] & \\ & C \end{tikzcd}$$ $k_1 = x\,hr^{-1}$; $k_1 : k_2 = 1 : 10$. Calculate $\frac{[C]}{[A]}$ after one hour from the start of the reaction. Assuming only A was present in the beginning.

Q.53 A substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as $$\begin{tikzcd}[row sep=small] & B \\ A \arrow[ur, "k_1"] \arrow[dr, "k_2"'] & \\ & C \end{tikzcd}$$; $k_1 = 1.26 \times 10^{-4}\ sec^{-1}$ and $k_2 = 3.6 \times 10^{-5}\ sec^{-1}$. Calculate the % distribution of B & C.

Q.54 For a reaction $A \longrightarrow B \longrightarrow C$ $t_{1/2}$ for A & B are 4 and 2 minutes respectively. How much time would be required for the B to reach maximum concentration.

TEMPERATURE DEPENDENCE OF RATE (ACTIVATION ENERGY)

Q.55 In gaseous reactions important for understanding the upper atmosphere, H_2O and O react bimolecularly to form two OH radicals. ΔH for this reaction is 72 kJ at 500 K and $E_a = 77\ kJ\ mol^{-1}$, then calculate E_a for the biolecular recombination of 2OH radicals to form H_2O & O at 500 K

Q.56 The energy of activation of a first order reaction is 104.5 kJ $mole^{-1}$ and pre – exponential factor (A) is $5 \times 10^{13}\ sec^{-1}$. At what temperature, will the reaction have a half life of 1 minute?

Q.57 The specific rate constant for a reaction increases by a factor of 4, if the temperature is changed from 27°C to 47°C. Find the activation energy for the reaction.

Q.58 The energy of activation and specific rate constant for a first order reaction at 25°C are 100 kJ/ mole and $3.46 \times 10^{-5}\ sec^{-1}$ respectively. Determine the temperature at which half life of the reaction is 2 hours.

$$2N_2O_5(g) \longrightarrow 2N_2O_4(g) + O_2\ (g)$$

Q.59 A first order reaction is 50% complete in 30 minutes at 27°C and in 10 minutes at 47°C. Calculate the

(a) rate constant for the reactiion at 27°C & 47°C and

(b) energy of activatioin for the reaction.

Q.60 A catalyst lowers the activation energy for a certain reaction from 75 kJ to 25 kJ mol^{-1}. What will be the effect on the rate of reaction at 25°C, after things being equal.

Q.61 Given that the temperature coefficient for the saponification of ethyl acetate by NaOH is 1.75. Calculate activation energy for the saponification of ethyl acetate.

MECHANISM OF REACTION

Q.62 The reaction $2NO + Br_2 \longrightarrow 2NOBr$, is supposed to follow the following mechanism

(i) $NO + Br_2 \overset{fast}{\rightleftharpoons} NOBr_2$

(ii) $NOBr_2 + NO \xrightarrow{slow} 2NOBr$

Suggest the rate of law expression.

Q.63 For the reaction $2H_2 + 2NO \longrightarrow N_2 + 2H_2O$, the following mechanism has been suggested:

$2NO \rightleftharpoons N_2O_2$ equilibrium constant K_1 (fast)

$N_2O_2 + H_2 \xrightarrow{K_2} N_2O + H_2O$ (slow)

$N_2O + H_2 \xrightarrow{K_3} N_2 + H_2O$ (fast)

Establish the rate law for given reaction.

Q.64 Write a stoichiometric equation for the reaction whose mechanism is detailed below. Determine the value of the equilibrium constant for the first step. Write a rate law equation for the overall reaction in terms of its initial reactants.

$A_2 \rightleftharpoons 2A$ $k_1 = 10^{10}s^{-1}$ (forward)
$k_{-1} = 10^{10}M^{-1}s^{-1}$ (reverse)
$A + C \longrightarrow AC$ $k_2 = 10^{-4}M^{-1}s^{-1}$ (slow)

Q.65 Reaction between NO and O_2 to form NO_2 is $2NO + O_2 \longrightarrow 2NO_2$ follows the following mechanism

$NO + NO \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} N_2O_2$ (in rapid equilibrium)

$N_2O_2 + O_2 \xrightarrow{K_2} 2NO_2$ (slow)

Show that the rate of reaction is given by $\frac{1}{2}\left(\frac{d[NO_2]}{dt}\right) = K[NO]^2[O_2]$

Q.66 Deduce rate law expressions for the conversion of H_2 and I_2 to HI at 400°C corresponding to each of the following mechanisms:

(a) $H_2 + I_2 \longrightarrow 2HI$ (one step)

(b) $I_2 \rightleftharpoons 2I$
$2I + H_2 \longrightarrow 2HI$ (slow)

(c) $I_2 \rightleftharpoons 2I$
$I + H_2 \rightleftharpoons IH_2$
$IH_2 + I \longrightarrow 2HI$ (slow)

(d) Can the observed rate law expression rate = $k[H_2][I_2]$ distinguish among these mechanisms?

(e) If it is known that ultraviolet light causes the reaction of H_2 and I_2 to proceed at 200°C with the same rate law expression, which of these mechanisms becomes most improbable? Are any of these mechanisms proved?

RADIOACTIVITY

Q.67 Classify each of the following nuclides as "beta emitter", or "positron emitter":

$^{49}_{20}Ca$ $^{195}_{80}Hg$ $^{8}_{5}B$ $^{150}_{67}Ho$ $^{30}_{13}Al$ $^{94}_{36}Kr$. Note: $^{200}_{80}Hg$ and $^{165}_{67}Ho$ are stable

Q.68 Of the three isobars $^{114}_{48}Cd$ $^{114}_{49}In$ and $^{114}_{50}Sn$, which is likely to be radioactive? Explain your choice.

Q.69 Complete the following nuclear equations:

(a) $^{14}_{7}N + ^{4}_{2}He \rightarrow ^{17}_{8}O + ...$

(b) $^{9}_{4}Be + ^{4}_{2}He \rightarrow ^{12}_{6}C + ...$

(c) $^{9}_{4}Be\ (p, \alpha)........$

(d) $^{30}_{15}P \rightarrow ^{30}_{14}S + ...$

(e) $^{3}_{1}H \rightarrow ^{3}_{2}He + ...$

(f) $^{43}_{20}Ca(\alpha, ...) \rightarrow ^{46}_{21}Sc$

Q.70 What symbol is needed to complete the nuclear equation $^{63}_{29}Cu(p, ...)^{62}_{29}Cu$?

Q.71 Complete the following equations.

(a) $^{23}_{11}Na + ^{4}_{2}He \rightarrow ^{26}_{12}Mg + ?$

(b) $^{64}_{29}Cu \rightarrow \beta^+ + ?$

(c) $^{106}Ag \rightarrow ^{106}Cd + ?$

(d) $^{10}_{5}B + ^{4}_{2}He \rightarrow ^{13}_{7}N + ?$

Q.72 How many α and β particle will be emitted when $^{a}_{c}X$ changes to $^{b}_{d}Y$?

Q.73 What is the α-activity in disintigration per minute 1 gm sample of ^{226}Ra. ($t_{1/2} = 1620$ year)

Q.74 The half life of the nuclide Rn^{220} is 54.5 sec. What mass of radon is equivalent to 1 millicurie.

Q.75 The activity of the radioactive sample drops to $\left(\frac{1}{64}\right)^{th}$ of its original value in 2 hr find the decay constant (λ).

Q.76 $_{84}Po^{210}$ decays with α to $^{206}_{82}Pb$ with a half life of 138.4 days. If 1.0 gm of Po^{210} is placed in a closed tube, how much helium accumlate in 69.2 days at STP.

Q.77 The half life period of $_{53}I^{125}$ is 60 days. What % of radioactivity would be present after 240 days.

Q.78 At a certain instant a piece of radioactive material contains 10^{12} atoms. The half life of material is 30 days. Calculate the no. of disintegrations in one second.

Q.79 Calculate the age of a vegetarian beverage whose tritium content is only 15% of the level in living plants. Given $t_{1/2}$ for $_1H^3 = 12.3$ years.

Q.80 A radioactive substance decays 20% in 10 min if at start there are 5×10^{20} atoms present, after what time will the number of atoms be reduced to 10^{18} atoms?

PROFICIENCY TEST

Q.1 ***Fill in the blanks with appropriate items :***

1. 1 Curie = _______ Bq.
2. ${}^{14}_{6}C$ decays by emission of _____________.
3. Emission of a β-particle by a nuclide results in the formation ______ of the element.
4. The number of α and β-particles emitted, when the following nuclear transformation takes place are _______ and ___________ respectively.

$${}^{238}_{92}X \longrightarrow {}^{206}_{82}Y$$

5. The nuclides with same difference of number of neutrons and number of protons are called _____.
6. When ${}^{30}_{15}P$ emits a position, the daughter nuclide formed is _________.
7. A nuclide which lies above the zone of stability is likely to emit ___________.
8. ${}^{3}_{1}H$ and ${}^{4}_{2}He$ are ____________.
9. The half-life period of radioactive element if 87.5% of it disintegrates in 40 min is __________.
10. For collision to be effective the energy possessed by the colliding molecules should be equal to or greater than the ____________.
11. In the reaction, $H_2 + I_2 \longrightarrow 2HI$, the rate of disappearance of H_2 is _______ the rate of appearance of HI.
12. For an endothermic process, the minimum value of activation energy can be _______.
13. The rate of a reaction is ________ to the collision frequency.
14. The rate constant for the zero order reaction has the dimensions ___________.
15. The reactions with molecularity more than three are _________.
16. A catalyst increases the rate of the reaction by __________ activation energy of reactants.
17. If activation energy of reaction is low, it proceeds at _______ rate.
18. In a multistep reaction, the ________ step is rate determining.
19. Rate constant of a reaction, generally __________ with increase in temperature.
20. The ratio $t_{7/8} / t_{1/2}$ for a first order reaction would be equal to __________.
21. For a zero order reaction, the rate of the reaction is equal to the ______ of the reaction.
22. The value of temperature coefficient is generally between _________.
23. For a certain reaction, $xM \longrightarrow yL$, the rate of reaction increases by 4 times when the concentration of M is doubled. The rate law is _________.
24. The rate equation $r = k[A][B]^{1/2}$ suggests that order of overall reaction is _______.
25. A plot of [A] vs t for a certain reaction $A \longrightarrow B$ with $r = k[A]^0$ will be a straight line with slope equal to ________.

26. $[E_{\text{activated complex}} - E_{\text{reactants}}]$ = ____________.

27. Among similar reactions, the endothermic reaction has ______ activation energy than exothermic reaction.

28. For a ______ order reaction the half-life ($t_{1/2}$) is independent of the initial conc. of the reactants.

29. For a first order reaction a graph of log [A] vs t has a slope equal to __________.

30. Average lifetime of a nuclei, T_{av} = __________________ $t_{1/2}$.

Q.2 ***True or False Statements :***

1. Order of a reaction can be written from the balanced chemical equation.
2. For a reaction having order equal to 3/2, the units for rate constant are sec^{-1}.
3. In a complex reaction the rate of overall reaction is governed by the slowest step.
4. $t_{1/2}$ for a first order reaction is 6.93 s, the value of rate constant for the reaction would be $10 s^{-1}$.
5. The ratio $t_{1/2} / t_{7/8}$ for a first order reaction is equal to 1/3.
6. The rate of an exothermic reaction increases with the rise in temperature.
7. Molecularity of a reaction is always whole number.
8. The reactants which are thermodynamically unstable are always kinetically unstable also.
9. Order and molecularity of a single step reaction may or may not be same.
10. The activation energy of a catalysed reaction is more than the activation energy of the uncatalysed reaction.
11. For a zero order reaction $t_{3/4}$ is related to $t_{1/2}$ as $t_{3/4} = 1.5\ t_{1/2}$.
12. A nuclide having one proton and one neutron is represented as ${}^{1}_{1}H$.
13. A radioactive element decays by emitting one α and two β-particles. The daughter element formed is an isotope of the parent element.
14. The daughter product formed by the emission of α-particle has mass number less by 4 units than the parent nuclide.
15. ${}^{27}_{13}Al$ is a stable isotope while ${}^{29}_{13}Al$ is expected to disintegrate by β-emission.
16. Half-life period of a radioactive substance can be changed by using some suitable catalyst.
17. Emission of a β-particle by a radioactive nuclide results in decrease in N / P ratio.
18. Positron has same mass as that of an electron.
19. ${}^{14}_{9}N$ and ${}^{16}_{8}O$ are isotones.
20. The S.I.unit of activity is Curie (Ci).

EXERCISE -II

Q.1 To investigate the decomposition of oxalic acid in concentrated H_2SO_4 at 50°C, a scientist prepared a 1/40 M solution of oxalic acid in 99.5 percent H_2SO_4, then removed aliquots at various reaction times t, and then determined the volumes υ of a potassium permanganate solution required to react with a 10 ml portion. The results are given below :

t, *min*	0	120	240	420	600	900	1440
υ,*mL*	11.45	9.63	8.11	6.22	4.79	2.97	1.44

Determine the reaction order with respect to oxalic acid and evaluate the specific rate constant.

Q.2 A solution of A is mixed with an equal volume of a solution of B containing the same number of moles, and the reaction A+B=C occurs. At the end of 1h, A is 75 % reacted. How much of A will be left unreacted at the end of 2 h if the reaction is (a) first order in A and zero order in B; (b) first order in both A and B ; and (c) zero order in both A and B ?

Q.3 The approach to the following equilibrium was observed kinetically from both directions:
$PtCl_4^{2-} + H_2O \rightleftharpoons [Pt(H_2O)Cl_3^-] + Cl^-$ at 25°C, it was found that

$$-\frac{\Delta}{\Delta t}[PtCl_4^{2-}] = [3.9\times10^{-5}\ sec^{-1}][PtCl_4^{2-}] - [2.1\times10^{-3}\ L.mol^{-1}\ sec^{-1}]\times[Pt(H_2O)Cl_3]^-[Cl^-]$$

What is the value of equilibrium constant for the complexation of the fourth Cl^- by Pt(II)?

Q.4 The oxidation of certain metals is found to obey the equation $\tau^2 = \alpha t + \beta$ where τ is the thickness of the oxide film at time t, α and β are contants. What is the order of this reaction?

Q.5 The complex $[Co(NH_3)_5F]^{2+}$ reacts with water according to the equation.
$[Co(NH_3)_5F]^{2+} + H_2O \rightarrow [Co(NH_3)_5(H_2O)]^{3+} + F^-$
The rate of the reaction = rate const. x$[complex]^a$x$[H^+]^b$. The reaction is acid catalysed i.e. $[H^+]$ does not change during the reaction. Thus rate = $k'[Complex]^a$ where $k' = k[H^+]^b$, calculate 'a' and 'b' given the following data at 25^0C.

[Complex]M	$[H^+]$M	$T_{1/2}$hr	$T_{3/4}$hr
0.1	0.01	1	2
0.2	0.02	0.5	1

Q.6 The reaction $CH_3{-}CH_2{-}NO_2 + OH^- \longrightarrow CH_3{-}CH{-}NO_2 + H_2O$ obeys the rate law for pseudo first order kinetics in the presence of a large excess of hydroxide ion. If 1% of nitro ethane undergoes reaction in half a minute when the reactant concentration is 0.002 M, What is the pseudo first order rate constant?

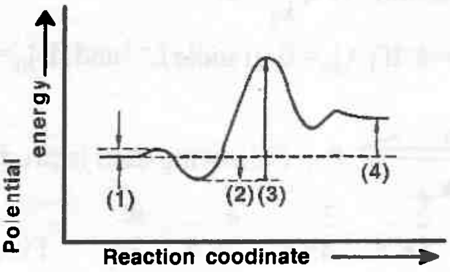
Q.7 A flask containing a solution a solution of N_2O_5 in CCl_4 was placed in a thermostat at 40°C. The N_2O_5 began to decompose by a first–order reaction, forming NO_2 and N_2O_4, which remained in the solution, and oxygen, which defined pressure. The measurements were started (t = 0) when 10.75ml gas had collected. At t = 2400 sec., 29.65ml was measured. After a very long time, (t = ∞)45.50ml was measured. Find the (a) rate constant, (b) half–life time for reaction at 40°C in CCl_4 solution. (c) What volume of gas should have collected after 4800 sec?

Q.8 At room temperature (20°C) orange juice gets spoilt in about 64 hours. In a referigerator at 3°C juice can be stored three times as long before it gets spoilt. Estimate (a) the activation energy of the reaction that causes the spoiling of juice. (b) How long should it take for juice to get spoilt at 40°C?

Q.9 A first order reaction, A → B, requires activation energy of 70 kJ mol^{-1}. When a 20% solution of A was kept at 25°C for 20 minutes, 25% decomposition took place. What will be the percent decomposition in the same time in a 30% solution maintianed at 40°C? Assume that activation energy remains constant in this range of temperature.

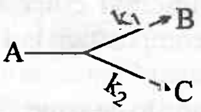
Q.10 Two reations (i) A → products (ii) B → products, follow first order kinetics. The rate of the reaction (i) is doubled when the temperature is raised from 300 K to 310K. The half life for this reaction at 310K is 30 minutes. At the same temperature B decomposes twice as fast as A. If the energy of activation for the reaction (ii) is half that of reaction (i), calculate the rate constant of the reaction (ii) at 300K.

Q.11 Choose the correct set of identifications.



	(1)	(2)	(3)	(4)
(A)	ΔE for $E + S \rightarrow ES$	E_a for $ES \rightarrow EP$	$\Delta E_{overall}$ for $S \rightarrow P$	E_a for $EP \rightarrow E + P$
(B)	E_a for $E + S \rightarrow ES$	ΔE for $E + S \rightarrow ES$	E_a for $ES \rightarrow EP$	$\Delta E_{overall}$ for $S \rightarrow P$
(C)	E_a for $ES \rightarrow EP$	E_a for $EP \rightarrow E + P$	$\Delta E_{overall}$ for $S \rightarrow P$	ΔE for $EP \rightarrow E + P$
(D)	E_a for $E + S \rightarrow ES$	E_a for $ES \rightarrow EP$	E_a for $EP \rightarrow E + P$	$\Delta E_{overall}$ for $S \rightarrow P$
(E)	ΔE for $E + S \rightarrow ES$	$\Delta E_{overall}$ for $S \rightarrow P$	ΔE for $EP \rightarrow E + P$	E_a for $EP \rightarrow E + P$

Q.12 A certain organic compound A decomposes by two parallel first order mechanism



If $k_1 : k_2 = 1 : 9$ and $k_1 = 1.3 \times 10^{-5}\ s^{-1}$.

Calculate the concentration ratio of C to A, if an experiment is started with only A and allowed to run for one hour.

Q.13 Decomposition of H_2O_2 is a first order reaction. A solution of H_2O_2 labelled as 20 volumes was left open. Due to this, some H_2O_2 decomposed. To determine the new volume strength after 6 hours, 10 mL of this solution was diluted to 100mL. 10mL of this diluted solution was titrated against 25mL of 0.025M $KMnO_4$ solution under acidic conditions. Calculate the rate constant for decomposition of H_2O_2.

Q.14 The reaction

$$\text{cis–Cr(en)}_2\text{(OH)}^+_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{trans–Cr(en)}_2\text{(OH)}^+_2$$

is first order in both directions. At 25°C the equilibrium constant is 0.16 and the rate constant k_1 is $3.3 \times 10^{-4} s^{-1}$. In an experiment starting with the pure *cis* form, how long would it take for half the equilibrium amount of the *trans* isomer to be formed ?

Q.15 A metal slowly forms an oxide film which completely protects the metal when the film thickness is 3.956 thousand ths of an inch. If the film thickness is 1.281 thou. in 6 weeks, how much longer will it be before it is 2.481 thou.? The rate of film formation follows first order kinetics.

Q.16 An optically active compound A upon acid catalysed hydrolysis yield two optically active compound B and C by pseudo first order kinetics. The observed rotation of the mixture after 20 min was 5° while after completion of the reaction it was – 20°. If optical rotation per mole of A, B & C are 60°, 40° & – 80°. Calculate half life and average life of the reaction.

Q.17 A bacterial preparation was inactivated in a chemical bath. The inactivation process was found to be first order in bacterial concentration having rate constant $1.7\times10^{-2}\ sec^{-1}$. Meanwhile the multiplication of bacteria (1bacterium → 2 bacteria) which also follows first order kinetics with rate constant $1.5\times10^{-3}\ sec^{-1}$ also continued. Calculate the number of bacteria left after 2 minutes if the initial number of bacteria is 10^3.

Q.18 The formation in water of *d*–potassium chromo–oxalate from its *l*–form is reversible reaction which is first order in both directions, the racemate being the equilibrium product. A polarimeter experiment at 22°C showed that, after 506 sec, 12 mole % of the *l*–isomer was converted to the *d*–form. Find the rate constant for the forward and the reverse reactions.

Q.19 For a reversible first–order reaction $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$

$k_1 = 10^{-2}\,s^{-1}$ and $[B]_{eq}/[A]_{eq} = 4$. If $[A]_0 = 0.01$ mole L^{-1} and $[B]_0 = 0$, what will be the concentration of B after 30 s ?

Q.20 For the reaction $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} P$. Following data is produced:

Time / Hr.	0	1	2	3	4	∞
% A	100	72.5	56.8	45.6	39.5	30

Find k , k_{-1} and k_{eq}.

Q.21 For the system $A_{(g)} \rightleftharpoons B_{(g)}$, ΔH for the forward reaction is –33 kJ/mol (Note : ΔH = ΔE in this case). Show that equilibrium constant $K = \frac{[B]}{[A]} = 5.572 \times 10^5$ at 300 K. If the activation energies E_f & E_b are in the ratio 20 : 31, calculate E_f and E_b at this temperature. Assume that the pre-exponential factor is the same for the forward and backward reactions.

Q.22 The conversion of A into B is an autocatalytic reaction $A \to B$ where B catalyzes the reaction. The rate equation is $-dx/dt = Kxy$ where x and y are concentrations of A and B at time t. Integrate this equation for initial concentrations x_0 and y_0 for A and B. Show that : $kt = \frac{2.303}{x_0 + y_0} \log \frac{x_0 y}{x y_0}$.

Q.23 A vessel contains dimethyl ether at a pressure of 0.4 atm. Dimethyl ether decomposes as $CH_3OCH_3(g) \longrightarrow CH_4(g) + CO(g) + H_2(g)$. The rate constant of decomposition is $4.78 \times 10^{-3}\,min^{-1}$. Calculate the ratio of initial rate of diffusion to rate of diffusion after 4.5 hours of initiation of decomposition. Assume the composition of gas present and composition of gas diffusing to be same.

Q.24(a) The reaction A proceeds in parallel channels $A \genfrac{}{}{0pt}{}{\nearrow B}{\searrow C}$ Although the $A \to C$ branch is thermodynamically more favorable than the branch $A \to B$, the product B may dominate in quantity over C. Why may this be so?

(b) In the above problem, suppose the half life values for the two branches are 60minutes and 90 minutes, what is the overall half-life value?

Q.25 For the two parallel reactions $A \xrightarrow{k_1} B$ and $A \xrightarrow{k_2} C$, show that the activation energy E′ for the disappearance of A is given in terms of activation energies E_1 and E_2 for the two paths by

$$E' = \frac{k_1 E_1 + k_2 E_2}{k_1 + k_2}$$

Q.26 For the mechanism $A + B \underset{K_2}{\overset{K_1}{\rightleftharpoons}} C \qquad C \xrightarrow{k_3} D$

(a) Derive the rate law using the steady-state approximation to eliminate the concentration of C.

(b) Assuming that $k_3 << k_2$, express the pre-exponential factor A and E_a for the apparent second-order rate constant in terms of A_1, A_2 and A_3 and E_{a1}, E_{a2} and E_{a3} for the three steps.

Q.27 The reaction of formation of phosgene from CO and Cl_2 is $CO + Cl_2 \longrightarrow COCl_2$

The proposed mechanism is

(i) $Cl_2 \underset{K-1}{\overset{K_1}{\rightleftharpoons}} 2Cl$ (fast equilibrium) (ii) $Cl + CO \underset{K-2}{\overset{K_2}{\rightleftharpoons}} COCl$ (fast equilibrium)

(iii) $COCl + Cl_2 \xrightarrow{K_3} COCl_2 + Cl$ (slow)

Show that the above mechanism leads to the following rate law $\frac{d[COCl_2]}{dt} = K[CO][Cl_2]^{3/2}$.

Where $K = k_3 . \frac{k_2}{k_{-2}} \left(\frac{k_1}{k-1}\right)^{1/2}$.

Q.28 The following kinetic data have been obtained at 250 °C, for the reaction

$$CO\,(g) + Cl_2\,(g) \longrightarrow COCl_2(g)$$

SET – 1

Initial Pressure CO = 400 Pa

$Cl_2 = 800 \times 10^3$ Pa

Time(sec)	Pressure of $COCl_2$ (Pa)
0	0
2072	200
4140	300
10280	375
infinity	400

SET – 2

Initial Pressure CO = 1600×10^3 Pa

$Cl_2 = 400$ Pa

Time(sec)	Pressure of $COCl_2$ (Pa)
0	0
2070	300
4140	375
infinity	400

(i) Determine the order of reaction with respect to CO and Cl_2

(ii) Calculate the rate constant. when pressure in pascal and time in seconds.

Q.29 The decomposition of a compound A, at temperature T according to the equation

$$2P_{(g)} \longrightarrow 4Q_{(g)} + R_{(g)} + S_{(l)}$$

is the first order reaction. After 30 minutes from the start of decomposition in a closed vessel, the total pressure developed is found to be 317 mm Hg and after a long period of time the total pressure observed to be 617 mm Hg. Calculate the total pressure of the vessel after 75 mintute, if volume of liquid S is supposed to be negligible. Also calculate the time fraction $t_{7/8}$.

Given : Vapour pressure of S (l) at temperature T = 32.5 mm Hg.

Q.30 A certain reactant B^{n+} is getting converted to $B^{(n+4)+}$ in solution. The rate constant of this reaction is measured by titrating a volume of the solution with a reducing reagent which only reacts with B^{n+} and $B^{(n+4)+}$. In this process, it converts B^{n+} to$B^{(n-2)+}$ and $B^{(n+4)+}$ to$B^{(n-1)+}$. At $t=0$, the volume of the reagent consumed is 25 ml and at t – 10 min, the volume used up is 32 ml. Calculate the rate constant of the conversion of B^{n+} to $B^{(n+4)+}$ assuming it to be a first order reaction.

Q.31 The catalytic decomposition of formic acid may take place in two ways :

(a) $HCOOH = H_2O + CO$ (b) $HCOOH = H_2 + CO_2$.

The rate constant and activation energy for reaction (a) are 2.79×10^{-3} min^{-1} at 236°C and 12.0 kcal $mole^{-1}$ respectively and for reaction (b) are 1.52×10^{-4} min^{-1} at 237°C and 24.5 kcal $mole^{-1}$ respectively. Find the temperature which will give a product made up of equimolar quantities of water vapour, carbon monoxide, hydrogen and carbon dioxide.

Q.32 The rate constant for the forward reaction A → Product is given by

$$\log k\,(sec^{-1}) = 14.34 - \frac{1.25\times10^4\,K}{T}$$

and the rate constant for the reverse reaction is 1.2×10^{-4} sec^{-1} at 50°C. Calculate the value of maximum rate constant possible for the backward reaction. Given : Enthalpy of the reaction = – 478 kJ/mol.

Q.33(a) The equilibrium between two isomers 'A' and 'B' can be represented as follow .

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

Where k_1 and k_2 are first order rate constants for forward and reverse reactions respectively. Starting with a non equilibrium mixture of conc. $[A]_0 = a$ and $[B]_0 = b$, it was found that 'x' mole of 'A' has reacted after time 't'. Give an expression for rate, $\frac{dx}{dt}$, and hence show that integerated rate expression

is $\log\left(\frac{P}{P-x}\right) = (k_1 + k_2)\,t$ where $P = \left(\frac{k_1 a - k_2 b}{k_1 + k_2}\right)$

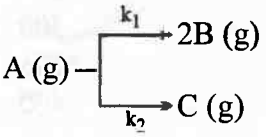
(b) After 69.3 minute $x = \frac{P}{2}$. Calculate k_1 and k_2 if equilibrium constant K = 4.

(Given : log2 = 0.3010)

Q.34 The gaseous reaction : $n_1A(g) \rightarrow n_2B(g)$ is first order with respect to A. It is studied at a constant pressure, with a_0 as the initial amount of A. Show that the volume of system at the concentration of A at time 't' are given by the expressions

$$V = V_0\left[\left(\frac{n_2}{n_1}\right)-\left(\frac{n_2}{n_1}-1\right)\exp(-n_1kt)\right] \quad ; \quad [A]_t = [A]_0\left[\frac{\exp(-n_1kt)}{(n_2/n_1)-\{(n_2/n_1)-1\}\exp(-n_1kt)}\right]$$

Q.35 For the following first order gaseous reaction



The initial pressure in a container of capacity V litres is 1 atm. Pressure at time t = 10 sec is 1.4 atm and after infinite time it becomes 1.5 atmosphere. Find the rate constant k_1 and k_2 for the appropriate reactions.

RADIOACTIVITY

Q.36 In a nature decay chain series starts with $_{90}Th^{232}$ and finally terminates at $_{82}Pb^{208}$. A thorium ore sample was found to contain 8×10^{-5} ml of helium at STP and 5×10^{-7} gm of Th^{232}. Find the age of ore sample assuming that source of He to be only due to decay of Th^{232}. Also assume complete retention of helium within the ore. (Half–life of $Th^{232} = 1.39 \times 10^{10}$Y)

Q.37 A 0.20 mL sample of a solution containing 1.0×10^{-7}Ci of ^3_1H is injected into the blood stream of a laboratory animal. After sfficient time for circulatory equilibrium to be established, 0.10 mL blood is found to have an activity of 20 dis/min. Calculate the blood volume of the animal.

Q.38 A sample of $^{131}_{53}I$, as iodine ion, was administered to a patient in a carrier consisting of 0.10 mg of stable iodide ion. After 4.00 days, 67.7% of the initial radioactivity was detected in the thyroid gland of the patient. What mass of the stable iodide ion had migrated to the thyroid gland? ($t_{1/2}$ = 8 days.)

Q.39 Potassium having atomic mass=39.1u contains 93.10 atom % ^{39}K, having atomic mass 38.96371 u; 0.0118 atom % ^{40}K, which has mass of 40.0 u and is radioactive with $t_{1/2} = 1.3 \times 10^9$y and 6.88 atom % ^{41}K having a mass of 40.96184 u. Calculate the specific activity of naturally occurring potassium.

Q.40 A mixture of ^{239}Pu and ^{240}Pu has a specific activity of 6×10^9 dis/s/g. The half lives of the isotopes are 2.44×10^4 y and 6.08×10^3 y respectively. calculate the isotopic composition of this sample.

Q.41 $_{92}U^{238}$ by successive radioactive decays changes to $_{82}Pb^{206}$. A sample of uranium ore was analyzed and found to contain 1.0g of U^{238} and 0.1g of Pb^{206}. Assuming that all the Pb^{206} had accumulated due to decay of U^{238}, find out the age of the ore. (Half life of $U^{238} = 4.5 \times 10^9$ years).

Q.42 Fallout from nuclear explosions contains ^{131}I and ^{90}Sr. Calculate the time required for the activity of each of these isotopes to fall to 1.0 % of its initial value. Radioiodine and radiostrontium tend to concentrate in the thyroid and the bones, respectively, of mammals which ingest them. Which isotope is likely to produce the more serious long-term effects? Half-life of ^{131}I = 8 days, ^{90}Sr = 19.9 yrs.

Q.43 $_{84}Po^{218}$ ($t_{/12}$ = 3.05 min) decay to $_{82}Pb^{214}$ ($t_{1/2}$ = 2.68 min) by α-emission, while Pb^{214} is a β-emitter. In an experiment starting with 1 gm atom of Pure Po^{218}, how much time would be required for the number of nuclei of $_{82}Pb^{214}$ to reach maximum.

Q.44 A sample pitch blende is found to contain 50% Uranium and 2.425% Lead. Of this Lead only 93% was Pb^{206} isotope, if the disintegration contant is 1.52×10^{-10} yr^{-1}. How old could be the pitch blende deposit.

Q.45 A sample of Uraninite, a Uranium containing mineral was found on analysis to contain 0.214 gm of Pb^{206} for every gram of Uranium. Assuming that the lead all resulted from the radioactive disintegration of the Uranium since the geological formation of the Uraninite and all isotopes of Uranium other than ^{238}U can be neglected. Estimate the day when the mineral was formed in the Earth's crust. [$t_{1/2}$ of $^{238}U = 4.5 \times 10^9$ years]

EXERCISE -III

Q.1 The rate of a reaction is expressed in different ways as follows :

$$+\frac{1}{2}\frac{d[C]}{dt} = -\frac{1}{3}\frac{d[D]}{dt} = +\frac{1}{4}\frac{d[A]}{dt} = -\frac{d[B]}{dt}$$

The reaction is:

(A) $4A + B \longrightarrow 2C + 3D$ (B) $B + 3D \longrightarrow 4A + 2C$

(C) $A + B \longrightarrow C + D$ (D) $B + D \longrightarrow A + C$

Q.2 Units of rate constant for first and zero order reactions in terms of molarity M unit are respectively

(A) sec^{-1}, M sec^{-1} (B) sec^{-1}, M (C) M sec^{-1}, sec^{-1} (D) M, sec^{-1}

Q.3 The rate constant for the forward reaction $A(g) \rightleftharpoons 2B(g)$ is $1.5 \times 10^{-3}\ s^{-1}$ at 100 K. If 10^{-5} moles of A and 100 moles of B are present in a 10 litre vessel at equilibrium then rate constant for the backward reaction at this temperature is

(A) $1.50 \times 10^{4}\ L\ mol^{-1}\ s^{-1}$ (B) $1.5 \times 10^{11}\ L\ mol^{-1}\ s^{-1}$

(C) $1.5 \times 10^{10}\ L\ mol^{-1}\ s^{-1}$ (D) 1.5×10^{-11}

Q.4 Reaction $A + B \longrightarrow C + D$ follow's following rate law : rate = $k = [A]^{+\frac{1}{2}}[B]^{\frac{1}{2}}$. Starting with initial conc. of one mole of A and B each, what is the time taken for amount of A of become 0.25 mole. Given $k = 2.31 \times 10^{-3}\ sec^{-1}$.

(A) 300 sec. (B) 600 sec. (C) 900 sec. (D) none of these

Q.5 Consider the following first order competing reactions:

$X \xrightarrow{k_1} A + B$ and $Y \xrightarrow{k_2} C + D$

if 50% of the reaction of X was completed when 96% of the reaction of Y was completed, the ratio of their rate constants (k_2/k_1) is

(A) 4.06 (B) 0.215 (C) 1.1 (D) 4.65

Q.6 A first order reaction is 50% completed in 20 minutes at 27°C and in 5 min at 47°C. The energy of activation of the reaction is

(A) 43.85 kJ/mol (B) 55.14 kJ/mol (C) 11.97 kJ/mol (D) 6.65 kJ/mol

Q.7 For the first order reaction $A \longrightarrow B + C$, carried out at 27 °C if 3.8×10^{-16} % of the reactant molecules exists in the activated state, the E_a (activation energy) of the reaction is

(A) 12 kJ/mole (B) 831.4 kJ/mole (C) 100 kJ/mole (D) 88.57 kJ/mole

Q.8 The reactions of higher order are rare because

(A) many body collisions involve very high activation energy

(B) many body collisions have a very low probability

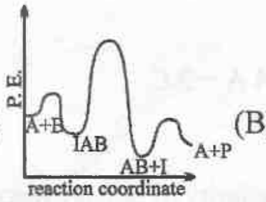
(C) many body collisions are not energetically favoured.

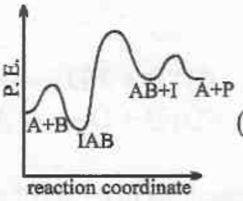
(D) many body collisions can take place only in the gaseous phase.

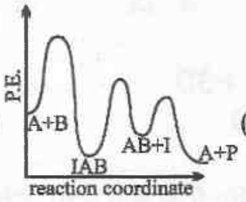
Q.9 The following mechanism has been proposed for the exothermic catalyzed complex reaction.

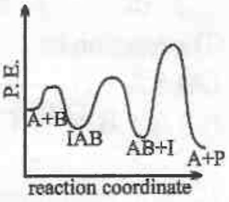
$$A + B \xrightleftharpoons{\text{fast}} IAB \xrightarrow{k_1} AB + I \xrightarrow{k_2} P + A$$

If k_1 is much smaller than k_2. The most suitable qualitative plot of potential energy (P.E.) versus reaction coordinate for the above reaction.

(A) 

(B) 

(C) 

(D) 

Question No. 10 to 11 (2 questions)

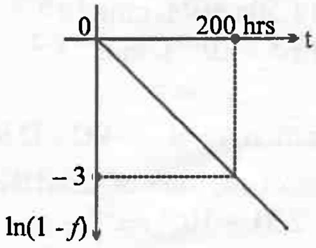
Oxidation of metals is generally a slow electrochemical reaction involving many steps. These steps involve electron transfer reactions. A particular type of oxidation involve overall first order kinetics with respect to fraction of unoxidised metal **(1–*f*)** surface thickness relative to maximum thickness **(T)** of oxidised surface, when metal surface is exposed to air for considerable period of time

Rate law : $\frac{df}{dt} = k(1 - f)$, **where** $f = x/T$,

x = thickness of oxide film at time 't'

& T = thickness of oxide film at t = ∞

A graph of $\ln(1 - f)$ vs t is shown in the adjacent figure.



Q.10 The time taken for thickness to grow 50% of 'T' is

(A) 23.1 hrs (B) 46.2 hrs (C) 100 hrs (D) 92.4 hrs

Q.11 The exponential variation of '*f*' with t(hrs) is given by

(A) $[1 - e^{-3t/200}]$ (B) $e^{-3t/200} - 1$ (C) $e^{-3t/200}$ (D) $e^{3t/200}$

Question No. 12 to 13 (.2 questions)

For a hypothetical elementary reaction $A \begin{matrix} \xrightarrow{k_1} 2B \\ \xrightarrow[k_2]{} 2C \end{matrix}$ where $\frac{k_1}{k_2} = \frac{1}{2}$

Initially only 2 moles of A are present.

Q.12 The total number of moles of A, B & C at the end of 50% reaction are

(A) 2 (B) 3 (C) 5 (D) None

Q.13 Number of moles of B are

(A) 2 (B) 1 (C) 0.666 (D) 0.333

Q.14 Two radioactive nuclides A and B have half lives of 50 min and 10 min respectively. A fresh sample contains the nuclides of B to be eight time that of A. How much time should elapse so that the number of nuclides of A becomes double of B

(A) 30 (B) 40 (C) 50 (D) None

Q.15 Give the correct order of initials **T** (true) or **F** (false) for following statements.

(i) On bombarding ${}_7N^{14}$ Nuclei with α-particle, the nuclei of the product formed after release of proton would be ${}_8O^{17}$.

(ii) ${}_{89}Ac^{228}$ and ${}_{90}Th^{229}$ belong respectively to Actinium and Neptunium series.

(iii) Nuclide and it's decay product after α-emission are called isodiaphers.

(iv) Half life of radium is 1580 years. Its average life will be 1097.22 years.

(A) TFTF (B) TTTF (C) FFTT (D) TFFF

EXERCISE-IV

OBJECTIVE PROBLEM

Q.1 For a first order reaction

(A) the degree of dissociation is equal to $(1 - e^{-kt})$

(B) a plot of reciprocal concentration of the reactent vs time gives a straight line.

(C) the time taken for completeion of 75% of reaction is thrice the $t_{1/2}$ of the reaction

(D) the pre-exponential factor in the Arrhenius equation has the dimensionof time, T^{-1}. **[JEE 1998]**

Q.2 The rate law for the reaction

$RCl + NaOH(aq) \longrightarrow ROH + NaCl$ is given by Rate = k[RCl]. The rate of the reaction will be

(A) Doubled on doubling the concentration of sodium hydroxide

(B) Halved on reducing the concentration of alkyl halide to one half

(C) Decreased on increasing the temperature of reaction

(D) Unaffected by increasing the temperature of the reaction. **[JEE 1998]**

Q.3 Which of the following statement(s) is (are) correct

(A) A plot of log K_p versus 1/T is linear

(B) A plot of log [X] versus time is linear for a first order reaction. $X \longrightarrow P$

(C) A plot of log P versus 1/T is linear at constant volume.

(D) A plot of P versus 1/V is linear at constant temperature. **[JEE 1999]**

Q.4 The rate constnat for the reaction **[JEE SCR 2000]**

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

is 3.0×10^{-5} sec^{-1}. if the rate is 2.4×10^{-5} mol litre^{-1} sec^{-1}, then the concentration of N_2O_5 (in mol litre^{-1}) is

(A) 1.4 (B) 1.2 (C) 0.004 (D) 0.8

Q.5 If I is the intensity of absorbed light and C is the concentration of AB for the photochemical proces $AB + h\nu \longrightarrow AB^*$, the rate of formation of AB* is directly proportional to **[JEE SCR 2001]**

(A) C (B) I (C) I^2 (D) CI

Q.6 Consider the chemical reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$. The rate of this reaction can be expressed in term of time derivative of concentration of $N_2(g)$, $H_2(g)$ or NH_3 (g). Identify the correct relationshiop amongst the rate expressions. **[JEE SCR 2002]**

(A) Rate $= -d[N_2]/dt = -1/3\, d[H_2]/dt = 1/2 d[NH_3]/dt$

(B) Rate $= -d[N_2]/dt = -3\, d[H_2]/dt = 2d[NH_3]/dt$

(C) Rate $= d[N_2]/dt = 1/3\, d[H_2]/dt = 1/2 d[NH_3]/dt$

(D) Rate $= -d[N_2]/dt = -d[H_2]/dt = d[NH_3]/dt$

Q.7 In a first order reaction the concentration of reactant decreases from 800 mol/dm^3 to 50 mol/dm^3 in 2×10^4 sec. The rate constant of reaction in sec^{-1} is **[JEE SCR 2003]**

(A) 2×10^4 (B) 3.45×10^{-5} (C) 1.3486×10^{-4} (D) 2×10^{-4}

Q.8 The reaction, $X \longrightarrow$ Product follows first order kinetics. In 40 minutes the concentration of X changes from 0.1 M to 0.025 M. Then the rate of reaction when concentration of X is 0.01 M

(A) 1.73×10^{-4} M min^{-1} (B) 3.47×10^{-5} M min^{-1}

(C) 3.47×10^{-4} M min^{-1} (D) 1.73×10^{-5} M min^{-1} **[JEE SCR 2004]**

Q.9 Which of the following statement is incorrect about order of reaction? **[JEE 2005]**

(A) Order of reaction is determined experimentally

(B) It is the sum of power of concentration terms in the rate law expression

(C) It does not necessarily depend on stoichiometric coefficients

(D) Order of the reaction can not have fractional value.

RADIOACTIVITY

Q.10 Loss of a β – particle is equivalent to **[JEE 1998]**
(A) Increase of one proton only (B) Decrease of one neutron only
(C) Both (A) and (B) (D) None of these.

Q.11 Decrease in atomic number is observed during **[JEE 1998]**
(A) α – emission (B) β – emission (C) Positron emission (D) Electron capture.

Q.12 The number of neutrons accompanying the formation of ${}_{54}X^{139}$ and ${}_{38}Sr^{94}$ from the absorption of slow neutron by ${}_{92}U^{235}$ followed by nuclear fision is **[JEE 1999]**
(A) 0 (B) 2 (C) 1 (D) 3

Question No. 13 to 15 (2 questions)

C^{14} radio carbon dating technique is used to determine the age of fossil fuel from archaeological excavations. This technique is based on simple principle of chemical kinetics.
Earth's atmosphere is constantly bombarded by cosmic rays (consisting of electrons, neutrons and atomic nuclei) of extremely high penetrating power. Atmospheric nitrogen (N^{14}) captures these neutrons (cosmic rays) to produce radioactive C^{14} isotope and hydrogen (${}_1H^1$).

$${}_7N^{14} + {}_0n^1 \longrightarrow {}_6C^{14} + {}_1H^1$$

The unstable carbon eventually forms ${}^{14}CO_2$, which mixes with the ordinary carbon dioxide (${}^{12}CO_2$) in the air. As the carbon –14 isotope decays, it emits β-particles.

$${}_6C^{14} \longrightarrow {}_7N^{14} + {}_{-1}\beta^{\circ}$$

The C^{14} isotope enters the biosphere when carbon dioxide is taken up in plant photosynthesis. Plants are eaten by animals, which exhale C^{14} as CO_2. Eventually, C^{14} participates in many aspects of the carbon cycle. The C^{14} lost by radioactive decay is constantly replenished by the production of new isotopes in the atmosphere. In this decay– replenishment process, a dynamic equilibrium is established whereby the ratio of C^{14} to C^{12} remains constant in living matter. But when an individual plant or an animal dies, the C^{14} isotope in it is no longer replenished, so the ratio decreases as C^{14} decays. So, the number of C^{14} nuclei after time t (after the death of living matter) would be less than in a living matter.
Now, using first order integrated rate law,

$$t_{1/2} = \frac{0.693}{\lambda}$$

For 30,000 year the cosmic rays have same intensity and organism are also have the same. But from some years the changes in this are observed due to excessive burning of fossil fuel and nuclear tests. **[JEE 2006]**

Q.13 Why we use the carbon dating to calculate the age of the fossil?
(A) Rate of exchange of carbon between atmosphere and living is slower than decay of C^{14}.
(B) It is not appropriate to use C^{14} dating to determine age.
(C) Rate of exchange of C^{14} between atmosphere and leaving organism is so fast that an equilibrium is set up between the intake of C^{14} by organism and its exponential decay.
(D) none of the above

Q.14 For how many old fossil can be process of C–dating be used.
(A) 6 years (B) 6000 year
(C) 60,000 year (D) any age it does depend on the age of the fossil.

Q.15 If C_1 is the conc. of C^{14} in the sample taken near nuclear site and C_2 is the concentration of the sample taken away from nuclear site

(A) $t_1 - t_2 = \frac{1}{\lambda} \ln \frac{C_1}{C_2}$ (there is a decrease in age of sample taken at nuclear site)

(B) $t_1 - t_2 = \frac{1}{\lambda} \ln \frac{C_1}{C_2}$ (there is a increase in age of sample taken at nuclear site)

(C) There is no change irrespective of value of C_1 and C_2

(D) $\frac{t_1}{t_2} = \frac{C_1}{C_2}$

SUBJECTIVE PROBLEM

Q.1(a) In the Arrhenius equation $k = A\exp(-E/RT)$, A may be termed as the rate constant at __________. **[JEE 1997]**

(b) The rate constant for the first order decomposition of a certain reaction is discribed by the equation

$$\ln k\,(s^{-1}) = 14.34 - \frac{1.25 \times 10^4 K}{T}$$

(i) What is the energy of activation for this reaction?
(ii) The rate constant at 500 K.
(iii) At what temperature will its half life period be 256 minutes? **[JEE 1997]**

(c) The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the pre exponential factor for the reaction is $3.56 \times 10^9\ s^{-1}$, calculate the rate constant at 318 K and also the energy of activation. **[JEE 1997]**

(d) The rate constant for an isomerisation reaction $A \rightarrow B$ is $4.5 \times 10^{-3}\ min^{-1}$. If the initial concentration of A is 1 M. Calculate the rate of the reaction after 1 h. **[JEE 1999]**

Q.2 A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20 kJmol^{-1}. **[JEE 2000]**

Q.3 The rate of a first order reaction is 0.04 mole litre^{-1} s^{-1} at 10 minutrs and 0.03 mol litre^{-1} s^{-1} at 20 minutes after initiation. Find the half life of the reaction. **[JEE 2001]**

Q.4 $2X(g) \longrightarrow 3Y(g) + 2Z(g)$

Time (in Min)	0	100	200
Partial pressure of X (in mm of Hg)	800	400	200

Assuming ideal gas condition. Calculate

(a) Order of reaction (b) Rate constant

(c) Time taken for 75% completion of reaction (d) Total pressure when $P_X = 700$ mm. **[JEE 2005]**

RADIOACTIVITY

Q.5 ^{64}Cu (half-life = 12.8 hr) decays by β^- emission (38%), β^+ emission (19%) and electron capture (43%). Write the decay product and calculate partial half-lives for each of the decay processes. **[JEE'2002]**

Q.6 Fill in the blanks

(a) $^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{137}_{52}A + ^{97}_{40}B +$ __________.

(b) $^{82}_{34}Se \longrightarrow 2\ ^{0}_{-1}e +$ ____________. **[JEE 2005]**

ANSWER KEY

EXERCISE-I

RATE OF REACTION AND STOICHIOMETRIC COEFFICIENT

Q.1 (a) 1×10^{-4} mol L^{-1} s^{-1} , (b) 3×10^{-4} mol L^{-1} s^{-1}

Q.2 (a) 0.019 mol L^{-1} s^{-1}, (b) 0.037 mol L^{-1} s^{-1}

Q.3 $2k_1 = k_2 = 4k_3$ Q.4 (i) $\frac{dx}{dt} = k[A][B]^2$, (ii) rate increases by 8 times

Q.5 rate increase by 27 times

Q.6 (i) $r = \frac{1}{4}\frac{d[NO]}{dt} = 9 \times 10^{-4}$mol litre^{-1} sec^{-1}, (ii) 36×10^{-4}mol litre^{-1}sec^{-1}, (iii) 54×10^{-4} mol litre^{-1}sec^{-1}

Q.7 (i) 7.2 mol litre^{-1}min^{-1}, (ii) 7.2 mol litre^{-1} min^{-1} Q.8 1/6

ZERO ORDER

Q.9 (i) 7.2 M, (ii) Think Q.10 $K = 0.01$ M min^{-1}

Q.11 0.75 M Q.12 6×10^{-9} sec Q.13 1.2 hr

FIRST ORDER

Q.14 (i) 36 min., (ii) 108 min. Q.15 (i) 0.0223 min^{-1}, (ii) 62.17 min Q.17 924.362 sec

Q.18 expiry time = 41 months Q.19 $3.3 \times 10^{-4} s^{-1}$ Q.20 $k = \frac{2.303}{t}\log\frac{1}{a}$ Q.21 11.2%

ORDER OF REACTION & RATE LAW

Q.22 (a) Third order, (b) $r = k[NO]^2[H_2]$, (c) 8.85×10^{-3} M sec^{-1}

Q.23 (a) order w.r.t NO = 2 and w.r.t Cl_2 = 1, (b) $r = K[NO]^2[Cl_2]$, (c) $K = 8$ $L^2mol^{-2}s^{-1}$, (d) rate = 0.256 mole $L^{-1}s^{1}$]

Q.24 (i) first order (ii) $k = 1.308 \times 10^{-2}$ min^{-1} (iii) 73%

Q.25 (i) rate=[A] [B] ; (ii) $k = 4 \times 10^{-2}M^{-1}s^{-1}$; (iii) rate = $2.8 \times 10^{-3}M{\cdot}s^{-1}$

Q.26 (i) Zero order, (ii) K = 5 Pa/s

Q.27 Zero order Q.28 (a) n =1, (b) $\frac{dx}{dt} = k[CH_3COCH_3]$, (c) 8.67×10^{-3} s^{-1}, (d) 1.56×10^{-5} M s^{-1}

HALF LIFE

Q.29 166.6 min Q.30 4.62×10^5 sec Q.32 (i) t = 13.96 hrs, (ii) 2.2176 litre

Q.33 54 min Q.34 15 min

CONCENTRATION REPLACED BY OTHER QUANTITIES IN FIRST ORDER INTEGRATED RATE LAW

Q.35 $k = \frac{1}{t}ln\frac{P_3}{2(P_3 - P_2)}$ Q.36 $k = \frac{1}{t}ln\frac{P_3}{(P_3 - P_2)}$

Q.37 $k = \frac{1}{t}ln\frac{V_1}{(2V_1 - V_2)}$ Q.38 $k = \frac{1}{t}ln\frac{4V_3}{5(V_3 - V_2)}$ Q.39 $k = \frac{1}{t}ln\frac{r_\infty}{(r_\infty - r_t)}$

Q.40 8.12×10^{-6} Ms^{-1}, 0.012 atm min^{-1}

Q.41 (a) 90 mm, (b) 47 mm, (c) 6.49×10^{-2} per minutes, (d) 10.677 min.
Q.42 First order Q.43 $k_1 = 2.605 \times 10^{-3}\ \text{min}^{-1}$
Q.44 (i) $r = K[(CH_3)_2O]$, 0.000428 sec^{-1} Q.45 First order
Q.46 (a) first order, (b) 13.75 minutes, (c) 0.716
Q.47 966 min Q.48 206.9 min Q.49 11.45 days
Q.50 0.180 atm, 47.69 sec

PARALLEL AND SEQUENTIAL REACTION

Q.51 $\dfrac{1}{e^{(K_1+K_2)}t - 1}$ Q.52 $\dfrac{[C]}{[A]} - \dfrac{10}{11}(e^{11x} - 1)$ Q.53 76.8, 23.2 Q.54 t = 4 min

TEMPERATURE DEPENDENCE OF RATE (ACTIVATION ENERGY)

Q.55 5 kJ mol^{-1} Q.56 349.1 k Q.57 55.33 kJ mole^{-1} Q.58 306 k
Q.59 (a) $2.31 \times 10^{-12}\ \text{min}^{-1}$, $6.93 \times 10^{-2}\ \text{min}^{-1}$, (b) 43.85 kJ mole^{-1}
Q.60 rate of reaction increases 5.81×10^{8} times
Q.61 10.757 k cal mol^{-1}

MECHANISM OF REACTION

Q.62 $r = K'\,[NO]^2[Br_2]$ Q.63 $r = K\,[NO]^2\,[H_2]$, where $K = k_2 \times K_1$
Q.64 $k_{eq} = 1$, rate = $k_2\,(C)\,(A_2)^{1/2}$ Q.66 (d) No, (e) mechanism (a) is incorrect

RADIOACTIVITY

Q.67 beta emitter : ^{49}Ca, ^{30}Al, 94 Kr, positron emitter : ^{195}Hg, ^{8}B, ^{150}Ho
Q.68 $^{114}_{49}In$, odd number of nucleons Q.69 (a) $^{1}_{1}H$, (b) $^{1}_{0}n$, (c) $^{6}_{3}Li$, (d) $^{0}_{+1}e$, (e) $^{0}_{-1}e$, (f) p (proton)
Q.70 d, deuteron Q.71 (a) $^{1}_{1}H$ (b) $^{54}_{28}Ni$ (c) $^{0}_{-1}\beta$ (d) $^{1}_{0}n$
Q.72 $\alpha = \dfrac{a-b}{4}$; $\beta = d + \dfrac{(a-b)}{2} - c$ Q.73 2.16×10^{12} events / min
Q.74 1.06×10^{-15} kg Q.75 $\lambda = 5.77 \times 10^{-4}\ \text{sec}^{-1}$ Q.76 32 ml
Q.77 6.25 % Q.78 2.674×10^{5} dps Q.79 33.67 years Q.80 4.65 hour

PROFICIENCY TEST

Q.1

1.	3.7×10^{10}	2.	β-rays	3.	isobar	4.	8, 6
5.	isodiaphers	6.	$^{30}_{14}Si$	7.	β-particles	8.	isotones
9.	10 min.	10.	threshold energy	11.	half	12.	equal to ΔH
13.	directly proportional			14.	$\text{mol L}^{-1}\text{s}^{-1}$	15.	rare
16.	lowering	17.	faster	18.	slowest	19.	increases
20.	3	21.	rate constant	22.	2 and 3	23.	rate = $k[M]^2$
24.	$1\frac{1}{2}$	25.	– k	26.	Activation energy		
27.	higher	28.	first	29.	$-\dfrac{k}{2.303}$	30.	1.44

Q.2

1.	False	2.	False	3.	True	4.	False
5.	True	6.	True	7.	True	8.	False
9.	False	10.	False	11.	True	12.	False
13.	True	14.	True	15.	True	16.	False
17.	True	18.	True	19.	False	20.	False

EXERCISE-II

Q.1 First order, k= 0.00144, 0.00144, 0.00145, 0.00145, 0.00150, 0.00140, average 0.00145min^{-1}
Q.2 (a) 6.25 ; (b) 14.3 ; (c) 0% Q.3 53.84 Q.4 $(d\tau/dt) = \alpha/2\tau$, –1 order
Q.5 a = b = 1 Q.6 2×10^{-2} min^{-1}
Q.7 (a) $3.27 \cdot 10^{-4} sec^{-1}$; (b) 2120 sec; (c) 38.27 (measured : 55.00ml)
Q.8 (a) 43.46$kJmol^{-1}$, (b) 20.47 hour Q.9 % decomposition = 67.21%
Q.10 k = 0.0327 min^{-1} Q.11 B Q.12 0.537 Q.13 k = 0.022 hr^{-1}
Q.14 4.83 mins Q.15 15.13 week Q.16 20 min, 28.66 min
Q.17 156 Q.18 $K_f = K_b =$ 0.00027 sec^{-1} Q.19 0.0025 m
Q.20 $k=9.74\times10^{-5}\ sec^{-1}, k_{-1} = 4.18\times10^{-5} sec^{-1}$ Q.21 $E_f = 6 \times 10^4 J$; $E_b = 9.3 \times 10^4 J$
Q.23 0.26 : 1 Q.24 (b)$t_{1/2}$ = 36min
Q.26 (a) $\frac{d(D)}{dt} = \frac{k_1k_3(A)(B)}{k_2 + k_3}$; (b) $E_a = E_{a1} + E_{a3} - E_{a2}$. $A = \frac{A_1A_3}{A_2}$
Q.28 Set – I : $3.5 \times 10^{-4} S^{-1}$; Set – II : $6.7 \times 10^{-4} S^{-1}$
Q.29 P_t = 379.55 mm Hg, $t_{7/8}$ = 399.96 min Q.30 0.0207 mm^{-1}
Q.31 399^0C ; R = 1.987$Kcal.mol^{-1}K^{-1}$ Q.33 $k_2 = 2 \times 10^{-3} sec^{-1}$, $k_1 = 8 \times 10^{-3} sec^{-1}$
Q.35 0.805

RADIOACTIVITY

Q.36 t = 4.89×10^9 years Q.37 V = 1.1 L Q.38 0.0958 mg
Q.39 Specific activity = 30.69 dis. $g^{-1}s^{-1}$ Q.40 ^{239}Pu = 45.1%, ^{240}Pu = 54.9%
Q.41 t = 7.1×10^8 years Q.42 53.1 days, 132 yrs, ^{90}Sr is likely to be serious, the iodine will soon be gone
Q.43 4125 min Q.44 3.3×10^8 years Q.45 1.4×10^9 yrs

EXERCISE-III

Q.1 B Q.2 A Q.3 D Q.4 B Q.5 D Q.6 B Q.7 C
Q.8 B Q.9 A Q.10 B Q.11 A Q.12 B Q.13 C Q.14 C
Q.15 A

EXERCISE-IV

OBJECTIVE PROBLEM

Q.1 A, D Q.2 B Q.3 A, B, D Q.4 D Q.5 B
Q.6 A Q.7 C Q.8 C Q.9 D

RADIOACTIVITY

Q.10 C Q.11 C, D Q.12 D Q.13 C Q.14 D
Q.15 B

SUBJECTIVE PROBLEM

Q.1 (a) infinte temperature ; (b) (i) 2.50×10^4 cal mol^{-1}, (ii) $2.35 \times 10^{-5} sec^{-1}$, (iii) 513 ;
(c) $K_{318} = 9.2 \times 10^{-4} sec^{-1}$, E_a = 18.33 K cal mol^{-1} ; (d) A = $5.40\times10^{10} sec^{-1}$, $E_a = 2.199\times10^4$ $Jmol^{-1}$
Q.2 100 $kJmol^{-1}$ Q.3 $t_{1/2}$ = 24.14 min Q.4 (a) 1, (b) $6.93 \times 10^{-3} mm^{-1}$, (c) 200, (d) 950 mm

RADIOACTIVITY

Q.5 $^{64}_{30}Zn$, $^{64}_{28}Ni$, $(t_{1/2})_1$ = 33.68 hr, $(t_{1/2})_2$ = 67.36 hr, $(t_{1/2})_3$ = 29.76 hr Q.6 (a) $2\,^1_0n$, (b) $^{82}_{36}Kr$

BANSAL CLASSES

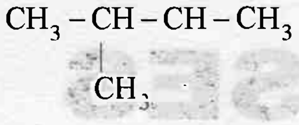
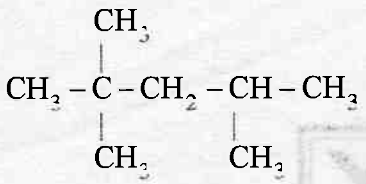
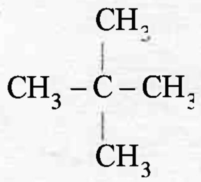
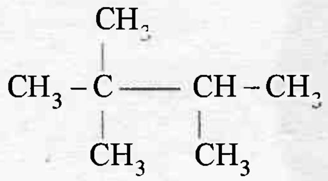
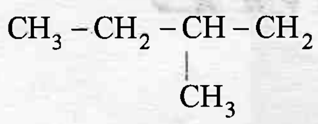
CHEMISTRY

TARGET IIT JEE 2007
XI (PQRS)

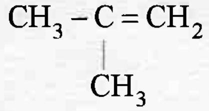
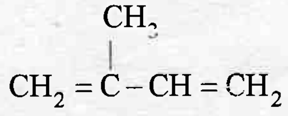
COMMON NAME

COMMON NAME

Group A: → ALKANES

S. No.	Compound	Common Name
1	 $CH_3-\underset{\underset{CH_3}{\vert}}{CH}-CH-CH_3$	Isopentane
2	 $CH_3-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-CH_2-\underset{\underset{CH_3}{\vert}}{CH}-CH_3$	Iso Octane
3	 $CH_3-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-CH_3$	Neo Pentane
4	 $CH_3-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-\underset{\underset{CH_3}{\vert}}{CH}-CH_3$	Triptane
5	 $CH_3-CH_2-\underset{\underset{CH_3}{\vert}}{CH}-CH_2$	Active Amyl Group

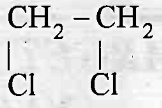
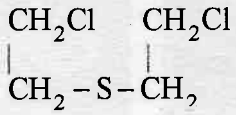
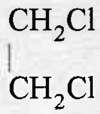
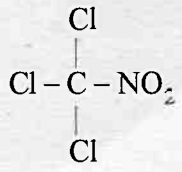
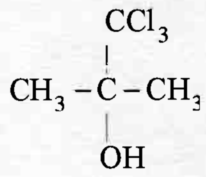
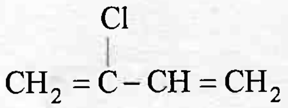
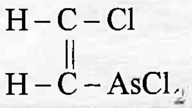
Group B: → ALKENES

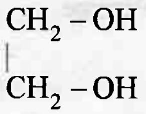
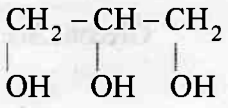
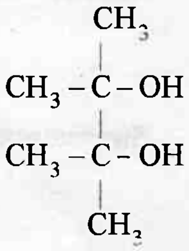
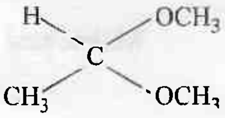
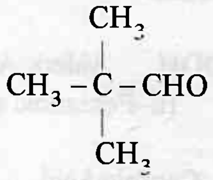
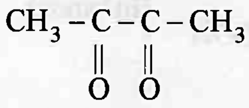
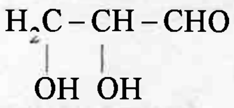
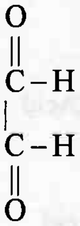
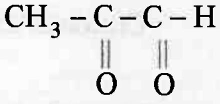
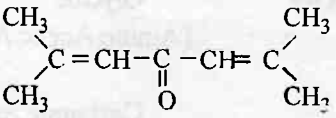
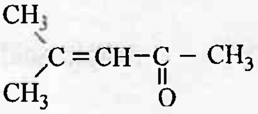
S. No.	Compound	Common Name
6	$CH_3-CH_2-CH=CH_2$	α–Butylene
7	$CH_3-CH=CH-CH_3$	β–Butylene
8	 $CH_3-\underset{\underset{CH_3}{\vert}}{C}=CH_2$	Iso Butylene
9	$CH_2=C=CH_2$	Allene
10	 $CH_2=\overset{\overset{CH_3}{\vert}}{C}-CH=CH_2$	Isoprene

Group C: → ALKYNES

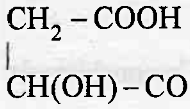
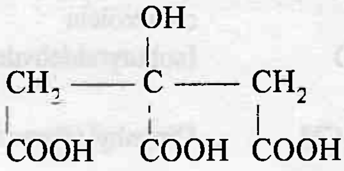
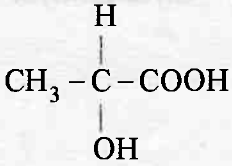
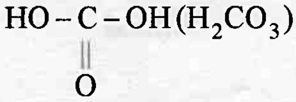
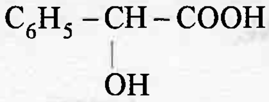
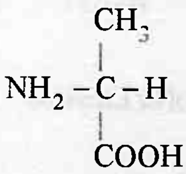
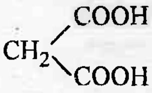
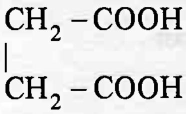
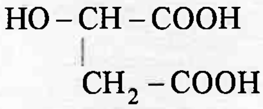
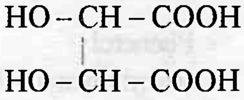
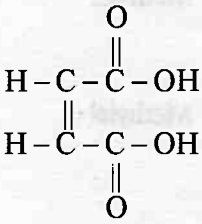
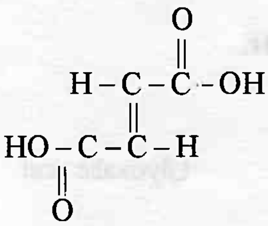
S. No.	Compound	Common Name
11	$CH=CH$	Purified Acetylene or Norcelyne
12	$CH_2=CH-C=CH$	Vinyl Acetylene
13	$CH_3-C\equiv CH$	Allylene

Group D: → ALKYL HALIDE

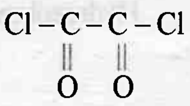
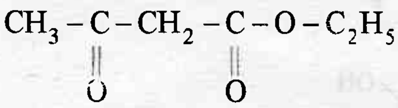
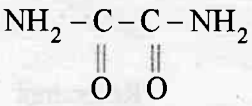
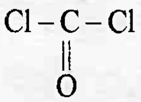
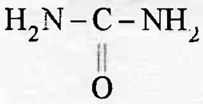
S. No.	Compound	Common Name
14	CH_3CHCl_2	Ethylidene Chloride (A Jem dihalide)
15	 $\underset{\underset{Cl}{\vert}}{CH_2}-\underset{\underset{Cl}{\vert}}{CH_2}$	Ethylene Dichloride (A Vinyl dihlide)
16	 $\overset{\overset{CH_2Cl}{\vert}}{CH_2}-S-\overset{\overset{CH_2Cl}{\vert}}{CH_2}$	Mustard Gas (Poisionous; used in war)
17	 $\underset{\underset{CH_2Cl}{\vert}}{CH_2Cl}$	Westron (Solvent)
18	$ClCH=CCl_2$	Westrosol or Triclean (Solvent)
19	$Cl_2C=CCl_2$	Tetraclean or Perclean
20	 $Cl-\overset{\overset{Cl}{\vert}}{\underset{\underset{Cl}{\vert}}{C}}-NO_2$	Chloropicrin (tear gas)
21	 $CH_3-\overset{\overset{CCl_3}{\vert}}{\underset{\underset{OH}{\vert}}{C}}-CH_3$	Chloretone
22	 $CH_2=\overset{\overset{Cl}{\vert}}{C}-CH=CH_2$	Chloroprene
23	 $\underset{\underset{H-C-AsCl_2}{\Vert}}{H-C-Cl}$	Lewisite

S. No.	Compound	Common Name
Group E:→ALCOHOL		
24	 $\begin{array}{l}CH_2-OH\\ \vert\\ CH_2-OH\end{array}$	Glycol or Ethylene
25	 $\begin{array}{ccccc}CH_2&-&CH&-&CH_2\\ \vert&&\vert&&\vert\\ OH&&OH&&OH\end{array}$	Glycerol
26	$CH{\equiv}C{-}CH_2{-}OH$	Propargyl Alcohol
27	$CH_2{=}CH{-}CH_2{-}OH$	Allyl Alcohol
28	$CH_2{=}CH{-}OH$	Vinyl Alcohol
29	 $\begin{array}{c}CH_3\\ \vert\\ CH_3-C-OH\\ \vert\\ CH_3-C-OH\\ \vert\\ CH_3\end{array}$	Pinacol
Group F:→ETHER		
30	$C_6H_5{-}O{-}CH_3$	Anesol (Methyl Phenyl Ether)
31	$C_6H_5{-}O{-}C_2H_5$	Phenetol (Ethyl Phenyl Ether)
32	$CH_3CH(OCH_3)_2$	Methylal
33	 or $CH_3CH(OCH_3)_2$	Methylal
Group G:→ALDEHYDE		
34	 $\begin{array}{l}CHO\\ \vert\\ COOH\end{array}$	Glyoxalic acid
35	 $\begin{array}{c}CH_3\\ \vert\\ CH_3-C-CHO\\ \vert\\ CH_3\end{array}$ or $(CH_3)_3C{-}CHO$	Pavaldehyde
36	$CH_3CH{=}CH{-}CHO$	Crotonaldehyde
37	$CH_2{=}CH{-}CHO$	Acraldehyde or Acrolein
38	$(CH_3)_2CHCHO$	Isobutyraldehyde
39	 $\begin{array}{ccccccc}CH_3&-&C&-&C&-&CH_3\\ &&\Vert&&\Vert&&\\ &&O&&O&&\end{array}$	Dimethyl Glyoxal
40	 $\begin{array}{ccccc}H_2C&-&CH&-&CHO\\ \vert&&\vert&&\\ OH&&OH&&\end{array}$	Glyceraldehyde
41	 $\begin{array}{c}O\\ \Vert\\ C-H\\ \vert\\ C-H\\ \Vert\\ O\end{array}$	Glyoxal
42	 $\begin{array}{ccccccc}CH_3&-&C&-&C&-&H\\ &&\Vert&&\Vert&&\\ &&O&&O&&\end{array}$	Methyl Glyoxal or Pyruvic Aldehyde
Group H:→KETONE		
43	CH_3COCH_3	Acetone
44		Phorone
45		Mesityl Oxide
46	$H_2C{=}C{=}O$	Ketene

Group I:→CARBOXYLIC ACID

S. No.	Compound	Common Name
47	$CH_3–CH_2–CH_2–CH_2–COOH$	Valeric Acide (n–Pentanoic acid)
48	$CH_3(CH_2)_4COOH$	Caproic Acid (n–Hexanoic acid)
49	 $\begin{array}{l}CH_2-COOH\\ \vert\\ CH(OH)-COOH\end{array}$	Malic Acid
50	 $\begin{array}{ccccc} & & OH & & \\ & & \vert & & \\ CH_2 & — & C & — & CH_2\\ \vert & & \vert & & \vert\\ COOH & & COOH & & COOH\end{array}$	Citric Acid (In lemon)
51	$CH_2=CH–COOH$	Acralic Acid
52	 $\begin{array}{l} \quad\quad H\\ \quad\quad \vert\\ CH_3-C-COOH\\ \quad\quad \vert\\ \quad\quad OH\end{array}$	Lactic Acid (In milk)
53	 $HO-\underset{\underset{O}{\Vert}}{C}-OH\,(H_2CO_3)$	Carbonic Acid
54	$CH_3–CO–COOH$	Pyruvic Acid
55	$CH_3–CH=CH–COOH$	Crotonic Acid
56	 $C_6H_5-\underset{\underset{OH}{\vert}}{CH}-COOH$	Mendalic Acid
57	$NH_2–CH_2–COOH$	Glycine (Amino Acetic Acid)
58	NH_2COOH	Carbamic Acid (Amino formic Acid)
59	$COOH–(CH_2)_4–COOH$	Adipic Acid
60	$C_6H_5CH=CHCOOH$	Cinnamic Acid
61	 $NH_2-\overset{\overset{CH_3}{\vert}}{\underset{\underset{COOH}{\vert}}{C}}-H$	Alanine
62	$HO\,CH_2\,COOH$	Glycolic Acid
63	 $\begin{array}{l}COOH\\ \vert\\ COOH\end{array}$	Oxalic acid
64	 $CH_2\begin{array}{l}\diagup COOH\\ \diagdown COOH\end{array}$	Malonic acid
65	 $\begin{array}{l}CH_2-COOH\\ \vert\\ CH_2-COOH\end{array}$	Succinic acid
66	 $\begin{array}{l}HO-CH-COOH\\ \quad\quad\;\vert\\ \quad\quad CH_2-COOH\end{array}$	Malic acid
67	 $\begin{array}{l}HO-CH-COOH\\ \quad\quad\;\vert\\ HO-CH-COOH\end{array}$	Tarteric acid
68	 $\begin{array}{l}\quad\quad\quad\;\; O\\ \quad\quad\quad\;\; \Vert\\ H-C-C-OH\\ \quad\;\; \Vert\\ H-C-C-OH\\ \quad\quad\quad\;\; \Vert\\ \quad\quad\quad\;\; O\end{array}$	Maleic acid
69	 $\begin{array}{l}\quad\quad\quad\quad\quad O\\ \quad\quad\quad\quad\quad \Vert\\ \quad\quad H-C-C-OH\\ \quad\quad\quad\quad \Vert\\ HO-C-C-H\\ \quad\quad \Vert\\ \quad\quad O\end{array}$	Fumeric acid

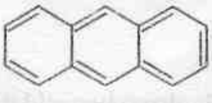
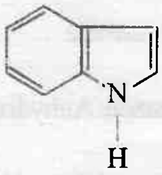
Group J:→ACID DERIVATIVES

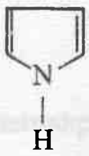
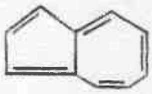
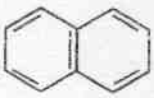
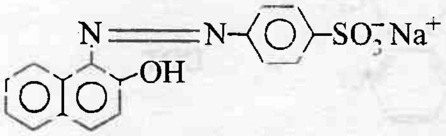
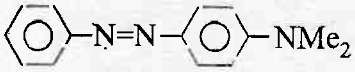
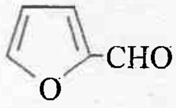
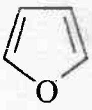
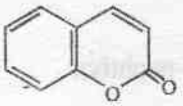
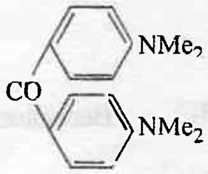
S. No.	Compound	Common Name
70	 $\mathrm{Cl}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{Cl}$	Oxalyl Chloride
71	NH_2COONH_4	Ammonium Carbamate
72	 $\mathrm{CH_3}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{CH_2}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{O}-\mathrm{C_2H_5}$	Aceto Acetic Ester or Ethyl Aceto Acetate
73	 $\mathrm{NH_2}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{NH_2}$	Oxanamide
74	 $\mathrm{Cl}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{Cl}$	Phosgene
75	 $\mathrm{H_2N}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{NH_2}$	Urea

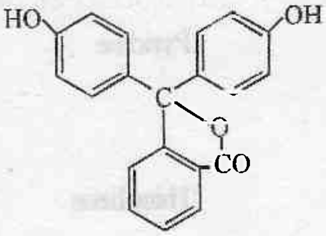
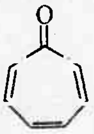
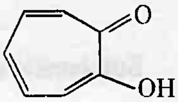
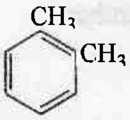
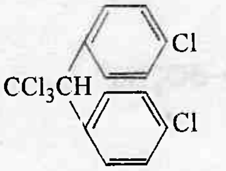
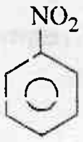
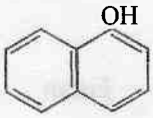
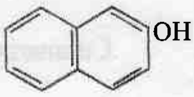
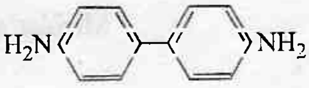
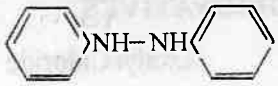
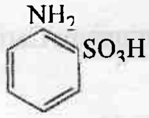
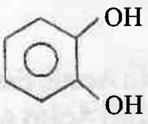
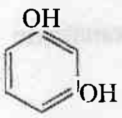
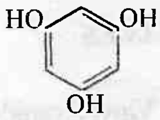
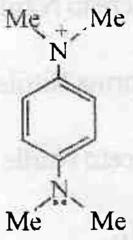
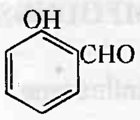
Group K:→N–DERIVATIVES

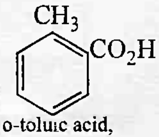
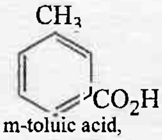
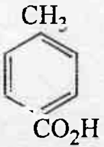
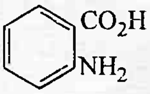
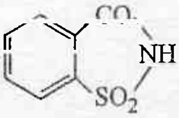
S. No.	Compound	Common Name
76	$CH_2=CH-C\equiv N$	Vinyl Cyanide or Acrelio Nitrile
77	$H-C\equiv N$	Forma Nitrile
78	$CH_3-C\equiv N$	Aceto Nitrile
79	CH_3-NCO	MIC

Group L:→AROMATIC COMPOUNDS

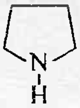
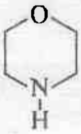
S. No.	Compound	Common Name
80		Anthracene
81		Indol

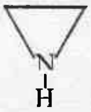
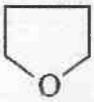
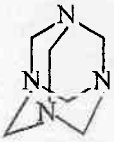
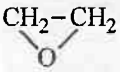
S. No.	Compound	Common Name
82		Pyridine
83		Thiophene
84		Pyrol
85		Sulphanilic acid
86		Azulene
87		Napthelene
88		Orange II
89		Butter Yellow
90		Furfurel
91		Furan
92		Conmarine
93		Michler's Ketone

S. No.	Compound	Common Name
94		Phenolphthalein
95		Tropone (Cycloheptatrienone)
96		Tropolone (Cycloheptatrienolone)
97		o–xylene
98		DDT (Dichlorodiphenyltrichloroethane)
99		Nitrobenzene (oil of mirbane)
100		α–naphthol
101		β–naphthol
102		Benzidine
103		Hydrazobenzene
104		Orthanilic Acid
105		Catechol
106		Resorcinol
107		Quinol
108		Phloroglucinol
109		Wurster salts
110		Salicylaldehyde(o-hydroxybenzaldehyde)
111	$C_6H_5CONH_2$	Benzamide
112	$(C_6H_5CO)_2O$	Benzoic Anhydride
113	$(C_6H_5CO)_2O_2$	Benzoyl Peroxide

S. No.	Compound	Common Name
114	$C_6H_5CO_2CH_3$	Perbenzoic acid
115	 o-toluic acid, m.p. 105°C  m-toluic acid, m.p. 111°C  p-toluic acid, m.p. 180°C	Toluic acids
116		Anthranilic acid (o-aminobenzoic acid)
117		Saccharin (o-sulphobenzoic imide)
118	$C_6H_5CH{=}CH_2$	Styrene
119	C_6H_5CHO	Benzaldehyde
120	$C_6H_5COCOC_6H_5$	Benzil
121	$(C_6H_5)_2C(OH)CO_2H$	Benzilic acid

Group M:→ HETROCYCLIC COMPOUNDS

S. No.	Compound	Common Name
122		Pyrrolidine
123		Piperidine
124		Morpholine

S. No.	Compound	Common Name
125		Aziridine
126		Tatrahydrofuran
127		Hexa-methlyenetetramine or Urotropene
128	 $\underset{O}{CH_2-CH_2}$	Oxirane or Ethylene Oxide or Oxo Cyclo Propane

BANSALCLASSES

TARGET IIT JEE 2007

INORGANIC CHEMISTRY

XII (ALL)

QUESTION BANK ON

COORDINATION COMPOUNDS

Q.1 Among TiF_6^{2-} , CoF_6^{3-} , Cu_2Cl_2 and $NiCl_4^{2-}$ the coloureless species are:

(A) CoF_6^{3-} and $NiCl_4^{2-}$ (B) TiF_6^{2-} and CoF_6^{3-}

(C) $NiCl_4^{2-}$ and Cu_2Cl_2 (D) TiF_6^{2-} and Cu_2Cl_2

Q.2 IUPAC name of complex $K_3[Al(C_2O_4)_3]$ is :

(A) Potassium alumino-oxalate (B) Potassium trioxalatoaluminate (III)

(C) Potassium aluminium (III) oxalate (D) Potassium trioxalatoaluminate (IV)

Q.3 Which ion has tetrahedral geometry:

(A) $[Fe(CO)_5]$ (B) $[Co(NH_3)_6]^{2+}$ (C) $[NiCl_4]^{2-}$ (D) $[Ni(CN)_4]^{2-}$

Q.4 Trioxalato aluminate (III) and tetrafluoro-borate (III) ions are:

(A) $[Al(C_2O_4)_3]$, $[BF_4]^{3-}$ (B) $[Al(C_2O_4)_3]^{3+}$, $[BF_4]^{3+}$

(C) $[Al(C_2O_4)_3]^{3-}$, $[BF_4]^{-}$ (D) $[Al(C_2O_4)_3]^{2-}$, $[BF_4]^{2-}$

Q.5 Which of the ligands can show linkage isomerism:

(A) CNS (B) NO_2 (C) CN (D) All of these

Q.6 Consider the following statements:

According the Werner's theory.

(1) Ligands are connected to the metal ions by covalent bonds.

(2) Secondary valencies have directional properties

(3) Secondary valencies are non-ionisable

Of these statements:

(A) 1, 2 and 3 are correct (B) 2 and 3 are correct

(C) 1 and 3 are correct (D) 1 and 2 are correct

Q.7 From the stability constant (hypothetical values), given below, predict which is the strongest ligand:

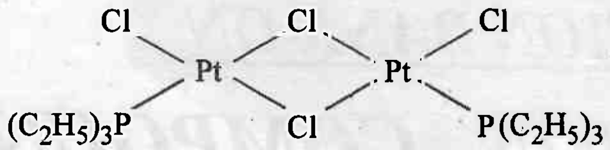
(A) $Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$, $K = 4.5 \times 10^{11}$

(B) Cu^{2+} $4CN^- \rightleftharpoons [Cu(CN)_4]^{2-}$, $K = 2.0 \times 10^{27}$

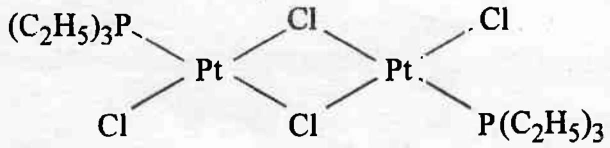
(C) $Cu^{2+} + 2en \rightleftharpoons [Cu(en)_2]^{2+}$, $K = 3.0 \times 10^{15}$

(D) $Cu^{2+} + 4H_2O \rightleftharpoons [Cu(H_2O)_4]^{2+}$, $K = 9.5 \times 10^{8}$

Q.8 The complexes given below show:



and



(A) Optical isomerism (B) Co-ordination isomerism

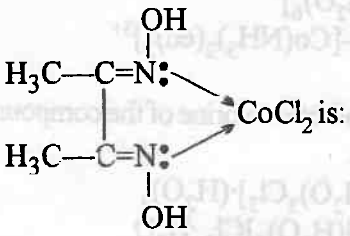
(C) Geometrical isomerism (D) Bridged isomerism

Q.9 In which of the following complexes the nickel metal is in highest oxidation state:
(A) $Ni(CO)_4$ (B) K_2NiF_6 (C) $[Ni(NH_3)_6](BF_4)_2$ (D) $K_4[Ni(CN)_6]$

Q.10 An ion M^{2+}, forms the complexes $[M(H_2O)_6]^{2+}$, $[M(en)_3]^{2+}$ and $[MBr_6]^{4-}$, match the complex with the appropriate colour.
(A) Green, blue and red (B) Blue, red and green
(C) Green, red and blue (D) Red, blue and green

Q.11 Name the metal M which is extracted on the basis of following reactions:
$4M + 8CN^- + 2H_2O + O_2 \longrightarrow 4[M(CN)_2]^- + 4OH^-$
$2[M(CN)_2]^- + Zn \longrightarrow [Zn(CN)_4]^{2-} + 2M$
(A) Nickel (B) Silver (C) Copper (D) Mercury

Q.12 The correct IUPAC name of the complex:



(A) Dichlorodimethylglyoximate cobalt (II) (B) Bis (dimethyglyoxime) dichloro cobalt (II)
(C) Dimethylglyoxime cobalt (II) chloride (D) Dichlorodimethylglyoxime cobalt (II)

Q.13 $[(C_6H_5)_2Pd(SCN)_2]$ and $[(C_6H_5)_2Pd(NCS)_2]$ are:
(A) Linkage isomers (B) Co-ordination isomers
(C) Ionisation isomers (D) Geometrical isomers

Q.14 Which one of the following will be able to show cis-trans isomerism:
(A) MA_3B (B) $M(AA)_2$ (C) MABCD (D) MA_4

Q.15 A complex of platinum, ammonia and chloride produces four ions per molecule in the solution. The structure consistent with the observation is:
(A) $[Pt(NH_3)_4]Cl_4$ (B) $[Pt(NH_3)_2Cl_4]$ (C) $[Pt(NH_3)_5Cl]Cl_3$ (D) $[Pt(NH_3)_4Cl_2]Cl_2$

Q.16 The total number of possible isomers of the compound $[Cu^{II}(NH_3)_4][Pt^{II}Cl_4]$ are:
(A) 3 (B) 5 (C) 4 (D) 6

Q.17 In the complex $Fe(CO)_x$, the value of x is:
(A) 3 (B) 4 (C) 5 (D) 6

Q.18 Cis-trans-isomerism is found in square planar complexes of the molecular formula : (A and B are monodenate ligands):
(A) MA_4 (B) MA_3B (C) MA_2B_2 (D) MAB_3

Q.19 The oxidation state of Mo in its oxo-complex species $[Mo_2O_4(H_2O)_2(C_2H_4)_2]^{2-}$ is:
(A) +2 (B) +3 (C) +4 (D) +5

Q.20 The hydridisation and unpaired electrons in $[Fe(H_2O)_6]^{2+}$ ion are :
(A) sp^3d^2 ; 4 (B) d^2sp^3 ; 3 (C) sp^3d ; 4 (D) $sp^3 d^2$; 2

Q.21 In which complex is the transition metal in zero oxidation state:
(A) $[Co(NH_3)_6]Cl_2$ (B) $[Fe(H_2O)_6SO_4]$ (C) $[Ni(CO)_4]$ (D) $[Fe(H_2O)_3](OH)_2$

Q.22 Formula of ferrocene is:
(A) $[Fe(CN)_6]^{4-}$ (B) $[Fe(CN)_6]^{3+}$ (C) $[Fe(CO)_5]$ (D) $[(C_5H_5)_2Fe]$

Q.23 The hybrisation involved in $[CoF_6]^{3-}$ is:
(A) d^2sp^3 (B) d^3sp^2 (C) dsp^3 (D) sp^3d^2

Q.24 Which of the following is π complex:
(A) Trimethyl aluminium (B) Ferrocene
(C) Diethyl zinc (D) Nickel carbonyl

Q.25 Which complex is likely to show optical activity:
(A) Trans-$[Co(NH_3)_4Cl_2]^+$ (B) $[Cr(H_2O)_6]^{3+}$
(C) Cis-$[Co(NH_3)_2(en)_2]^{3+}$ (D) Trans-$[Co(NH_3)_2(en)_2]^{3+}$

Q.26 Which one is the most likely structure of $CrCl_3 \cdot 6H_2O$ if 1/3 of total chlorine of the compound is precipitate by adding $AgNO_3$ to its aqueous solution:
(A) $CrCl_3 \cdot 6H_2O$ (B) $[Cr(H_2O)_3Cl_3] \cdot (H_2O)_3$
(C) $[CrCl_2(H_2O)_4] \cdot Cl \cdot 2H_2O$ (D) $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$

Q.27 The complex $[Co(NH_3)_5Br]SO_4$ will give white ppt. with:
(A) $PbCl_2$ (B) $AgNO_3$ (C) KI (D) None of these

Q.28 The two compounds $[Co(SO_4)(NH_3)_5]Br$ and $[Co(SO_4)(NH_3)_5]Cl$ represent:
(A) Linkage isomerism (B) Ionisation isomerism
(C) Co-ordination isomerism (D) No isomerism

Q.29 The structure of iron pentacarbonyl is:
(A) Square planar (B) Trigonal bipyramid (C) Triangular (D) None of these

Q.30 The EAN of platinum in potassium hexachloroplatinate (IV) is:
(A) 46 (B) 86 (C) 36 (D) 84

Q.31 Diethylene triamine is:
(A) Chelating agent (B) Polydentate ligand (C) Tridentate ligand (D) All of these

Q.32 How many moles of AgCl would be obtained, when 100 ml of 0.1 M $Co(NH_3)_5Cl_3$ is treated with excess of $AgNO_3$?
(A) 0.01 (B) 0.02 (C) 0.03 (D) none of these

Q.33 0.001 mol of $Co(NH_3)_5(NO_3)(SO_4)$ was passed through a cation exchanger and the acid coming out of it required 20 ml of 0.1 M NaOH for neutralisation. Hence, the complex is
(A) $[Co(NH_3)_5SO_4]NO_3$ (B) $[Co(NH_3)_5NO_3]SO_4$
(C) $[Co(NH_3)_5](SO_3)(NO_3)$ (D) none of these

Q.34 Cu^{2+} shows a coordination number of
(A) 2 only (B) 2 or 4 (C) 4 only (D) 4 or 6

Q.35 Which of the following is not chelating agent?
(A) thiosulphato (B) oxalato (C) glycinato (D) ethylene diamine

Q.36 Which of the following has five donor (coordinating) sites?
(A) Triethylene tetramine (B) Ethylenediamine tetracetate ion
(C) Ethylenediamine triacetate ion (D) Diethylene triamine

Q.37 A compound contains 1.08 mol of Na, 0.539 mol of Cu and 2.16 mol of F. Its aqueous solution shows osmotic pressure which is three times that of urea having same molar concentration. The formula of the compound is
(A) $Na_4[CuF_6]$ (B) $Na[CuF_4]$ (C) $Na_2[CuF_4]$ (D) $Na_2[CuF_3]$

Q.38 The IUPAC name of the red coloured complex $[Fe(C_4H_7O_2N_2)_2]$ obtained from the reaction of Fe^{2+} and dimethyl glyoxime
(A) bis (dimethyl glyoxime) ferrate (II) (B) bis (dimethyl glyoximato) iron (II)
(C) bis (2, 3-butanediol dioximato) iron (II) (D) bis (2, 3-butanedione dioximato) iron (II)

Q.39 The molar ionic conductances of the octahedral complexes.
(1) $PtCl_4{\cdot}5NH_3$ (2) $PtCl_4{\cdot}4NH_3$ (3) $PtCl_4{\cdot}3NH_3$ (4) $PtCl_4{\cdot}2NH_3$
(A) I < II < III < IV (B) IV < III <II < I (C) III < IV < II < I (D) IV < III < I < II

Q.40 On treatment of 10 ml of 1M solution of the complex $CrCl_3{\cdot}6H_2O$ with excess of $AgNO_3$, 4.305 g of AgCl was obtained. The complex is
(A) $[Cr(H_2O)_3Cl_3]{\cdot}3H_2O$ (B) $[Cr(H_2O)_4Cl_2]Cl{\cdot}2H_2O$
(C) $[Cr(H_2O)_5Cl]Cl_2{\cdot}H_2O$ (D) $[Cr(H_2O)_6]Cl_3$

Q.41 Which of the following species is not expected to be a ligand
(A) $\overset{+}{NO}$ (B) NH_4^+ (C) $NH_2-NH_3^+$ (D) CO

Q.42 The number of donor sites in dimethyl glyoxime, glycinato, diethylene triamine and EDTA are respectively:
(A) 2, 2, 3 and 4 (B) 2, 2, 3 and 6 (C) 2, 2, 2 and 6 (D) 2, 3, 3 and 6

Q.43 EAN of the central metal in the complexes – $K_2[Ni(CN_4)]$, $[Cu(NH_3)_4]SO_4$ and $K_2[PtCl_6]$ are respectively.
(A) 36, 35, 86 (B) 34, 35, 84 (C) 34, 35, 86 (D) 34, 36, 86

Q.44 Which of the following pair of complexes have the same EAN of the central metal atoms/ions?
(A) $[Cu(NH_3)_4]SO_4$ and $K_3[Fe(CN)_6]$ (B) $K_4[Fe(CN)_6]$ and $[Co(NH_3)_6]Cl_3$
(C) $K_3[Cr(C_2O_4)_3$ and $[Cr(NH_3)_6]Cl(NO_2)_2$ (D) all

Q.45 The complex that violates the Sidgwicks's rule of EAN is
(A) Potassium ferrocyanide (B) Hexamine cobalt (III) Chloride
(C) Tetramine copper (II) sulphate (D) Potassium dichlorodioxalato cobaltate (III)

Q.46 The IUPAC name for the coordination compound $Ba[BrF_4]_2$ is
(A) Barium tetrafluorobromate (V) (B) Barium tetrafluorobromate (III)
(C) Barium bis (tetrafluorobromate) (III) (D) none of these

Q.47 The formula of the complex hydridotrimethoxyborate (III) ion is:
(A) $[BH(OCH_3)_3]^{2-}$ (B) $[BH_2(OCH_3)_2]^{2-}$ (C) $[BH(OCH_3)_3]^{-}$ (D) $[BH(OCH_3)_3]^{+}$

Q.48 The complex ion which has no 'd' electrons in the central metal atom is:
(A) $[Co(NH_3)_6]^{3+}$ (B) $[Fe(CN)_6]^{3-}$ (C) $[Cr(H_2O)_6]^{3+}$ (D) $[MnO_4]^{-}$

Q.49 Oxidation number of Fe in violet coloured complex $Na_4[Fe(CN)_5(NOS)]$ is:
(A) 0 (B) 2 (C) 3 (D) 4

Q.50 Complexes $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$ can be distinguished by
(A) conductance measurement (B) using $BaCl_2$
(C) using $AgNO_3$ (D) all

Q.51 Amongst the following ions, which one has the highest paramagnetism?
(A) $[Cr(H_2O)_6]^{3+}$ (B) $[Fe(H_2O)_6]^{2+}$ (C) $[Zn(H_2O)_6]^{2+}$ (D) $[Cu(H_2O)_6]^{2+}$

Q.52 $Ni(CO)_4$ and $[Ni(NH_3)_4]^{2+}$ do not differ in
(A) magnetic moment (B) oxidation number of Ni
(C) geometry (D) EAN

Q.53 Which of the following statements is not correct?
(A) $Ti(NO_3)_4$ is a colourless compound (B) $[Cr(NH_3)_6)]Cl_3$ is a coloured compound
(C) $K_3[VF_6]$ is a colourless compound (D) $[Cu(NCCH_3)_4]BF_4$ is a colourless compound

Q.54 The geometry of $Ni(CO)_4$ and $[Ni(P Ph_3)_2Cl_2]$ are
(A) both square planar (B) tetrahedral and square planar
(C) both tetrahedral (D) square planar and tetrahedral

Q.55 Of the following which is diamagnetic in nature?
(A) $[CoF_6]^{3+}$ (B) $[NiCl_4]^{2-}$ (C) $[CuCl_4]^{2-}$ (D) $[Ni(CN)_4]^{2-}$

Q.56 The $[Fe(CN)_6]^{3-}$ complex ion
(A) exhibits planar geometry (B) is diamagnetic
(C) should be very stable (D) has 2 unpaired electrons

Q.57 50 ml of 0.2 M solution of a compound with empirical formula $CoCl_3.4NH_3$ on treatment with excess of $AgNO_3(aq)$ yields 1.435 g of AgCl. Ammonia is not removed by treatment with concentrated H_2SO_4. The formula of the compound is:
(A) $Co(NH_3)_4Cl_3$ (B) $[Co(NH_3)_4Cl_2]Cl$ (C) $[Co(NH_3)_4Cl_3$ (D) $[CoCl_3(NH_3)]NH_3$

Q.58 In the process of extraction of gold,

Roasted gold ore $+CN^- + H_2O \xrightarrow{O_2} [x] + OH^-$; $[x] + Zn \longrightarrow [y] + Au$
[x] and [y] are:
(A) $[x] = [Au(CN)_2]^-$, $[y] = [Zn(CN)_4]^{2-}$ (B) $[x] = [Au(CN)_4]^{3-}$, $[y] = [Zn(CN)_4]^{2-}$
(C) $[x] = [Au(CN)_2]^-$, $[y] = [Zn(CN)_6]^{4-}$ (D) $[x] = [Au(CN)_4]^-$, $[y] = [Zn(CN)_4]^{2-}$

Q.59 Which of the following is non–conducting?
(A) $CoCl_3.6NH_3$ (B) $CoCl_3.5NH_3$ (C) $CoCl_3.4NH_3$ (D) $CoCl_3.3NH_3$

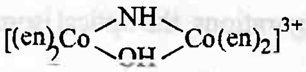
Q.60 Aqueous solution of $FeSO_4$ gives tests for both Fe^{2+} and SO_4^{2-} but after addition of excess of KCN, solution ceases to give test for Fe^{2+}. This is due to the formation of
(A) the double salt $FeSO_4.2KCN.6H_2O$ (B) $Fe(CN)_3$
(C) the complex ion $[Fe(CN)_6]^{4-}$ (D) the complex ion $[Fe(CN)_6]^{3-}$

Q.61 Which of the following statement(s) is/are correct with reference to Fe^{2+} and Fe^{3+} ions?
(1) Fe^{3+} gives brown colour with potassium ferricyanide
(2) Fe^{2+} gives blue colour with potassium ferricyanide
(3) Fe^{3+} gives red colour with potassium thiocyanate
(4) Fe^{2+} gives brown colour with ammonium thiocyanate
(A) 1, 2 (B) 1, 4 (C) 1, 2, 3 (D) all of these

Q.62 The number of sigma bonds in Ziese's salt is:
(A) 4 (B) 6 (C) 8 (D) none of these

Q.63 The disodium salt of ethylene diamine tetracetic acid can be used to estimate the following ion(s) in the aqueous solution
(A) Mg^{2+} ion (B) Ca^{2+} ion (C) Na^{+} ion (D) both Mg^{2+} and Ca^{2+}

Q.64 The oxidation number of Co in the complex ion



$[(en)_2Co\langle^{NH}_{OH}\rangle Co(en)_2]^{3+}$

(A) +2 (B) +3 (C) +4 (D) +6

Q.65 $[Cu(NH_3)_4]^{2+}$ has hybridisation and magnetic moment
(A) sp^3, 1.73 B.M. (B) sp^3d, 1.73 B.M. (C) dsp^2, 2.83 B.M. (D) dsp^2, 1.73 B.M.

Q.66 $[FeF_6]^{3-}$ has Fe atom ---hybridised with unpaired ----electrons
(A) d^2sp^3, 4 (B) d^2sp^3, 5 (C) sp^3d^2, 5 (D) sp^3d^2, 3

Q.67 Which of the following statements about $Fe(CO)_5$ is correct?
(A) It is paramagnetic and high spin complex (B) It is diamagnetic and high spin complex
(C) It is diamagnetic and low spin complex (D) It is paramagnetic and low spin complex

Q.68 Which of the following statements is not true?
(A) $MnCl_4^-$ ion has tetrahedral geometry and is paramagnetic
(B) $[Mn(CN)_6]^{2-}$ ion has octahedral geometry and is paramagnetic
(C) $[CuCl_4]^{2-}$ has square planar goemetry and is paramagnetic
(D) $[Ni(Ph_3P)_2Br_3]$ has trigonal bipyramidal geometry and one unpaired electron

Q.69 The increasing order of magnetism of
(I) $MnSO_4.4H_2O$ (II) $FeSO_4.7H_2O$ (III) $NiSO_4.6H_2O$ (IV) $CuSO_4.5H_2O$
(A) I < II < III < IV (B) IV < III < II < I (C) III < IV < II < I (D) III < IV < I < II

Q.70 Which of the following statements is correct?
(A) Geometrical isomerism is not observed in complexes of C.N.4 having tetrahedral geometry
(B) Square planar complexes generally do not show geometrical isomerism
(C) The square planar complex of general formulae Ma_3b or Mab_3 exhibits cis–trans isomerism
(D) The platinum glycinato complex, $[Pt(Gly)_2]$ does not show geometrical isomerism

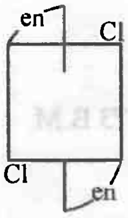
Q.71 Geometrical isomerism can be shown by
(A) $[Ag(NH_3)(CN)]$ (B) $Na_2[Cd(NO_2)_4]$ (C) $[PtCl_4I_2]$ (D) $[Pt(NH_3)_3Cl][Au(CN)_4]$

Q.72 $[Co(en)_3]^{3+}$ ion is expected to show
(A) two optically active isomers: d and *l* forms
(B) three optically active isomers: d, *l* and meso forms
(C) four optically active isomers: cis, d and *l* isomers and trans d and *l* isomers
(D) none of these

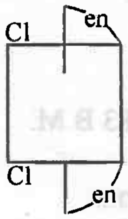
Q.73 The number of geometrical isomers for octahedral $[Co(NH_3)_2Cl_4]^-$, square planar $[AuCl_2Br_2]^-$ and $[Pt(en)Cl_2]$ are
(A) 2, 2, 2 (B) 2, 2, no isomerism (C) 3, 2, 2 (D) 2, 3, no isomerism

Q.74 Which of the following statements is not true about the complex ion $[Cr(en)_2Cl_2]^+$
(A) It has two geometrical isomers – cis and strans
(B) Both the cis and trans isomers display optical activity
(C) Only the cis isomer displays optical activity
(D) Only the cis isomer has non–superimpossible mirror image

Q.75 Of the following configurations, the optical isomers are

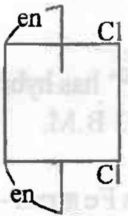


I



II

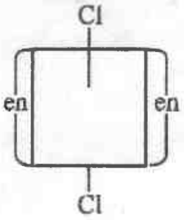
III



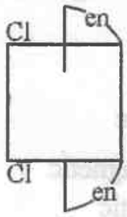
IV

(A) I and II (B) I and III (C) II and IV (D) II and III

Q.76 Identify the geometrical isomers of the following:

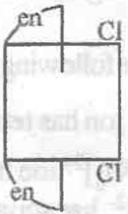


I



II

III



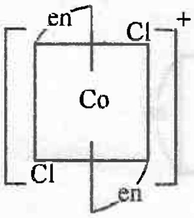
IV

(A) I with III (B) II with IV (C) I with II and IV (D) none of these

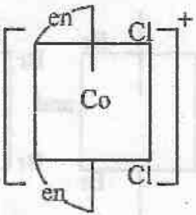
Q.77 Other than the X–ray diffractions, how could be the following pairs of isomers be distinguished from one another by
$[Cr(NH_3)_6][Cr(NO_2)_6]$ and $[Cr(NH_3)_4(NO_2)_2][Cr(NH_3)_2(NO_2)_4]$
(A) electrolysis of an aqueous solution (B) measurement of molar conductance
(C) measuring magnetic moments (D) observing their colours

Q.78 How the isomeric complexes $[Co(NH_3)_6][Cr(NO_2)_6]$ and $[Cr(NH_3)_6][Co(NO_2)_6]$ can be distinguished from one another by
(A) conductivity measurement (B) measuring magnetic moments
(C) electrolysis of their aqueous solutions (D) optical measurement

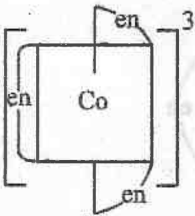
Q.79 Which of the following ions are optically active?



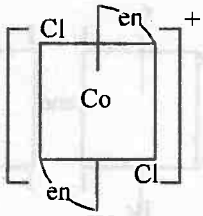
I



II



III



IV

(A) I only (B) II only (C) II and III (D) IV only

Q.80 Which of the following polymerisation isomers of the compound having empirical formula $Cr(NH_3)_3(NO_2)_3$ has the lowest molecular mass?

(A) $[Cr(NH_3)_4(NO_2)_2]^+ [Cr(NH_3)_2(NO_2)_4]^-$ (B) $[Cr(NH_3)_6]^{3+}[Cr(NO_2)_6]^{3-}$
(C) $[Cr(NH_3)_5(NO_2)]^{2+}[Cr(NH_3)(NO_2)_5]^{2-}$ (D) all

Q.81 Octahedral complex of Ni(II) must be
(A) inner orbital
(B) outer orbital
(C) inner or outer orbital depending upon the strong or weak field ligand
(D) none of these

Q.82 For the correct assignment of electronic configuration of a complex, the valence bond theory often requires the measurement of
(A) molar conductance (B) optical activity (C) magnetic moment (D) dipole moment

Q.83 Mn^{2+} forms a complex with Br^- ion. The magnetic moment of the complex is 5.92 B.M. What could not be the probable formula and geometry of the complex?
(A) $[MnBr_6]^{4-}$, octahedral (B) $[MnBr_4]^{2-}$, square planar
(C) $[MnBr_4]^{2-}$, tetrahedral (D) $[MnBr_5]^{3-}$, trigonal bipyramidal

Q.84 How many isomers are possible for the complex ion $[Cr(NH_3)(OH)_2Cl_3]^{2-}$
(A) 2 (B) 3 (C) 4 (D) 5

Q.85 A complex of certain metal has the magnetic moment of 4.91 BM whereas another complex of the same metal with same oxidation state has zero magnetic moment. The metal ion could be
(A) Co^{2+} (B) Mn^{2+} (C) Fe^{2+} (D) Fe^{3+}

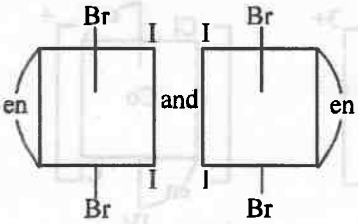
Q.86 The tetrahedral $[CoI_4]^{2-}$ and square planar $[PdBr_4]^{2-}$ complex ions are respectively
(A) low spin, high spin (B) high spin, low spin (C) both low spin (D) both high spin

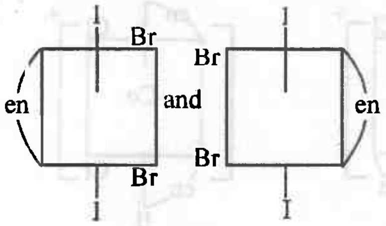
Q.87 Ethylenediaminetetraacetic acid (EDTA) is the antidote for lead poisoning. It is administered in the form of
(A) free acid (B) sodium dihydrogen salt
(C) Calcium dihydrogen salt (D) none of these

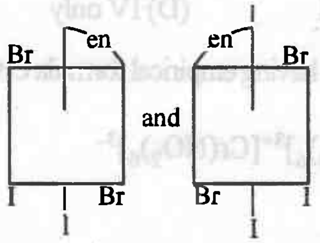
Q.88 The species having tetrahedral shape is
(A) $[PdCl_4]^{2-}$ (B) $[Ni(CN)_4]^{2-}$ (C) $[Pd(CN)_4]^{2-}$ (D) $[NiCl_4]^{2-}$

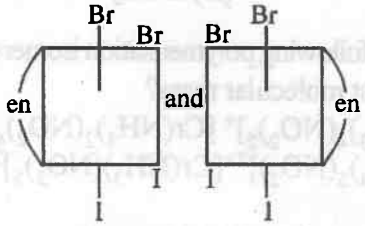
Q.89 Which one of the following species does not represent cationic species of vanadium formed in aqueous solution
(A) VO_2^+ (B) VO^{2+} (C) $[V(H_2O)_6]^{3+}$ (D) VO_2^{2+}

Q.90 The complex ion has two optical isomers. Their correct configurations are:

(A)


(B)


(C)


(D)


Q.91 The EAN of metal atoms in $Fe(NO)_2(CO)_2$ and $Co_2(CO)_8$ respectively are
(A) 34, 35 (B) 34, 36 (C) 36, 36 (D) 36, 35

Q.92 Following Sidgwick's rule of EAN, $Co(CO)_x$ will be
(A) $Co_2(CO)_4$ (B) $Co_2(CO)_3$ (C) $Co_2(CO)_8$ (D) $CO_2(CO)_{10}$

Q.93 On treatment of $[Ni(NH_3)_4]^{2+}$ with concentrated HCl, two compounds I and II having the same formula, $Ni(NH_3)_2Cl_2$ are obtained, I can be converted into II by boiling with dilute HCl. A solution of I reacts with oxalic acid to form $[Ni(NH_3)_2(C_2O_4)]$ wheras II does not react. Point out the correct statement of the following
(A) I cis, II trans; both tetrahedral (B) I cis, II trans; both square planar
(C) I trans, II cis; both tetrahedral (D) I trans, II cis; both square planar

Q.94 Coordination isomerism could be shown by
(A) $[Ag(NH_3)_2][CuCl_2]$ (B) $[Al(H_2O)_6][Co(CN)_6]$
(C) $[Fe(NH_3)_6]_2[Pt(CN)_6]_3$ (D) $[Co(NH_3)_5Cl]SO_4$

Q.95 Point out the correct statements amongst the following
(A) $[Cu(CN)_4]^{3-}$ has tetrahedral geometry and dsp^2 hybridization
(B) $[Ni(CN)_6]^{4-}$ is octahedral and Ni has d^2sp^3 hybridization
(C) $[ZnBr_4]^{2-}$ is tetrahedral and diamagnetic
(D) $[Cr(NH_3)_6]^{3+}$ has octahedral geometry and sp^3d^2 hybridization

Q.96 Among the following ions which one has the highest paramagnetism
(A) $[Cr(H_2O)_6]^{3+}$ (B) $[Fe(H_2O)_6]^{2+}$ (C) $[Cu(H_2O)_6]^{2+}$ (D) $[Zn((H_2O)_6]^{2+}$

Q.97 Among the following, the compound that is both paramagnetic and coloured is
(A) $K_2Cr_2O_7$ (B) $(NH_4)_2[TiCl_6]$ (C) $VOSO_4$ (D) $K_3[Cu(CN)_4]$

Q.98 Which of the following compounds is expected to be coloured
(A) Ag_2SO_4 (B) CuF_2 (C) MgF_2 (D) CuCl

Q.99 Which compound is formed when excess of KCN is added to aqueous solution of copper sulphate?
(A) $Cu(CN)_2$ (B) $K_2[Cu(CN)_4]$ (C) $K[Cu(CN)_2]$ (D) $K_3[Cu(CN)_4]$

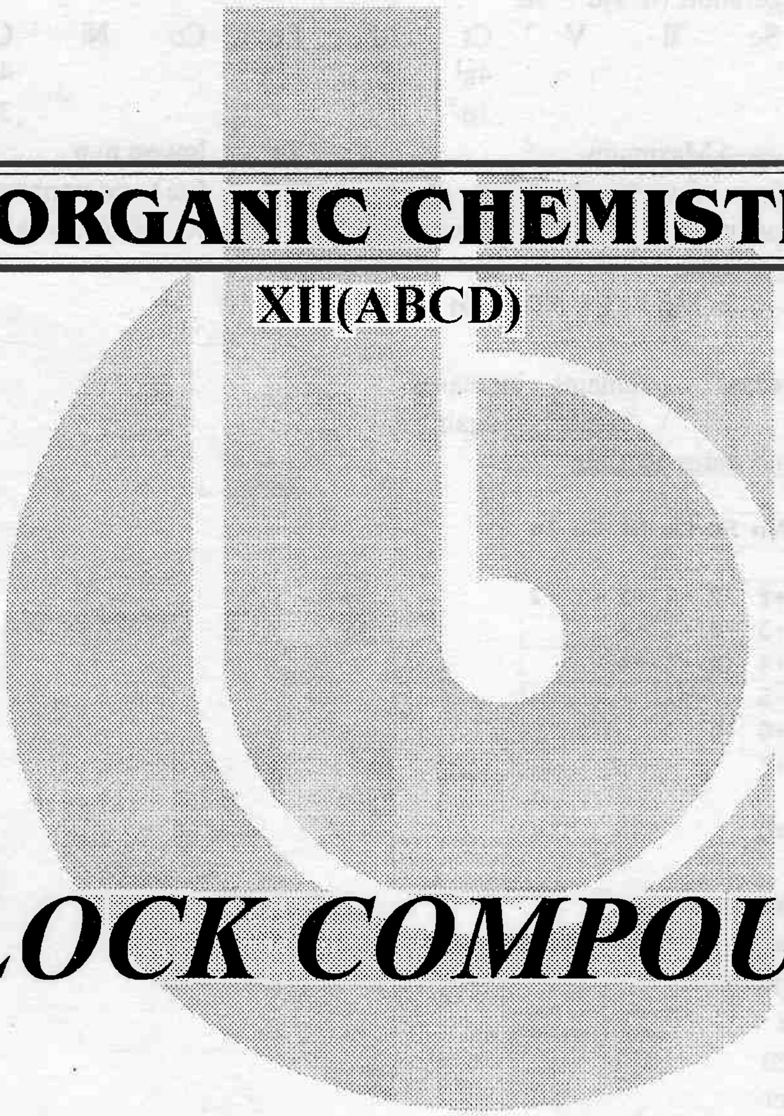
Q.100 Which of the following complex shows ionization isomerism
(A) $[Cr(NH_3)_6]Cl_3$ (B) $[Cr(en)_2]Cl_2$ (C) $[Cr(en)_3]Cl_3$ (D) $[Co(NH_3)_5Br]SO_4$

ANSWER KEY

Q.1 D	Q.2 B	Q.3 C	Q.4 C
Q.5 D	Q.6 B	Q.7 B	Q.8 C
Q.9 B	Q.10 B	Q.11 B	Q.12 D
Q.13 A	Q.14 C	Q.15 C	Q.16 C
Q.17 C	Q.18 C	Q.19 B	Q.20 A
Q.21 C	Q.22 D	Q.23 D	Q.24 B
Q.25 C	Q.26 C	Q.27 A	Q.28 D
Q.29 B	Q.30 B	Q.31 D	Q.32 B
Q.33 B	Q.34 D	Q.35 A	Q.36 C
Q.37 C	Q.38 B	Q.39 B	Q.40 D
Q.41 B	Q.42 B	Q.43 C	Q.44 D
Q.45 C	Q.46 B	Q.47 C	Q.48 D
Q.49 B	Q.50 D	Q.51 B	Q.52 A
Q.53 C	Q.54 C	Q.55 D	Q.56 C
Q.57 B	Q.58 A	Q.59 D	Q.60 C
Q.61 C	Q.62 C	Q.63 D	Q.64 B
Q.65 D	Q.66 C	Q.67 C	Q.68 C
Q.69 B	Q.70 A	Q.71 C	Q.72 A
Q.73 B	Q.74 B	Q.75 C	Q.76 C
Q.77 B	Q.78 C	Q.79 C	Q.80 D
Q.81 B	Q.82 C	Q.83 B	Q.84 B
Q.85 C	Q.86 B	Q.87 C	Q.88 D
Q.89 D	Q.90 D	Q.91 C	Q.92 C
Q.93 B	Q.94 A, B	Q.95 C	Q.96 B
Q.97 C	Q.98 B	Q.99 D	Q.100 D

BANSALCLASSES

TARGET IIT JEE 2007



INORGANIC CHEMISTRY

XII(ABCD)

d -BLOCK COMPOUNDS

TRANSITION ELEMENTS:

Definition: They one often called 'transition elements' because their position in the periodic table is between s-block and p-block elements

Typically, the transition elements have an incompletely filled d-level. Since Zn group has d^{10} configuration and are not considered as transition elements but they are d-block elements.

General Characteristics:

(i) Metallic character: They are all metal and good conductor of heat & electricity

(ii) Electronic configuration: $(n-1)d^{1-10}ns^{1-2}$

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
others are				$4s^1$					$4s^1$	
as usual				$3d^5$					$3d^{10}$	

(iii) M.P.
Cr, Mo, W } ⟶ Maximum
6 no. of unpaired e^-s are involved in metallic bonding

Zn, Cd, Hg } lowest m.p.
due to no unpaired e^- for metallic bonding

(iv) Variation in atomic radius:

$$Sc \longrightarrow Mn\ \underbrace{Fe\ Co\ Ni}\ Cu\ Zn$$

decreases — remains same — increases again

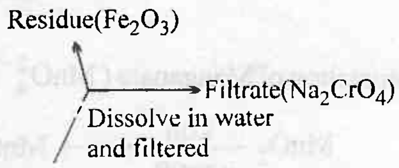
(v) Variable oxidation states possible

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
			1					+1	
	+2	+2	+2	**+2**	**+2**	**+2**	**+2**	**+2**	**+2**
+3	**+3**	**+3**	**+3**	+3	**+3**	**+3**	+3		
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5					
			+6	+6	+6				
				+7					

Colour: (aquated)

$Sc^{3+} \longrightarrow$ colourless
$Ti^{4+} \longrightarrow$ colourless
$Ti^{3+} \longrightarrow$ purple
$V^{4+} \longrightarrow$ blue
$V^{3+} \longrightarrow$ green
$V^{2+} \longrightarrow$ violet
$Cr^{2+} \longrightarrow$ blue
$Cr^{3+} \longrightarrow$ green
$Mn^{3+} \longrightarrow$ violet
$Mn^{2+} \longrightarrow$ pink
$Fe^{2+} \longrightarrow$ green(light)
$Fe^{3+} \longrightarrow$ yellow
$Co^{2+} \longrightarrow$ pink
$Ni^{2+} \longrightarrow$ green
$Cu^{2+} \longrightarrow$ blue
$Zn^{2+} \longrightarrow$ colourless

CHROMATE -DICHROMATE



Preparation:→ $\underset{\text{(chromite ore)}}{4FeCr_2O_4} + 8Na_2CO_3 + 7O_2 \xrightarrow[\text{red hot in presence of air}]{1000°-1300°C} 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

[Lime (CaO) added with Na_2CO_3 which keeps the mass porous so that air has access to all parts and prevents fusion]

Then, $2Na_2CrO_4 + \underset{\text{conc.}}{H_2SO_4} \longrightarrow Na_2SO_4\downarrow + Na_2Cr_2O_7 + H_2O$

It's solubility upto 32°C increases and then decreases } Hence, suitable temp. is to be employed to crystallise out Na_2SO_4 first.

Then $Na_2Cr_2O_7$ is crystallised out as $\underset{\text{(red crystal)}}{Na_2Cr_2O_7{\cdot}2H_2O}$ on evaporation.

Ques. In laboratory $K_2Cr_2O_7$ is used mainly not $Na_2Cr_2O_7$. Why?

Sol. $Na_2Cr_2O_7$ is deliquescent enough and changes its concentration and can not be taken as primary standard solution whereas $K_2Cr_2O_7$ has no water of crystallisation and not deliquescent.

How to get $K_2Cr_2O_7$: $\underset{\text{hot conc.}}{Na_2Cr_2O_7} + KCl \xrightarrow[\text{decomposition}]{\text{double}} K_2Cr_2O_7 + 2NaCl$

NaCl crystallises out first and filtered off. Then less soluble $K_2Cr_2O_7$ crystallised out on cooling

Ques. How to standardise $Na_2S_2O_3$ solution in iodometry?

Sol. $K_2Cr_2O_7$ is primary standard ⇒ strength is known by weighing the salt in chemical balance and dissolving in measured amount of water.

Then in acidic solution add. KI

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

This I_2 is liberated can be estimated with $S_2O_3^{2-}$.

Other props & test of $CrO_4^{2-} - Cr_2O_7^{2-}$: Already done

* Similarities between hexavalent Cr & S-compounds:

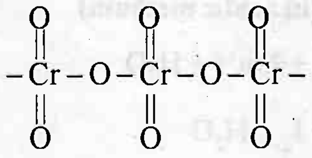
(i) SO_3 & $CrO_3 \longrightarrow$ both acidic.

(ii) $S \longrightarrow SO_4^{2-}$, $S_2O_7^{2-}$, $Cr \longrightarrow CrO_4^{2-}$, $Cr_2O_7^{2-}$

(iii) CrO_4^{-2} & SO_4^{2-} are isomorphous

(iv) SO_2Cl_2 & $CrO_2Cl_2 \xrightarrow{OH^-} SO_4^{2-}$ & CrO_4^{2-} respectively.

(v) SO_3Cl^- & $SrO_3Cl^- \xrightarrow{OH^-} SO_4^{2-}$ & CrO_4^{2-}

(vi) CrO_3 & β(SO_3) has same structure 

$$-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}}-$$

MANGANATE & PERMANGANATE

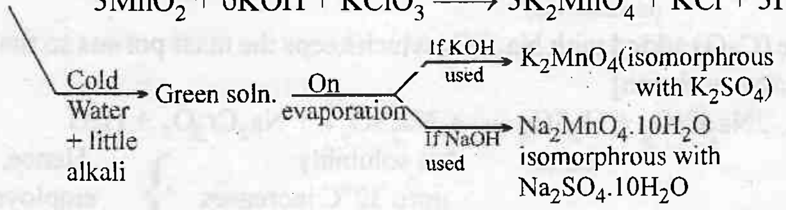
Preparation of Manganate (MnO_4^{2-}):-

$MnO_2 \xrightarrow[\text{or NaOH, } \Delta \text{ in presence of air}]{KOH} MnO_4^{2-}$ $[2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O]$

green melt

$MnO_2 + 2KOH + KNO_3 \longrightarrow K_2MnO_4 + KNO_2 + H_2O$

$3MnO_2 + 6KOH + KClO_3 \longrightarrow 3K_2MnO_4 + KCl + 3H_2O$



In presence of $KClO_3$ & KNO_3 the above reaction is more faster because these two on decomposition provides O_2 easily.

* Manganate is also obtained when $KMnO_4$ is boiled with KOH.

$4KMnO_4 + 4KOH \xrightarrow{\text{boiled}} 4K_2MnO_4 + 2H_2O + O_2$

Props : The above green solution is quite stable in alkali, but in pure water and in presence of acids, depositing MnO_2 and giving a purple solution of permanganate.

$3K_2MnO_4 + 2H_2O \rightleftharpoons \underset{\text{purple}}{2KMnO_4} + \underset{\text{drak brown}}{MnO_2 \downarrow} + 4KOH$

Prob. : $E^o_{MnO_4^{2-}/MnO_2} = 2.26\ V$; $E^o_{MnO_4^{2-}/MnO_4^-} = -0.56\ V$

Prove that MnO_4^{2-} will disproportionate in acidic medium.

Another Method of Prep^n. : $3K_2MnO_4 + 2H_2SO_4 \longrightarrow 2KMnO_4 + MnO_2 \downarrow + 2K_2SO_4 + 2H_2O$

or $3K_2MnO_4 + 2H_2O + 4CO_2 \longrightarrow 2KMnO_4 + MnO_2 + 4KHCO_3$

But in the above method $\frac{1}{3}$ of Mn is lost as MnO_2 but when oxidised either by Cl_2 or by O_3

$2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$ [Unwanted MnO_2 does not form]

OR

$2K_2MnO_4 + O_3 + H_2O \longrightarrow 2KMnO_4 + 2KOH + O_2$

Prop.: $2KMnO_4 \xrightarrow[200°C]{\Delta} K_2MnO_4 + MnO_2 + O_2$

$2K_2MnO_4 \xrightarrow[\text{hot}]{\text{at red}} 2K_2MnO_3 + O_2$

Oxidising Prop. of $KMnO_4$: (in acidic medium)

(i) $MnO_4^- + Fe^{+2} + H^+ \longrightarrow Fe^{+3} + Mn^{+2} + H_2O$

(ii) $MnO_4^- + I^- + H^+ \longrightarrow Mn^{+2} + I_2 + H_2O$

(iii) $MnO_4^- + H_2O_2 + H^+ \longrightarrow Mn^{+2} + O_2 + H_2O$

(iv) $MnO_4^- + SO_2 \xrightarrow{H^{\oplus}} Mn^{+2} + H_2SO_4$

(v) $MnO_4^- + NO_2^- + H^+ \longrightarrow Mn^{+2} + NO_3^- + H_2O$

(vi) $MnO_4^- + H_2C_2O_4 + H^+ \longrightarrow Mn^{+2} + CO_2 + H_2O$

(vii) $MnO_4^- + H_2S \longrightarrow Mn^{2+} + S\downarrow + H_2O$

* (1) It is not a primary standard since it is difficult to get it in a high degree of purity and free from traces of MnO_2.

*(2) It is slowly reduced to MnO_2 especially in presence of light or acid

$4MnO_4^- + 4H^+ \longrightarrow 4MnO_2 + 2H_2O + 3O_2$

Hence it should be kept in dark bottles and standardise just before use.

(viii) $2KMnO_4 + 16HCl \longrightarrow 2KCl + 5Cl_2 + 8H_2O + 2MnCl_2$

Oxidising Prop. of $KMnO_4$ in alk. medium :

$2MnO_4^- + 2OH^- \longrightarrow 2MnO_4^{2-} + H_2O + O$. Then $2MnO_4^{2-} + 2H_2O \longrightarrow 2MnO_2 + 4OH^- + 2O$

(i) $2KMnO_4 + H_2O + KI \longrightarrow 2MnO_2 + 2KOH + KIO_3$

(ii) $2KMnO_4 + 3HCO_2K \longrightarrow 2MnO_2 + KHCO_3 + 2K_2CO_3 + H_2O$

(iii) $2KMnO_4 + 3H_2O_2 \longrightarrow 2KOH + 2MnO_2 + 2H_2O + 3O_2$

Oxidising Prop. in neutral or weakly acidic solution:

(i) $2KMnO_4 + 3MnSO_4 + 2H_2O \xrightarrow{\text{in presence } Zn^{+2} \text{ or } ZnO} 5MnO_2 + K_2SO_4 + 2H_2SO_4$

or $MnO_4^- + Mn^{+2} + 2H_2O \longrightarrow 5MnO_2 + 4H^+$

In absence of Zn^{+2} ions, some of the Mn^{+2} ion may escape, oxidation through the formation of insoluble $Mn^{II}[Mn^{IV}O_3]$ manganous permanganite.

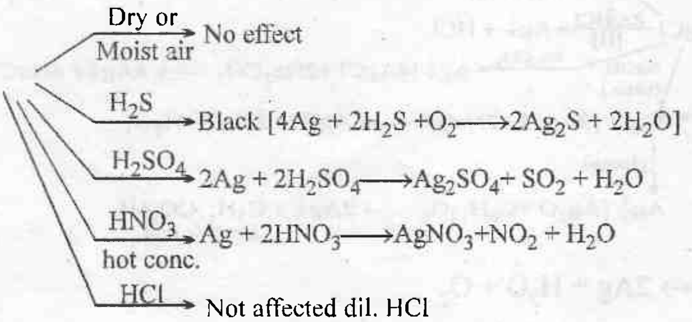
(ii) $8KMnO_4 + 3Na_2S_2O_3 + H_2O \longrightarrow 8MnO_2 + 3Na_2SO_4 + 3K_2SO_4 + 2KOH$

** Conversion of Mn^{+2} to MnO_4^- :

(i) PbO_2 (ii) $Pb_3O_4 + HNO_3$ (iii) $Pb_2O_3 + HNO_3$ (iv) $NaBiO_3 / H^+$
(v) $(NH_4)_2S_2O_8 / H^+$ (vi) KIO_4 / H^+

Prep^n : Properties of Ag, $AgNO_3$, AgBr, $Ag_2S_2O_3$

(I) Metallic Ag



$E^{o}_{Ag/Ag^+} < E^{o}_{H_2/H^+}$

Hence in presence of O_2.

Ag reacts with dil.HCl

$4Ag + 4HCl + O_2 \longrightarrow 4AgCl\downarrow + 2H_2O$

In the same way in presence of O_2, Ag complexes with NaCN / KCN.

$$4Ag + 8KCN + 2H_2O + O_2 \longrightarrow 4K[Ag(CN)_2] + 4KOH$$

(II) $AgNO_3$: (i) Prep^n.: already done.

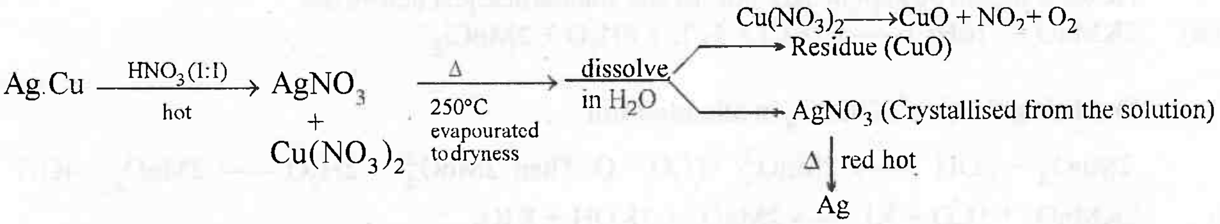
Properties.: (i) It is called as lunar caustic because in contact with skin it produces burning sensation like that of caustic soda with the formation of finely devided silver (black colour)

(ii) Thermal decomposition:

$$2AgNO_3 \xrightarrow{212°C} 2AgNO_2 + O_2$$

$$2AgNO_2 \xrightarrow{500°C} 2Ag + 2NO + O_2$$

How to separate Ag from Ag – Cu alloy : [Principle : decomposition temperature of $AgNO_3$ is much higher than $Cu(NO_3)_2$.]



(iii) Props. of $AgNO_3$: [Already done in basic radical]

$6AgNO_3 + 3I_2 + 3H_2O \longrightarrow 5AgI + AgIO_3 + 6HNO_3$
(excess)

(iv) $Ag_2SO_4 \xrightarrow{\Delta} 2Ag + SO_2 + O_2$

(v) $A(AgNO_3) \xrightarrow[\text{added}]{B}$ white ppt appears quickly

$B(Na_2S_2O_3) \xrightarrow[\text{added}]{A}$ It takes time to give white ppt.

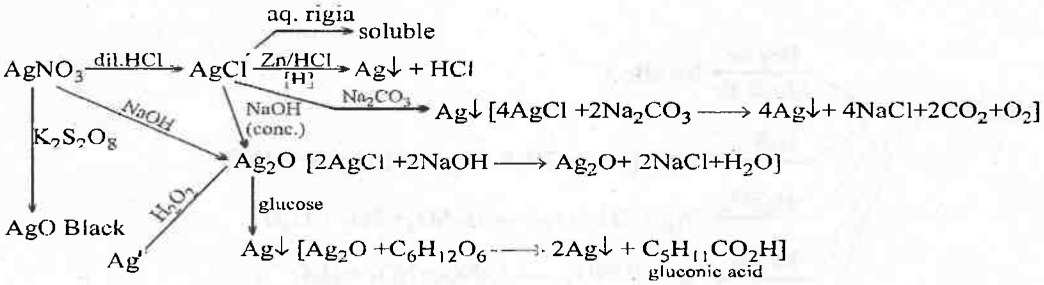
} Explain

(vi) $Ag_2S_2O_3 + H_2O \xrightarrow{\Delta} Ag_2S + H_2SO_4$

AgCl . AgBr. AgI (but not Ag_2S) are soluble in $Na_2S_2O_3$ forming $[Ag(S_2O_3)_2]^{-3}$, $Na_5[Ag_3(S_2O_3)_4]$ complexes

(vii) AgBr : $AgNO_3 \xrightarrow{KBr} AgBr\downarrow + KNO_3$
Pale yellow
ppt.

(viii)



$$Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$$

$$K_2S_2O_8 + 2AgNO_3 + 2H_2O \longrightarrow 2AgO + 2KHSO_4 + 2HNO_3$$

* AgO supposed to be paramagnetic due to d^9 configuration. But actually it is diamagnetic and exists as $Ag^{I}[Ag^{III}O_2]$

* Reaction involved in developer :
$K_2Fe^{II}(C_2O_4)_2 + AgBr \longrightarrow KFe^{III}(C_2O_4)_2 + Ag\downarrow + KBr$

ZINC COMPOUNDS

ZnO: It is called as phillospher's wool due to its wooly flock type appearance

Preparation:
1] $2Zn + O_2 \longrightarrow 2ZnO$
2] $ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$
3] $2Zn(NO_3)_2 \xrightarrow{\Delta} 2ZnO + 4NO_2 + O_2$
4] $Zn(OH)_2 \xrightarrow{\Delta} ZnO + H_2O$

Purest ZnO : $4ZnSO_4 + 4Na_2CO_3 + 3H_2O \longrightarrow \underset{\text{white basic zinc carbonate}}{ZnCO_3 \cdot 3Zn(OH)_2} \downarrow + 4Na_2SO_4 + 3CO_2$

$$\Big\downarrow \Delta$$

$$\underset{\text{pure}}{4ZnO} + 3H_2O\uparrow + CO_2\uparrow$$

Properties:
1] $\underset{\text{white}}{ZnO(cold)} \overset{\Delta}{\rightleftharpoons} \underset{\text{yellow}}{ZnO(hot)}$
2] It is insoluble in water
3] It sublimes at 400°C
4] It is amphoteric oxide
$ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$
$ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$
$ZnO + 2NaOH \longrightarrow Na_2ZnO_2 + H_2O$
5] $ZnO \longrightarrow Zn$ by H_2 & C
$ZnO + H_2 \xrightarrow{>400^\circ C} Zn + H_2O$
$ZnO + C \longrightarrow Zn + CO$
6] It forms Rinmann's green with $Co(NO_3)_2$
$2Co(NO_3)_2 \longrightarrow 2CoO + 4NO_2 + O_2$
$CoO + ZnO \longrightarrow \underset{\text{Rinmann's green}}{CoZnO_2 \text{ or } CoO\cdot ZnO}$

Uses:
(1) As white pigment. It is superior than white lead because it does not turn into black
(2) Rinmann's green is used as green pigment
(3) It is used as zinc ointment in medicine

$ZnCl_2$

Preparation:

$$\left.\begin{aligned}&ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O\\&ZnCO_3 + 2HCl \longrightarrow ZnCl_2 + H_2O + CO_2\\&Zn(OH)_2 + 2HCl \longrightarrow ZnCl_2 + 2H_2O\end{aligned}\right\}\text{It crystallises as } ZnCl_2\cdot 2H_2O$$

Anh. $ZnCl_2$ cannot be made by heating $ZnCl_2\cdot 2H_2O$ because

$$ZnCl_2\cdot 2H_2O \xrightarrow{\Delta} Zn(OH)Cl + HCl + H_2O$$

$$Zn(OH)Cl \xrightarrow{\Delta} ZnO + HCl$$

To get anh. $ZnCl_2$: $Zn + Cl_2 \longrightarrow ZnCl_2$

$Zn + 2HCl(dry) \longrightarrow ZnCl_2 + H_2$

or $Zn + HgCl_2 \longrightarrow ZnCl_2 + Hg$

Properties: (i) It is deliquescent white solid (when anhydrous)

(ii) $ZnCl_2 + H_2S \longrightarrow ZnS$

" $+ NaOH \longrightarrow Zn(OH)_2 \xrightarrow{\text{excess}} Na_2[Zn(OH)_4]$

" $+ NH_4OH \longrightarrow Zn(OH)_2 \xrightarrow{\text{excess}} [Zn(NH_3)_4]^{2+}$

Uses:
1] Used for impregnating timber to prevent destruction by insects
2] As dehydrating agent when anhydrous
3] $ZnO\cdot ZnCl_2$ used in dental filling

$ZnSO_4$:-

Preparation:→

$$Zn + \text{dil } H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

$$ZnO + \text{dil } H_2SO_4 \longrightarrow ZnSO_4 + H_2O$$

$$ZnCO_3 + \text{dil } H_2SO_4 \longrightarrow ZnSO_4 + H_2O + CO_2$$

$$\left.\begin{aligned}&ZnS + 2O_2 \longrightarrow ZnSO_4\\&ZnS + \frac{3}{2}O_2 \longrightarrow ZnO + SO_2\end{aligned}\right\}\text{parallel reaction}$$

$$ZnS + 4O_3 \longrightarrow ZnSO_4 + 4O_2$$

Props. 1]

$$ZnSO_4\cdot 7H_2O \xrightarrow{39-70°C} ZnSO_4\cdot 6H_2O \xrightarrow{>70°C} ZnSO_4\cdot H_2O \xrightarrow{>280°C} ZnSO_4$$

$$ZnSO_4 \xrightarrow{>800°C} \frac{1}{2}O_2 + SO_2 + ZnO$$

Uses:
1] in eye lotion
2] Lithophone making ($ZnS + BaSO_4$) as white pigment

COPPER COMPOUNDS

CuO:

Preparation:→ (i) $CuCO_3.Cu(OH)_2 \xrightarrow{\Delta} 2CuO + H_2O + CO_2$ (Commercial process)
Malachite Green
(native Cu-carbonate)

(ii) $2Cu + O_2 \longrightarrow 2CuO$ & $Cu_2O + \frac{1}{2}O_2 \longrightarrow 2CuO$

(iii) $Cu(OH)_2 \xrightarrow{\Delta} CuO + H_2O$

(iv) $2Cu(NO_3)_2 \xrightarrow{250°C} 2CuO + 4NO_2 + O_2$

Properties:→ (i) CuO is insoluble in water

(ii) Readily dissolves in dil. acids
$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$
$HCl \longrightarrow CuCl_2$
$HNO_3 \longrightarrow Cu(NO_3)_2$

(iii) It decomposes when, heated above 1100°C
$4CuO \longrightarrow 2Cu_2O + O_2$

(iv) CuO is reduced to Cu by H_2 or C under hot condition
$CuO + C \longrightarrow Cu + CO\uparrow$
$CuO + H_2 \longrightarrow Cu + H_2O\uparrow$

$CuCl_2$:

Preparation:→ $CuO + 2HCl(conc.) \longrightarrow CuCl_2 + H_2O$
$Cu(OH)_2{\cdot}CuCO_3 + 4HCl \longrightarrow 2CuCl_2 + 3H_2O + CO_2$

Properties:→ (i) It is crystallised as $CuCl_2{\cdot}2H_2O$ of Emerald green colour

(ii) dil. solution in water is blue in colour due to formation of $[Cu(H_2O)_4]^{2+}$ complex.

(iii) conc. HCl or KCl added to dil. solution of $CuCl_2$ the colour changes into yellow, owing to the formation of $[CuCl_4]^{2-}$

(iv) The conc. aq. solution is green in colour having the two complex ions in equilibrium $2[Cu(H_2O)_4]Cl_2 \rightleftharpoons [Cu(H_2O)_4]^{2+} + [CuCl_4]^{2-} + 4H_2O$

(v) $CuCl_2 \longrightarrow CuCl$ by no. of reagents

(a) $CuCl_2$ + Cu-turnings $\xrightarrow{\Delta} 2CuCl$
(b) $2CuCl_2 + H_2SO_3 + H_2O \longrightarrow 2CuCl + 2HCl + 2H_2SO_4$
(c) $2CuCl_2 + Zn/HCl \longrightarrow 2CuCl + ZnCl_2$
(d) $CuCl_2 + SnCl_2 \longrightarrow CuCl + SnCl_4$

** $CuF_2{\cdot}2H_2O \longrightarrow$ light blue
$CuCl_2{\cdot}2H_2O \longrightarrow$ green
$CuBr_2 \longrightarrow$ almost black

{ Anh. $CuCl_2$ is dark brown mass obtained by heating $CuCl_2{\cdot}2H_2O$ at 150°C in presence of HCl vap.

CuI_2 does not exist

$$CuCl_2{\cdot}2H_2O \xrightarrow[\text{HCl gas}]{150°C} CuCl_2 + 2H_2O$$

$CuSO_4$:

Preparation:→ $CuO + H_2SO_4(dil) \longrightarrow CuSO_4 + H_2O$

$Cu(OH)_2 + H_2SO_4(dil) \longrightarrow CuSO_4 + 2H_2O$

$Cu(OH)_2\cdot CuCO_3 + H_2SO_4\ (dil) \rightarrow CuSO_4 + 3H_2O + CO_2$

$Cu + H_2SO_4 + \frac{1}{2}O_2 \longrightarrow CuSO_4 + H_2O$ [Commercial scale]

(Scrap)

$Cu + dil.\ H_2SO_4 \longrightarrow$ no reaction {Cu is a below H in electrochemical series}

Properties:→ (i) It is crystallised as $CuSO_4\cdot 5H_2O$

(ii)

$$\begin{tikzcd}[column sep=huge]
\underset{\text{Blue}}{CuSO_4\cdot 5H_2O} \arrow[r, shift left, "\text{On exposure}"] & \underset{\text{Pale blue}}{CuSO_4\cdot 3H_2O} \arrow[l, shift left, "\text{effloresence take places}"] \arrow[r, shift left, "100°C"] & \underset{\text{Bluish white}}{CuSO_4\cdot H_2O} \arrow[l, shift left] \arrow[d, shift left, "230°C"] \\
 & & \underset{\text{white}}{CuSO_4(anh.)} \arrow[u, shift left] \arrow[dl, "800°C"'] \arrow[d, "750°C"] \\
 & CuO + SO_2 + \frac{1}{2}O_2 & CuO + SO_3
\end{tikzcd}$$

(iii) Revision with all others reagent

IRON COMPOUNDS

$FeSO_4\cdot 7H_2O$:

Preparation:→ (i) Serap $Fe + \underset{\text{(dil.)}}{H_2SO_4} \longrightarrow FeSO_4 + H_2\uparrow$

(ii) From Kipp's waste

$FeS + H_2SO_4(dil) \longrightarrow FeSO_4 + H_2S\uparrow$

(iii) $FeS_2 + 2H_2O + \frac{7}{2}O_2 \longrightarrow FeSO_4 + H_2SO_4$

Properties:→ (i) It undergoes aerial oxidation forming basic ferric sulphate

$4FeSO_4 + H_2O + O_2 \longrightarrow 4Fe(OH)SO_4$

(ii) $FeSO_4\cdot 7H_2O \xrightarrow{300°C} \underset{\text{anh. white}}{FeSO_4} \xrightarrow[\text{temp.}]{\text{high}} Fe_2O_3 + SO_2 + SO_3$

(iii) Aq. solution is acidic due to hydrolysis

$FeSO_4 + 2H_2O \rightleftharpoons \underset{\text{weak base}}{Fe(OH)_2} + H_2SO_4$

(iv) It is a reducing agent

(a) $Fe^{2+} + MnO_4^- + H^+ \longrightarrow Fe^{3+} + Mn^{2+} + H_2O$

(b) $Fe^{2+} + Cr_2O_7^{2-} + H^+ \longrightarrow Fe^{3+} + Cr^{3+} + H_2O$

(c) $Au^{3+} + Fe^{2+} \longrightarrow Au + Fe^{3+}$

(d) $Fe^{2+} + HgCl_2 \longrightarrow \underset{\text{white ppt.}}{Hg_2Cl_2\downarrow} + Fe^{3+}$

(v) It forms double salt. Example $(NH_4)_2SO_4\cdot FeSO_4\cdot 6H_2O$

FeO(Black): Prep^n: $FeC_2O_4 \xrightarrow[\text{in absence of air}]{\Delta} FeO + CO + CO_2$

Props:→ It is stable at high temperature and on cooling slowly disproportionates into Fe_3O_4 and iron

$4FeO \longrightarrow Fe_3O_4 + Fe$

$FeCl_2$:

Preparation:→ $Fe + 2HCl \xrightarrow[\text{a current of HCl}]{\text{heated in}} FeCl_2 + H_2$

OR

$2FeCl_3 + H_2 \xrightarrow{\Delta} 2FeCl_2 + 2HCl$

Properties:→ (i) It is deliquescent in air like $FeCl_3$

(ii) It is soluble in water, alcohol and ether also because it is sufficiently covalent in nature

(iii) It volatilises at about 1000°C and vapour density indicates the presence of Fe_2Cl_4. Above 1300°C density becomes normal

(iv) It oxidises on heating in air

$12FeCl_2 + 3O_2 \longrightarrow 2Fe_2O_3 + 8FeCl_3$

(v) H_2 evolves on heating in steam

$3FeCl_2 + 4H_2O \longrightarrow Fe_3O_4 + 6HCl + H_2$

(vi) It can exist as different hydrated form

$FeCl_2\cdot 2H_2O \longrightarrow$ colourless

$FeCl_2\cdot 4H_2O \longrightarrow$ pale green

$FeCl_2\cdot 6H_2O \longrightarrow$ green

BANSAL CLASSES

CHEMISTRY

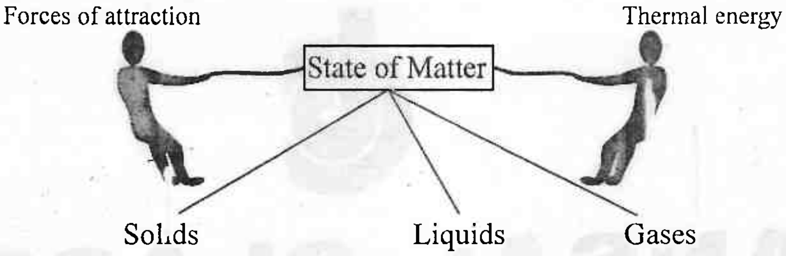
TARGET IIT JEE 2007
XI (P, Q, R, S - BATCH)

GASEOUS STATE

PREREQUISITE:
Basic unit conversion of pressure, volume. Basic mathematics of differentiation & integration, maximum value of a given function & plotting graphs.

CONTENTS

KEY CONCEPTS



Parameters:

		Solids	Liquids	Gases
(i)	Forces of attraction	👍	✋	👎
(ii)	Thermal energy	down	moderate	up
(iii)	Space	down	moderate	up
(iv)	Shape	up	down	down
(v)	Volume	up	up	down
(vi)	Density	up	up	down

GASEOUS STATE : The state is characterized by sensitivity of volume change with change of pressure and temperature. It is due to large distance between molecules as compared to their own dimensions. There exists weak Vander Waal's forces, molecules move independent of each other with speed about 400 m s^{-1}.

Are volume of solids & liquid totally independent of pressure??

IDEAL GAS : A gas with no intermolecular attractions & having very negligible volume occupied by molecules when compared with volume of gas is termed as ideal gas. A theoretical concept which for gases present can be obtained only under certain condition.

REAL GAS : Considerable forces of attraction & appreciable size of molecules. These under " certain conditions" behalve like ideal. [Refer : section of real gas behaviour]

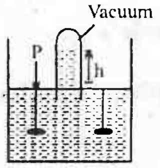
Parameter associated with the gas : P, V, T, n
where
P represents pressure exerted by the gas molecules on the walls of the container assuming negilible intermolecular attractions,
V represents free volume available for motion (equal to the volume of the container),
T represents absolute temperature, **n** represents no of moles.

Conversion factors : Pressure → 1 **atm** = 1.013 × 10^5 **Pa** = 760 **mm of Hg** = 760 **torr** = 1.013 **bar**
Volume → 1 **l** = 1**dm^3** = 10^{-3} **m^3** = 1000 **ml** = 1000 **cm^3**

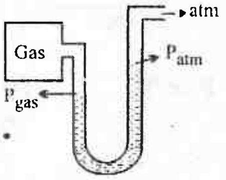
$$\text{Temperature} \rightarrow T_K = T_C^\circ + 273 = \frac{5}{9}T_F^\circ + 255.22$$

INSTRUMENTS FOR PRESSURE CALCULATIONS :

Barometer : $P = \dfrac{A \times h \times d \times g}{A}$ where
d = density of fluid
h = vertical height
g = acceleration due to



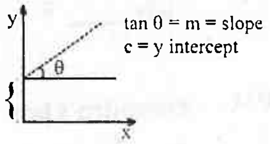
Manometer : $P_{gas} = P_{atm} + hdg$



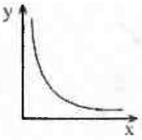
EQUATION & GRAPHS OF EXTENSIVE UTILITY IN GASEOUS STATE :

Two Parameters 'y' & 'x' if are related as

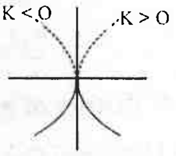
(a) $y = mx + C$ (where m & C are constants) [then there will be a <u>direct relationship</u> between them & graph will be a straight line as shown]
$y = mx + C$ (straight line)



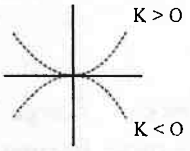
(b) xy = constant (rect hyperbola) / $y = \dfrac{m}{x} + C$ (where m & C are constant)



(c) $y^2 = Kx$ (K is a constant)



(d) $x^2 = Ky$ (K is a constant)



Experimental Gas laws ⟶ Relationship between various parameter of the gas. Gaseous state is the only state that allows a quantitative descriptive between the four parameters, P, V, T & n. The relationship which connects the four variables is known as equation of state, which can be obtained experimentally from the following gas laws.

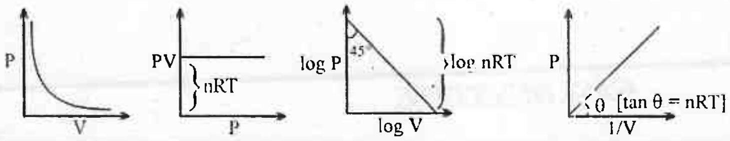
\# All are based on experimental data.

\# All are applicable for ideal gases only.

\# Get yourselves comfortable with all the various types of graphs to get a 'feel' of them.

I. **Boyle's law** $V \propto \dfrac{1}{P}$ $\left(\begin{matrix}T, \text{constant} \\ n \ \text{constant}\end{matrix}\right)$ $P_1V_1 = P_2V_2$

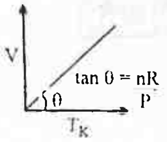
graphs are Isotherms

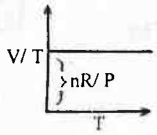


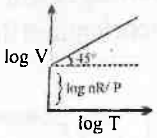
Plot the different curves for difference values of n & V to compare.

II. **Charle's law** $V \propto T$ $\left(\begin{matrix} P\text{, constant} \\ n \text{ constant}\end{matrix}\right)$ $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

graphs are Isobars



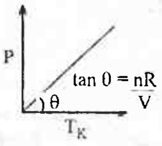


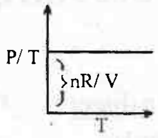


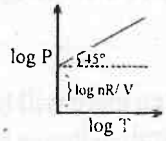
Plot graphs of V vs T꜀ & V vs T_F

III. **Gay Lussac's law** $P \propto T$ $\left(\begin{matrix} V\text{, constant} \\ n \text{ constant}\end{matrix}\right)$ $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

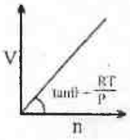
graphs are Isochor

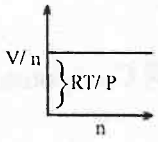


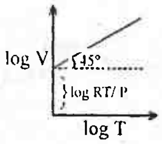




IV. **Avogadro's law** $V \propto n$ (T , P constant) $\frac{V_1}{n_1} = \frac{V_2}{n_2}$







Combined Gas Law : $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

Equation Of State : $PV = nRT$

d = density of gas

$\Rightarrow PV = \frac{w}{M}RT$ R = Universal Gas constant = 0.0821 atm litres /kelvin/mol

$\Rightarrow PM = dRT$ = 8.314 joule/kelvin = 2cal / kelvin/mol

Dalton's law of partial pressure :

$P_{total} = P_A + P_B + \ldots\ldots$; $P_{wet\ gas} = P_{dry\ gas} + P_{H_2O\ vapour}$ i.e. aq. tension.

P_A, P_B are partial pressures . ; P_A = mole fraction$_A$ × Total pressure

and % of gas in mixture = $\frac{\text{Partial pressure}}{\text{Total pressure}} \times 100$.

Amagat's Law :

The total volume of a mixture of gases is equal to the sum of the partial volumes of the constituent gases, at same Temperature & Pressure.

Graham's law of Diffusion & Effusion :

$r \propto \frac{1}{\sqrt{d}}$ or $r \propto \frac{1}{\sqrt{M}}$ $r \propto \frac{P}{\sqrt{M}}$ [For gases effusing at different pressures]

r is rate of diffusion of any gas.

$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$; $\frac{\text{volume / time}}{\text{volume / time}} = \sqrt{\frac{M_2}{M_1}}$ **d** is density at some temperature.

$$r = \frac{\text{moles diffused}}{\text{time taken}} = \frac{\text{distance travelled in a narrow tube}}{\text{time taken}} = \frac{\text{Pressure drop I}}{\text{Pressure drop II}}$$

It should be noted that the rate of diffusion or effusion actually depends on pressure difference of the gas and not simply on its pressure. Moreover the pressure difference is to be measured for this gas only i.e. if a container holds [He] at a pressure of 0.1 atm and if a small pin-hole is made in the container and if the container is placed in a room, then the rate of effusion of He gas from the container to outside depends only on its pressure difference, which is 0.1 - 0 (as there is no He in the atmosphere). This implies that the diffusion of a gas is not dependent on the diffusion of any other gas.

Whenever we consider the diffusion of a gas under experimental conditions, we always assume that the gas diffuses in vaccum and during the time period for which the diffusion is studied the rate of diffusion (or the composition of diffusing or effusing mixture of gases) remains constant.

Miscellaneous concepts used in Gaseous State:

(a) **Bursting of containers :** two concepts used depending upon type of container.

(i) **Bubble type** (very thin skin) cannot tolerate difference in pressure on the skin

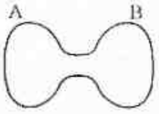
outside pressure = inside pressure

Any change in these cause change in volume & the container burst due to maximum stretching.

(ii) **Cylinder type** (thick skin) can withstand pressure difference till a limit but cannot have volume change.

Any change cause a change in pressure & when it exceeds the limits the container burst.

(b) **Connecting containers having gases**



On removal of nozzel the gas from higher pressure will travel so as to have equal pressure at both the containers.... from idea of total moles & final temperature each parameter can be calculated.

(c) **Changes in Open vessel :** Pressure of gas remains constant & so is the volume.

$$\therefore\ n_1 T_1 = n_2 T_2$$

(e) **Changes in closed vessel :** $\frac{P_1}{n_1} = \frac{P_2}{n_2}$

(f) **Barometric pressure distr.butor in a gas** [To calculate pressure at various height in a gas]

$$\ln\frac{P_2}{P_1} = \frac{-Mg}{RT}[H_2 - H_1] \qquad P_2 = P_1\, e^{-\frac{Mg}{RT}[H_2 - H_1]}$$

(g) **I separation**

For separating lighter gas from a mixture.

Separation Factor :

$$f = \frac{n_1^1/n_2^1}{n_1/n_2} = f$$

n_1, n_2 and n_1^1, n_2^1 are the concentration of two isotopes before and after processing.

Theoretical separation factor $f' = \sqrt{\frac{M_2}{M_1}}$

If required enrichment of species (1) is attained after 'x' times, then :

$$(f')^x = \frac{n_1^1/n_2^1}{n_1/n_2} = f.$$

Solving using Graham's law, $x = \frac{2\log f}{\log\left(\frac{M_2}{M_1}\right)}$.

(h) **Payload / lifting power** [based on Buoyancy]

L.P. of balloon = $V(d - d_1)g - Mg$

V = Volume of balloon

d = density of outside gas

d = density of gas in the balloon

M = Mass of balloon

Analysis of a reaction involving gaseous

$A(g) + B(g) \longrightarrow C(g)$

→ What happens to pressure as reaction proceeds (in a closed container)

(j) **Vapour density and degree of dissociation** $\alpha = \frac{D - d}{(n-1)d}$

Kinetic theory of gases :

$$PV = \frac{1}{3}\ [illegible] = \frac{1}{3} Mu^2 \text{ (For 1 mole)}$$

Types of velocities :

$$u^2 = \frac{u_1^2 + u_2^2 + \ldots\ldots + u_N^2}{N}$$; u = **root mean square speed** .

??

Finds applications in K.E.

$$u = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{d}}$$

$$\textbf{Average speed} = \frac{u_1 + u_2 + \ldots\ldots + u_N}{N} = \sqrt{\frac{8RT}{\pi M}}$$

??

Finds application in Collision theroy

$$\textbf{most probable speed} = \sqrt{\frac{2RT}{M}}$$

most probable : average : r. m. s. = 1 : 1.13 : 1.22

$= \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$ *Relationship between three types of speeds*

$$u_{rms} > u_{av} > u_{mp}$$

Average kinetic energy of a single molecule $= \frac{3}{2} \cdot \frac{R}{N} \cdot T = \frac{3}{2}\,\mathbf{k}T$

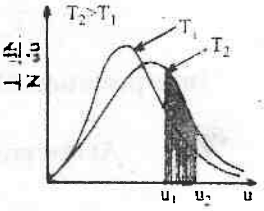
k = Boltzman constant $= 1.3806 \times 10^{-16}$ erg deg^{-1}.

Total kinetic energy for **one mole** of a gas $= \frac{3}{2}RT$.

kinetic energy of **n moles** of a gas $= n \times \frac{3}{2}RT$

Maxwell distribution Laws: $dN_u = 4\pi N\left(\frac{M}{2\pi RT}\right)^{3/2} \exp(-Mu^2/2RT)\,u^2\,du$

$$= 4\pi N\left(\frac{M}{2\pi kT}\right)^{3/2} \exp(-mu^2/2kT)\,u^2\,du$$



Collision frequency & Mean Free Path :

$$\text{Mean free path } \lambda = \frac{d_1 + d_2 + \ldots\ldots + d_n}{n}$$

$$\lambda = \frac{\text{Average velocity / RMS velocity}}{\text{collision number or frequency}} = \frac{kT}{\sqrt{2}\,\pi\sigma^2 P}$$

k = Boltzman constant ; σ = collision diameter.

$Z_1 = \sqrt{2}\,\sigma^2 \bar{u} N^*$ [collisions made by one molecule]

THE REAL PATH

Vander Waals equation of state :

$$\left(P + \frac{a}{v^2} \cdot n^2\right)(v - nb) = nRT.$$

a, b are Vander Waals constants ; different for each gas

unit of a ⟶ atm $L^2\,mol^{-2}$; S.I. unit ⟶ $P_a\,m^6\,mol^{-2}$

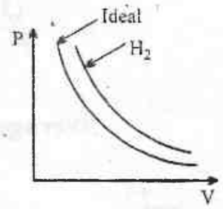
unit of b ⟶ $L\,mol^{-1}$; S.I. unit ⟶ $m^3\,mol^{-1}$

greater the value of 'a', more easily the gas is liquefiable ; $a = \frac{PV^2}{n^2}$

greater the value of 'b' greater the molecular size, $b = 4\nu$.

ν = volume occupied by all the gas molecules .

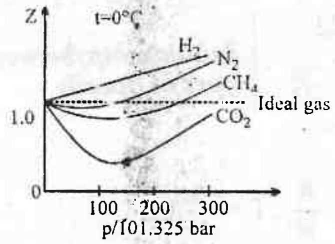
Real gases : Deviation from ideal behaviour

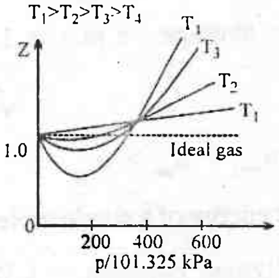


The curve for the real gas has a tendency to coincide with that of an ideal gas at low pressures when the volume is large. At higher pressures, however deviations are observed.

Compressibility factor : z

$$z = \frac{PV}{nRT} = \frac{\text{volume observed}}{\text{volume ideal}}$$





Boyle Temperature :

$$T_B = \frac{a}{bR}$$

Inversion Temperature :

$$T_i = \frac{2a}{bR}$$

Interpretation Of Deviation From Vander Waals Equation :

(i) At low pressure (below Boyle temperature) $z = \frac{PV}{RT} = 1 - \frac{a}{VRT}$

(ii) At high pressure (above Boyle temperature) $z = \frac{PV}{RT} = 1 + \frac{Pb}{RT}$

(iii) At extremely low pressure (at Boyle temperature) $z = \frac{PV}{RT} = 1$; $Pb = \frac{a}{V}$

HEAT CAPACITIES

C_P = Molar heat capacity at constant pressure

C_V = Molar heat capacity at constant volume

c_p = specific heat capacity at constant pressure

c_v = specific heat capacity at constant volume

$\Rightarrow C_P - C_V = R$

$\Rightarrow \frac{C_P}{C_V} = r$ r = 1.66 (monoatomic); 1.4 (diatomic)

Molar Specific Heat :

= specific heat × molecular mass

$$C_P - C_V = R/J \ ; \quad \frac{C_P}{C_V} = 1.66 \text{ for monoatomic} \ ; \quad \frac{C_P}{C_V} = 1.4 \text{ for diatomic}$$

Degree Of Freedom :

Three for monoatomic gas ; Five for diatomic gas .

For a molecule having N atoms, total are 3N

Translational : 3 for all types [at all temp.]

Rotational : 2 for linear
3 for N-linear

] *Each contributing* $\frac{1}{2}$ *KT*

Vibrational : 3N – 5 for linear
3N – 6 for N-linear

] *Each contributing KT*

Law Of Equipartition Of Energy :

Translational Motion : $\overline{E}_{trans} = \frac{1}{2} mv^2 = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2 \Rightarrow \frac{3}{2} KT$

Rotational Motion : $\overline{E}_{rot} = \frac{1}{2} I_x w_x^2 , \frac{1}{2} I_y w_y^2$ (linear)

$$= \frac{1}{2} I_x w_x^2 + \frac{1}{2} I_y w_y^2 + \frac{1}{2} I_z w_z^2 \text{ (N.L.)}$$

∴ linear = KT ; N.L. = $\frac{3}{2}$ KT

Vibrational Motion : $\overline{E}_{vib} = \frac{1}{2} KT + \frac{1}{2} KT = KT$

SOME OTHER EQUATION OF STATE

Dieterici Equation :

$$Pe^{na/VRT} \times (V - nb) = nRT$$

Berthelot Equation :

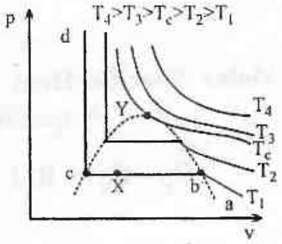
$$\left(P + \frac{n^2 a}{T V^2}\right)(V - nb) = nRT$$ (a & b are Berthlot's constant different from vander Waal's constant)

Virial Equation Of State For 1 Mole Of Gas :

$$z = \frac{PV}{RT} = 1 + B\frac{1}{V} + C\frac{1}{V^2} + D\frac{1}{V^3} + \ldots\ldots$$ (B, C, D... are temp. dependent constant)

B = second virial co–efficient = $b - \frac{a}{RT}$
C = third virial co–efficient = b^2 .

] *gas dependent*



Critical Phenomenon : Critical Temp , Critical pressure , Critical volume

$$T_c = \frac{8a}{27Rb}\ , \quad P_c = \frac{a}{27b^2}\ ; \quad V_c = 3b$$

The law of corresponding states :

$$p_r = \frac{p}{p_c}, \qquad T_r = \frac{T}{T_c} \qquad \text{and} \qquad V_r = \frac{V_m}{V_c}$$

$$p = p_r p_c, \qquad T = T_r T_c \qquad \text{and} \qquad V_m = V_r V_c$$

Substituting these expression in the van der Waals equation

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

we obtain $\left(p_r p_c + \frac{a}{V_r^2 V_c^2}\right)(V_r V_c - b) = RT_r T_c$

Replacing p_c, V_c and T_c in terms of a, b and R, we get

$$\left\{p_r \frac{a}{27b^2} + \frac{a}{V_r^2(3b)^2}\right\}\{V_r(3b) - b\} = RT_r\left(\frac{8a}{27Rb}\right)$$

i.e. $\quad (p_r + 3/V_r^2)(3V_r - 1) = 8T_r$

$$Z = \frac{pV_m}{RT} = \frac{(p_r p_c)(V_r V_c)}{R(T_r T_c)} = \frac{p_c V_c}{T_c}\left(\frac{p_r V_r}{T_r}\right) = \frac{3}{8}\frac{p_r V_r}{T_r}$$

EXERCISE # I

EXPERIMENTAL GAS LAW AND APPLICATION OF IDEAL GAS EQUATION.

Q.1 3.6 gm of an ideal gas was injected into a bulb of internal volume of 8L at pressure P atmp and temp T-K. The bulb was then placed in a thermostat maintained at (T+ 15) K.0.6 gm of the gas was let off to keep the original pressure. Find P and T if mol weight of gas is 44.

Q.2 A toy balloon originally held 1.0 gm of He gas and had a radius 10 cm. During the night, 0.25 gm of the gas effused from the balloon. Assuming ideal gas behaivour, under these constant P and T conditions, what was the radius of the balloon the next morning.

Q.3 If a scuba diver is to remain submerged for 1 hr, what pressure must be applied to force sufficient air into the tank to be used . Assume 0.5 dm^3 of air per breath at standard atmospheric pressure, a respiration rate of 38 breaths per minute, and a tank capacity of 30 dm^3.

Q.4 While resting, the average human male use 0.2 dm^3 of O_2 per hour at S T P for each kg of body mass. Assume that all this O_2 is used to produce energy by oxidising glucose in the body . What is the mass of glucose required per hour by a resting male having mass 60 kg . What volume, at S T P of CO_2 would be produced.

Q.5 In a basal metabolism measurement timed at 6.00 min, a patient exhaled 52.5 L of air, measured over water at 20^0C. The vapour pressure of water at 20^0C is 17.5 torr. The barometric pressure was 750 torr. The exhaled air analyzed 16.75 vol% oxygen and the inhaled air 20.32 vol% oxygen, both on dry basis. Neglecting any solubility of the gases in water and any difference in the total volumes of inhaled and exhaled air, calculate the rate of oxygen consumption by the patient in ml (S.T.P) per minute.

Q.6 One mole of NH_4Cl is kept in an open container & then covered with a lid. The container is now heated to 600 K where all NH_4Cl dissociates into NH_3 & HCl. If volume of the container is 24.63 litres, calculate what will be the final pressure of gases inside the container. Also find whether the lid would stay or bounce off if it can with stand a pressure difference of 5.5 atm. Assume that outside air is at 300 K and 1 atm pressure.

DALTON'S LAW OF PARTIAL PRESSURE

Q.7 12 g N_2, 4 gm H_2 and 9 gm O_2 are put into a one litre container at 27°C. What is the total pressure.

Q.8 1.0×10^{-2} kg of hydrogen and 6.4×10^{-2} kg of oxygen are contained in a 10×10^{-3} m^3 flask at 473 K. Calculate the total pressure of the mixture. If a spark ignities the mixture. What will be the final pressure.

GRAHAM'S LAW OF DIFFUSION AND EFFUSION

Q.9 At room temp , NH_3 gas at one atmp & HCl gas at "P" atmp are allowed to effuse through identical pin holes to the opposite ends of a glass tube 1m long & uniform cross-section. A white deposit is observed at a distance of 60 cm from the HCl end. What is "P".

Q.10 A gas mixture contains equal number of molecules of N_2 and SF_6, some of it is passed through a gaseous effusion apparatus . Calculate how many molecules of N_2 are present in the product gas for every 100 molecules of SF_6.

Q.11 Two gases NO and O_2 were introduced at the two ends of a one metre long tube simultaneously (tube of uniform cross-section). At what distance from NO gas end, Brown fumes will be seen.

Q.12 At 20 °C two balloons of equal volume and porosity are filled to a pressure of 2 atm, one with 14 kg N_2 & other with 1 kg H_2. The N_2 balloon leaks to a pressure of $\frac{1}{2}$ atm in one hour. How long will it take for H_2 balloon to leaks to a pressure of $\frac{1}{2}$ atm.

Q.13 Naturally occurring Fluorine is entirely ^{19}F, but suppose that it were 50% F^{19} and 50% F^{20} whether gaseous diffusion of UF_6 would then work to separate U^{235} from U^{238}.

Q.14 Pure O_2 diffuses through an aperture in 224 sec, whereas mixture of O_2 and another gas containing 80 % O_2 diffuses from the same in 234 sec. What is molecular weight of the gas?

Q.15 A space capsule is filled with neon gas at 1.00 atm and 290 K. The gas effuses through a pin-hole into outer space at such a rate that the pressure drops by 0.3 torr/sec

(a) If the capsule were filled with ammonia at the same temperature and pressure, what would be the rate of pressure drop.

(b) If the capsule were filled with 30.0 mol % helium, 20.0 mol % oxygen & 50.0 mol % nitrogen at a total pressure of 1.00 atm & a temp. of 290 K, what would be the corresponding rate of pressure drop.

Q.16 The composition of the equilibrium mixture ($Cl_2 \Leftrightarrow 2\,Cl$) which is attained at 1200 °C is determined by measuring the rate of effusion through a pin hole. It is observed that at 1.8 mm Hg pressure, the mixture effuses 1.16 times as fast as Kr effuses under the same conditions. Calculate the fraction of chlorine molecules dissociated into atoms. [Kr = 84 a. m. u.]

APPLICATION OF CONCEPT OF GASOUS STATE

Q.17 Show that the height at which the atmospheric pressure is reduced to half its value is given by

$$h = \frac{0.6909\,RT}{Mg}$$

Q.18(a)How much H_2 (in mol) is needed to inflate a balloon of radius 3m to a pressure of 1 atmp in an ambient temp at 25^0 C at sea level.

(b) What mass can the balloon lift at sea level, where the density of air is 1·22 Kg m^{-3}.

(c) What would be the pay load if He were used instead of H_2.

Q.19 Calculate the pressure of a barometer on an aeroplane which is at an altitude of 10 Km. Assume the pressure to be 101.325 Kpa at sea level & the mean temperature 243 K. Use the average molar mass of air (80% N_2, 20 % O_2)

Q.20 Automobile air bags are inflated with N_2 gas which is formed by the decomposition of solid sodium azide (NaN_3). The other product is Na - metal. Calculate the volume of N_2 gas at 27°C and 756 Torr formed by the decomposing of 125 gm of sod azide.

Q.21 What will be the temperature difference needed in a hot air balloon to lift 1.0 kg of mass ? Assume that the volume of balloon is 100 m^3, the temperature of ambient air is 25 °C, the pressure is 1 bar, and air is an ideal gas with an average molar mass of 29 g mol^{-1} (hot and cold both).

& 27°c.

Q.22 An iron cylinder contains helium at a pressure of 250 k pa. The cylinder can withstand a pressure of 1×10^6 pa. The room in which cylinder is placed catches fire. Predict whether the cylinder will blow up before it metls or not. [melting point of cylinder = 1800 k]

Q.23 Determine the molar mass of a gas if its pressure is to fall to one-half of its value in a vertical distance of one meter at 298 K.

KINETIC THEORY OF GASEOUS LAW MAXWELL DISTRIBUTION OF SPEEDS

Q.24 The time taken for a given volume of gas E to effuse through a hole is 75 sec. Under identical conditions the same volume of a mix of CO & N_2 (containing 40% of N_2 by volume) effused in 70 seconds. Calculate

(i) the relative mol mass of E, and

(ii) the RMS velocity (in ms^{-1} units) of E at 0^0C.

Q.25 At what temperature in °C, the U_{rms} of SO_2 is equal to the average velocity of O_2 at 27°C.

Q.26 Calculate U_{rms} of molecules of H_2 at 1 atmp density of H_2 is 0.00009 g/cc.

Q.27 A bulb of capacity 1 dm^3 contains 1.03×10^{23} H_2 molecules & pressure exerted by these molecules is 101.325 kPa. Calculate the average square molecular speed and the temperature.

Q.28 The mean kinetic energy of a molecule at 0^0C is 5.621×10^{-14} ergs. Calculate the number of molecules in gm molecule of gas.

Q.29 The density of CO at 273 K and 1 atm is 1.2504 kg m^{-3}. Calculate (a) root mean square speed (b) the average speed and (c) most probable speed.

Q.30 Calculate the temperature values at which the molecules of the first two members of the homologous series, C_nH_{2n+2} will have the same rms speed as CO_2 gas at 770 K. The normal b.p. of n-butane is 273 K. Assuming ideal gas behaviour of n-butane upto this temperature, calculate the mean velocity and the most probable velocity of its molecules at this temperature.

Q.31 Calculate the temperature at which the root mean square velocity, average velocity and most probable velocity of oxygen gas are all equal to 1500 ms^{-1}.

Q.32 Calculate the fraction of N_2 molecules at 101.325 kPa and 300 K whose speeds are in the range of $u_{mp} - 0.005\, u_{mp}$ to $u_{mp} + 0.005\, u_{mp}$.

Q.33 What is the ratio of the number of molecules having speeds in the range of $2u_{mp}$ and $2u_{mp} + du$ to the number of molecules having speeds in the range of u_{mp} and $u_{mp} + du$?

COLLISIONS AMONG GASEOUS MOLECULES

Q.34 At low pressure and high temperature, the vander Waals equation is reduced to

(A) $PV_m = RT$

(B) $(P + a/V_m^2)(V_m - b) = RT$

(C) $P(V_m - b) = RT$

(D) $(P + a/V_m^2)(V_m) = RT$

Q.35 Calculate the mean free path in CO_2 at 27°C and a pressure of 10^{-6} mm Hg. (molecular diameter = 460 pm)

Q.36 Calculate the value of σ, λ, Z_1 and Z_{11} for nitrogen molecules at 25°C and at pressure of 10^{-3} mm Hg. Given that b for nitrogen is 39.1 cm^3 mol^{-1}.

Q.37 A mixture of hydrogen and helium is prepared such that the number of wall collisions per unit time by molecules of each gas is the same. Which gas has the higher concentration?

Q.38 The mean free path of the molecule of a certain gas at 300 K is 2.6×10^{-5} m. The collision diameter of the molecule is 0.26 nm. Calculate
(a) pressure of the gas, and (b) number of molecules per unit volume of the gas.

REAL GAS AND VANDER WAALS EQUATION OF STATE

Q.39 The density of mercury is 13.6 g/cm^3. Estimate the b value.

Q.40 Calculate the pressure exerted by 22 g of carbon dioxide in 0.5 dm^3 at 298.15 K using:
(a) the ideal gas law and (b) vander waals equation. Given:
[a = 363.76 kPa dm^6 mol^{-2} and b = 42.67 cm^3 mol^{-1}]

COMPRESSIBILITY FACTOR

Q.41 The compressibility factor for N_2 at – 50°C and 800 atmp pressure is 1.95 and at 100°C and 200 atmp, it is 1.10. A certain mass of nitrogen occupied one litre at – 50°C and 800 atmp. Calculate the volume occupied by the same quantity of N_2 at 100°C and 200 atmp.

Q.42 At 273.15 K and under a pressure of 10.1325 MPa, the compressibility factor of O_2 is 0.927. Calculate the mass of O_2 necessary to fill a gas cylinder of 100 dm^3 capacity under the given conditions.

BOYLE'S TEMPERATURE CRITICAL PHENOMENON AND INVERSION TEMPERATURE

Q.43 The vander waals constant for O_2 are a = 1.36 atm L^2 mol^{-2} and b = 0.0318 L mol^{-1}. Calculate the temperature at which O_2 gas behaves, ideally for longer range of pressure.

Q.44 The vander Waals constants for gases A, B and C are as follows

Gas	a/dm^6 kPa mol^{-1}	b/dm^3 mol^{-1}
A	405.3	0.027
B	1215.9	0.030
C	607.95	0.032

Which gas has (i) the highest critical temperature, (ii) the largest molecular volume, and (iii) most ideal behaviour around STP?

HEAT CAPACITY

Q.45 One mole of a non linear triatomic gas is heated in a closed rigid container from 500°C to 1500°C. Calculate the amount of energy required if vibrational degree of freedom become effective only above 1000°C.

OTHER EQUATION OF STATE

Q.46 A commercial cylinder contains 6.91 m^3 of O_2 at 15.18 M Pa and 21^0C. the critical constants for O_2 are $T_C = -118.4^0C$, $P_C = 50.1$ atmp. Determine the reduced pressure and reduced temperature for O_2 under these conditions.

Q.47 Show that at low densities, the vander waals equation

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

and the Dieterici's equation

$$p(V_m - b) = RT \exp(-a/RTV_m)$$

give essentially the same value of p.

SOME PROBLEMS ON REAL GAS & VANDER WAALS

Q.48 Calculate from the vander waal's equation, the temperature at which 192 gm of SO_2 would occupy a vol. of 10 dm^3 at 15 atm pressure.[a = 6.7 atm lit^2 mol^2, b = 0.0564 lit mol^{-1}]

Q.49 Calculate the pressure of 15 mol neon at 30° C in a 12 lit container using
(i) the ideal gas equation (ii) the vander waals equation
[a = 0.2107 atm lit^2 mol^{-2}, b = 0.0171 lit mol^{-1}]

Q.50 The molar volume of He at 10.1325 MPa and 273 K is 0.011075 of its molar volume at 101.325 KPa at 273 K.Calculate the radius of helium atom. The gas is assumed to show real gas nature. Neglect the value of a for He.

Q.51 The density of water vapour at 327.6 atm and 776.4 K is 133.2 gm/dm^3.
(a) Determine the molar volume, V_m of water and the compression factor, from above given data.
(b) Calculate Z from the vander waals equation with a = 5.464 L^2 atm mol^{-2} and b = 0.0305 L mol^{-1}

Q.52 N_2 molecule is spherical of radius 100 pm.
(a) What is the volume of molecules is one mole of a gas?
(b) What is the value of vander waal's constant b?
(c) What is the actual volume of the gas at STP?

-Free

EXERCISE # II

Q.1 A 50 litre vessel is equally divided into three parts with the help of two stationary semi permeable membrane (SPM). The vessel contains 60 g H_2 gas in the left chamber, 160 g O_2 in the middle & 140 g N_2 in the right one. The left SPM allows transfer of only H_2 gas while the right one allows the transfer of both H_2 & N_2. Calculate the final ratio of pressure in the three chambers.

Q.2 Militants are hiding at the top of the kargil peak which is 7000 m above the plains. Major of a troop of soldiers wants to send few soldiers to the peak to kill the enemies by balloons, then find the minimum volume of each balloon (volume remain constant throughout the mission) if he attach 10 balloons to each soldier. Given
(i) Change in density in atmosphere is $d = d_0 e^{-Mgh/RT}$
(where d_0 is density at plain and d is density at height 'h')
(ii) M = 29 gm/mole (constant)
(iii) T = 27°C (constant)
(iv) g = 10 m/sec^2
(v) Each balloon contains 10 moles of H_2
(vi) weigth of each soldier is 75 kg.

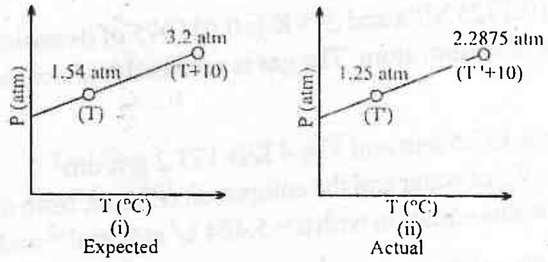
Q.3 There are two vessels of same volume consisting same no of moles of two different gases at same temperature. One of the gas is CH_4 & the other is unknown X. Assuming that all the molecular of X are under random motion whereas in CH_4 except one all are stationary. Calculate Z_1 for X in terms of Z_1 of CH_4. Given that the collision diameter for both the gases are same & $(U_{rms})_x = \frac{1}{\sqrt{6}}(Uav)_{CH_4}$.

Q.4 A mixture of CH_4 & O_2 is used as an optimal fuel if O_2 is present in thrice the amount required theoretically for combustion of CH_4. Calculate number of effusions steps required to convert a mixture containing 1 part of CH_4 in 193 parts mixture (parts by volume). If calorific value (heat evolved when 1 mole is burnt) of CH_4 is 100 cal/mole & if after each effusion 90% of CH_4 is collected, find out what initial mole of each gas in initial mixture required for producing 1000 cal of energy after processing.
[Given $(0.9)^5 = 0.6$]

Q.5 A closed vessel of known volume containing known amount of ideal gaseous substance 'A' was observed for variation of pressure with temperature. The expected graph was to be like as in (i) However actual observations revealed the graph to be like. (ii) The deviation was attributed to polymerisation of gas molecules as $nA(g) \rightleftharpoons A_n(g)$. If it is known that the above reaction gives only 50% yield

a) Calculate the ratio of $\frac{n_{\text{experiment}}}{n_{\text{theoritical}}}$ (where $n_{\text{exp.}}$ = Total no. of gaseous mole acutally present
$n_{\text{theoritical}}$ = Total no. of mole original taken)

(b) Find the value of n to which the gas A is being polymerised into



(i) Expected

(ii) Actual

Q.6 You are told to prepare a closed experimental environment (a box) for student mice. The box volume will be 294 liters (about 10 ft^3) and the entire air volume will be changed every minute. The relative humidity of the air entering the box is to be controlled at 40% at 21°C. What weight of H_2O must be added to the flow of dry air per minute? (Equilibrium vapour pressure for H_2O at $21^0C \simeq 19$ torr). ($R = 0.082$ liter atm mole^{-1}deg^{-1} mol wt: $H_2O = 18$)

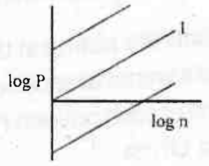
Q.7 Graph between log P (atm) v/s log n is plotted for an ideal gas enclosed in 24.63 litre container at three different temperatures. If $T_1 = \frac{T_2}{3} = 2T_3$ [where T_1, T_2, T_3 are temperature in kelvin of graph 1, 2 & 3] then

(a) Mention graph 2 & graph 3.

(b) Calculate T_1, T_2, T_3.

(c) Calculate slope of graphs 1, 2 & 3.

(d) Calculate intercept of graphs 2 & 3.



Q.8 During one of his adventure, Chacha chaudhary got trapped in an underground cave which was sealed two hundred year back. The air inside the cave was poisonous, having some amount of carbon monoxide in addition to O_2 and N_2. Sabu, being huge could not enter into the cave, so in order to save chacha choudhary be started sucking the poisonous air out of the cave by mouth. Each time, he filled his lunge with cave air and exhaled it out in the surroundings. In the mean time fresh air from surrounding effused into the cave till the pressure was again one atmosphere. Each time Sabu sucked out some air, the pressure in the cave dropped to half of its initial value of one atmosphere.
If the initial sample of air from the cave contain 5% by volume CO.
If the safe level of CO in the atmosphere is less than 0.001% by volume how many times does Sabu need to suck out air in order to save Chacha chaudhary.

Q.9 The density of the vapour of a substance at 1 atm pressure and 500 K is 0.36 Kg m^{-3}. The vapour effuses through a small hole at a rate of 1.33 times faster than oxygen under the same condition.

(a) Determine
(i) molecular weight ;
(ii) molar volume at given condition ;
(iii) compression factor (z) of the vapour and
(iv) which forces among the gas molecules are dominating, the attractive or the repulsive

(b) If the vapour behaves ideally at 1000K, determine the average translational K.E. of a molecule

Q.10 A compound exists in the gaseous state both as a monomer (A) and dimer (A_2). The molecular weight of the monomer is 48. In an experiment, 96 g of the compound was confined in a vessel of volume 33.6 litres and heated to 273^0 C. Calculate the pressure developed, if the compound exists as a dimer to the extent of 50 per cent by weight, under these conditions. (R = 0.082)

Q.11 The following reaction is carried out in a flask at 101325 pascal and 383 k with the initial concentration of CH_4, O_2 as 0.01 & 0.03 mole.

$$2\,CH_4 + 3\,O_2 \longrightarrow 2\,CO + 4\,H_2O.$$

All reactants and products are gases at 383 k. A shortwhile after the completion of reaction the flask is cooled to 283 k at which H_2O is completely condensed. Calculate :
(a) Volume of flask.
(b) Total pressure and partial pressure of various species at 383 k, 283 k.
(c) number of molecules of various substance before and after reaction.

Q.12 A closed vertical cylinder is divided into two parts by a frictionless piston, each part contains 1 mole of air. At 27 °C the volume of the upper part is 4 times than that of the lower part. Calculate the temperature when volume of the upper part will be three times than that of the lower part.

Q.13 A water gas mixture has the compsition by volume of 50% H_2, 45% CO and 5% CO_2.
(i) Calculate the volume in litres at STP of the mixture which on treatment with excess steam will contain 5 litres of H_2. The stoichiometry for the water gas shift reaction is

$$CO + H_2O \rightarrow CO_2 + H_2$$

(ii) Find the density of the water gas mixture in kg/m^3.
(iii) Calculate the moles of the absorbants KOH, $Ca(OH)_2$ and ethanolamine.
$HO{-}CH_2{-}CH_2{-}NH_2$ required respectively to collect the CO_2 gas obtained.

EXERCISE # III

Q.1 A mixture of ideal gases is cooled upto liquid He temperature (4.22 K) to form an ideal solution. Is this statement **true** or **false**. Justify your answer in not more than two lines. **[JEE 1996]**

Q.2 The ratio between the r. m. s. velocity of H_2 at 50 K and that of O_2 at 800 k is : **[JEE 1996]**
(A) 4 (B) 2 (C) 1 (D) 1/4

Q.3 X ml of H_2 gas effuses through a hole in a container in 5 sec. The time taken for the effusion of the same volume of the gas specified below under identical conditions is : **[JEE 1996]**
(A) 10 sec, He (B) 20 sec, O_2 (C) 25 sec, CO (D) 55 sec, CO_2

Q.4 One mole of N_2O_4 (g) at 300 k is kept in a closed container under one atmp. It is heated to 600 k when 20 % by mass of N_2O_4 (g) decomposes to NO_2 (g). The resultant pressure is : **[JEE 1996]**
(A) 1.2 atm (B) 2.4 atm (C) 2.0 atm (D) 1.0 atm

Q.5 The absolute temperature of an ideal gas is ______ to/than the average kinetic energy of the gas molecules. **[JEE 1997]**

Q.6 One way of writing the equation for state for real gases is,

$$P\bar{V} = RT\left[1 + \frac{B}{\bar{V}} + ...\right] \quad \text{where } B \text{ is a constant.}$$

Derive an approximate expression for 'B' in terms of Vander Waals constant 'a' & 'b'. **[JEE 1997]**

Q.7 Calculate the total pressure in a 10 litre cylinder which contains 0.4 g He, 1.6 g oxygen and 1.4 g of nitrogen at 27 °C. Also calculate the partial pressure of He gas in the cylinder. Assume ideal behavious for gases. **[JEE 1997]**

Q.8 According to Graham's law, at a given temperature the ratio of the rates of diffusion $\frac{r_A}{r_B}$ of gases A and B is given by : **[JEE 1998]**

(A) $\frac{P_A}{P_B}\left(\frac{M_A}{M_B}\right)^{1/2}$ (B) $\left(\frac{M_A}{M_B}\right)\left(\frac{P_A}{P_B}\right)^{1/2}$ (C) $\frac{P_A}{P_B}\left(\frac{M_B}{M_A}\right)^{1/2}$ (D) $\frac{M_A}{M_B}\left(\frac{P_B}{P_A}\right)^{1/2}$

Q.9 An evacuated glass vessel weighs 50.0 g when empty, 148.0 gm when filled with a liquid of density 0.98 g /mL and 50.5 g when filled with an ideal gas at 760 mm Hg at 300 k. Determine the molecular weight of the gas. **[JEE 1998]**

Q.10 Using Vander Waals equation, calculate the constant "a" when 2 moles of a gas confined in a 4 litre flask exerts a pressure of 11.0 atmp at a temperature of 300 k. The value of "b" is 0.05 litre mol^{-1}. **[JEE 1998]**

Q.11 The pressure exerted by 12 g of an ideal gas at temperature t °C in a vessel of volume V is one atmp. When the temperature is increased by 10 degrees at the same volume, the pressure increases by 10 %. Calculate the temperature 't' and volume 'V'. [molecular weight of gas = 120] **[JEE 1999]**

Q.12 One mole of N_2 gas at 0.8 atmp takes 38 sec to diffuse through a pin hole, whereas one mole of an unknown compound of Xenon with F at 1.6 atmp takes 57 sec to diffuse through the same hole. Calculate the molecular formula of the compound. **[JEE 1999]**

Q.13 A gas will approach ideal behaviour at : **[JEE 1999]**
(A) low temperature and low pressure (B) low temperature and high pressure
(C) low pressure and high temperature (D) high temperature and high pressure.

Q.14 The compressibility of a gas is less than unity at STP. Therefore **[JEE 2000]**
(A) $V_m > 22.4$ L (B) $V_m < 22.4$ L (C) $V_m = 22.4$ L (D) $V_m = 44.8$ L

Q.15 The r.m.s. velocity of hydrogen is $\sqrt{7}$ times the r.m.s. velocity of nitrogen. If T is the temperature of the gas : **[JEE 2000]**

(A) $T(H_2) = T(N_2)$ (B) $T(H_2) > T(N_2)$

(C) $T(H_2) < T(N_2)$ (D) $T(H_2) = \sqrt{7}\ T(N_2)$

Q.16 The pressure of a fixed amount of an ideal gas is proportional to its temperature. Frequency of collision and their impact both increase in proportion to the square root of temperature. True/False. **[JEE 2000]**

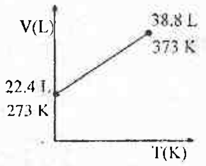
Q.17 Calculate the pressure exerted by one mole of CO_2 gas at 273 k, if the Vander Waals constant $a = 3.592\ dm^6\ atm\ mol^{-2}$. Assume that the volume occupied by CO_2 molecules is negligible. **[JEE 2000]**

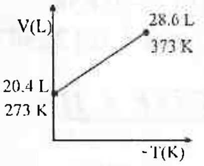
Q.18 The root mean square velocity of an ideal gas at constant pressure varies with density as

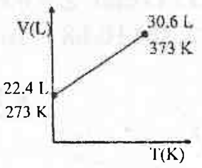
(A) d^2 (B) d (C) $d^{1/2}$ (D) $1/d^{1/2}$ **[JEE 2001]**

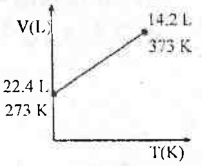
Q.19 The compression factor (compressibility factor) for one mole of a vander Waals gas at 0^0C and 100 atmosphere pressure is found to be 0.5. Assuming that the volume of a gas molecule is negligible, calculate the vander waals constant 'a'. **[JEE 2001]**

Q.20 Which one of the following V, T plots represents the behaviour of one mole of an ideal gas at one atmp?

(A)


(B)


(C)


(D)


[JEE 2002]

Q.21 The density of the vapour of a substance at 1 atm pressure and 500 K is 0.36 Kg m^{-3}. The vapour effuses through a small hole at a rate of 1.33 times faster than oxygen under the same condition.

(a) Determine

(i) mol. wt.; (ii) molar volume; (iii) compression factor (z) of the vapour and

(iv) which forces among the gas molecules are dominating, the attractive or the repulsive

(b) If the vapour behaves ideally at 1000K, determine the average translational K.E. of a molecule. **[JEE 2002]**

Q.22 The average velocity of gas molecules is 400 m/sec. Calculate its (rms) velocity at the same temperature. **[JEE 2003]**

Q.23 C_V value of He is always 3R/2 but C_V value of H_2 is 3R/2 at low temperature and 5R/2 at moderate temperature and more than 5R/2 at higher temperature explain in two to three lines. **[JEE 2003]**

Q.24 Positive deviation from ideal behaviour takes place because of **[JEE 2003]**

(A) molecular interaction between atoms and $\frac{PV}{nRT} > 1$

(B) molecular interation between atoms and $\frac{PV}{nRT} < 1$

(C) finite size of atoms and $\frac{PV}{nRT} > 1$

(D) finite size of atoms and $\frac{PV}{nRT} < 1$

Q.25 For a real gas obeying van der Waal's equation a graph is plotted between PV_m (y-axis) and P(x-axis) where V_m is molar volume. Find y-intercept of the graph. **[JEE 2004]**

ANSWER KEY

EXERCISE # I

Q.1 P = 0.062 atm , T = 75 K Q.2 0.08 cm Q.3 3.8×10^3 kpa
Q.4 16.07 gm ; 12 dm^3 Q.5 280 ml/min Q.6 6 atm, No Q.7 66.74 atm
Q.8 $P_{total} = 27.54\times10^5\ N/m^2$, $P_{final} = 19.66\times10^5 N/m^2$ Q.9 2.19 atmp Q.10 228
Q.11 50.8 cm Q.12 16 min Q.13 yes Q.14 46.6
Q.15 (a) 0.33 Torr/sec , (b) 0.29 Torr/sec Q.16 0.137 Q.18 4.62×10^3 moles, 128.79 Kg, 119.55Kg
Q.19 25.027 Kpa Q.20 71.4 L Q.21 2.53°C Q.22 yes
Q.23 175.133 kg mol^{-1} Q.24 32.14 g / mol , 460.28 m/s Q.25 236.3°C
Q.26 183,800 cm/sec Q.27 $8.85\times10^5 (m/s)^2$; 71.27 K
Q.28 6.06×10^{23} molecules mol^{-1} Q.29 U_{RMS} = 493 m/s ,U_{mp} = 403m/s ,U_{av} =454.4 m/s
Q.30 280 K 525 K , 3.157 $\times10^2$ m/sec, 2.798×10^2 m/sec
Q.31 T_{RMS} = 2886 K, T_{av} = 3399 K, T_{mp} =4330K Q.32 8.303×10^{-3}
Q.33 0.199 Q.34 A Q.35 3.93×10^3 cm
Q.36 157.09 pm, 7.015 cm, 6742 s^{-1}, $1.09\times10^{17}\ cm^{-1}s^{-1}$ Q.37
Q.38 (a) $1.281\times10^{23}\ m^{-3}$, (b) 5.306×10^2 Pa Q.39 58.997 cm^3
Q.40 (a) 2.479×10^3 kPa, (b) 2225.55 kPa Q.41 3.77 L Q.42 15.40 kg
Q.43 521 K Q.44 (i) B, (ii) C, (iii) A Q.45 4500 RJ Q.46 π = 2.99 , θ = 1.90
Q.48 350.5°C Q.49 (i) 31.1 atm, (ii) 31.4 atm Q.50 $r = 1.33\times10^{-8}$
Q.51 (a) Molar vol = 0.1353 L/mol; Z = 0.6957, (b) Z = 0.658
Q.52 (a) 2.52×10^{-3} l mol^{-1}, (b) $10.08\times10^{-3}\ dm^3\ mol^{-1}$, (c) 22397.48 cm^3

EXERCISE # II

Q.1 4 : 7 : 5 Q.2 ~~13.580 lit.~~ [illegible] Q.3 $\frac{2\sqrt{2}}{3\sqrt{\pi}}Z_1$
Q.4 10 Steps Q8 → 13 lines Q.5 (a) 0.625, (b) 4. Q.6 2.2 g
Q.9 (a) (i) 18 g/mol, (ii) 50 L mol^{-1}, (iii) 1.22, (iv) repulsive, (b) 2.07×10^{-20} J/molecules Q.10 2 atmp
Q.11 (a) 1.257 L ; (b) At 383 K P_T = 113.99 kpa , P_{O_2} = 38 kpa , P_{CO} = 25.33 kpa , P_{H_2O} = 50.66 kpa,
At 283 K P_T = 46.81 kpa , P_{O_2} = 28.086 kpa , P_{CO} = 18.724 kpa , P_{CH_4} = 0
(c) Before reaction : $CH_4 = 0.01\ N_A$, $O_2 = 0.03\ N_A$
After reaction : $O_2 = 0.015\ N_A$, $CO = 0.01\ N_A$, $H_2O = 0.02\ N_A$
Q.12 421.9 K
Q.13 (i) 5.263 L ,(ii) 0.7 Kg/m^3 ,(iii) K_{OH}=0.2348 moles, $Ca(OH)_2$=0.1174 moles, ethanolamine=0.2348 moles

EXERCISE # III

Q.1 yes it is false statement Q.2 C Q.3 B Q.4 B Q.5 directly proportional
Q.6 $B = \left(b - \frac{\alpha}{RT}\right)$ Q.7 0.492 atmp ; 0.246 atmp Q.8 C Q.9 123
Q.10 6.46 atmp $L^2\ mol^{-2}$ Q.11 –173°C , 0.82 L Q.12 XeF_4 Q.13 C
Q.14 B Q.15 C Q.16 Both statements are correct Q.17 0.9928 atmp
Q.18 D Q.19 1.2544 atmp $L^2\ mol^{-2}$ Q.20 C
Q.21 (a) (i) 18.1 g/mol , (ii) 50.25 L mol^{-1} , (iii) 1.224 , (iv) repulsive Q.22 434.17 m/sec
Q.23 Since H_2 is diatomic and He is monoatomic degree of freedom for mono is 3 and only translational but for diatomic, vibrational and rotational are also to be considered
Q.24 C (25) R7

BANSALCLASSES

TARGET IIT JEE 2007

INORGANIC CHEMISTRY

XII(ABCD) & XIII(XYZ)

HEATING EFFECTS

HEATING EFFECTS

Heating effect of carbonate & bicarbonate salts

All carbonates except (Na, K, Rb, Cs) decompose on heating giving CO_2

$Li_2CO_3 \longrightarrow Li_2O + CO_2$

$MCO_3 \longrightarrow MO + CO_2$ [M = Be, Mg, Ca, Sr, Ba]

$$\underset{\text{Yellow}}{Ag_2CO_3} \longrightarrow \underset{\text{Black}}{2Ag} + CO_2 + \frac{1}{2}O_2$$

$$\underbrace{Cu(OH)_2.CuCO_3}_{\text{Basic Cu(II) carbonate}} \xrightarrow{\Delta} 2CuO + CO_2 + H_2O$$

$$\underset{\text{white}}{ZnCO_3} \longrightarrow \underset{\substack{\text{Yellow(hot)}\\ \text{white(cold)}}}{ZnO} + CO_2$$

$$PbCO_3 \longrightarrow \underset{\text{Yellow}}{PbO} + CO_2 \quad \left[\underset{\text{White}}{2PbCO_3.Pb(OH)_2} \xrightarrow{450°C} Pb_3O_4 + CO + CO_2 + H_2O\right]$$

$HgCO_3 \longrightarrow Hg + \frac{1}{2}O_2\uparrow + CO_2$

$(NH_4)_2CO_3 \longrightarrow 2NH_3 + H_2O + CO_2$

All bicarbonates decompose to give carbonates and CO_2. eg.

$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O$

[General reaction $2HCO_3^- \longrightarrow CO_3^{2-} + H_2O + CO_2$]

Heating effect of ammonium salts

$(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$

$NH_4NO_2 \longrightarrow N_2 + 2H_2O$

$NH_4NO_3 \longrightarrow N_2O + 2H_2O$

$2NH_4\,ClO_4 \longrightarrow N_2 + Cl_2 + 2O_2 + 4H_2O$

$2NH_4\,IO_3 \longrightarrow N_2 + I_2 + O_2 + 4H_2O$

[If anionic part is oxdising in nature, then N_2 will be the product (some times N_2O).]

$(NH_4)_2HPO_4 \longrightarrow HPO_3 + H_2O + 2NH_3$

$(NH_4)_2SO_4 \longrightarrow 2NH_3 + H_2SO_4$

$2(NH_3)_3PO_4 \longrightarrow 2NH_3 + P_2O_5 + 3H_2O$

$(NH_4)_2CO_3 \longrightarrow 2NH_3 + H_2O + CO_2$

[If anionic part weakly oxidising or non oxidising in nature then NH_3 will be the product.]

Heating effect of nitrate salts

$MNO_3 \longrightarrow KNO_2 + \frac{1}{2}O_2$

[M = Na, K, Rb, Cs]

$2LiNO_3 \longrightarrow Li_2O + 2NO_2 + \frac{1}{2}O_2$

$2M(NO_3)_2 \longrightarrow 2MO + 4NO_2 + O_2$

[M = all bivalent metals eg. Zn^{+2}, Mg^{+2}, Sr^{+2}, Ca^{+2}, Ba^{+2}, Cu^{+2}, Pb^{+2}]

$Hg(NO_3)_2 \longrightarrow Hg + 2NO_2 + O_2$; $2AgNO_3 \longrightarrow 2Ag + 2NO_2 + O_2$

Heating effect of Halides salts

$2FeCl_3 \longrightarrow 2FeCl_2 + Cl_2$; $AuCl_3 \longrightarrow AuCl + Cl_2$

$Hg_2Cl_2 \longrightarrow HgCl_2 + Hg$; $NH_4Cl \longrightarrow NH_3 + HCl$

$Pb(SCN)_4 \longrightarrow Pb(SCN)_2 + (SCN)_2$

$PbCl_4 \longrightarrow PbCl_2 + Cl_2$ [$PbBr_2 \longrightarrow PbBr_2 + Br_2$ & PbI_4 does not exists]

Heating effect of hydrated chloride salts

$$MgCl_2 . 6H_2O \xrightarrow{\Delta} MgO + 2HCl + 5H_2O$$
$$2FeCl_3 . 6H_2O \longrightarrow Fe_2O_3 + 6HCl + 9H_2O$$
$$2AlCl_3 . 6H_2O \longrightarrow Al_2O_3 + 6HCl + 9H_2O$$
$$\underset{\text{Pink}}{CoCl_2.6H_2O} \xrightarrow[-2H_2O]{50°C} \underset{\text{Pink}}{CoCl_2.4H_2O} \xrightarrow[-2H_2O]{58°C} \underset{\text{Red violet}}{CoCl_2.2H_2O} \xrightarrow[-2H_2O]{140°C} \underset{\text{Blue}}{CoCl_2}$$

Heating effect of hydrated Sulphate salts

$$\underset{\text{Blue vitriol}}{CuSO_4.5H_2O} \xrightarrow[-4H_2O]{100°C} \underset{\text{Bluish White}}{CuSO_4.H_2O} \xrightarrow[-H_2O]{220°C} \underset{\text{White}}{CuSO_4} \xrightarrow{>800°C} CuO + SO_2 + \frac{1}{2}O_2$$
$$CuSO_4 \xrightarrow{750°C} \underset{\text{Black}}{CuO} + SO_3$$

$$\underset{\text{Green Vitriol}}{FeSO_4.7H_2O} \xrightarrow[-7H_2O]{300°C} FeSO_4 \xrightarrow{\Delta} \underset{Fe_2O_3}{\cancel{Fe_2SO_3}} + SO_2 + SO_3 \text{ (very important)}$$

$$Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 + 3SO_3$$

$$\underset{\text{epsom salt}}{MgSO_4.7H_2O} \xrightarrow[-7H_2O]{\Delta} MgSO_4 \downarrow \text{[Same as } ZnSO_4\text{]}$$

$$\underset{\text{gypsum}}{CaSO_4.2H_2O} \xrightarrow{120°C} \underset{\text{Plaster of pairs}}{(CaSO_4.\frac{1}{2}H_2O)} + 1\frac{1}{2}H_2O$$

$$CaSO_4.2H_2O \xleftarrow{+1\frac{1}{2}H_2O} \text{Plaster of pairs} \xrightarrow{\Delta} \underset{\text{Dead burnt}}{CaSO_4} + \frac{1}{2}H_2O$$

$$Na_2S_2O_3.5H_2O \xrightarrow{220°C} Na_2S_2O_3 + 5H_2O$$
$$Na_2S_2O_3 \xrightarrow[\text{(From 4 moles)}]{\Delta} 3Na_2SO_4 + Na_2S_5$$

$$ZnSO_4.7H_2O \xrightarrow{70°C} ZnSO_4.6H_2O \xrightarrow{70°-200°C} ZnSO_4.H_2O \xrightarrow{>200°C} ZnSO_4$$
$$ZnSO_4 \xrightarrow{\Delta\ >800°C} ZnO + SO_2 + \frac{1}{2}O_2$$

$$2NaHSO_3 \longrightarrow Na_2S_2O_5 + H_2O$$
$$Na_2S_2O_5 \xrightarrow{\Delta} Na_2SO_3 + SO_2$$
$$Na_2SO_3 \longrightarrow Na_2S + Na_2SO_4$$

$$2NaHSO_4 \xrightarrow{\Delta} Na_2SO_4 + H_2O + SO_3$$

Heating effect of Oxide salts

$2Ag_2O \xrightarrow[300°C]{\Delta} 4Ag + O_2$; $\underset{\text{yellow}}{HgO} \xrightarrow[400°C]{\Delta} \underset{\text{red}}{HgO} \xrightarrow[\text{strong heating}]{\Delta} Hg + \frac{1}{2}O_2$

$PbO_2 \xrightarrow{\Delta} PbO + \frac{1}{2}O_2$; $\underset{\text{Red lead}}{Pb_3O_4} \xrightleftharpoons[340°C]{>470°C} \underset{\text{Litharge}}{6PbO} + O_2$

$3MnO_2 \xrightarrow{900°C} Mn_3O_4 + O_2$; $\underset{\text{white}}{ZnO} \xrightleftharpoons[\text{Cold}]{\text{Hot}} \underset{\text{yellow}}{ZnO}$

$2CrO_5 \longrightarrow Cr_2O_3 + \frac{1}{2}O_2$; $\underset{\text{(Massicot)}}{\underset{\text{yellow}}{PbO}} \xrightleftharpoons[\text{Cold}]{\text{Hot}} \underset{\text{(Litharge)}}{\underset{\text{Red}}{PbO}}$

$2CrO_3 \xrightarrow{420°C} Cr_2O_3 + \frac{3}{2}O_2$; $I_2O_5 \longrightarrow I_2 + \frac{5}{2}O_2$

Heating effect of dichromate & chromate salts

$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O$

$K_2Cr_2O_7 \xrightarrow{\Delta} 2K_2CrO_4 + Cr_2O_3 + \frac{7}{2}O_2$

Heating effect of phosphate salts

$\underset{1^\circ \text{ phosphate salt}}{NaH_2PO_4} \xrightarrow{\Delta} H_2O + NaPO_3$

$\underset{2^\circ \text{ phosphate salt}}{Na_2HPO_4} \xrightarrow{\Delta} H_2O + Na_2P_2O_7$

$\underset{3^\circ \text{ phosphate salt}}{Na_3PO_4} \xrightarrow{\Delta} \text{No effect}$

$Na(NH_4)HPO_4.4H_2O \xrightarrow[-4H_2O]{\Delta} NaNH_4HPO_4 \xrightarrow{\text{High temp.}} NaPO_3 + NH_3 + H_2O$

$2Mg(NH_4)PO_4 \xrightarrow{\Delta} Mg_2P_2O_7 + 2NH_3 + H_2O$

Heating effect of Acids

$2HNO_3 \xrightarrow{\Delta} H_2O + 2NO_2 + \frac{1}{2}O_2$

$H_2SO_4 \xrightarrow{444°C} H_2O + SO_3$

$H_2SO_4 \xrightarrow{>800°C} H_2O + SO_2 + \frac{1}{2}O_2$

$3H_2SO_3 \longrightarrow 2H_2SO_4 + S\downarrow + H_2O$
$3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$
$HClO_2 \longrightarrow HClO_4 + ClO_2 + H_2O$
$3HOCl \longrightarrow 2HCl + HClO_3$
$4H_3PO_3 \xrightarrow[200°C]{\Delta} 3H_3PO_4 + PH_3$
$2H_3PO_2 \longrightarrow H_3PO_4 + PH_3$
$2NaH_2PO_2 \longrightarrow Na_2HPO_4 + PH_3$

Undergoes dispropor-tionation reaction

$H_3PO_4 \xrightarrow{220°C} H_4P_2O_7 \xrightarrow{320°C} 4HPO_3 \xrightarrow{>320°C} 2P_2O_5 + 2H_2O$

$H_3BO_3 \xrightarrow{100°C} 4HBO_2 \xrightarrow{140°C} H_2B_4O_7 \xrightarrow[\text{hot}]{\text{Red}} 2B_2O_3 + H_2O$

$H_2C_2O_4 \xrightarrow{\Delta} H_2O + CO + CO_2$

Heating effects of acetate, formate, oxalate salts

$CH_3CO_2K \xrightarrow{\Delta} K_2CO_3 + CH_3COCH_3$
$Pb(OAc)_2 \xrightarrow{\Delta} PbO + CO_2 + CH_3COCH_3$
$Mg(OAc)_2 \longrightarrow MgO + CO_2 + CH_3COCH_3$
$Be(OAc)_2 \longrightarrow BeO + CO_2 + CH_3COCH_3$
$Ca(OAc)_2 \longrightarrow CaCO_3 + CH_3COCH_3$
$Ba(OAc)_2 \longrightarrow BaCO_3 + CH_3COCH_3$
$HCO_2Na \xrightarrow{350°C} Na_2C_2O_4 + H_2\uparrow$
$2HCOOAg \xrightarrow{\Delta} HCOOH + 2Ag + CO_2$
$(HCOO)_2Hg \longrightarrow HCOOH + Hg + CO_2$

$Na_2C_2O_4 \longrightarrow Na_2CO_3 + CO$
$SnC_2O_4 \xrightarrow{\Delta} SnO + CO_2 + CO$
$FeC_2O_4 \longrightarrow FeO + CO + CO_2$
$Ag_2C_2O_4 \xrightarrow{\Delta} 2Ag + 2CO_2$
$HgC_2O_4 \longrightarrow Hg + 2CO_2$

BANSAL CLASSES

TARGET IIT JEE 2007

PHYSICAL CHEMISTRY

XII (ALL)

IONIC EQUILIBRIUM

" A SPECIALLY DESIGNED KIT FOR LEARNING."

CONTENTS

THE KEY	⟶	Basic principles of subjects. An outline of the topics to be discussed in class lectures.
THE ATLAS	⟶	Basic layout of subject. A route map correlating different subtopics in coherent manner.
GLOSSARY	⟶	A list of important terms in brief
EXERCISE I	⟶	Introductory problems to get first hand experience of problem solving.
PROFICIENCY TEST	⟶	To check you newly acquired concepts.
BEWARE OF SNAKES	⟶	A list of common mistakes made by students's.
EXERCISE II	⟶	A collection of good problems.
EXERCISE III	⟶	Test your objective skill.
EXERCISE IV	⟶	A collection of previous ten years JEE problems.

THE KEY

Fundamentals of Acids, Bases & Ionic Equilibrium

Acids & Bases

When dissolved in water, acids release H^+ ions, base release OH^- ions.

Arrhenius Theory

When dissolved in water, the substances which release

(i) H^+ ions are called acids (ii) OH^- ions are called bases

Bronsted & Lowry Concept

Acids are proton donors, bases are proton acceptors

Note that as per this definition, water is not necessarily the solvent.

When a substance is dissolved in water, it is said to react with water e.g.

$HCl + H_2O \rightarrow H_3O^+ + Cl^-$; HCl donates H^+ to water, hence acid.

$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$; NH_3 takes H^+ from water, hence base.

For the backward reaction, NH_4^+ donates H^+, hence it is an acid; OH^- accepts H^+, hence it is base.

NH_3 (base) & NH_4^+ (acid) from conjugate acid base pair.

Conjugate acid and bases

To get *conjugate acid* of a given species add H^+ to it. e.g. conjugate acid of N_2H_4 is $N_2H_5^+$.

To get *conjugate base* of any species subtract H^+ from it. e.g. Conjugate base of NH_3 is NH_2^-.

Note: Although Cl^- is conjugate base of HCl, it is not a base as an independent species. In fact, anions of all strong acid like Cl^-, NO_3^-, ClO_4^- etc. are neutral anions. Same is true for cations of strong bases like K^+, Na^+, Ba^{++} etc. When they are dissolved in water, they do not react with water (i.e. they do not undergo hydrolysis) and *these ions* do not cause any change in pH of water (others like CN^- do).

Some examples of :

Basic Anions : CH_3COO^-, OH^-, CN^- (Conjugate bases of weak acids)

Acid Anions: HSO_3^-, HS^- etc. Note that these ions are *amphoteric*, i.e. they can behave both as an acid and as a base. e.g. for $H_2PO_4^-$:

$HS^- + H_2O \rightleftharpoons S^{2-} + H_3O^+$ (functioning as an acid)

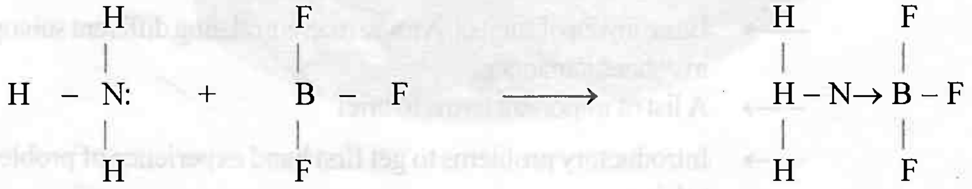
$HS^- + H_2O \rightleftharpoons H_2S + OH^-$ (functioning as a base)

Acid Cations : NH_4^+, H_3O^+ etc.(Conjugate acids of weak bases)

Note : Acid anions are rare.

Lewis Concept : Acids are substances which accept a pair of electrons to form a coordinate bond and bases are the substances which donate a pair of electrons to form a coordinate bond.

e.g.



$$H-\overset{H}{\underset{H}{N}}: + \overset{F}{\underset{F}{B}}-F \longrightarrow H-\overset{H}{\underset{H}{N}}\rightarrow\overset{F}{\underset{F}{B}}-F$$

(Lewis base) (Lewis acid)

Important : $Ca + S \rightarrow Ca^{2+} + S^{2-}$ is not a Lewis acid–base reaction since dative bond is not formed.

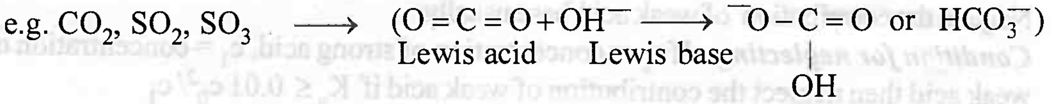
Lewis Acids : As per Lewis concept, following species can acts as Lewis Acids :

(i) Molecules in which central atom has *incomplete octet.* (e.g. BF_3, $AlCl_3$ etc.)

(ii) Molecules which have a central atom with empty d– orbitals (e.g. SiX_4, GeX_4, PX_3, $TiCl_4$ etc.)

(iii) *Simple Cations:* Though all cations can be expected to be Lewis acids, Na^+, Ca^{++}, K^+ etc. show no tendency to accept electrons. However H^+, Ag^+ etc. act as Lewis acids.

(iv) Molecules having multiple bond between atoms of dissimilar electronegativity.



$$\text{e.g. } CO_2, SO_2, SO_3 \longrightarrow (\underset{\text{Lewis acid}}{O=C=O} + \underset{\text{Lewis base}}{OH^-} \longrightarrow {}^{-}O-\underset{\underset{OH}{|}}{C}=O \text{ or } HCO_3^-)$$

Lewis bases are typically :

(i) Neutral species having at least one lone pair of electrons.

$$\text{e.g. } \ddot{N}H_2-\ddot{N}H_2, R-\ddot{\underset{..}{O}}-H$$

(ii) Negatively charged species (anions). e.g. CN^-, OH^-, Cl^- etc.

pH and pOH $pH = -\log_{10}[H_3O^+]$, $pOH = -\log_{10}[OH^-]$

Note : * pH of very dilute (~ 10^{-8}M or Lower) acids (or bases) is nearly 7 (not simply −log[acid] etc. due to ionization of water.

* pH of strong acids with concentration > 1M is never negative. It is zero only.

* At 25°C, if pH = 7, then solution is neutral, pH > 7 than solution is basic.

Autoprotolysis of water (or any solvent)

Autoprotolysis (or self–ionization) constant $(K_w) = [H_3O^+][OH^-]$

Hence, $pH + pOH = pK_w$ at all temperatures

Condition of neutrality $[H_3O^+] = [OH^-]$ (for water as solvent)

At 25°C, $K_W = 10^{-14}$. K_W increases with increase in temperature. Accordingly, the neutral point of water (pH = 7 at 25°C) also shifts to a value lower than 7 with increase in temperature.

Important: $K_W = 10^{-14}$ is a value at (i) 25°C (ii) for water only. If the temperature changes or if some other solvent is used, autoprotolysis constant will not be same.

Ionisation Constant

* For dissociation of weak acids (eg. HCN), $HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$ the equilibrium constant expression is written as $K_a = \dfrac{[H_3O^+][CN^-]}{[HCN]}$

* For the Polyprotic acids (e.g. H_3PO_4), sucessive ionisation constants are denoted by K_1, K_2, K_3 etc. For H_3PO_4,

$$K_1 = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} \qquad K_2 = \frac{[H_3O^+][HPO_4^{2-}]}{[H_3PO_4^-]} \qquad K_3 = \frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]}$$

Similarly, K_b denotes basic dissociation constant for a base.

Also, $pK_a = -\log_{10}K_a$, $pK_b = -\log_{10}K_b$

Some Important Results: $[H^+]$ concentration of

Case (i) A weak acid in water

(a) if $\alpha = \sqrt{\dfrac{K_a}{C}}$ is < 0.1, then $[H^+] \approx \sqrt{K_a c_0}$.

(b) **General Expression :** $[H^+] = 0.5(-K_a + \sqrt{K_a^2 + 4K_a c_o})$

Similarly for a weak base, substitute $[OH^-]$ and K_b instead of $[H^+]$ and K_a respectively in these expressions.

Case (ii)(a) A weak acid and a strong acid $[H^+]$ is entirely due to dissociation of strong acid

(b) **A weak base and a strong base** $[H^+]$ is entirely due to dissociation of strong base

Neglect the contribution of weak acid/base usually.

Condition for neglecting : If c_0 = concentration of strong acid, c_1 = concentration of weak acid then neglect the contribution of weak acid if $K_a < 0.01\, c_0^2/c_1$

Case (iii) Two (or more) weak acids

Proceed by the general method of applying two conditions

(i) of electroneutrality (ii) of equilibria.

The accurate treatement yields a cubic equation. Assuming that acids dissociate to a negligible extent [i.e. $c_0 - x \approx c_0$] $[H^+] = (K_1c_1 + K_2c_2 + ... + K_w)^{1/2}$

Case (iv) When dissociation of water becomes significant:

Dissociation of water contributes significantly to $[H^+]$ or $[OH^-]$ only when for

(i) strong acids (or bases) : $10^{-8}M < c_0 < 10^{-6}M$. Neglecting ionisation of water at $10^{-6}M$ causes 1% error (approvable). Below $10^{-8}M$, contribution of acid (or base) can be neglected and pH can be taken to be practically 7.

Weak acids (or bases) : When $K_ac_0 < 10^{-12}$, then consider dissociation of water as well.

HYDROLYSIS

* ***Salts of strong acids and strong bases*** do not undergo hydrolysis.

* ***Salts of a strong acids and weak bases*** give an acidic solution. e.g. NH_4Cl when dissolved, it dissociates to give NH_4^+ ions and $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$.

$K_h = [NH_3][H_3O^+] / [NH_4^+] = K_w/K_b$ of conjugate base of NH_4^+

Important! In general : K_a(of an acid)xK_b(of its conjugate base) = K_w

If the degree of hydrolysis(h) is small (<<1), $h = \sqrt{K_hc_0}$.

Otherwise $h = \dfrac{-K_h + \sqrt{K_h^2 + 4K_hc_0}}{2c_0}$, $[H^+] = c_0h$

* ***Salts of strong base and weak acid*** give a basic solution (pH>7) when dissolved in water, e.g. NaCN, $CN^- + H_2O \rightleftharpoons HCN + OH^-$ $[OH^-] = c_0h$, $h = \sqrt{K_hc_0}$

* ***Salts of weak base and weak acid***

Assuming degree of hydrolysis to be same for the both the ions,

$K_h = K_w / (K_a.K_b)$, $[H^+] = [K_a\, K_w/K_b]^{1/2}$

Note: Exact treatment of this case is difficult to solve. So use this assumption in general cases. Also, degree of anion or cation will be much higher in the case of a salt of weak acid and weak base. This is because each of them gets hydrolysed, producing H^+ and OH^- ions. These ions combine to form water and the hydrolysis equilibrium is shifted in the forward direaction.

Buffer Solutions are the solutions whose pH does not change significantly on adding a small quantity of strong base or on little dilution.

These are typically made by mixing a weak acid (or base) with its conjugate base (or acid). e.g. CH_3COOH with

CH_3COONa, NH_3(aq) with NH_4Cl etc.

If K_a for acid (or K_b for base) is not too high, we may write :

Henderson's Equation

$pH = pK_a + \log\{[salt]/[acid]\}$ for weak acid with its conjugate base.

or $pOH = pK_b + \log\{[salt]/[base]\}$ for weak base with its conjugate acid.

Important : For good buffer capacity, [salt] : [acid ratios should be as close to one as possible. In such a case, $pH = pK_a$. (This also is the case at midpoint of titration)

Buffer capacity = (no. of moles of acid (or base) added to 1L) / (change in pH)

Indicators. Indicator is a substance which indicates the point of equivalence in a titration by undergoing a change in its colour. They are weak acids or weak bases.

Theory of Indicators. The ionized and unionized forms of indicators have different colours. If 90 % or more of a particular form (ionised or unionised) is present, then its colour can be distinclty seen.In general, for an indicator which is weak acid, $HIn \rightleftharpoons H^+ + In^-$, the ratio of ionized to unionized form can be determined from

$$pH = pK_a + \log \frac{[In^-]}{[HIn]}$$

So, for detectable colour change, $pH = pK_a \pm 1$

This roughly gives the range of indicators. Ranges for some popular indicators are

Table 1 : Indicators

Indicators	pH range	Colour	
		acid medium	basic medium
Methyl Orange	3.1-4.4	pink	yellow
Methyl red	4.2-6.3	red	yellow
Litmus	5.5-7.5	red	blue
Phenol red	6.8-8.4	yellow	red
Phenolphathlene	8.3-10	colourless	pink
Thymol blue	1.2-2.8	red	yello

Equivalence point. The point at which exactly equivalent amounts of acid and base have been mixed.

Acid Base Titration. For choosing a suitable indicator titration curves are of great help. In a titration curve, change in pH is plotted against the volume of alkali to a given acid. Four cases arise.

(a) **Strong acid vs strong base.** The curve is almost vertical over the pH range 3.5-10. This abrupt change corresponds to equivalence point. Any indicator suitable.

(b) **Weak acid vs strong base.** Final solution is basic 9 at equivalence point. Vertical region (not so sharp) lies in pH range 6.5-10. So, phenolphathlene is suitable.

(c) **Strong acid vs weak base.** Final solution acidic. Vertical point in pH range 3.8-7.2. Methyl red or methyl orange suitable.

(d) **Weak acid vs weak base.** No sharp change in pH. No suitable indicator.

Note : at midpoint of titration, $pH = pK_a$, thus by pH measurements, K_a for weak acids (or K_b for weak bases) can be determined.

Polyprotic acids and bases. Usually K_2, K_3 etc. can be safely neglected and only K_1 plays a significant role.

Solubility product (K_{sp}). For sparingly soluble salts (eg. $Ag_2C_2O_4$) an equilibrium which exists is

$$Ag_2C_2O_4 \rightleftharpoons 2Ag^+ (aq.)\ C_2O_4^{2-} (aq.)$$

$$\text{Then } K_{sp} = [Ag^+]^2[C_2O_4^{2-}]$$

Precipitation. Whenever the product of concentrations (raised to appropriate power) exceeds the solubility product, precipitation occurs.

Common ion effects. Suppression of dissociation by adding an ion common with dissociation products. e.g. Ag^+ or $C_2O_4^{2-}$ in the above example.

Simultaneous solubility. While solving these problems, go as per general method i.e.

(i) First apply condition of electroneutrality and
(ii) Apply the equilibria conditions.

THE ATLAS

The concept of ionic equilibria as equilibria involving ions in solution

(i) Arrhenius theory of electrolytes.

(ii) Ostwards dilution law for weak electrolyte $K_a = \left(\frac{\alpha^2}{1-\alpha}\right)\left(\frac{1}{V}\right)$

(iii) Acid & Bases

(a) Arrhenius H^+/OH^- theory.

(b) Bronsted lowery - protonic concept.

(c) Lewis concept - electronic concept of acids and bases.

Some basic concept

pH scale : $pH = -\log[H^+]$.

(i) Water as amphiprotic solvent.

(ii) Autoionization of water : $K_w = [H^+][OH^-]$.

(iii) $K_a[H_2O] = K_w/[H_2O]$

(iv) Change in pH of neutral H_2O with temperature.

Homogenous Ionic equilibria

(i) Acid/ base equilibrium.

(a) Strong acid/ base-$[H]^+ = \frac{c}{2} + \sqrt{\frac{c^2}{4} + K_w}$;c=conc. of (acid)

(b) pH due to polyprotic weak acids

(c) Weak monobasic acid/base $[H]^+ = \sqrt{K_a.c}$ (if $\alpha < 0.1$)

(d) Mixture of S.A./W.A.

(e) Mixture of W.A./ W.A. $H^+ = \sqrt{K_1c_1 + K_2c_2}$

(f) Buffer solutions : $pH = pK_a + \log\left(\frac{salt}{acid}\right)$

$pOH = pK_b + \log\left(\frac{salt}{base}\right)$

(g) Salt hydrolysis – (W.A./S.B) $pH = \frac{1}{2}(pK_w + pK_a + \log c)$

(W.B/S.A.) $pH = \frac{1}{2}(pK_w - pK_b - \log c)$

(W.A./W.B.) $pH = \frac{1}{2}(pK_w + pK_a - pK_b)$

Heterogenons equilibria

Solubility of sparingly soluble salt's $(AB, AB_2, A_xB_y) K_{sp} = (S^{x+y})X^xY^y$

(i) Effect of pH on solubility.

(ii) Simultaneous solubility.

Application of both heterogenous and homogenous equilibrium

(i) Extent of hydrolysis in buffer solution.

(ii) Change in solubility due to complex formation.

(iii) Solubility and hydrolysis.

GLOSSARY

Amphoteric substance. A molecule which can act both as an acid and as a base.

Autoprotolysis constant. The equilibrium constant for the reaction in which one solvent molecule loses a proton to another, as $2H_2O \rightleftharpoons H_3O^+ + OH^-$.

Amphiprotic solvent. A solvent which possesses both acidic and basic properties.

Aprotic solvent. A solvent which is neither appreciably acidic or basic.

Bronsted acid. A substance which furnishes a proton.

Bronsted base. A substance which accepts a proton.

Buffer capacity. A measure of the effectiveness of a buffer in resisting changes in pH; the capacity is greater the concentrations of the conjugate acid-base pair.

Buffer solution. A solution which contains a conjugated acid-base pair. Such a solution resists large changes in pH when H_3O^+ or OH^- ions are added and when the solution is diluted.

Charge-balance equation. The equation expressing the electroneutrality principle; i.e., the total concentration of positive charge must equal the total concentration of negative charge.

Common-ion effect. The effect produced by an ion, say from a salt, which is the same ion produced by the dissociation of a weak electrolyte. The "common" ion shifts the dissociation equilibrium in accordance with LeChatelier's principle.

Central metal atom. A cation which accepts electrons from a ligand to form a complex ion.

Conjugate acid-base pair. An acid-base pair which differ only by a proton, as HCl and Cl^-.

Diprotic acid. An acid which furnishes two protons.

Electrolyte. A compound which produces positive and negative ions in solution. Strong electrolytes are completely dissociated, whereas weak electrolytes are only partially dissociated.

Hydrolysis. An acid-base reaction of a cation or anion with water.

Isoelectric point. The pH at which there is an exact balance of positive and negative charge on an amino acid.

Indicator. A visual acid-base indicator is a weak organic acid or base which shows different colors in the molecular and ionic forms.

Ligand. An anion or neutral molecule which forms a complex ion with a cation by donating one or more pairs of electrons.

Nonelectrolyte. A substance which does not dissociate into ions in solution.

pH. The negative logarithm of the hydrogen ion concentration.

pK. The negative logarithm of an equilibrium constant.

Polyprotic acid. An acid which furnishes two or more protons.

Range of an indicator. That portion of the pH scale over which an indicator changes color, roughly the pK of the indicator ± 1 unit.

Salt. The product other than water which is formed when an acid reacts with a base; usually an ion solid.

Simultaneous equilibria. Equilibria established in the same solution in which one molecule or ions is a participant in more than one of the equilibria.

Solubility product constant, K_{sp}. The constant for the equilibrium established between a slightly soluble salt and its ions in solution.

Stability constant. The equilibrium constant for a reaction in which a complex is formed. Also called a formation constant.

EXERCISE I

IONIZATION CONSTANTS AND pH

Q.1.1 Calculate
(i) K_a for H_2O ($K_w = 10^{-14}$)
(ii) K_b for $B(OH)_4^-$, $K_a(B(OH)_3) = 6 \times 10^{-10}$
(iii) K_a for HCN, $K_b(CN^-) = 2.5 \times 10^{-5}$

Q.1.2 Calculate the ratio of degree of dissociation (α_2/α_1) when 1 M acetic acid solution is diluted to $\frac{1}{100}$ times. [Given $K_a = 1.8 \times 10^{-5}$]

Q.1.3 Calculate the ratio of degree of dissociation of acetic acid and hydrocyanic acid (HCN) in 1 M their respective solution of acids.[Given $K_{a(CH_3COOH)} = 1.8 \times 10^{-5}$; $K_{a(HCN)} = 6.2 \times 10^{-10}$]

Q.1.4 Calculate :
(a) K_a for a monobasic acid whose 0.10 M solution has pH of 4.50.
(b) K_b for a monoacidic base whose 0.10 M solution has a pH of 10.50.

Q.1.5 Calculate pH of following solutions :
(a) 0.1 M HCl
(b) 0.1 M H_2SO_4 (50 ml) + 0.4 M HCl 50 (ml)
(c) 0.1 M CH_3COOH ($K_a = 1.8 \times 10^{-5}$)
(d) 0.1 M NH_4OH ($K_b = 1.8 \times 10^{-5}$)
(e) 10^{-8} M HCl
(f) 10^{-10} M NaOH
(g) 10^{-6} M CH_3COOH
(h) 10^{-8} M CH_3COOH
(i) 0.1 M HA + 0.1 M HB [$K_a(HA) = 2 \times 10^{-5}$; $K_a(HB) = 4 \times 10^{-5}$]
(j) Decimolar solution of Baryta ($Ba(OH)_2$), diluted 100 times.
(k) 10^{-3} mole of KOH dissolved in 100 L of water.
(l) 0.5 M HCl (25 ml) + 0.5 M NaOH (10 ml) + 40 ml H_2O
(m) equal volume of HCl solution (PH = 4) + 0.0019 N HCl solution

Q.1.6 The value of K_w at the physiological temperature (37°C) is 2.56×10^{-14}. What is the pH at the neutral point of water at this temperature, where there are equal number of H^+ and OH^-?

Q.1.7 Calculate the number of H^+ present in one ml of solution whose pH is 13.

Q.1.8 Calculate change in concentration of H^+ ion in one litre of water, when temperature changes from 298 K to 310 K. Given $K_w(298) = 10^{-14}$ $K_w(310) = 2.56 \times 10^{-14}$.

Q.1.9
(i) K_w for H_2O is 9.62×10^{-14} at 60°C. What is pH of water at 60°C.
(ii) What is the nature of solution at 60°C whose
(a) pH = 6.7
(b) pH = 6.35

Q.1.10 pH of a dilute solution of HCl is 6.95. Calculate molarity of HCl solution.

Q.1.11 The pH of aqueous solution of ammonia is 11.5. Find molarity of solution. $K_b(NH_4OH) = 1.8 \times 10^{-5}$.

Q.1.12 The solution of weak monoprotic acid which is 0.01 M has pH = 3. Calculate K_a of weak acid.

Q.1.13 Boric acid is a weak monobasic acid. It ionizes in water as

$$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+ : K_a = 5.9 \times 10^{-10}$$

Calculate pH of 0.3 M boric acid.

Q.1.14 Calculate $[H^+]$ and $[CHCl_2COO^-]$ in a solution that is 0.01 M in HCl and 0.01 M in $CHCl_2COOH$. Take ($K_a = 2.55 \times 10^{-2}$).

Q.1.15 Calculate the percent error in the $[H_3O^+]$ concentration made by neglecting the ionization of water in a 10^{-6}M NaOH solution.

Q.1.16 Calculate $[H^+]$, $[CH_3COO^-]$ and $[C_7H_5O_2^-]$ in a solution that is 0.02 M in acetic acid and 0.01M in benzoic acid. K_a(acetic) = 1.8×10^{-5}, K_a (benzoic) = 6.4×10^{-5}.

Q.1.17 At 25°C, the dissociation constant of HCN and HF are 4×10^{-10} and 6.7×10^{-4}. Calculate the pH of a mixture of 0.1 M HF and 0.1 M HCN.

POLYPROTIC ACIDS & BASES

Q.2.1 Determine the $[S^{2-}]$ in a saturated (0.1M) H_2S solution to which enough HCl has been added to produce a $[H^+]$ of 2×10^{-4}. $K_1 = 10^{-7}$, $K_2 = 10^{-14}$.

Q.2.2 Calculate $[H^+]$, $[H_2PO_4^-]$, $[HPO_4^{2-}]$ and $[PO_4^{3-}]$ in a 0.01M solution of H_3PO_4.
Take $K_1 = 7.225 \times 10^{-3}$, $K_2 = 6.8 \times 10^{-8}$, $K_3 = 4.5 \times 10^{-13}$.

Q.2.3 Calculate the pH of a 0.1M solution of $H_2NCH_2CH_2NH_2$; ethylenediamine (en). Determine the en H_2^{2+}. Concentration in the solution. K_{b_1} and K_{b_2} values of ethylenediamine are 8.5×10^{-5} and 7.1×10^{-8} respectively.

Q.2.4 What are the concentrations of H^+, HSO_4^-, SO_4^{2-} and H_2SO_4 in a 0.20 M solution of sulphuric acid?

Given: $H_2SO_4 \longrightarrow H^+ + HSO_4^-$; strong

$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$; $K_2 = 1.3 \times 10^{-2}$ M

Q.2.5 What are the concentration of H^+, $H_2C_2O_4$, $HC_2O_4^-$ and $C_2O_4^{2-}$ in a 0.1 M solution of oxalic acid? [$K_1 = 5.9 \times 10^{-2}$ M and $K_2 = 6.4 \times 10^{-5}$ M]

Q.2.6 Nicotine, $C_{10}H_{14}N_2$, has two basic nitrogen atoms and both can react with water to give a basic solution

$Nic\,(aq) + H_2O\,(l) \rightleftharpoons NicH^+\,(aq) + OH^-\,(aq)$

$NicH^+\,(aq) + H_2O\,(l) \rightleftharpoons NicH_2^{2+}\,(aq) + OH^-\,(aq)$

K_{b1} is 7×10^{-7} and K_{b2} is 1.1×10^{-10}. Calculate the approximate pH of a 0.020 M solution.

Q.2.7 Ethylenediamine, $H_2N{-}C_2H_4{-}NH_2$, can interact with water in two steps, giving OH^- in each step. Calculate the concentration of OH^- and $[H_3N{-}C_2H_4{-}NH_3]^{2+}$ in a 0.15 M aqueous solution of the amine. $K_1 = 8.5 \times 10^{-5}$, $K_2 = 2.7 \times 10^{-8}$ for the base.

BUFFER SOLUTION

Q.3.1 Determine $[OH^-]$ of a 0.050 M solution of ammonia to which has been added sufficient NH_4Cl to make the total $[NH_4^+]$ equal to 0.100. [$K_{b(NH_3)} = 1.8 \times 10^{-5}$]

Q.3.2 Calculate the pH of a solution prepared by mixing 50.0 mL of 0.200 M $HC_2H_3O_2$ and 50.0 mL of 0.100 M NaOH. [$K_{a(CH_3COOH)} = 1.8 \times 10^{-5}$]

Q.3.3 A buffer of pH 9.26 is made by dissolving x moles of ammonium sulphate and 0.1 mole of ammonia into 100 mL solution. If pK_b of ammonia is 4.74, calculate value of x.

Q.3.4 50 mL of 0.1 M NaOH is added to 75 mL of 0.1 M NH_4Cl to make a basic buffer. If pK_a of NH_4^+ is 9.26, calculate pH.

Q.3.5
(a) Determine the pH of a 0.2 M solution of pyridine C_5H_5N . $K_b = 1.5 \times 10^{-9}$
(b) Predict the effect of addition of pyridinium ion $C_5H_5NH^+$ on the position of the equilibrium. Will the pH be raised or lowered ?
(c) Calculate the pH of 1.0 L of 0.10 M pyridine solution to which 0.3 mol of pyridinium chloride $C_5H_5NH^+Cl$, has been added, assuming no change in volume.

Q.3.6 Calculate the pH of a solution which results from the mixing of 50.0 ml of 0.3 M HCl with 50.0 ml of 0.4 M NH_3 . $[K_b\ (NH_3) = 1.8 \times 10^{-5}]$

Q.3.7 Calculate the pH of a solution made by mixing 50.0 ml of 0.2M NH_4Cl & 75.0 ml of 0.1 M NaOH. $[\ K_b\ (NH_3\ ) = 1.8 \times 10^{-5}\ ]$

Q.3.8 A buffer solution was prepared by dissolving 0.02 mol propionic acid & 0.015 mol sodium propionate in enough water to make 1.00 L of solution .(K_a for propionic acid is 1.34×10^{-5})
(a) What is the pH of the buffer?
(b) What would be the pH if 1.0×10^{-5} mol HCl were added to 10 ml of the buffer ?
(c) What would be the pH if 1.0×10^{-5} mol NaOH were added to 10 ml of the buffer.
(d) Also report the percent change in pH of original buffer in cases (b) and (c).

Q.3.9 A solution was made up to be 0.01 M in chloroacetic acid, $ClCH_2COOH$ and also 0.002 M in sodium chloroacetate $ClCH_2COONa$. What is $[H^+]$ in the solution ? $K_a = 1.5 \times 10^{-3}$.

INDICATORS

Q.4.1 A certain solution has a hydrogen ion concentration 4×10^{-3} M. For the indicator thymol blue, pH is 2.0 when half the indicator is in unionised form. Find the % of indicator in unionised form in the solution with $[H^+] = 4 \times 10^{-3}$ M.

Q.4.2 At what pH does an indicator change colour if the indicator is a weak acid with $K_{ind} = 4 \times 10^{-4}$. For which one(s) of the following neutralizations would the indicator be useful ? Explain.
(a) NaOH + CH_3COOH (b) HCl + NH_3 (c) HCl + NaOH

Q.4.3 What indicator should be used for the titration of 0.10 M KH_2BO_3 with 0.10 M HCl ?
$K_a\ (H_3BO_3) = 7.2 \times 10^{-10}$.

Q.4.4 Bromophenol blue is an indicator with a K_a value of 6×10^{-5} . What % of this indicator is in its basic form at a pH of 5 ?

Q.4.5 An acid base indicator has a K_a of 3×10^{-5}. The acid form of the indicator is red & the basic form is blue. By how much must the pH change in order to change the indicator form 75% red to 75 % blue?

HYDROLYSIS

Q.5.1 What is the OH^- concentration of a 0.08 M solution of CH_3COONa. $[K_a(CH_3COOH)=1.8 \times 10^{-5}]$

Q.5.2 Calculate the pH of a 2.0 M solution of NH_4Cl. $[K_b\ (NH_3) = 1.8 \times 10^{-5}]$

Q.5.3 0.25 M solution of pyridinium chloride $C_5H_6N^+Cl^-$ was found to have a pH of 2.699. What is K_b for pyridine, C_5H_5N ?

Q.5.4 Calculate the extent of hydrolysis & the pH of 0.02 M CH_3COONH_4.
$[K_b\ (NH_3)= 1.8 \times 10^{-5},\ K_a(CH_3COOH)=1.8 \times 10^{-5}]$

Q.5.5 Calculate the percent hydrolysis in a 0.06 M solution of KCN. $[K_a(HCN) = 6 \times 10^{-10}]$

Q.5.6 Calculate the extent of hydrolysis of 0.005 M K_2CrO_4. [$K_2 = 3.1 \times 10^{-7}$ for H_2CrO_4]
(It is essentially strong for first ionization).

Q.5.7 Calculate the percent hydrolysis in a 0.0100 M solution of KCN.($K_a = 6.2 \times 10^{-10}$)

Q.5.8 A 0.010 M solution of $PuO_2(NO_3)_2$ was found to have a pH of 4.0. What is the hydrolysis constant, K_h, for PuO_2^{2+}, and what is K_b for PuO_2OH^+?

Q.5.9 Calculate the pH of 1.0×10^{-3} M sodium phenolate, $NaOC_6H_5$. K_a for HOC_6H_5 is 1.05×10^{-10}.

Q.5.10 What is the pH of 0.1M $NaHCO_3$? $K_1 = 4.5 \times 10^{-7}$, $K_2 = 4.5 \times 10^{-11}$ for carbonic acids.

Q.5.11 Calculate pH of 0.05M potassium hydrogen pnthalate, $KHC_8H_4O_4$.

$$H_2C_8H_4O_4 + H_2O \rightleftharpoons H_3O^+ + HC_8H_4O_4^- \qquad pK_1 = 2.94$$

$$HC_8H_4O_4^- + H_2O \rightleftharpoons H_3O^+ + C_8H_4O_4^{2-} \qquad pK_2 = 5.44$$

Q.5.12 Calculate OH^- concentration at the equivalent point when a solution of 0.1 M acetic acid is titrated with a solution of 0.1 M NaOH. K_a for the acid $= 1.9 \times 10^{-5}$.

Q.5.13 The acid ionization (hydrolysis) constant of Zn^{2+} is 1.0×10^{-9}
(a) Calculate the pH of a 0.001 M solution of $ZnCl_2$
(b) What is the basic dissociation constant of $Zn(OH)^+$?

ACID BASE REACTIONS & TITRATIONS

Q.6.1 Calculate the hydronium ion concentration and pH at the equivalence point in the reaction of 22.0 mL of 0.10M acetic acid, CH_3COOH, with 22.0 mL of 0.10 M NaOH.

Q.6.2 Calculate the hydronium ion concentration and the pH at the equivalence point in a titration of 50.0 mL of 0.40 M NH_3 with 0.40M HCl.

Q.6.3 In the titration of a solution of a weak acid HX with NaOH, the pH is 5.8 after 10.0 mL of NaOH solution has been added and 6.402 after 20.0 mL of NaOH has been added. What is the ionization constant of HX? Nothing known → concn of NaOH/ concn of HX or its volume

Q.6.4 The equivalent point in a titration of 40.0 mL of a solution of a weak monoprotic acid occurs when 35.0 mL of a 0.10M NaOH solution has been added. The pH of the solution is 5.75 after the addition of 20.0 mL of NaOH solution. What is the dissociation constant of the acid?

Q.6.5 Phenol, C_6H_5OH, is a weak organic acid that has many uses, and more than 3 million ton are produced annually around the world. Assume you dissolve 0.515 g of the compound in exactly 100mL of water and then titrate the resulting solution with 0.123M NaOH.

$$C_6H_5OH\,(aq) + OH^-\,(aq) \rightarrow C_6H_5O^-\,(aq) + H_2O(l)$$

What are the concentrations of all of the following ions at the equivalence point: Na^+, H_3O^+, OH^- and $C_6H_5O^-$? What is the pH of the solution? [K_a (phenol) $= 1.3 \times 10^{-10}$]

Q.6.6 A weak base (50.0mL) was titrated with 0.1 M HCl. The pH of the solution after the addition of 10.0 mL and 25.0 mL were found to be 9.84 and 9.24, respectively. Calculate K_b of the base and pH at the equivalence point.

Q.6.7 A weak acid (50.0mL) was titrated with 0.1 M NaOH. The pH values when 10.0 mL and 25.0 mL of base have been added are found to be 4.16 and 4.76, respectively. Calculate K_a of the acid and pH at the equivalence point.

Q.6.8 CH_3COOH (50 ml, 0.1 M) is titrated against 0.1 M NaOH solution. Calculate the pH at the addition of 0 ml, 10 ml 20 ml, 25 ml, 40 ml, 50 ml of NaOH. K_a of CH_3COOH is 2×10^{-5}.

SOLUBILITY & SOLUBILITY PRODUCT'S

Q.7.1 The values of K_{sp} for the slightly soluble salts MX and QX_2 are each equal to 4.0×10^{-18}. Which salt is more soluble? Explain your answer fully.

Q.7.2 The solubility of $PbSO_4$ water is 0.038 g/L. Calculate the solubility product constant of $PbSO_4$.

Q.7.3 Calculate the solubility of $Mg(OH)_2$ in water. $K_{sp} = 1.2 \times 10^{-11}$.

Q.7.4 How many mol CuI ($K_{sp} = 5 \times 10^{-12}$) will dissolve in 1.0 L of 0.10 M NaI solution ?

Q.7.5 A solution of saturated CaF_2 is found to contain 4.1×10^{-4} M fluoride ion. Calculate the K_{sp} of CaF_2. Neglect hydrolysis.

Q.7.6 The solubility of ML_2 (formula weight, 60 g/mol) in water is 2.4×10^{-5} g/100 mL solution. Calculate the solubility product constant for ML_2.

Q.7.7 What is the solubility (in mol/L) of $Fe(OH)_3$ in a solution of pH = 8.0 ? [K_{sp} for $Fe(OH)_3 = 1.0 \times 10^{-36}$]

Q.7.8 The solubility of Ag_2CrO_4 in water is 0.044 g/L. Determine the solubility product constant.

Q.7.9 Calculate the solubility of A_2X_3 in pure water, assuming that neither kind of ion reacts with water. For A_2X_3, [$K_{sp} = 1.1 \times 10^{-23}$]

Q.7.10 Determine the solubility of AgCl in 0.1 M $BaCl_2$. [K_{sp} for AgCl = 1×10^{-10}]

Q.7.11 What mass of Pb^{2+} ion is left in solution when 50.0 mL of 0.20M $Pb(NO_3)_2$ is added to 50.0 mL of 1.5 M NaCl ?[Given K_{sp} for $PbCl_2 = 1.7 \times 10^{-4}$]

Q.7.12 A solution has a Mg^{2+} concentration of 0.0010 mol/L. Will $Mg(OH)_2$ precipitate if the OH^- concentration of the solution is [$K_{sp} = 1.2 \times 10^{-11}$]

(a) 10^{-5} mol/L (b) 10^{-3} mol/L ?

Q.7.13 Calculate solubility of PbI_2 ($K_{sp} = 1.4 \times 10^{-8}$) in water at 25°, which is 90% dissociated.

Q.7.14 Calculate solubility of AgCN ($K_{sp} = 4 \times 10^{-16}$) in a buffer solution of PH = 3.

SIMULTANEOUS SOLUBILITY

Q.8.1 Calculate the Simultaneous solubility of AgSCN and AgBr. K_{sp} (AgSCN) = 1.1×10^{-12}, $K_{sp}(AgBr) = 5 \times 10^{-13}$.

Q.8.2 Calculate F^- in a solution saturated with respect of both MgF_2 and SrF_2. $K_{sp}(MgF_2) = 9.5 \times 10^{-9}$, $K_{sp}(SrF_2) = 4 \times 10^{-9}$

Q.8.3 Equal volumes of 0.02M $AgNO_3$ and 0.02M HCN were mixed. Calculate $[Ag^+]$ at equilibrium . Take $K_a(HCN) = 9 \times 10^{-10}$, K_{sp} (AgCN) = 4×10^{-16}.

COMPLEXATION EQUILIBRIA

Q.9.1 Assuming no change in volume, calculate the minimum mass of NaCl necessary to dissolve 0.010 mol AgCl in 100 L solution. [$K_f(AgCl_2^-) = 3 \times 10^5$, $K_{sp} = (AgCl) = 1 \times 10^{-10}$]

Q.9.2 A recent investigation of the complexation of SCN^- with Fe^{3+} led of 130, 16, and 1.0 for K_1, K_2, and K_3, respectively. What is the overall formation constant of $Fe(SCN)_3$ from its component ions, and what is the dissociation constant of $Fe(SCN)_3$ into its simplest ions on the basis of these data ?

Q.9.3 How much AgBr could dissolve in 1.0 L of 0.40 M NH_3 ? Assume that $Ag(NH_3)_2^+$ is the only complex formed. [$K_f(Ag(NH_3)_2^+) = 1 \times 10^8$; K_{sp} (AgBr) = 5×10^{-13}]

PROFICIENCY TEST

Q.1 True / False. When a solution of a weak monoprotic acid is titrated against a strong base, at half-neutralization point, $pH = \frac{1}{2} pK_a$.

Q.2 True / False. A solution of sodium acetate and ammonium acetate can act as a buffer.

Q.3 True / False. If the solubility of the salt $Li_3Na_3(AlF_6)_2$ is x, then its solubility product would be $2916\,x^8$.

Q.4 True / False. A buffer has maximum buffer capacity when the ratio of salt to acid is 10.

Q.5 True / False. In the presence of a common ion (incapable of froming complex ion), the solubility of salt decreases.

Q.6 In a mixture of waek acid and its salt, the ratio of concentration of salt to acid is increased ten fold. The pH of the solution would __________ by __________ unit.

Q.7 The solubilty of CH_3COOAg in water considering hydrolysis of CH_3COO^- ions would be ________ than that ignoring the hydrolysis.

Q.8 From an equimolar solution of Cl^- and Br^- ions, the addition of Ag^+ will selectively precipitates _____ (K_{sp} of AgCl & AgBr are 1×10^{-10} & 1×10^{-13} respectively).

Q.9 The solubility of AgCl in NH_3 is ______ than the solubility in pure water because of complex ion, $[Ag(NH_3)_2]^+$ formation.

Q.10 The hydrolytic constant K_h for the hydrolytic equilibrium

$$H_2PO_4^- + H_2O \longrightarrow H_3PO_4 + OH^- \text{ is } 1.4 \times 10^{-12}$$

What is the value of ionization constant for the $H_3PO_4 + H_2O \longrightarrow H_2PO_4^- + H_3O^+$?

Q.11 Given the equilibrium constants

$$HgCl^+ + Cl^- \rightleftharpoons HgCl_2 \quad ; K_1 = 3 \times 10^6$$

$$HgCl_2 + Cl^- \rightleftharpoons HgCl_3^- \quad ; K_2 = 8.9$$

The equilibrium constant for the dispropotionation equilibrium.

$$2HgCl_2 \rightleftharpoons HgCl^+ + HgCl_3^- \text{ is}$$

Q.12 Under which set of conditions is the ionic product of water, K_w, constant at a given temperature in aqueous system?

Q.13 If the salts M_2X, QY_2 and PZ_3 have same solubilities (<<<1), their K_{sp} values are related as _____.

Q.14 K_a for an acid HA is 1×10^{-6}. K_b for A^- would be __________.

Q.15 An aqueous solution of K_2SO_4 has pH nearly equal to ______.

Q.16 The pH of a solution which is 0.1 M in sodium acetate and 0.01 M in acetic acid ($pK_a = 4.74$) would be ________.

Q.17 The conjugate acid of sulphate (SO_4^{2-}) is ____________.

Q.18 The value of K_w ________ with increase in temperature.

Q.19 AgCl is _______ soluble in aqueous sodium chloride solution than in pure water.

Q.20 The buffer HCOOH / HCOONa will have pH __________ than 7.

Q.21 In the reaction $I_2 + I^- \longrightarrow I_3^-$, I_2 acts as __________.

Q.22 An equimolar solution of $NaNO_2$ and HNO_2 can act as a ________ solution.

Q.23 Larger the value of pK_a, _________ is the acid.

Q.24 An aqueous solution of potash alum is ______ in nature.

Q.25 Salts of strong acids and weak bases undergo __________ hydrolysis.

Q.26 For salts of weak acid with weak bases, degree of hydrolysis is _______ of concentration of the salt in solution.

BEWARE OF SNAKES

1. ***General Mistake :*** pH of a neutral water solution is always equal to 7.

   Explanation : pH of neutral water depend on temperature. Since pH (neutral point) = $\frac{pK_w}{2}$; pK_w decreases with temperature hence pH of neutral solution.

2. ***General Mistake :*** If a solution is diluted half times pH of solution becomes double.
   Explanation : Infact pH increases by 0.3010 unit. If it is diluted x times pH increases by log x.
   e.g. If solution is diluted 10 times pH increases by $\log_{10}10 = 1$ unit.

3. ***General Mistake :*** For calculation of pH of 10^{-6} M CH_3COOH the formula $(H^+) = \sqrt{K_a c}$ will give

   $$pH = -\log\left(\sqrt{1.8\times10^{-5}\times10^{-6}}\right) = 5.37.$$

   Explanation : 5.37 is incorrect answer. pH should be calculated by taking $\alpha = \frac{-K_a + \sqrt{K_a^2 + 4K_a c}}{2c}$

4. ***General Mistake :*** If 10^3 mole CH_3COONa and 1 mole CH_3COOH is added in 10^4 litres water the pH of resulting solution is equal to $pH = pK_a + \log\frac{10^3}{1} = 7.74$.

   Explanation : 7.74 is incorrect answer. The CH_3COOH concentration is too low to be taken as constituent of buffer solution. Use salt hydrolysis formula instead to calculate the pH.

5. ***General Mistake :*** The equilibrium concentration of anion and cation of a sparingly soluble salt (A_2C_3) are a and c moles lit^{-1} respectively. The solubility product is $(2a)^2\,(3c)^3 = K_{sp}$
   Explanation : $K_{sp} = a^2c^3$.

6. ***General Mistake :*** pH of 10^{-8} M HCl is equal to 8.
   Explaination : pH = 8 means basic solution. Contribution of water can not be neglected in this case.

7. ***General Mistake :*** If NaOH is added to NH_4Cl so that NaOH is limiting, the resulting solution is containing some remaining conc. of NH_4Cl. Now use salt hydrolysis condition to calculate pH of solution.
   Explanation : The addition of NaOH in NH_4Cl results in a basic buffer solution.

8. ***General Mistake :*** Do not use the K_1K_2 form of equation unless you have an independent method of calculating $[H^+]$ or $[S^{2-}]$
   Explanation : Determine the $[S^{2-}]$ in a saturated H_2S solution to which enough HCl has been added to produce a $[H^+]$ of 2×10^{-4}.

   Sol. : $$K_1K_2 = \frac{[H^+]^2[S^{2-}]}{[H_2S]} = \frac{(2\times10^{-4})^2[S^{2-}]}{0.10} = 1.0 \times 10^{-21} \text{ or}$$

   $$[S^{2-}] = \frac{1.0\times10^{-22}}{4\times10^{-8}} = 2.5 \times 10^{-15}.$$

EXERCISE II

Q.1 At 25°C, the degree of dissociation of water was found to be 1.8×10^{-9}. Calculate the ionization constant and ionic product of water at this temperature.

Q.2 A solution contains HCl, $Cl_2HC\ COOH$ & CH_3COOH at concentrations 0.09 M in HCl, 0.09 M in $Cl_2HC\ COOH$ & 0.1 M in $CH_3\ COOH$. pH for the solution is 1. Ionization constant of $CH_3\ COOH = 10^{-5}$. What is the magnitude of K for dichloroacetic acid ?

Q.3 A solution of chloroacetic acid, $ClCH_2COOH$ containing 9.45 grams in 500 ml of the solution has a pH of 2.0. What is the degree of ionization of the acid.

Q.4 A solution of ammonia bought for cleaning the windows was found to be 10% ammonia by mass, having a density of $0.935\ g.ml^{-1}$. What is the pH of the solution. Take K_b for protonation of ammonia = 5.5×10^{-6}.

Q.5 The K_w of water at two different temperatures is :

T	25°C	50°C
K_w	1.08×10^{-14}	$5.474 \times 10^{--14}$

Assuming that ΔH of any reaction is independent of temperature, calculate the enthalpy of neutralization of a strong acid and strong base.

Q.6 What is the pH of a 1.0 M solution of acetic acid ? To what volume must 1 litre of the solution be diluted so that the pH of the resulting solution will be twice the original value. Given $K_a = 1.8 \times 10^{-5}$.

Q.7 A handbook states that the solubility of methylamine $CH_3NH_2(g)$ in water at 1 atm pressure at 25°C is 959 volumes of $CH_3NH_2(g)$ per volume of water ($pk_b = 3.39$)

(a) Estimate the max. pH that can be attained by dissolving methylamine in water.

(b) What molarity NaOH (aq.) would be required to yield the same pH ?

Q.8 The equilibrium constant of the reaction

$$2Ag(s) + 2I^- + 2H_2O \rightleftharpoons 2AgI(s) + H_2(g) + 2OH^-$$

is 1.2×10^{-23} at 25°C. Calculate the pH of a solution at equilibrium with the iodine ion concentration = 0.10 and the pressure of H_2 gas = 0.60 atm.

Q.9 For the reaction

$$A + B \rightleftharpoons C + D$$

(all reactants in solution) calculate the value of the equilibrium constant for the following percentages of conversion of A and B into products. (Assume the initial concentrations of A and B are each 1.0 M)
(a) 67%; (b) 95%; (c) 99%.

Q.10 Mixtures of soutions. Calculate the pH of the following solutions. (Use data of Q.14)

(a) 50 ml of 0.12 M H_3PO_4 + 20 ml of 0.15 M NaOH;

(b) 50 ml of 0.12 M H_3PO_4 + 40 ml of 0.15 M NaOH;

(c) 40 ml of 0.12 M H_3PO_4 + 40 ml of 0.18 M NaOH;

(d) 40 ml of 0.10 M H_3PO_4 + 40 ml of 0.25 M NaOH.

Q.11 Mixtures of solution. Calculate the pH of the following solution.(Use data of Q.14)

(a) 40 ml of 0.050 M Na_2CO_3 + 50 ml of 0.040 M HCl;

(b) 40 ml of 0.020 M Na_3PO_4 + 40 ml of 0.040 M HCl;

(c) 50 ml of 0.10 M Na_3PO_4 + 50 ml of 0.10 M NaH_2PO_4;

(d) 40 ml of 0.10 M H_3PO_4 + 40 ml of 0.10 M Na_3PO_4.

Q.12 The electrolytic reduction of an organic nitro compound was carried out in a solution buffered by acetic acid and sodium acetate. The reaction was

$$RNO_2 + 4H_3O^+ + 4e \longrightarrow RNHOH + 5H_2O$$

300 ml of a 0.0100 M solution of RNO_2 buffered initially at pH 5.00 was reduced, with the reaction above going to completion. The total acetate concentration, $[HOAc] + [OAc^-]$, was 0.50 M.Calculate the pH of the solution after the reduction is complete.

Q.13(a) It is desired to prepare 100 ml of a buffer of pH 5.00.Acetic, benzoic and formic acids and their salts are available for use. Which acid should be used for maximum effectiveness against increase in pH? What acid-salt ratio should be used ?pK_a values of these acids are : acetic 4.74; benzoic 4.18 and formic 3.68.

(b) If it is desired that the change in pH of the buffer be no more than 0.10 unit for the addition of 1 m mol of either acid or base, what minimum concentrations of the acid and salt should be used ?

Q.14 Calculate the pH of 0.1 M solution of (i) $NaHCO_3$, (ii) Na_2HPO_4 and (iii) NaH_2PO_4. Given that:

$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$; $K_1 = 4.2 \times 10^{-7}$ M

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$; $K_2 = 4.8 \times 10^{-11}$ M

$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$; $K_1 = 7.5 \times 10^{-3}$ M

$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$; $K_2 = 6.2 \times 10^{-8}$ M

$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$; $K_3 = 1.0 \times 10^{-12}$ M

Q.15 When a 40 mL of a 0.1 M weak base is titrated with 0.16M HCl, the pH of the solution at the end point is 5.23. What will be the pH if 15 mL of 0.12 M NaOH is added to the resulting solution.

Q.16 A buffer solution was prepared by dissolving 0.05 mol formic acid & 0.06 mol sodium formate in enough water to make 1.0 L of solution. K_a for formic acid is 1.80×10^{-4}.

(a) Calculate the pH of the solution .

(b) If this solution were diluted to 10 times its volume, what would be the pH ?

(c) If the solution in (b) were diluted to 10 times its volume,what would be the pH?

Q.17 How many moles of sodium hydroxide can be added to 1.00 L of a solution 0.1 M in NH_3 & 0.1 M in NH_4Cl without changing the pOH by more than 1.00 unit ? Assume no change in volume. $K_b(NH_3) = 1.8 \times 10^{-5}$.

Q.18 20 ml of a solution of 0.1 M CH_3COOH solution is being titrated against 0.1 M NaOH solution. The pH values after the addition of 1 ml & 19 ml of NaOH are $(pH)_1$ & $(pH)_2$, what is ΔpH ?

Q.19 Calculate the OH^- concentration and the H_3PO_4 concentration of a solution prepared by dissolving 0.1 mol of Na_3PO_4 in sufficient water to make 1L of solution. $K_1 = 7.1 \times 10^{-3}$, $K_2 = 6.3 \times 10^{-8}$, $K_3 = 4.5 \times 10^{-13}$.

Q.20 Find the pH of 0.068M Na_2HPO_4 solution. Use K values from the above problem if required.

Q.21 Calculate the values of the equilibrium constants for the reactions with water of $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} as bases. Comparing the relative values of the two equilibrium constants of $H_2PO_4^-$ with water, deduce whether solutions of this ion in water are acidic or basic. Deduce whether solutions of HPO_4^{2-} are acidic or basic. Take $K_1 = 5 \times 10^{-3}$, $K_2 = 5 \times 10^{-8}$, $K_3 = 5 \times 10^{-13}$.

Q.22 Determine the equilibrium carbonate ion concentration after equal volumes of 1.0M sodium carbonate and 1.0M HCl are mixed. $K_1 = 5 \times 10^{-7}$, $K_2 = 5 \times 10^{-11}$.

Q.23 K_1 and K_2 for oxalic acid, $H_2C_2O_4$, are 5.6×10^{-2} and 5.0×10^{-5}. What is $[OH^-]$ in a 0.4mM solution of $Na_2C_2O_4$?

Q.24 If 0.00050 mol $NaHCO_3$ is added to 1 litre of a buffered solution at pH 8.00, how much material will exist in each of the three forms H_2CO_3, HCO_3^- and CO_3^{2-}? For H_2CO_3, $K_1 = 5 \times 10^{-7}$, $K_2 = 5 \times 10^{-13}$.

Q.25 Equilibrium constant for the acid ionization of Fe^{3+} to $Fe(OH)^{+2}$ and H^+ is 6.5×10^{-3}. What is the max.pH, which could be used so that at least 95% of the total Fe^{3+} in a dilute solution. exists as Fe^{3+}.

Q.26 Hydrazine, N_2H_4, can interact with water in two stages.

$$N_2H_4\,(aq) + H_2O\,(l) \rightleftharpoons N_2H_5^+\,(aq) + OH^-\,(aq.) \qquad K_{b1} = 8.5 \times 10^{-7}$$

$$N_2H_5^+\,(aq) + H_2O\,(l) \rightleftharpoons N_2H_6^{2+}\,(aq) + OH^-\,(aq.) \qquad K_{b2} = 8.9 \times 10^{-16}$$

(i) What are the concentration of OH^-, $N_2H_5^+$ and $N_2H_6^{2+}$ in a 0.010 M aqueous solution of hydrazine?
(ii) What is pH of the 0.010 M solution of hydrazine?

Q.27 How much Na_2HPO_4 must be added to one litre of 0.005M solution of NaH_2PO_4 in order to make a 1L of the solution of pH 6.7? $K_1 = 7.1 \times 10^{-3}$, $K_2 = 6.3 \times 10^{-8}$, $K_3 = 4.5 \times 10^{-13}$ for H_3PO_4.

Q.28 A solution of volume V contains n_1 moles of QCl and n_2 moles of RCl where QOH and ROH are two weak bases of dissociation constants K_1 and K_2 respectively. Show that the pH of the solution is given

by $$\text{pH} = \frac{1}{2}\log\left[\left(\frac{K_1K_2}{K_W}\right)\frac{V}{(n_1K_2 + K_1n_2)}\right]$$

State assumptions, if any.

Q.29 The indicator phenol red is half in the ionic form when pH is 7.2. If the ratio of the undissociated form to the ionic form is 1 : 5, find the pH of the solution. With the same pH for solution, if indicator is altered such that the ratio of undissociated form to dissociated form becomes 1 : 4, find the pH when 50 % of the new indicator is in ionic form.

Q.30 A buffer solution, 0.080 M in Na_2HPO_4 and 0.020 M in Na_3PO_4, is prepared. The electrolytic oxidation of 1.00 mmol of the organic compound RNHOH is carried out in 100 ml of the buffer. The reaction is

$$RNHOH + H_2O \longrightarrow RNO_2 + 4H^+ + 4e$$

Calculate the approximate pH of the solution after the oxidation is complete.

Q.31 A solution of weak acid HA was titrated with base NaOH. The equivalence point was reached when 36.12 ml of 0.1 M NaOH has been added. Now 18.06 ml of 0.1 M HCl were added to titrated solution, the pH was found to be 4.92. What will be the pH of the solution obtained by mixing 10 ml of 0.2 M NaOH and 10 ml of 0.2 M HA.

Q.32 A weak base BOH was titrated against a strong acid. The pH at 1/4th equivalence point was 9.24. Enough strong base was now added (6m.eq.) to completely convert the salt. The total volume was 50ml. Find the pH at this point.

Q.33 An organic monoprotic acid [0.1M] is titrated against 0.1M NaOH. By how much does the pH change between one fourth and three fourth stages of neutralization? If at one third stage of neutralization, the pH is 4.45 what is the dissociation constant of the acid? Between what stages of neutralisation may the pH change by 2 units?

Q.34 50 ml of a solution which is 0.050 M in the acid HA, $pK_a = 3.80$ and 0.10 M in HB, $pK_a = 8.20$, is titrated with 0.2 M NaOH. Calculate the pH
(a) at the first equivalence point and
(b) at the second equivalence point.

Q.35 Calculate the solubility of solid zinc hydroxide at a pH of 5, 9 and 13. Given

$$Zn(OH)_2(s) \rightleftharpoons Zn(OH)_2(aq) \qquad K_1 = 10^{-6}\ M \qquad (1)$$
$$Zn(OH)_2(aq) \rightleftharpoons Zn(OH)^+ + OH^- \qquad K_2 = 10^{-7}\ M \qquad (2)$$
$$Zn(OH)^+ \rightleftharpoons Zn^{2+} + OH^- \qquad K_3 = 10^{-4}\ M \qquad (3)$$
$$Zn(OH)_2\,(aq) + OH^- \rightleftharpoons Zn(OH)_3^- \qquad K_4 = 10^{3}\ M^{-1} \qquad (4)$$
$$Zn(OH)_3^- + OH^- \rightleftharpoons Zn(OH)_4^{2-} \qquad K_5 = 10\ M^{-1} \qquad (5)$$

Q.36 The salt $Zn(OH)_2$ is involved in the following two equilibria,
$Zn(OH)_2\,(s) \rightleftharpoons Zn^{2+}\,(aq) + 2OH^-(aq)$; $K_{sp} = 1.2 \times 10^{-17}$
$Zn(OH)_2\,(s) + 2OH^-\,(aq) \rightleftharpoons [Zn(OH)_4]^{2-}(aq.)$; $K_c = 0.13$
Calculate the pH of solution at which solubility is minimum.

Q.37 What is the solubility of AgCl in 0.20 M NH_3?
Given : $K_{sp}(AgCl) = 1.7 \times 10^{-10}\ M^2$, $K_1 = [Ag(NH_3)^+] / [Ag^+][NH_3] = 2.33 \times 10^3\ M^{-1}$ and $K_2 = [Ag(NH_3)_2^+] / [Ag(NH_3)^+]\,[NH_3] = 7.14 \times 10^3\ M^{-1}$.

Q.38 H_2S is bubbled into a 0.2 M NaCN solution which is 0.02 M in each $Ag(CN)_2^-$ and $Cd(CN)_4^{2-}$.
Determine which sulphide precipitates first.
Given: $K_{sp}(Ag_2S) = 1.0 \times 10^{-50}\ M^3$
$K_{sp}(CdS) = 7.1 \times 10^{-28}\ M^2$
$K_{inst}(Ag(CN)_2^-) = 1.0 \times 10^{-20}\ M^2$
$K_{inst}(Cd(CN)_4^{2-}) = 7.8 \times 10^{-18}\ M^4$

Q.39 Predict whether or not AgCl will be precipitated from a solution which is 0.02 M in NaCl and 0.05 M in $KAg(CN)_2$. Given $K_{inst}(Ag(CN)_2^-) = 4.0 \times 10^{-19}\ M^2$ and $K_{sp}(AgCl) = 2.8 \times 10^{-10}\ M^2$.

Q.40 Show that solubility of a sparingly soluble salt $M^{2+}A^{2-}$ in which A^{2-} ions undergoes hydrolysis is given by

$$S = \sqrt{K_{sp}\left(1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1K_2}\right)}.$$

where K_1 and K_2 are the dissociation constant of acid H_2A. K_{sp} is solubility product of MA.

EXERCISE III

Q.1 The conjugate acid of NH_2^- is

(A) NH_3 (B) NH_2OH (C) NH_4^+ (D) N_2H_4

Q.2 pH of an aqeous solution of NaCl at 85°C should be

(A) 7 (B) > 7 (C) < 7 (D) 0

Q.3 1 CC of 0.1 N HCl is added to 99 CC solution of NaCl. The pH of the resulting solution will be

(A) 7 (B) 3 (C) 4 (D) 1

Q.4 10 ml of $\frac{M}{200}$ H_2SO_4 is mixed with 40 ml of $\frac{M}{200}$ H_2SO_4. The pH of the resulting solution is

(A) 1 (B) 2 (C) 2.3 (D) none of these

Q.5 The pH of an aqueous solution of 1.0 M solution of a weak monoprotic acid which is 1% ionised is

(A) 1 (B) 2 (C) 3 (D) 11

Q.6 If K_1 & K_2 be first and second ionisation constant of H_3PO_4 and $K_1 >> K_2$ which is incorrect.

(A) $[H^+] = [H_2PO_4^-]$ (B) $[H^+] = \sqrt{K_1[H_3PO_4]}$

(C) $K_2 = [HPO_4^{--}]$ (D) $[H^+] = 3[PO_4^{3-}]$

Q.7 The degree of hydrolysis of a salt of weak acid and weak base in it's 0.1 M solution is found to be 50%. If the molarity of the solution is 0.2 M, the percentage hydrolysis of the salt should be

(A) 100% (B) 50% (C) 25% (D) none of these

Q.8 What is the percentage hydrolysis of NaCN in N/80 solution when the dissociation constant for HCN is 1.3×10^{-9} and $K_w = 1.0 \times 10^{-14}$

(A) 2.48 (B) 5.26 (C) 8.2 (D) 9.6

Q.9 The compound whose 0.1 M solution is basic is

(A) Ammonium acetate (B) Ammonium chloride

(C) Ammonium sulphate (D) Sodium acetate

Q.10 Which of the following solution will have pH close to 1.0?

(A) 100 ml of M/100 HCl + 100 ml of M/10 NaOH

(B) 55 ml of M/10 HCl + 45 ml of M/10 NaOH

(C) 10 ml of M/10 HCl + 90 ml of M/10 NaOH

(D) 75 ml of M/5 HCl + 25 ml of M/5 NaOH

Q.11 The ≈ pH of the neutralisation point of 0.1 N ammonium hydroxide with 0.1 N HCl is

(A) 1 (B) 6 (C) 7 (D) 9

Q.12 If equilibrium constant of

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^-$

Is 1.8×10^{-5}, equilibrium constant for

$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$ is

(A) 1.8×10^{-9} (B) 1.8×10^{9} (C) 5.55×10^{-9} (D) 5.55×10^{10}

Q.13 If 40 ml of 0.2 M KOH is added to 160 ml of 0.1 M HCOOH [$K_a = 2\times10^{-4}$], the pOH of the resulting solution is

(A) 3.4 (B) 3.7 (C) 7 (D) 10.3

Q.14 The range of most suitable indicator which should be used for titration of $X^- Na^+$ (0.1 M, 10 ml) with 0.1 M HCl should be (Given: $k_{b(X^-)} = 10^{-6}$)

(A) 2–3 (B) 3–5 (C) 6–8 (D) 8–10

Q.15 When NO_2 is bubbled into water, it disproportionates completely into HNO_2 and HNO_3.

$$2NO_2 + H_2O\,(l) \longrightarrow NHO_2\,(aq.) + HNO_3\,(aq.)$$

The concentration of NO_2^- in a solution prepared by dissolving 0.05 mole of NO_2 gas in 1 litre H_2O is $\{K_a\,(HNO_2) = 5\times10^{-4}\}$ is

(A) ~ 5×10^{-4} (B) ~ 4.8×10^{-5} (C) ~ 4.8×10^{-3} (D) ~ 2.55×10^{-2}

Q.16 Which of the following is most soluble in water?

(A) MnS ($K_{sp} = 8\times10^{-37}$) (B) ZnS ($K_{sp} = 7\times10^{-16}$)

(C) Bi_2S_3 ($K_{sp} = 1\times10^{-72}$) (D) $Ag_3(PO_4)$ ($K_{sp} = 1.8\times10^{-18}$)

Q.17 The precipitate of CaF_2($K_{sp} = 1.7\times10^{-10}$) is obtained when equal volumes of the following are mixed

(A) 10^{-4} M Ca^{3+} + 10^{-4} M F^- (B) 10^{-2} M Ca^{2+} + 10^{-3} M F^-

(C) 10^{-5} M Ca^{2+} + 10^{-3} M F^- (D) 10^{-3} M Ca^{2+} + 10^{-5} M F^-

Q.18 The solubility of AgCl in water, 0.01 M $CaCl_2$, 0.02 M NaCl and 0.05 M $AgNO_3$ are denoted by S_1, S_2, S_3 and S_4 respectively. Which of the following relationship is correct?

(A) $S_1 > S_2 > S_3 > S_4$ (B) $S_1 = S_2 = S_3 = S_4$

(C) $S_1 > S_3 > S_2 > S_1$ (D) $S_1 > S_2 = S_3 > S_4$

Q.19 How many moles NH_3 must be added to 2.0 litre of 0.80 M $AgNO_3$ in order to reduce the Ag^+ concentration to 5×10^{-8} M. K_f of $[Ag(NH_3)_2^+] = 10^8$

(A) 0.4 (B) 2 (C) 3.52 (D) 4

Q.20 The solubility of metal sulphides in saturated solution of H_2S **{[H_2S] = 0.1 M}** can be represented by

$$MS + 2H^+ \rightleftharpoons M^{2+} + H_2S\ ;\ K_{eq} = \frac{[M^{2+}][H_2S]}{[H^+]^2}$$

The value of K_{eq} is given for few metal sulphide. If conc. of each metal ion in solution is **0.01 M**, which metal sulphides are selectively ppt at total **[H^+] = 1M** in saturated H_2S solution.

Metal sulphides	MnS	ZnS	CoS	PbS
$K_{eq} = \frac{[M^{2+}][H_2S]}{[H^+]^2}$	3×10^{10}	3×10^{-2}	3	3×10^{-7}

(A) MnS, ZnS, CoS (B) PbS, ZnS, CoS (C) PbS, ZnS (D) PbS

EXERCISE IV

Q.1 In the reaction $I^- + I_2 \longrightarrow I_3^-$. the Lewis acid is ______ . **[JEE '97, 1]**

Q.2 Between Na^+ & Ag^+ which is a stronger Lewis acid & why ? **[JEE '97, 2]**

Q.3 Select the correct alternative . **[JEE'97,1+1]**
If pK_b for fluoride ion at 25° C is 10.83, the ionisation constant of hydrofluoric acid in water at this temperature is :
(A) 1.74×10^{-5} (B) 3.52×10^{-3} (C) 6.75×10^{-4} (D) 5.38×10^{-2}

Q.4 The solubility of A_2X_3 is y mol dm^{-3}. Its solubility product is **[JEE 97]**
(A) $6\ y^2$ (B) $64\ y^4$ (C) $36\ y^5$ (D) $108\ y^5$

Q.5 Which of the following statement(s) is/are correct ? **[JEE '98, 2]**
(A) the pH of 1.0×10^{-8} M solution of HCl is 8
(B) the conjugate base of $H_2PO_4^-$ is HPO_4^{2-}
(C) autoprotolysis constant of water increases with temperature
(D) when a solution of a weak monoprotic acid is titrated again a strong base, at half-neutralization point pH = (1/2) pKa .

Q.6 A buffer solution can be prepared from a mixture of **[JEE 99]**
(A) sodium acetate and acetic acid in water
(B) sodium acetate and hydrochloric acid in water
(C) ammonia and ammonium chloride in water
(D) ammonia and sodium hydroxide in water.

Q.7 The pH of 0.1 M solution of the following salts increases in the order **[JEE 99]**
(A) $NaCl < NH_4Cl < NaCN < HCl$ (B) $HCl < NH_4Cl < NaCl < NaCN$
(C) $NaCN < NH_4Cl < NaCl < HCl$ (D) $HCl < NaCl < NaCN < NH_4Cl$

Q.8 An aqueous solution of 6.3 g oxalic acid dihydrate is made up to 250 mL. The volume of 0.1 N NaOH required to completely neutralise 10 mL of this solution is **[JEE 2001]**
(A) 40 mL (B) 20 mL (C) 10 mL (D) 4 mL

Q.9 For sparingly soluble salt ApBq, the relationship of its solubility product (Ls) with its solubility (S) is
(A) $Ls = S^{p+q}, p^p . q^q$ (B) $Ls = S^{p+q}, p^p . q^p$ (C) $Ls = S^{pq}, p^p . q^q$ (D) $Ls = S^{pq}, (p.q)^{p+q}$
[JEE 2001]

Q.10 A solution which is 10^{-3} M each in Mn^{2+}, Fe^{2+}, Zn^{2+} and Hg^{2+} is treated with 10^{-16}M sulphide ion. If K_{sp}, MnS, FeS, ZnS and HgS are 10^{-15}, 10^{-23}, 10^{-20} and 10^{-54} respectively, which one will precipitate first ?
(A) FeS (B) MnS (C) HgS (D) ZnS
[JEE 2003]

Q.11 HX is a weak acid ($K_a = 10^{-5}$). It forms a salt NaX (0.1 M) on reacting with caustic soda. The degree of hydrolysis of NaX is
(A) 0.01% (B) 0.0001% (C) 0.1% (D) 0.5% **[JEE 2004]**

Q.12 CH_3NH_2 (0.1 mole, $K_b = 5 \times 10^{-4}$) is added to 0.08 moles of HCl and the solution is diluted to one litre, resulting hydrogen ion concentration is
(A) 1.6×10^{-11} (B) 8×10^{-11} (C) 5×10^{-5} (D) 2×10^{-2} **[JEE 2005]**

SUBJECTIVES

Q.13 An acid type indicator, HIn differs in colour from its conjugate base (In^-). The human eye is sensitive to colour differences only when the ratio $[In^-]/[HIn]$ is greater than 10 or smaller than 0.1 . What should be the minimum change in the pH of the solution to observe a complete colour change ($K_a = 1.0 \times 10^{-5}$)? **[JEE '97, 2]**

Q.14 A sample of AgCl was treated with 5.00 ml of 1.5 M Na_2CO_3 solution to give Ag_2CO_3. The remaining solution contained 0.0026 g of Cl^- per litre . Calculate the solubility product of AgCl. (K_{sp} $Ag_2CO_3 = 8.2 \times 10^{-12}$) **[JEE '97, 5]**

Q.15 Given : $Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2\,NH_3$, $K_c = 6.2 \times 10^{-8}$ & K_{sp} of AgCl $= 1.8 \times 10^{-10}$ at 298 K . Calculate the concentration of the complex in 1.0 M aqueous ammonia . **[JEE '98, 5]**

Q.16 What will be the resultant pH when 200 ml of an aqueous solution of HCl (pH = 2.0) is mixed with 300 ml of an aqueous solution of NaOH (pH = 12.0) ? **[JEE '98, 2]**

Q.17 The solubility of $Pb(OH)_2$ in water is 6.7×10^{-6}M. Calculate the solubility of $Pb(OH)_2$ in a buffer solution of pH = 8. **[JEE '99, 4]**

Q.18 The average concentration of SO_2 in the atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of SO_2 in water at 298 K is 1.3653 moles litre^{-1} and the pK_a of H_2SO_3 is 1.92, estimate the pH of rain on that day. **[JEE 2000]**

Q.19 500 ml of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 25°C.

(a) Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.

(b) If 6 g of NaOH is added to the above solution, determine final pH. Assume there is no change in volume on mixing. K_a of acetic acid is 1.75×10^{-5} M. **[JEE 2002]**

Q.20 Will the pH of water be same at 4°C and 25°C ? Explain. **[JEE 2003]**

Q.21 0.1 M of HA is titrated with 0.1 M NaOH, calculate the pH at end point. Given $Ka(HA) = 5 \times 10^{-6}$ and $\alpha << 1$. **[JEE 2004]**

ANSWER KEY

EXERCISE I

IONIZATION CONSTANTS AND pH

Q.1.1 (i) 1.8×10^{-16}, (ii) 1.66×10^{-5}, (iii) 4×10^{-10} Q.1.2 10 Q.1.3 170.4
Q.1.4 (a) $K_a = 10^{-8}$, (b) $K_b = 10^{-6}$
Q.1.5 (a) +1, (b) 0.522, (c) 2.87, (d) 11.13 (e) 6.97, (f) 7, (g) 6.01, (h) 6.97, (i) 2.61, (j) 11.30 (k) 9 (l) 1 , (m) 3
Q.1.6 6.81 Q.1.7 6.022×10^{7} Q.1.8 0.6×10^{-7}
Q.1.9 (i) 6.51 ; (ii) (a) Basic , (b) Acidic Q.1.10 2.31×10^{-8} M Q.1.11 0.556 M
Q.1.12 1.11×10^{-4} Q.1.13 4.87 Q.1.14 $[H^+] = 1.612 \times 10^{-2}$M, $[CHCl_2COO^-] = 6.126 \times 10^{-3}$M
Q.1.15 error = 1% Q.1.16 $[H^+] = 10^{-3}$M, $[CH_3COO^-] = 3.6 \times 10^{-4}$M, $[C_7H_5O_2^-] = 6.4 \times 10^{-4}$M
Q.1.17 2.08

POLYPROTIC ACIDS & BASES

Q.2.1 $[S^{2-}] = 2.5 \times 10^{-15}$
Q.2.2 $[H^+] = [H_2PO_4^-] = 5.623 \times 10^{-3}$, $[HPO_4^{2-}] = 6.8 \times 10^{-8}$, $[PO_4^{3-}] = 5.441 \times 10^{-18}$
Q.2.3 pH = 11.46, $[enH_2^{2+}] = 7.1 \times 10^{-8}$ M Q.2.4 0.2116 M, 0.1884 M, 0.0116 M, 0
Q.2.5 0.0528 M, 0.0472 M, 0.0528 M, 0.000064 M Q.2.6 10.07
Q.2.7 $[OH^-] = 3.57 \times 10^{-3}$ M, $[H_2en]^{2+} = 2.7 \times 10^{-8}$ M

BUFFER SOLUTION

Q.3.1 $[OH^-] = 9.0 \times 10^{-6}$ Q.3.2 4.74 Q.3.3 0.05 mol
Q.3.4 9.56 Q.3.5 (a) pH = 9.239 (b) lowered (c) pH = 4.699
Q.3.6 8.7782 Q.3.7 9.7324
Q.3.8 (a) 4.7525 (b) 4.697, (c) 4.798 (d) 1.134% on acid addition 0.96% on base addition.
Q.3.9 $[H^+] = 2.5 \times 10^{-3}$

INDICATORS

Q.4.1 $[HI_n] = 28.57\%$ Q.4.2 (b), (c)
Q.4.3 (methyl red), one with pH = 5.22 as midpoint of colour range
Q.4.4 85.71% Q.4.5 ∆pH = 0.954

HYDROLYSIS

Q.5.1 $[OH^-] = 6.664 \times 10^{-6}$ Q.5.2 pH = 4.477 Q.5.3 $K_b = 6.25 \times 10^{-10}$
Q.5.4 0.56%, pH = 7 Q.5.5 1.667% Q.5.6 0.26%
Q.5.7 4.0% Q.5.8 10^{-6} ; 10^{-8} Q.5.9 pH = 10.43
Q.5.10 8.34 Q.5.11 4.19 Q.5.12 5.12×10^{-6} M
Q.5.13 (a) 6, (b) 1×10^{-5}

ACID BASE REACTIONS & TITRATIONS

Q.6.1 8.71 Q.6.2 4.98 Q.6.3 6.1
Q.6.4 2.37×10^{-6} Q.6.5 pH = 8.73, $[Na^+] = 0.0379$, $[C_6H_5O^-] = 0.0373$
Q.6.6 $K_b = 1.8 \times 10^{-5}$, 5.27 Q.6.7 8.73
Q.6.8 (i) 2.85, (ii) 4.0969, (iii) 4.5229, (iv) 4.699, (v) 5.301, (vi) 8.699

SOLUBILITY & SOLUBILITY PRODUCT'S

Q.7.1 QX_2 is more soluble Q.7.2 1.6×10^{-8} Q.7.3 1.4×10^{-4}
Q.7.4 $[Cu^+] = 5 \times 10^{-11}$ M Q.7.5 3.4×10^{-11} Q.7.6 2.6×10^{-16}
Q.7.7 1.0×10^{-18} M Q.7.8 8.8×10^{-12} Q.7.9 1.0×10^{-5} mol/lit
Q.7.10 5×10^{-10} M Q.7.11 12 mg
Q.7.12 (a) no precipitation will occur, (b) a precipitate will form Q.7.13 1.6×10^{-3}
Q.7.14 2.1×10^{-5}

SIMULTANEOUS SOLUBILITY

Q.8.1 4×10^{-7}mol/L AgBr, 9×10^{-7} mol/L AgSCN Q.8.2 $[F^-] = 3 \times 10^{-3}$M
Q.8.3 $[Ag^+] = 6.667 \times 10^{-5}$M

COMPLEXATION EQUILIBRIA

Q.9.1 19.3 kg Q.9.2 $K_d = 1/K_f = 4.8 \times 10^{-4}$ Q.9.3 2.8×10^{-3} M

PROFICIENCY TEST

Q.1 False Q.2 False Q.3 True Q.4 False Q.5 True
Q.6 Increase, one Q.7 Greater Q.8 Br^- ion Q.9 Greater
Q.10 7.14×10^{-3} Q.11 3×10^{-6} Q.12 in both dil acidic and alkaline solution
Q.13 $M_2X = QY_2 > PZ_3$
Q.14 10^{-8} Q.15 7 Q.16 5.74 Q.17 HSO_4^-
Q.18 increases Q.19 less Q.20 less Q.21 Lewis acid
Q.22 Buffer Q.23 Weaker Q.24 acidic Q.25 cationic Q.26 independent

EXERCISE II

Q.1 $1.8 \times 10^{-16}, 10^{-14}$ Q.2 $K_a = 1.25 \times 10^{-2}$ Q.3 $\alpha = 0.05$
Q.4 11.74 Q.5 $\Delta H_{neut} = -51.963$ kJ mol^{-1}
Q.6 $V = 2.77 \times 10^4$ litre Q.7 (a) 13.1, (b) 0.13 M Q.8 1.650
Q.9 (a) 4.1, (b) 3.6×10^2, (c) 9.8×10^3 Q.10 (a) 2.12 (b) 4.66 (c) 7.2 (d) 12
Q.11 (a) 8.34 (b) 4.66 (c) 9.6 (d) 7.20 Q.12 5.158
Q.13 (a) acetic acid, salt-acid molar ratio 1.8 :1 ;
(b) [HOAc] = 0.066 mmol/ml and $[OAc^-] = 0.119$ mmol/ml
Q.14 8.35, 9.60, 4.66 Q.15 9.168 Q.16 (a) pH = 3.83 (b) pH = 3.85 , (c) = 3.99
Q.17 0.0818 moles Q.18 2.558 Q.19 $[OH^-] = 3.73 \times 10^{-2}M, [H_3PO_4] = 6 \times 10^{-18}M$
Q.20 9.7736
Q.21 $K_h(H_2PO_4^-) = 2 \times 10^{-12}$; $K_h(HPO_4^{2-}) = 2 \times 10^{-7}$, $K_h(PO_4^{3-}) = 2 \times 10^{-2}$; acidic, basic
Q.22 $[CO_3^{2-}] = 4.9 \times 10^{-3}M$ Q.23 $[OH^-] = 3 \times 10^{-7}M$
Q.24 $[H_2CO_3] = 9.85 \times 10^{-6}M$; $[HCO_3^-] = 4.9 \times 10^{-4}$ $[CO_3^{2-}] = 2.45 \times 10^{-8}$
Q.25 0.908 Q.26 (a) 9.21×10^{-5} M, 9.21×10^{-5}, 8.9×10^{-16} (b) 9.96
Q.27 1.6 mmol Q.29 pH = 7.3 Q.30 7.81 Q.31 8.96
Q.32 11.22 Q.33 0.9542, $pK_a = 4.751$, $\frac{1}{11}$th & $\frac{10}{11}$th stages of neutralisation
Q.34 (a) 5.85 (b) 10.48 Q.35 10 M, 1.12×10^{-6}M, 2×10^{-4} M
Q.36 9.99, $s = 2.5 \times 10^{-5}$ M Q.37 9.66×10^{-3} Q.38 $[Cd^{2+}]$
Q.39 Precipitation will occur

EXERCISE III

Q.1 A Q.2 C Q.3 B Q.4 B Q.5 C Q.6 D Q.7 B
Q.8 A Q.9 D Q.10 D Q.11 B Q.12 B Q.13 D Q.14 B
Q.15 A Q.16 D Q.17 B Q.18 D Q.19 D Q.20 D

EXERCISE IV

Q.1 I_2 Q.2 Ag^+, Na^+ has no tendency to accept e^- Q.3 C Q.4 D
Q.5 B, C Q.6 A, B, C Q.7 B Q.8 A Q.9 A
Q.10 C Q.11 A Q.12 B

SUBJECTIVES

Q.13 $\Delta pH = 2$ Q.14 $K_{sp} = 1.71 \times 10^{-10}$ Q.15 $[Ag(NH_3)_2^+] = 0.0539$
Q.16 pH = 11.3010 Q.17 $s = 1.203 \times 10^{-3}$M Q.18 think ?
Q.19 (a) 0.0175% , (b) 4.757 Q.20 No it will be > 7 Q.21 pH = 9

BANSAL CLASSES

PHYSICS

TARGET IIT JEE 2007
XI (PQRS & J)

KINETIC THEORY OF GASES
&
THERMODYNAMICS

CONTENTS

KEY CONCEPTS

Kinetic Theory Of Gases

1. Assumption of kinetic theory of gases

(1) A gas consist of particles called molecules which move randomly in all directions.
(2) These molecules obey Newton's law of motion.
(3) Size of molecule negligible in comparison to average separation between the molecules.
(4) The forces on molecule are negligible except at the time of collision.
(5) All collision between molecules or between molecules and wall are pefectly elastic. Time of collision is very small.
(6) For large number of molecules the density and distribution of molecules with different velocities are independent of position, direction and time.

2. Pressure of an ideal gas

$$\boxed{P = \frac{1}{3}\rho\overline{v}^2 = \frac{1}{3}\rho\overline{v}^2_{rms}}$$

Here v = mean square speed

v_{rms} = root mean square speed
ρ = density of gas

$$P = \frac{2}{3}\left(\frac{1}{2}\rho v^2_{rms}\right)$$

$$P = \frac{2}{3}E$$

$$E = \frac{3}{2}P$$

So total K.E. $\boxed{K = \frac{3}{2}PV}$

3. R.M.S. velocity – depends on tempearture only for any gas.

$$\bar{v}_{rms} = \frac{\sqrt{v_1^2+v_2^2+v_3^2+..........+v_n^2}}{n}$$

$$P = \frac{1}{3}\rho v^2_{rms}$$

$$\boxed{v_{rms} = \sqrt{\frac{3P}{\rho}} = \sqrt{\frac{3RT}{M}}}$$

4. Most Probable velocity – velocity which maximum number of molecules may have

$$\boxed{v_{mp} = \sqrt{\frac{2RT}{M}}}$$

5. Average velocity

$$v_{avg} = \frac{v_1+v_2+........+\bar{v}_n}{n} = 0$$

6. Average speed

$$\boxed{V_{avg} = \frac{|\vec{v}_1| + |\vec{v}_2| + |\vec{v}_3| + \ldots\ldots + |v_n|}{n} = \sqrt{\frac{8RT}{\pi M}}}$$

7. Ideal gas equation

PV= nRT (container form of gas law/ pressure volume form)

$P = \left(\frac{\rho}{M}\right)RT$ (open atmosphere / pressure density form)

8. Graham's law of diffusion :–

When two gases at the same pressure and tempearture are allowed to diffuse into each other the rate of diffusion of each gas is inversely proportional to the square root of the density of the gas

$r \alpha v_{rms}$ where r = rate of diffusion

so, $$\boxed{\frac{r_1}{r_2} = \sqrt{\frac{\rho_2}{\rho_1}}}$$

9. Degree of Freedom (f) – No. of ways in which a gas molecule can distribute its energy

10. Law of equipartition of energy : – Energy in each degree of freedom = 1/2 KT joules

If degree of freedom is f. Energy = $\frac{f}{2}$ KT joules.

$$U = \frac{f}{2} KTnN_A = \frac{f}{2} nRT$$

11. Degree of freedom(f) in different gas molecules

Molecules	Translational	Rotational
Monoatomic	3	0
Diatomic	3	2
Polyatomic	3	2 (linear molecule) 3 (non-linear molecule)

Translational energy for all type of molecules = $\frac{3}{2}$ **(nRT)**

Law of Thermodynamics

1. Zeroth law of thermodynamics :– If two bodies A and B are in thermal equilibrium and A and C are also in thermal equilibrium. Then B and C are also in thermal equilibrium.

2. First law of Thermodynamics:– Energy conservation for gaseous system.

Heat supplied to the gas = Increment in internal energy + work done by the gas.

$\Delta Q = \Delta U + \Delta W$ ΔQ is +ve for heat supplied

in differential form $dQ = dU + dW$ ΔQ is –ve for heat rejected and $dQ = nCdT$ C = molar specific heat

$C = C_P$ (constant pressure) ; $C = C_V$ = (constant volume)

$$dU = \frac{f}{2}\, nRdT$$

$$dW = \int_{v_1}^{v_2} P\,dv$$ (P = pressure of the gas of which work is to be calculated)

ΔW = +ve for work done by gas (in expansion of gas)

ΔW = –ve for work done on the gas (in contraction of gas)

Molar specific heat for a given process $C = \frac{f}{2} R + \frac{R\,PdV}{PdV + VdP} = C_V + \frac{R\,PdV}{PdV + VdP}$

Process	**C**	**Monoatomic**	**Diatomic**	**Polyatomic**
V= constant	$C_V = (f/2)R$	(3/2)R	(5/2)R	3R
P = constant	$C_P = \frac{f+2}{2}R$	(5/2)R	(7/2)R	4R

Mayor's Relation $C_P = C_V + R$

Note :– C of a gas depends on the process of that gas, which can be infinite in types.

Ratio of specific heat :– $\gamma = \frac{C_P}{C_V} = \frac{f+2}{f}$

$\xrightarrow{\text{monoatomic}}$ 5/3 = 1.67

$\xrightarrow{\text{diatomic}}$ 7/5 = 1.4

$\xrightarrow{\text{polyatomic}}$ 4/3 = 1.33

and $f = \frac{2}{\gamma - 1}$

$C_V = \frac{R}{\gamma - 1}$; $C_P = \frac{\gamma R}{\gamma - 1}$

Isochoric Process (V= constant)

$dV = 0 \Rightarrow dW = 0$

By FLT $dQ = dU = nC_V\,dT$

$$\boxed{Q = \int_{T_1}^{T_2} nC_V\,dT = nC_V(T_2 - T_1)}$$

* Be careful if $\Delta V = 0$ then not necessarily an Isochoric Process.

Isobaric Process (P = constant)

$dP = 0$

By FLT $dQ = dU + dW$

$n_{C_P}(T_2 - T_1) = (\frac{f}{2})nR(T_2 - T_1) + nR(T_2 - T_1)$

$$\boxed{W = nR(T_2 - T_1)}$$

* If $\Delta P = 0$ then not necessarily an Isobaric Process.

Isothermal Process (T = constant)

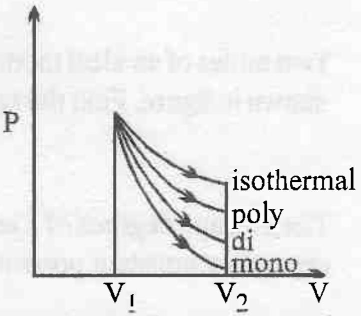
$dT = 0$, $dU = 0$

$$Q = W = (nRT) \int_{v_1}^{v_2} dV/V$$

$$\boxed{W = nRT\, ln\frac{V_2}{V_1} = nRT\, ln\frac{P_1}{P_2}} \qquad \left(\frac{V_2}{V_1} = \frac{P_1}{P_2} = \text{compression ratio}\right)$$

Adiabatic Process dQ = 0 but if ΔQ = 0, it is not necessaserily adibatic.
dW = –dU By FLT

$$\boxed{W = \int_{T_1}^{T_2} \frac{nRdT}{\gamma - 1} = \frac{nR(T_1 - T_2)}{\gamma - 1} = \frac{P_1V_1 - P_2V_2}{\gamma - 1}}$$



So PdV + VdP = (γ–1) ....(ii)

For Adiabatic Process PV^γ = constant

Work done is least for monoatomic gas

$$\left|\frac{dP}{dV}\right|_{adiabatic} = \gamma\left|\frac{dP}{dV}\right|_{isothermal}$$

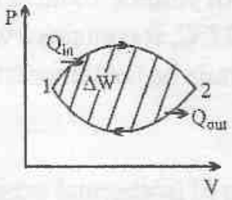
Polytropic process

PV^n= constant

$$\boxed{P = \frac{K}{V^n} \Rightarrow \frac{dP}{dV} = -n\left|\frac{K}{V^{n+1}}\right|} \quad ; \qquad C = \frac{R}{\gamma - 1} + \frac{R}{1-n}$$

So C is constant for polytropic process

Efficiency of a cyclic process



$\Delta U = 0$

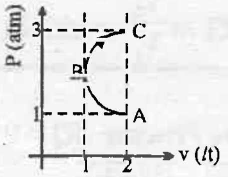
so $\Delta Q = \Delta W$

Efficiency $\eta = \frac{\text{work done by gas}}{\text{heat input}}$

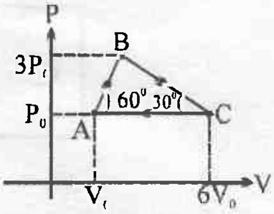
$$\eta = \frac{W}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}$$

EXERCISE – I

Q.1 In the P-V diagram shown in figure, ABC is a semicircle. Find the workdone in the process ABC.



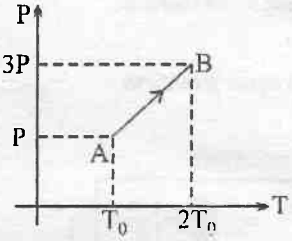
Q.2 Two moles of an ideal monoatomic gas undergone a cyclic process ABCA as shown in figure. Find the ratio of temperatures at B and A.



Q.3 The average degrees of freedom per molecules for a gas is 6. The gas performs 25 J of work when it expands at constant pressure. Find the heat absorbed by the gas.

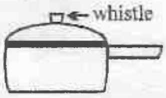
Q.4 1 mole of an ideal gas at initial temperature T was cooled isochorically till the gas pressure decreased n times. Then by an isobaric process, the gas was restored to the initial temperature T. Find the net heat absorbed by the gas in the whole process.

Q.5 Pressure versus temperature graph of an ideal gas is shown. Density of gas at point A is ρ_0. Find the density of gas at B.

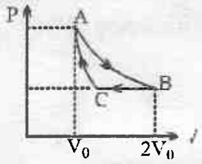


Q.6 PV-diagram of a monoatomic ideal gas is a straight line passing through origin. Find the molar heat capacity in the process.

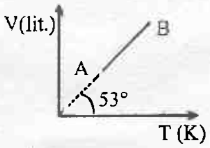
Q.7 An empty pressure cooker of volume 10 litres contains air at atmospheric pressure 10^5 Pa and temperature of 27°C. It contains a whistle which has area of 0.1 cm^2 and weight of 100 gm. What should be the temperature of air inside so that the whistle is just lifted up?



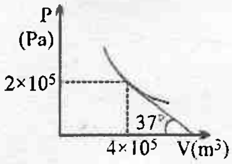
Q.8 In a cycle ABCA consisting of isothermal expansion AB, isobaric compression BC and adiabatic compression CA, find the efficiency of cycle (Given : $T_A = T_B = 400$ K, $\gamma = 1.5$)



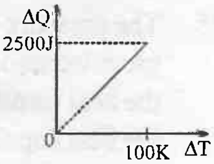
Q.9 V-T curve for 2 moles of a gas is straight line as shown in the graph here. Find the pressure of gas at A.



Q.10 P-V graph for an ideal gas undergoing polytropic process PV^m = constant is shown here. Find the value of m.



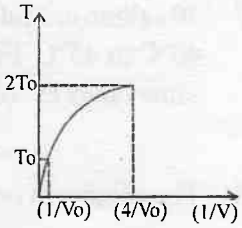
Q.11 Air at temperature of 400 K and atmospheric pressure is filled in a balloon of volume 1 m^3. If surrounding air is at temperature of 300 K, find the ratio of Buoyant force on balloon and weight of air inside



Q.12 One mole of a gas mixture is heated under constant pressure, and heat required ΔQ is plotted against temperature difference acquired. Find the value of γ for mixture.

Q.13 Ideal diatomic gas is taken through a process $\Delta Q = 2\Delta U$. Find the molar heat capacity for the process (where ΔQ is the heat supplied and ΔU is change in internal energy)

Q.14 A gas is undergoing an adiabatic process. At a certain stage A, the values of volume and temperature $\equiv (V_0, T_0)$ and the magnitude of the slope of V-T curve is m. Find the value of C_P and C_V.



Q.15 Figure shows a parabolic graph between T and $\frac{1}{V}$ for a mixture of a gas undergoing an adiabatic process. What is the ratio of V_{rms} and speed of sound in the mixture?

Q.16 The height of mercury is a faulty barometer is 75 cm and the tube above mercury having air is 10 cm long. The correct barometer reading is 76 cm. If the faulty barometer reads 74 cm, find the true barometer reading.

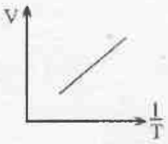
Q.17 A piston divides a closed gas cylinder into two parts. Initially the piston is kept pressed such that one part has a pressure P and volume 5V and the other part has pressure 8P and volume V. The piston is now left free. Find the new pressures and volumes for the adiabatic and isothermal processes. For this gas $\gamma = 1.5$.

Q.18 A closed vessel of volume V_0 contains oxygen at a pressure P_0 and temperature T_0. Another closed vessel of the same volume V_0 contains helium at a pressure of P_0 and temperature $T_0/2$. Find the ratio of the masses of oxygen to the helium.

Q.19 A gas undergoes a process in which the pressure and volume are related by VP^n = constant. Find the bulk modulus of the gas.

Q.20 An ideal gas has a molar heat capacity C_V at constant volume. Find the molar heat capacity of this gas as a function of volume, if the gas undergoes the process : $T = T_0 e^{\alpha V}$.

Q.21 A standing wave of frequency 1000 Hz in a column of methane at 27°C produces nodes which are 20.4 cm apart. Find the ratio of heat capacity of methane at constant pressure to that at constant volume (Take gas constant, $R = 8.31\ J{\cdot}K^{-1}mol^{-1}$)



Q.22 One mole of an ideal monoatomic gas undergoes a process as shown in the figure. Find the molar specific heat of the gas in the process.

Q.23 One mole of an ideal gas is compressed from 0.5 lit to 0.25 lit. During the compression, 23.04×10^2 J of work is done on the gas and heat is removed to keep the temperature of the gas constant at all times. Find the temperature of the gas. (Take universal gas constant $R = 8.31\ J\ mol^{-1}K^{-1}$)

Q.24 A mixture of 4 gm helium and 28 gm of nitrogen in enclosed in a vessel of constant volume 300°K. Find the quantity of heat absorbed by the mixture to doubled the root mean velocity of its molecules.
(R = Universal gas constant)

Q.25 The pressure of an ideal gas changes with volumes as $P = aV$ where 'a' is a constant. One moles of this gas is expanded to 3 times its original volume V_0. Find

(i) the heat transferred in the process.

(ii) the heat capacity of the gas.

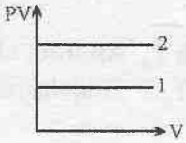
Q.26 If heat is added at constant volume, 6300 J of heat are required to raise the temperature of an ideal gas by 150 K. If instead, heat is added at constant pressure, 8800 joules are required for the same temperature change. When the temperature of the gas changes by 300 K. Determine the change is the internal energy of the gas.

Q.27 70 calorie of heat is required to raise the temperature of 2 mole of an ideal gas at constant pressure from 40°C to 45°C. Find the amount of heat required to raise the temperature of the same gas through the same range at constant volume ($R = 2$ cal/mol-K)

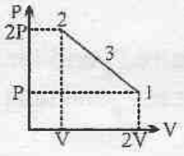
Q.28 The volume of one mole of an ideal gas with specific heat ratio γ is varied according to the law $V = \frac{a}{T^2}$, where a is a constant. Find the amount of heat obtained by the gas in this process if the gas temperature is increased by ΔT.

Q.29 Find the molecular mass of a gas if the specific heats of the gas are $C_P = 0.2$ cal/gm°C and $C_V = 0.15$ cal/gm°C. [Take $R = 2$ cal/mole°C]

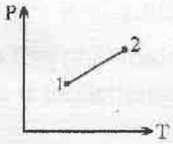
Q.30 Examine the following plots and predict whether in (i) $P_1 < P_2$ and $T_1 > T_2$, in (ii) $T_1 = T_2 < T_3$, in (iii) $V_1 > V_2$, in (iv) $P_1 > P_2$ or otherwise.



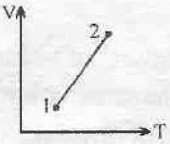
(i)



(ii)



(iii)



(iv)

EXERCISE – II

Q.1 A barometer is faulty. When the true barometer reading are 73 and 75 cm of Hg, the faulty barometer reads 69 cm and 70 cm respectively.

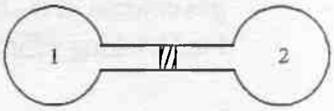
(i) What is the total length of the barometer tube?

(ii) What is the true reading when the faulty barometer reads 69.5 cm ?

(iii) What is the faulty barometer reading when the true barometer reads 74 cm?

Q.2 Two bulbs of equal volume joined by a narrow tube of negligible volume contain hydrogen at 0°C and one atmospheric pressure. What is the pressure of the gas when one of the bulbs is immersed in steam at 100°C and the other in liquid oxygen at –190°C ? The volume of each bulb is $10^{-3}m^3$ and density of hydrogen is 0.09 kg/m^3 at 0°C and at 1 atmosphere. What mass of hydrogen passes along the connecting tube?

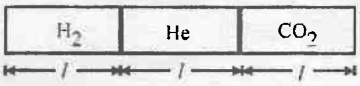
Q.3 Two spherical flasks having a volume $V_0 = 1.0$ L each containing air are connected by a tube of diameter d = 6 mm and length *l* = 1 m. A small droplet of mercury contained in the tube is at its middle at 0°C. By what distance do the mercury droplets move if the flask 1 is heated by 2°C while flask 2 is cooled by 2°C. Ignore any expansion of flask wall.



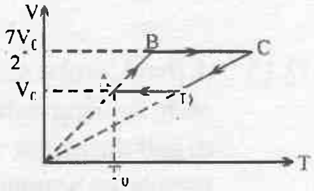
Q.4 A vessel of volume V = 30*l* is seperated into three equal parts by stationary semipermeable thin membranes as shown in the Figure. The left, middle and right parts are filled with $m_{H_2} = 30g$ of hydorgen, $m_{O_2} = 160g$ of oxygen, and $m_{N_2} – 70g$ of nitrogen respectively. The left partition lets through only hydrogen, while the right partition lets through hydrogen and nitrogen. What will be the pressure in each part of the vessel after the equilibrium has been set in if the vessel is kept at a constant temperature T = 300K?

Q.5 A freely moving piston divides a vertical cylinder, closed at both ends, into two parts each containing 1 mole of air. In equilibrium, at T = 300 K, volume of the upper part is η = 4 times greater than the lower *p* part. At what temperature will the ratio of these volumes be equal to η' = 2?

Q.6 A non-conducting cylindrical vessel of length 3*l* is placed horizontally and is divided into three parts by two easily moving piston having low thermal conductivity as shown in figure. These parts contain H_2, He and CO_2 gas at initial temperatures $\theta_1 = 372°C$, $\theta_2 = – 15°C$ and $\theta_3 = 157°C$ respectively. If initial length and pressure of each part are *l* and P_0 respectively, calculate final pressure and length of each part. Use : $\gamma_{CO_2} = 7/5$

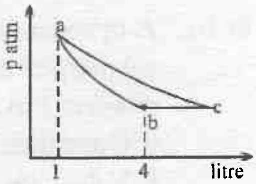


Q.7 A sample of an ideal non linear tri-atomic gas has a pressure P_0 and temperature T_0 taken through the cycle as shown starting from A. Pressure for process C → D is 3 times P_0. Calculate heat absorbed in the cycle and work done.



Q.8 RMS velocity of molecules of a di-atomic gas is to be increased to 1.5 times. Calculate ratio of initial volume to final volume, if it is done.
(i) Adiabatically ; (ii) Isobarically ; (iii) Calculate, also ratio of work done by gas during these processes.

Q.9 Figure shows three processes for an ideal gas. The temperature at 'a' is 600 K, pressure 16 atm and volume 1 litre. The volume at 'b' is 4 litre. Out of the two process ab and ac, one is adiabatic and he other is isothermal. The ratio of specific heats of the gas is 1.5. Answer the following :



(i) Which of ab and ac processes is adiabatic. Why?

(ii) Compute the pressure of the gas at b and c.

(iii) Compute the temperature at b and c.

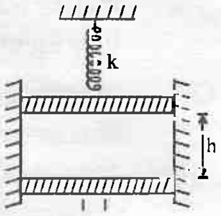
(iv) Compute the volume at c.

Q.10 Two vessels A and B both containing an ideal diatomic gas are connected together by a narrow tube of negligible volume fitted with a valve. A contains 5 mole of the gas at temperature 35°C and pressure 1.6×10^5 Nm^{-2}, while B contains 2 moles of gas at temperature 17°C and pressure 8.3×10^4 Nm^{-2}. The valve between the two vessel is opened to allow the contents to mix and achieve an equilibrium temperature of 27°C.

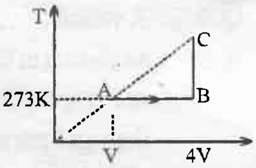
(i) Find the final pressure and the amount of heat transferred to the surrounding.

(ii) If the vessels along with the tube are perfectly insulated, calculate the final temperature and pressure.

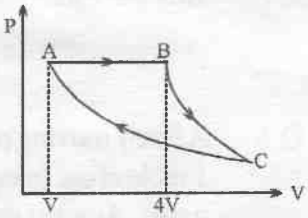
Q.11 An ideal gas at NTP is enclosed in a adiabatic vertical cylinder having area of cross section A = 27 cm^2, between two light movable pistons as shown in the figure. Spring with force constant k = 3700 N/m is in a relaxed state initially. Now the lower piston is moved upwards a height h/2, h being the initial length of gas column. It is observed that the upper piston moves up by a distance h/16. Find h taking γ for the gas to be 1.5. Also find the final temperature of the gas.



Q.12 At a temperature of T_0 = 273°K, two moles of an ideal gas undergoes a process as shown. The total amount of heat imparted to the gas equals Q = 27.7 kJ. Determine the ratio of molar specific heat capacities.

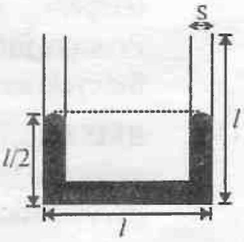


Q.13 A fixed mass of a gas is taken through a process A → B → C → A. Here A → B is isobaric. B → C is adiabatic and C → A is isothermal. Find efficiency of the process. (take γ = 1.5)

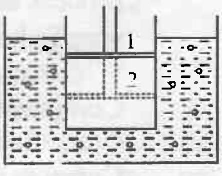


Q.14 A vessel of volume 30 litre is separated into three equal parts by stationary semipermeable membrane. The left, middle and right parts are filled with 30 gms of hydrogen, 160 gms of oxygen and 70 gms of nitrogen respectively. The left partition lets through only hydrogen while the right partition lets through hydrogen and nitrogen. If the temperature in all is 300 K find the ratio of pressure in the three compartments.

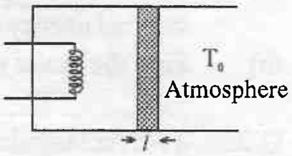
Q.15 A thin U–tube sealed at one end consists of three bends of length l = 250mm each, forming right angles. The vertical parts of the tube are filled with mercury to half the height as shown in the figure. All of mercury can be displaced from the tube by heating slowly the gas in the sealed end of the tube, which is separated from the atmospheric air by mercury. Determine the work A done by the gas thereby if the atmospheric pressure is $p_0 = 10^5$Pa, the density of mercury is $\rho_{mer} = 13.6 \times 10^3 kg/m^3$, and the cross-sectional area of the tube is S = 1cm^2.



Q.16 A cylinder containing a gas is closed by a movable piston. The cylinder is submerged in an ice-water mixture. The piston is quickly pushed down from position 1 to position 2. The piston is held at position 2 until the gas is again at 0°C and then slowly raised back to position 1. Represent the whole process on P-V diagram. If m = 100 gm of ice are melted during the cycle, how much work is done on the gas. Latent heat of ice = 80 cal/gm.



Q.17 An adiabatic vessel containing n moles of a ideal diatomic gas is fitted with a light conducting piston. The cross-sectional area, thickness and thermal conductivity of piston are A, l and K respectively. The other side of the piston is open to atmosphere of temperature T_0. Heat is supplied to the gas by means of an electric heater at a small constant rate q. Initial temperature of gas is T_0.



(a) Find the temperature of the gas as a function of time,

(b) Find the maximum temperature of the gas and

(c) What is the ratio of the maximum volume to the minimum volume?

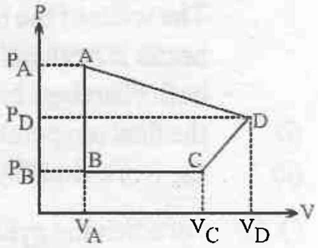
Q.18 A parallel beam of particles of mass m moving with velocities v impinges on a wall at an angle θ to its normal. The number of particles per unit volume in the beam is n. If the collision of particles with the wall is elastic, then find the pressure exerted by this beam on the wall.

Q.19 For the thermodynamic process shown in the figure.

$P_A = 1 \times 10^5$ Pa; $P_B = 0.3 \times 10^5$ Pa

$P_D = 0.6 \times 10^5$ Pa; $V_A = 0.20$ litre

$V_D = 1.30$ litre.

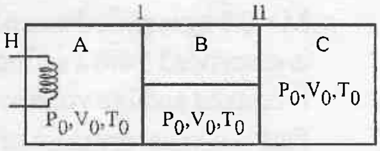


(a) Find the work performed by the system along path AD.

(b) In the total work done by the system along the path ADC is 85J find the volume at point C.

(c) How much work is performed by the system along the path CDA?

Q.20 The figure shows an insulated cylinder divided into three parts A, B and C. Pistons I and II are connected by a rigid rod and can move without friction inside the cylinder. Piston I is perfectly conducting while piston II is perfectly insulating. The initial state of the gas (γ = 1.5) present in each compartment A, B and C is as shown. Now, compartment A is slowly given heat through a heater H such that the final volume of C becomes $\frac{4V_0}{9}$. Assume the gas to be ideal and find.



(a) Final pressures in each compartment A, B and C

(b) Final temperatures in each compartment A, B and C

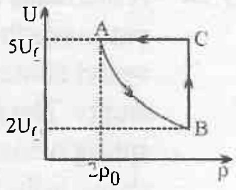
(c) Heat supplied by the heater

(d) Work done by gas in A and B.

(e) Heat flowing across piston I.

Q.21 How many atoms do the molecules of a gas consist of if γ increases 1.20 times when the vibrational degrees of freedom are "frozen"? Assume that molecules are non linear.

Q.22 Figure shows the variation of the internal energy U with the density ρ of one mole of ideal monoatomic gas for a thermodynamic cycle ABCA. Here process AB is a part of rectangular hyperbola.



(a) Draw the P-V diagram for the above process.

(b) Find the net amount of heat absorbed by the system for the cyclic process.

(c) Find the work done in the process AB.

Q.23 An ideal monoatomic gas undergoes a process where its pressure is inversely proportional to its temperature.

(i) Calculate the specific heat for the process.

(ii) Find the work done by two moles of gas if the temperature changes from T_1 to T_2.

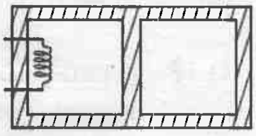
Q.24 An ideal diatomic gas undergoes a process in which its internal energy relates to the volume as

$$U = a\sqrt{V}$$, where α is a constant.

(a) Find the work performed by the gas and the amount of heat to be transferred to this gas to increase its internal energy by 100 J.

(b) Find the molar specific heat of the gas for this process.

Q.25 Two rectangular boxes shown in figure has a partition which can slide without friction along the length of the box. Initially each of the two chambers of the box has one mole of a monoatomic ideal gas ($\gamma = 5/3$) at a pressure p_0 volume V_0 and temperature T_0. The chamber on the left is slowly heated by an electric heater. The walls of the box and the partitions are thermally insulated. Heat loss through the lead wires of the heater is negligible. The gas in the left chamber expands, pushing the partition until the final pressure in both chambers becomes $243\ P_0/32$. Determine

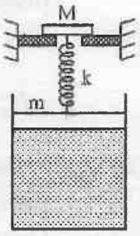


(i) the final temperature of the gas in each chamber and

(ii) the work-done by the gas in the right chamber.

Q.26 An adiabatic cylinder of length $2l$ and cross-sectional area A is closed at both ends. A freely moving non-conducting this piston divides the cylinder in two parts. The piston is connected with right end by a spring having force constat K and natural length l. Left part of the cylinder contains one mole of helium and right part contains 0.5 mole of each of helium and oxygen. If initial pressure of gas in each part is P_0, calculate heat supplied by the heating coil, connected to left part, to compress the spring through half of its natural length.

Q.27 0.01 moles of an ideal diatomic gas is enclosed in an adiabatic cylinder of cross-sectional area $A = 10^{-4} m^2$. In the arrangement shown, a block of mass $M = 0.8$ kg is placed on a horizontal support, and another block of mass $m = 1$ kg is suspended from a spring of stiffness constant $k = 16$ N/m. Initially, the spring is relaxed and the volume of the gas is $V = 1.4 \times 10^{-4}\ m^3$.

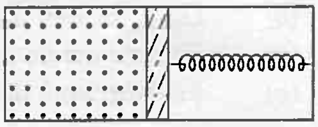


(a) Find the initial pressure of the gas.

(b) If block *m* is gently pushed down and released it oscillates harmonically, find its angular frequency of oscillation.

(c) When the gas in the cylinder is heated up the piston starts moving up and the spring gets compressed so that the block *M* is just lifted up. Determine the heat supplied.
Take atmospheric pressure $P_0 = 10^5\ Nm^{-2}$, $g = 10 m/s^2$.

Q.28 A thermally insulated vessel is divided into two parts by a heat-insulating piston which can move in the vessel without the friction. The left part of the vessel contains one mole of an ideal monatomic gas, & the right part is empty. The piston is connected to the right wall of the vessel through a spring whose length in free state is equal to the length of the vessel as shown in the figure. Determine the heat capacity C of the system, neglecting the heat capacities of the vessel, piston and spring.



EXERCIES – III

Q.1 The kinetic energy, due to translational motion, of most of the molecules of an ideal gas at absolute temperature T is ______ . **[REE '94, 1]**

Q.2 A vessel of volume 2×10^{-2} m^3 contains a mixture of hydrogen and helium at 47° C temperature and 4.15×10^5 N/m^2 pressure. The mass of the mixture is 10^{-2} kg. Calculate the masses of hydrogen and helium in the given mixture. **[REE '94, 4]**

Q.3 There are two vessels . Each of them contains one mole of a mono-atomic ideal gas . Initial volume of the gas in each vessel is 8.3×10^{-3} m^3 at 27° C . Equal amount of heat is supplied to each vessel . In one of the vessels, the volume of the gas is doubled isothermally, whereas the volume of the gas is held constant in the second vessel . The vessels are now connected to allow free mixing of the gas. Find the final temperature and pressure of the combined gas system . **[REE '94, 6]**

Q.4 An ideal gas with pressure P, volume V & temperature T is expanded isothermally to a volume 2 V and a final pressure P_i . If the same gas is expanded adiabatically to a volume 2 V, the final pressure is P_a. The ratio of the specific heats for the gas is 1.67 . The ratio P_a/P_i is ______ . **[JEE '94, 2]**

Q.5 An ideal gas is taken through a cyclic thermodynamic process through four steps. The amounts of heat involved in these steps are $Q_1 = 5960$ J, $Q_2 = -5585$ J, $Q_3 = -2980$ J and $Q_4 = 3645$ J respectively. The corresponding works involved are $W_1 = 2200$ J, $W_2 = -825$ J, $W_3 = -1100$ J and W_4 respectively.
(i) Find the value of W_4. (ii) What is the efficiency of the cycle ? **[JEE '94, 6]**

Q.6 A closed container of volume 0.02 m^3 contains a mixture of neon and argon gases, at a temperature of 27° C & pressure of 1×10^5 Nm^{-2} . The total mass of the mixture is 28 gm. If the gram molecular weights of neon and argon are 20 & 40 respectively, find the masses of the individual gases in the container, assuming them to be ideal. [Universal gas constant R = 8.314 J/mol K] **[JEE '94, 6]**

Q.7 A gaseous mixture enclosed in a vessel of volume V consists of one gram mole of a gas A with $\gamma = Cp/Cv = 5/3$ & another gas B $\gamma - 7/5$ with at a certain temperature T. The gram molecular weights of the gases A & B are 4 & 32 respectively. The gases A & B do not react with each other and are assumed to be ideal. The gaseous mixture follows the equation; $PV^{19/13}$ = const. in adiabatic processes.
(a) Find the number of gram moles of the gas B in the gaseous mixture.
(b) Compute the speed of sound in the gaseous mixture at T = 300 K.
(c) If T is raised by 1 K from 300 K, find the percentage change in the speed of sound in the gaseous mixture.
(d) The mixture is compressed adiabatically to 1/5 its initial volume V . Find the change in its adiabatic compressibility in terms of the given quantities. **[JEE '95]**

Q.8 The pressure in a monoatomic gas increases linearly from 4×10^5 N m^{-2} to 8×10^5 N m^{-2} when its volume increases from 0.2 m^3 to 0.5 m^3. Calculate the following: **[REE '95, 5]**
(a) work done by the gas, (b) increase in the internal energy, (c) amount of heat supplied,
(d) molar heat capacity of the gas.

Q.9 The temperature of an ideal gas is increased from 120 K to 480 K . If at 120 K the root-mean-square velocity of the gas molecules is v, at 480 K it becomes : **[JEE '96, 2]**
(A) 4v (B) 2v (C) v/2 (D) v/4

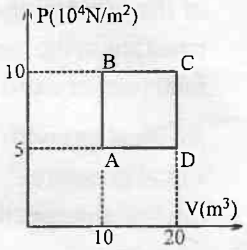
Q.10 At 27° C two moles of an ideal monoatomic gas occupy a volume V. The gas expands adiabatically to a volume 2V. Calculate : (i) the final temperature of the gas , (ii) change in its internal energy & (iii) the work done by the gas during the process . **[JEE '96, 5]**

Q.11 There is a soap bubble of radius 2.4×10^{4} m in air cylinder which is originally at the pressure of 10^5 Nm^{-2}. The air in the cylinder is now compressed isothermally until the radius of the bubble is halved. Calculate now the pressure of air in the cylinder. The surface tension of the soap film is 0.08 Nm^{-1}. **[REE '96, 5]**

Q.12 A vertical hollow cylinder contains an ideal gas. The gas is enclosed by a 5kg movable piston with an area of cross-section 5×10^{-3} m^2. Now, the gas is slowly heated from 300 K to 350K and the piston rises by 0.1 m. The piston is now clamped at this position and the gas is cooled back to 300 K. Find the difference between the heat energy added during heating process & energy lost during the cooling process.
[1 atm pressure = 10^5 N m^{-2}] **[REE '96, 5]**

Q.13 The average translational energy and the rms speed of molecules in a sample of oxygen gas at 300 K are 6.21×10^{-21} J & 484 m/s respectively. The corresponding values at 600K are nearly (assuming ideal gas behaviour)
(A) 12.42×10^{-21} J, 968 m/s (B) 8.78×10^{-21} J, 684 m/s
(C) 6.21×10^{-21} J, 968 m/s (D) 12.42×10^{-21} J, 684 m/s **[JEE '97, 1]**

Q.14 A sample of 2 kg of monoatomic Helium (assumed ideal) is taken through the process ABC and another sample of 2 kg of the same gas is taken through the process ADC as in figure. Given, molecular mass of Helium = 4



(i) what is the temperature of Helium in each of the states A, B, C & D ?
(ii) Is there any way of telling afterwards which sample of Helium went through the process ABC and which went through the process ADC? Write Yes or No.
(iii) How much is the heat involved in each of the processes ABC ADC. **[JEE '97, 5]**

Q.15 The average translational kinetic energy of a molecule in a gas becomes equal to 1 eV at a temperature ______. **[REE '97, 1]**

Q.16 Two moles of an ideal monoatomic gas are confined within a cylinder by a massless & frictionless spring loaded piston of cross-sectional area 4×10^{-3} m^2. The spring is, initially in its relaxed state. Now the gas is heated by an electric heated, placed inside the cylinder, for some time. During this time, the gas expands and does 50 J of work in moving the piston through a distance 0.10 m. The temperature of the gas increases by 50 K. Calculate the spring constant & the heat supplied by the heater. **[REE '97, 5]**

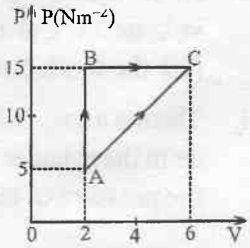
Q.17 Two vessels A & B, thermally insulated, contain an ideal monoatomic gas. A small tube fitted with a valve connects these vessels. Initially the vessel A has 2 litres of gas at 300 K and 2×10^5 Nm^{-2} pressure while vessel B has 4 litres of gas at 350 K & 4×10^5 N m^{-2} pressure. The valve is now opened and the system reaches equilibrium in pressure & temperature. Calculate the new pressure & temperature. **[REE '97, 5]**

Q.18 One mole of a diatomic ideal gas ($\gamma = 1.4$) is taken through a cyclic process starting from point A. The process A → B is an adiabatic compression. B → C is isobaric expansion. C → D an adiabatic expansion & D → A is isochoric. The volume ratios are $V_a/V_b = 16$ and $V_c/V_b = 2$ & the temperature at A is $T_A = 300^0$K. Calculate the temperature of the gas at the points B & D and find the efficiency of the cycle.
[($16^{0\,4} = 3.03$) $(1/8)^{0\,4} = 0.435$] **[JEE '97, 5]**

Q.19 The average translational kinetic energy of O_2 (molar mass 32) molecules at a particluar temperature is 0.048 eV. The translational kinetic energy of N_2 (molar mass 28) molecules in eV at the same temperature is
(A) 0.0015 (B) 0.003 (C) 0.048 (D) 0.768 **[JEE '97, 3]**

Q.20 Select the correct alternative. **[JEE '97, 3]**
A vessel contains 1 mole of O_2 gas (molar mass 32) at a temperature T. The pressure of the gas is P. An identical vessel containing one mole of He gas (molar mass 4) at a temperature 2 T has a pressure of:
(A) P/8 (B) P (C) 2 P (D) 8 P

Q.21 In the given figure an ideal gas changes its state from state A to state C by two paths ABC and AC. (a) Find the path along which work done is the least. (b) The internal energy of gas at A is 10J and amount of heat supplied to change its state to C through the path AC is 200J. Calculate the internal energy at C. (c) The internal energy of gas at state B is 20J. Find the amount of heat supplied to the gas from A to B. **[REE '98]**



Q.22 Two cylinders A and B fitted with pistons contain equal amounts of an ideal diatomic gas at 300K. The piston of A is free to move, while that of B is held fixed. The same amount of heat is given to the gas in each cylinder. If the rise in temperature of the gas is A is 30K, then rise in temperature of the gas in B is
(A)30K (B) 18K (C) 50K (D) 42K **[JEE' 98]**

Q.23 Two identical containers A and B with frictionless pistons contain the same ideal gas at the same temperature and the same volume V. The mass of the gas in A is m_A and that in B is m_B. The gas in each cylinder is now allowed to expand isothermally to the same final volume 2V. The change in the pressure in A and B are found to be ΔP and $1.5\ \Delta P$ respectively. Then **[JEE' 98]**
(A) $4m_A=9m_B$ (B) $2m_A=3m_B$ (C) $3m_A=2m_B$ (D) $9m_A=4m_B$

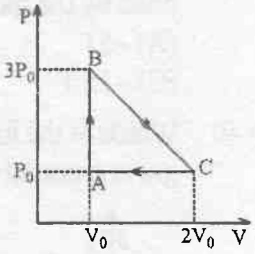
Q.24 A vessel contains a mixture of one mole of oxygen and two moles of nitrogen at 300K. The ratio of the average rotational kinetic energy per O_2 molecule the that per N_2 molecule is **[JEE' 98]**
(A) 1:1 (B) 1:2 (C) 2:1 (D) depend on the moment of inertia of two molecules.

Q.25 Let v_{av}, v_{rms} and v_p respectively denote mean speed, root mean square speed and the most probable speed of the molecule in an ideal monoatomic gas at absolute temperature T. The mass of a molecule is m then :
(A) no molecule can have speed greater than $\sqrt{2}\ v_{rms}$ **[JEE'98]**
(B) no molecule can have speed less than $v_u / \sqrt{2}$
(C) $v_p < v_{av} < v_{rms}$ (D) the average kinetic energy of a molecule is $3/4\ mv_p^2$

Q.26 A given quantity of an ideal gas is at pressure P and absolute temperature T. The isothermal bulk modulus of the gas is :
(A) 2P/3 (B) P (C) 3P/2 (D) 2P **[JEE'98]**

Q.27 During the melting of a slab of ice at 273K at atmospheric pressure:
(A) positive work is done by the ice-water system on the atmosphere.
(B) positive work is done on the ice-water system by the atmosphere
(C) the internal energy of the ice-water system increases
(D) the internal energy of ice-water system decreases. **[JEE' 98]**

Q.28 One mole of an ideal monoatomic gas is taken round the cyclic process ABCA as shown in figure, calculate



(a) the work done by the gas
(b) the heat rejected by the gas in the path CA and the heat absorbed by the gas in the path AB.
(c) the net heat absorbed by the gas in the path BC
(d) the maximum temperature attained by the gas during the cycle. **[JEE' 98]**

Q.29 The ratio of the speed of sound in nitrogen gas to that in helium gas, at 300K is
(A) $\sqrt{(2/7)}$ (B) $\sqrt{(1/7)}$ (C) $(\sqrt{3})/5$ (D) $(\sqrt{6})/5$ **[JEE' 99]**

Q.30 A gas mixture consists of 2 moles of oxygen and 4 moles of argon at temperature T. Neglecting all vibrational modes, the total internal energy of the system is
(A) 4 RT (B) 15 RT (C) 9 RT (D) 11 RT **[JEE' 99]**

Q.31 Two moles of an ideal monoatomic gas, initially at pressure p_1 and volume V_1, undergo an adiabatic compression until its volume is V_2. Then the gas is given heat Q at constant volume V_2. (a) Sketch the complete process on a p-V diagram. (b) Find the total work done by the gas, the total change in its internal energy and the final temperature of the gas. [Given answers in terms of p_1, V_1, V_2, Q and R] **[JEE' 99]**

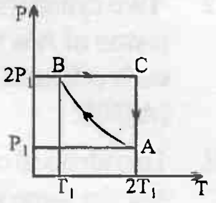
Q.32 A gas has molar heat capacity $C = 37.35\ \text{J mole}^{-1}\text{K}^{-1}$ in the process PT = constant. Find the number of degrees of freedom of molecules in the gas. **[REE' 99]**

Q.33 A weightless piston divides a thermally insulated cylinder into two parts of volumes V and 3V. 2 moles of an ideal gas at pressure P = 2 atmosphere are confined to the part with volume V = 1 litre. The remainder of the cylinder is evacuated. The piston is now released and the gas expands to fill the entire space of the cylinder. The piston is then pressed back to the initial position. Find the increase of internal energy in the process and final temperature of the gas. The ratio of the specific heat of the gas $\gamma = 1.5$.
[REE' 99]

Q.34 Two moles of an ideal monatomic gas is taken through a cycle ABCA as shown in the P-T diagram. During the process AB, pressure and temperature of the gas vary such that PT = constant. If $T_1 = 300$ K, calculate:

(a) the work done on the gas in the process AB and

(b) the heat absorbed or released by the gas in each of the processes. Give answers in terms of the gas constant R. **[JEE' 2000]**



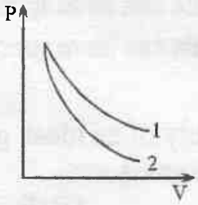
Q.35 One mole of an ideal gas is heated isobarically from the freezing point to the boiling point of water each under normal pressure. Find out the work done by the gas and the change in its internal energy. The amount of heat involved is 1kJ. **[REE' 2000]**

Q.36 A vertical cylinder of cross-sectional area 0.1m² closed at both ends is fitted with a fricitonless piston of mass M dividing the cylinder into two parts. Each part contains one mole of an ideal gas in equilibrium at 300K. The volume of the upper part is 0.1m³ and that of the lower part is 0.05m³. What force must be applied to the piston so that the volumes of the two parts remain unchanged when the temperature is increased to 500K? **[REE' 2000]**

Q.37 P-V plots for two gases during adiabatic processes are shown in the figure. Plots 1 and 2 should correspond respectively to

(A) He and O_2 (B) O_2 and He

(C) He and Ar (D) O_2 and N_2



[JEE' 2001]

Q.38 In a given process on an ideal gas, dW = 0 and dQ < 0. then for the gas

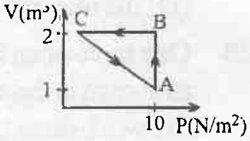
(A) the temperature will decrease. (B) the volume will increase

(C) the pressure will remain constant (D) the temperature will increase **[JEE' 2001]**

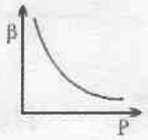
Q.39 An ideal gas is taken through the cycle A → B → C → A, as shown in the figure. If the net heat supplied to the gas in the cycle is 5J, the work done by the gas in the process C → A is **[JEE(Scr)2002]**

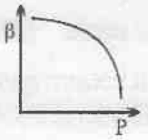
(A) –5J (B) –10 J

(C) –15 J (D) –20 J



Q.40 Which of the following graphs correctly represents the variation of $\beta = -(dV/dP)/V$ with P for an ideal gas at constant temperature? **[JEE (Scr)2002]**

(A)


(B)


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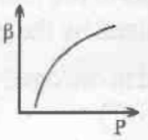
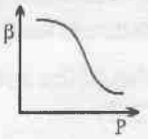


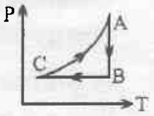
(D)


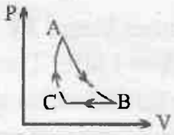
Q.41 A cubical box of side 1 meter contains helium gas (atomic weight 4) at a pressure of 100 N/m². During an observation time of 1 second, an atom travelling with the root mean square speed parallel to one of the edges of the cube, was found to make 500 hits with a particular wall, without any collision with other atoms. Take R = 25/3 J/mol-K and k = 1.38 × 10^{-23} J/K. **[JEE'2002]**

(a) Evaluate the temperature of the gas ; (b) Evaluate the average kinetic energy per atom

(c) Evaluate the total mass of helium gas in the box.

Q.42 In the figure AC represent Adiabatic process. The corresponding PV graph is **[JEE (Scr) 2003]**



(A)


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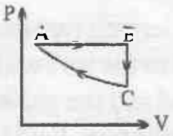
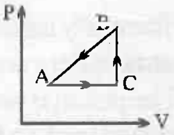


(C)


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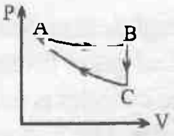
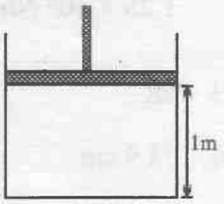


Q.43 An insulated container containing monoatomic gas of molar mass m is moving with a velocity v_0. If the container is suddenly stopped, find the change in temperature. **[JEE 2003]**

Q.44 An ideal gas expands isothermally from a volume V_1 to V_2 and then compressed to original volume V_1 adiabatically. Initial pressure is P_1 and final pressure is P_3. The total work done is W. Then

(A) $P_3 > P_1$, $W > 0$ (B) $P_3 < P_1$, $W < 0$ **[JEE' 2004 (Scr)]**
(C) $P_3 > P_1$, $W < 0$ (D) $P_3 = P_1$, $W = 0$

Q.45 The piston cylinder arrangement shown contains a diatomic gas at temperature 300 K. The cross-sectional area of the cylinder is 1 m^2. Initially the height of the piston above the base of the cylinder is 1 m. The temperature is now raised to 400 K at constant pressure. Find the new height of the piston above the base of the cylinder. If the piston is now brought back to its original height without any heat loss, find the new equilibrium temperature of the gas. You can leave the answer in fraction. **[JEE' 2004]**



Q.46 An ideal gas is filled in a closed rigid and thermally insulated container. A coil of 100Ω resistor carrying current 1A for 5 minutes supplies heat to the gas. The change in internal energy of the gas is

(A) 10 KJ (B) 20 KJ (C) 30 KJ (D) 0 KJ

[JEE' 2005 (Scr)]

Q.47 When the pressure is changed from $p_1 = 1.01 \times 10^5$ Pa to $p_2 = 1.165 \times 10^5$ a then the volume changes by 10%. The bulk modulus is

(A) 1.55×10^5Pa (B) 0.0015×10^5Pa (C) 0.015×10^5Pa (D) none of these

[JEE' 2005 (Scr)]

Q.48 A cylinder of mass 1 kg is given heat of 20000 J at atmospheric pressure. If initially temperature of cylinder is 20°C, find

(a) final temperature of the cylinder
(b) work done by the cylinder.
(c) change in internal energy of the cylinder.

(Given that specific heat of cylinder = 400 J kg^{-1} $°C^{-1}$, Coefficient of volume expansion $= 9 \times 10^{-5}$ $°C^{-1}$, Atmospheric pressure = 10^5 N/m^2 and density of cylinder = 9000 kg/m^3) **[JEE 2005]**

ANSWER KEY

EXERCISE – I

Q.1 $\pi/2$atm-lt Q.2 27 : 4 Q.3 100 J Q.4 $RT\left[1-\frac{1}{n}\right]$

Q.5 $\frac{3}{2}\rho_0$ Q.6 2 R Q.7 327 °C Q.8 $1-\frac{3\left(1-\frac{1}{2^{1/3}}\right)}{ln2}$

Q.9 1.25×10^4 N/m^2 Q.10 1.5 Q.11 4/3 Q.12 1.5

Q.13 5R Q.14 $\frac{mRT_0}{V_0}\left(1+\frac{T_0 m}{V_0}\right)R$ Q.15 $\sqrt{2}$

Q.16 74.9 cm Q.17 1.84P, 10V/3, 8V/3 (adiabatic), 13P/6, 30V/13, 48V/13 (isothermal)

Q.18 4 : 1 Q.19 P/n Q.20 $C_V+\frac{R}{\alpha V}$ Q.21 16/15

Q.22 $\frac{R}{2}$ Q.23 400 K Q.24 3600 R

Q.25 (i) $\left(\frac{\gamma+1}{\gamma-1}\right)4aV_0^2$, (ii) $\left(\frac{\gamma+1}{\gamma-1}\right)\frac{R}{2}$ Q.26 12600 J Q.27 50 calorie

Q.28 $R\Delta T\left(\frac{3-2\gamma}{\gamma-1}\right)$

Q.29 the molar mass of the gas is 40 gm, the number of degrees of freedom of the gas molecules is 6

Q.30 (i) $P_1 < P_2$, $T_1 < T_2$; (ii) $T_1 = T_2 < T_3$; (iii) $V_2 > V_1$; (iv) $P_1 > P_2$

EXERCISE – II

Q.1 (i) 74 cm, (ii) 73.94 cm, (iii) 69.52 cm Q.2 0.497 atm, 0.0572 gm Q.3 0.263

Q.4 $p_1 = p_{H_2} \simeq 1.25 \times 10^6$ Pa ; $p_2 = p_{H_2} + p_{O_2} + p_{N_2} \simeq 2.8125 \times 10^6$ Pa ; $p_3 = p_{H_2} + p_{N_2} \simeq 1.5625 \times 10^6$ P.

Q.5 750 K Q.6 $P = \frac{13}{12}P_0$, $l_1 = 0.6\,l$, $l_2 = 1.5\,l$, $l_3 = 0.9\,l$

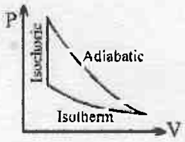
Q.7 $31P_0V_0$; $-5P_0V_0$ Q.8 (i) 7.594, (ii) 4/9, (iii) – 2.5

Q.9 (ii) $P_b = P_c = 2$ atm, (iii) $T_b = 300$ K, $T_c = 600$ K, (iv) $V_c = 8$ litre

Q.10 (i) 1.263×10^5 Nm^{-2} ; 415 J, (ii) 302.8 K ; 1.275×10^5 Nm^{-2} Q.11 1.6 m, 364 K

Q.12 1.63 Q.13 $\frac{3-2\,ln2}{3}$ Q.14 4 : 9 : 5 Q.15 7.71 J

Q.16 8000 cal.



Q.17 (a) $\frac{L}{kA}\left(q-qe^{-\frac{kAt}{nLC_P}}\right)+T_0$, (b) $T_0+\frac{qL}{kA}$, (c) $\frac{qL}{kAT_0}+1$

Q.18 $2mnv^2\cos^2\theta$ Q.19 (a) $W_{AD} = 88$ J, (b) $V_C = 1.223$ litre, (c) $W_{CDA} = -85$ J

Q.20 (a) Final pressure in A = $\frac{27}{8}P_0$ = Final pressure in C, Final pressure in B = $\frac{21}{4}P_0$

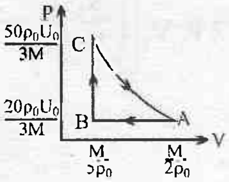
(b) Final temperature in A (and B) = $\frac{21}{4}T_0$, Final temperature in C = $\frac{3}{2}T_0$,

(c) $18\,P_0V_0$,

(d) work done by gas in A = $+P_0V_0$, work done by gas in B = 0,

(e) $\frac{17}{2}P_0V_0$

Q.21 four Q.22 (a)



, (b) $Q = \left(\frac{10}{3}\ln 2.5 - 2\right)U_0$, (c) $-2U_0$

Q.23 $\frac{7R}{2M}$, $4R(T_2 - T_1)$ Q.24 (a) 80 J, 180 J, (b) 4.5 R

Q.25 $T_1 = (207/16)\,T_0$; $T_2 = \frac{9}{4}T_0$, $-\frac{15}{8}P_0V_0$ Q.26 $\frac{5}{4}Kl^2 + \frac{1}{2}(13\sqrt{2} - 7)P_0Al$

Q.27 (a) 2×10^5 N/m^2 ; (b) 6 rad/s, (c) 75 J Q.28 C = 2 R

EXERCISE – III

Q1. K T Q2. $m_H = 2.5 \times 10^{-3}$ kg, $m_{He} = 7.5 \times 10^{-3}$ kg

Q3. 369.3 K, 2.462×10^5 Pa Q4. $1/2^{0.67}$

Q5. (i) 765 J, (ii) 10.83% Q6. 23.928 g ; 4.072 g

Q7. $n_B = 2$; 401 ms^{-1} ; 0.167 % ; – 0.0248 V/T

Q8. (a) 1.8×10^5J ; (b) 4.8×10^5J ; (c) 6.6×10^5J ; (d) 17J/mol-K Q9. B

Q10. (i) 189 K, (ii) –2767 J, (iii) 2767 J Q11. 8.08 x 10^5 Pa

Q 12. 55 J Q13. D

Q14. (i) $T_A = 120.33$ K, $T_B = 240.66$ K, $T_C = 481.32$ K, $T_D = 240.66$ K, (ii) No,
(iii) $\Delta Q_{ABC} = 3.25 \times 10^6$ J ; $\Delta Q_{ADC} = 2.75 \times 10^6$ J

Q15. 7730 K Q16. 2000N/m, 1295J

Q17. 3.3×10^5 N/m^2, 338.71 K Q18. $T_B = 909$ K, $T_D = 791$ K, $\eta = 61.4$ %

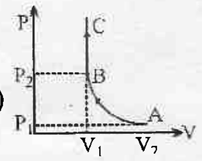
Q19. C Q20. C Q21. AC, 170 J, 10 J Q22. D

Q23. C　　Q24. A　　Q25. C, D　　Q26. B

Q27. B,C　　Q28. (a) P_oV_o, (b) $5/2\ P_oV_o$, $3P_oV_o$, (c) $1/2\ P_oV_o$, (d) $T_{max} = 25/8\ P_oV_o/R$

Q29. C　　Q30. D

Q31. (a)



(b) $$W = 3/2P_1V_1\left[1-\left(\frac{V_1}{V_2}\right)^{2/3}\right];\ \Delta U = 3/2\,P_1V_1\left[\left(\frac{V_1}{V_2}\right)^{2/3}-1\right]+Q,\ \text{Final } T = \frac{Q}{3R}+\frac{P_1V_2}{2R}\left(\frac{V_1}{V_2}\right)^{5/3}$$

Q32. 5　　Q33. 400 J, 2 T_0

Q34. (a) 1200R, (b) $Q_{AB} = -2100R$, $Q_{BC} = 1500R$, $Q_{CA} = 1200\ R\ ln2$　　Q35. W = 830 J, U=170 J

Q36. 1660 N　　Q37. B　　Q38. A　　Q.39 A

Q.40 A　　Q.41 160 K, 3.3×10^{-21} J, 0.3 gm　　Q 42. A

Q.43 $\Delta T = \dfrac{mv_0^2}{3R}$　　Q.44 C　　Q.45 $T_3 = 400\left(\dfrac{4}{3}\right)^{0.4}$ K

Q.46 C　　Q.47 A　　Q.48 (a) $T_{final} = 70°C$, (b) 0.05 J, (c) 19999.95 J

BANSAL CLASSES

PHYSICS

TARGET IIT JEE 2007
XI (PQRS & J)

QUESTION BANK ON

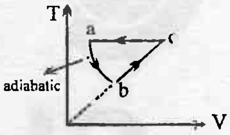
KTG & THERMODYNAMICS

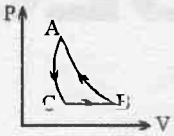
Time Limit : 2 Sitting Each of 60 minutes. duration approx.

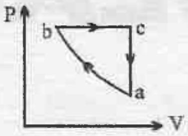
QUESTION ON KTG & THERMODYNAMICS

There are 48 questions in this question bank.

Q.1 PV curve for the process whose VT curve is



(A)


(B)


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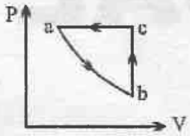

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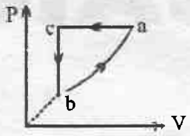
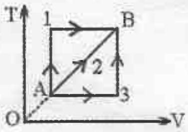
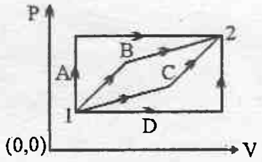


Q.2 A given mass of a gas expands from a state A to the state B by three paths 1, 2 and 3 as shown in T-V indicator diagram. If W_1, W_2 and W_3 respectively be the work done by the gas along the three paths, then



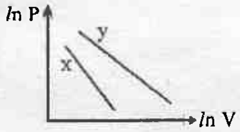
(A) $W_1 > W_2 > W_3$
(B) $W_1 < W_2 < W_3$
(C) $W_1 = W_2 = W_3$
(D) $W_1 < W_2$, $W_1 > W_3$

Q.3 An ideal gas is taken from state 1 to state 2 through optional path A, B, C & D as shown in P-V diagram. Let Q, W and U represent the heat supplied, work done & internal energy of the gas respectively. Then



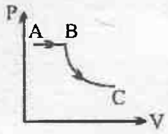
(A) $Q_B - W_B > Q_C - W_C$
(B) $Q_A - Q_D = W_A - W_D$
(C) $W_A < W_B < W_C < W_D$
(D) $Q_A > Q_B > Q_C > Q_D$

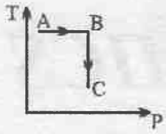
Q.4 For two different gases X and Y, having degrees of freedom f_1 and f_2 and molar heat capacities at constant volume C_{V_1} and C_{V_2} respectively, the *l*n P versus *l*n V graph is plotted for adiabatic process, as shown



(A) $f_1 > f_2$
(B) $f_2 > f_1$
(C) $C_{V_2} > C_{V_1}$
(D) $C_{V_1} > C_{V_2}$

Q.5 A process is shown in the diagram. Which of the following curves may represent the same process ?



(A)


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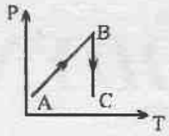

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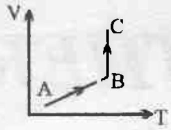

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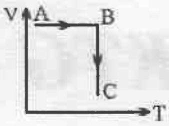


Q.6 The ratio of average translational kinetic energy to rotational kinetic energy of a diatomic molecule at temperature T is
(A) 3
(B) 7/5
(C) 5/3
(D) 3/2

Q.7 A student records ΔQ, ΔU & ΔW for a thermodynamic cycle $A \to B \to C \to A$. Certain entries are missing. Find correct entry in following options.

	AB	BC	CA
ΔW	40J		30J
ΔU		50J	
ΔQ	150J	10J	

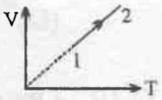
(A) $W_{BC} = -70$ J
(B) $\Delta Q_{CA} = 130$ J
(C) $\Delta U_{AB} = 190$ J
(D) $\Delta U_{CA} = -160$ J

Q.8 According to kinetic theory of gases, which of following statement will be true.
(A) Ideal gases can not be liquified
(B) The molecules of ideal gas do not obey newtons laws of motion.
(C) Pressure of gas is always inversely proportional to its volume
(D) molecules of gas never move in straight line.

Q.9 Find the approx. number of molecules contained in a vessel of volume 7 litres at 0°C at 1.3×10^5 pascal
(A) 2.4×10^{23} (B) 3×10^{23} (C) 6×10^{23} (D) 4.8×10^{23}

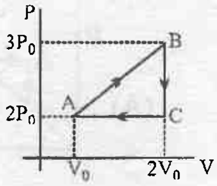
Q.10 A diatomic gas follows equation PV^m = constant, during a process. What should be the value of m such that its molar heat capacity during process = R
(A) 2/3 (B) 1 (C) 1.5 (D) 5/3

Q.11 An ideal gas undergoes the process $1 \to 2$ as shown in the figure, the heat supplied and work done in the process is ΔQ and ΔW respectively. The ratio $\Delta Q : \Delta W$ is
(A) $\gamma : \gamma - 1$ (B) γ
(C) $\gamma - 1$ (D) $\gamma - 1/\gamma$



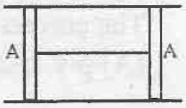
Q.12 Two moles of monoatomic gas is expanded from (P_0, V_0) to $(P_0, 2V_0)$ under isobaric condition. Let ΔQ_1, be the heat given to the gas, ΔW_1 the work done by the gas and ΔU_1 the change in internal energy. Now the monoatomic gas is replaced by a diatomic gas. Other conditions remaining the same. The corresponding values in this case are ΔQ_2, ΔW_2, ΔU_2 respectively, then
(A) $\Delta Q_1 - \Delta Q_2 = \Delta U_1 - \Delta U_2$ (B) $\Delta U_2 + \Delta W_2 > \Delta U_1 + \Delta W_1$
(C) $\Delta U_2 > \Delta U_1$ (D) All of these

Q.13 In the above thermodynamic process, the correct statement is
(A) Heat given in the complete cycle ABCA is zero
(B) Work done in the complete cycle ABCA is zero
(C) Work done in the complete cycle ABCA is $(1/2\ P_0V_0)$
(D) None



Q.14 For an ideal gas
(A) The change in internal energy in a constant pressure process from temperature T_1 to T_2 is equal to
$n\,C_v\,(T_2 - T_1)$ where C_v is the molar specific heat at constant volume and n is the number of the moles of the gas.
(B) The change in internal energy of the gas and the work done by the gas are equal in magnitude in an adiabatic proces.
(C) The internal energy does not change in an isothermal process.
(D) A, B and C

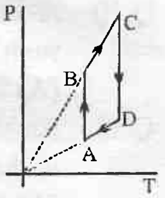
Q.15 A cylindrical tube of cross-sectional area A has two air tight frictionless pistons at its two ends. The pistons are tied with a straight two ends. The pistons are tied with a straight piece of metallic wire. The tube contains a gas at pressure P_0 and temperature T_0. If temperature of the gas is doubled then the tension in the wire is
(A) $4\,P_0\,A$ (B) $P_0A/2$
(C) $P_0\,A$ (D) $2\,P_0\,A$



Q.16 According to kinetic theory of gases,
(A) The velocity of molecules decreases for each collision
(B) The pressure exerted by a diatomic gas is proportional to the mean velocity of the molecule.
(C) The K.E. of the gas decreases on expansion at constant temperature.
(D) The mean translational K.E. of a diatomic gas increases with increase in absolute temperature.

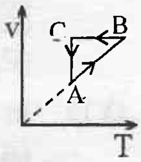
Q.17 An ideal gas mixture filled inside a balloon expands according to the relation $PV^{2/3}$ = constant. The temperature inside the balloon is
(A) increasing (B) decreasing (C) constant (D) can't be said

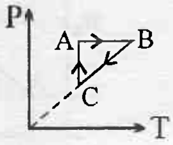
Q.18 Pressure versus temperature graph of an ideal gas is shown in figure
(A) During the process AB work done by the gas in positive
(B) during the process CD work done by the gas is negative
(C) during the process BC internal energy of the gas is increasing
(D) None

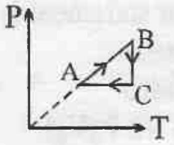


Q.19 One mole of an ideal gas at temperature T_1 expends according to the law $\frac{P}{V^2}$ = a (constant). The work done by the gas till temperature of gas becomes T_2 is :
(A) $\frac{1}{2}R(T_2 - T_1)$ (B) $\frac{1}{3}R(T_2 - T_1)$ (C) $\frac{1}{4}R(T_2 - T_1)$ (D) $\frac{1}{5}R(T_2 - T_1)$

Q.20 An ideal gas undergoes a thermodynamics cycle as shown in figure. Which of the following graphs represents the same cycle?



(A)


(B)


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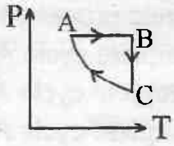

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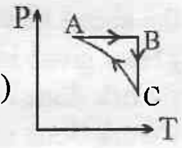


Q.21 A reversible adiabatic path on a P-V diagram for an ideal gas passes through state A where $P=0.7\times10^5$ N/m^{-2} and $v = 0.0049$ m^3. The ratio of specific heat of the gas is 1.4. The slope of path at A is :
(A) 2.0×10^7 Nm^{-5} (B) 1.0×10^7 Nm^{-5} (C) -2.0×10^7 Nm^{-5} (D) -1.0×10^7 Nm^{-5}

Q.22 An ideal gas at pressure P and volume V is expanded to volume 2V. Column I represents the thermodynamic processes used during expansion. Column II represents the work during these processes in the random order.

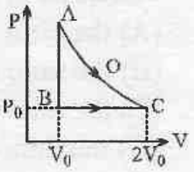
Column I	**Column II**
(p) isobaric	(x) $\frac{PV(1-2^{1-\gamma})}{\gamma-1}$
(q) isothermal	(y) PV
(r) adiabatic	(z) PV ln 2

The correct matching of column I and column II is given by :
(A) p-y, q-z, r-x (B) p-y, q-x, r-z (C) p-x, q-y, r-z (D) p-z, q-y, r-x

Q.23 An ideal gas expands in such a way that PV^2 = constant throughout the process.

(A) The graph of the process of T-V diagram is a parabola.
(B) The graph of the process of T-V diagram is a straight line.
(C) Such an expansion is possible only with heating.
(D) Such an expansion is possible only with cooling.

Q.24 An ideal gas is taken from point A to point C on P-V diagram through two process AOC and ABC as shown in the figure. Process AOC is isothermal



(A) Process AOC requires more heat than process ABC.
(B) Process ABC requires more heat than process AOC.
(C) Both process AOC & ABC require same amount of heat.
(D) Data is insufficient for comparison of heat requirement for the two processes.

Q.25 One mole of an ideal gas at STP is heated in an insulated closed container until the average velocity of its molecules is doubled. Its pressure would therefore increase by factor.

(A) 1.5 (B) $\sqrt{2}$ (C) 2 (D) 4

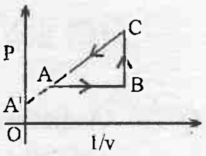
Q.26 A rigid tank contains 35 kg of nitrogen at 6 atm. Sufficient quantity of oxygen is supplied to increase the pressure of 9 atm, while the temperature remains constant. Amount of oxygen supplied to the tank is :

(A) 5 kg (B) 10 kg (C) 20 kg (D) 40 kg

Q.27 Three particles have speeds of 2u , 10u and 11u. Which of the following statements is correct?

(A) The r.m.s. speed exceeds the mean speed by about u.
(B) The mean speed exceeds the r.m.s. speed by about u.
(C) The r.m.s. speed equals the mean speed.
(D) The r.m.s. speed exceeds the mean speed by more than 2u.

Q.28 An enclosed ideal gas is taken through a cycle as shown in the figure. Then



(A) Along AB, temperature decreases while along BC temperature increases
(B) Along AB, temperature increases while along BC the temperature decreases.
(C) Along CA work is done by the gas and the internal energy remains constant.
(D) Along CA work is done on the gas and internal energy of the gas increases.

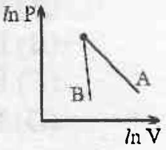
Q.29 One mole of an ideal gas is contained with in a cylinder by a frictionless piston and is initially at temperature T. The pressure of the gas is kept constant while it is heated and its volume doubles. If R is molar gas constant, the work done by the gas in increasing its volume is

(A) RT $ln2$ (B) 1/2 RT (C) RT (D) 3/2 RT

Q.30 The ratio of specific heats of a gas is $\frac{9}{7}$, then the number of degrees of freedom of the gas molecules for translational motion is :

(A) 7 (B) 3 (C) 6 (D) none

Q.31 The figure, shows the graph of logarithmic reading of pressure and volume for two ideal gases A and B undergoing adiabatic process. From figure it can be concluded that



(A) gas B is diatomic (B) gas A and B both are diatomic
(C) gas A is monoatomic (D) gas B is monoatomic & gas A is diatomic

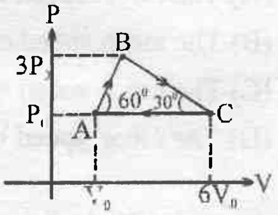
Q.32 A perfect gas of a given mass is heated first in a small vessel and then in a large vessel, such that their volumes remain unchanged. The P-T curves are
(A) parabolic with same curvature
(B) parabolic with different curvature
(C) linear with same slopes
(D) linear with different slopes

Q.33 Two vessels of the same volume contain the same gas at same temperature. If the pressure in the vessels be in the ratio of 1 : 2, then
(A) the ratio of the average kinetic energy is 1 : 2
(B) the ratio of the root mean square velocity is 1 : 1
(C) the ratio of the average velocity is 1 : 2
(D) the ratio of number of molecules is 1 : 2

Q.34 At a temperature T K, the pressure of 4.0g argon in a bulb is p. The bulb is put in a bath having temperature higher by 50K than the first one. 0.8g of argon gas had to be removed to maintained original pressure. The temperature T is equal to
(A) 510 K
(B) 200 K
(C) 100 K
(D) 73 K

Q.35 The total kinetic energy of translatory motion of all the molecules of 5 litres of nitrogen exerting a pressure P is 3000 J.
(A) the total k.e. of 10 litres of N_2 at a pressure of 2P is 3000 J
(B) the total k.e. of 10 litres of He at a pressure of 2P is 3000 J
(C) the total k.e. of 10 litres of O_2 at a pressure of 2P is 20000 J
(D) the total k.e. of 10 litres of Ne at a pressure of 2P is 12000 J

Q.36 Two moles of an ideal monoatomic gas undergone a cyclic process ABCA as shown in figure. The ratio of temperatures at B and A is



(A) $16 : \sqrt{3}$
(B) 27 : 4
(C) $20\sqrt{3} : 5$
(D) 6 : 1

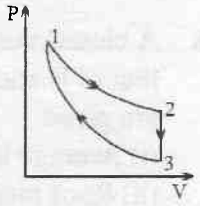
Q.37 A diatomic gas of molecules weight 30 gm/mole is filled in a container at 27°C. It is moving at a velocity 100 m/s. If it is suddenly stopped, the rise in temperature of gas is :
(A) $\frac{60}{R}$
(B) $\frac{600}{R}$
(C) $\frac{6\times10^4}{R}$
(D) $\frac{6\times10^5}{R}$

Q.38 A thermodynamic cycle takes in heat energy at a high temperature and rejects energy at a lower temperature. If the amount of energy rejected at the low temperature is 3 times the amount of work done by the cycle, the efficiency of the cycle is
(A) 0.25
(B) 0.33
(C) 0.67
(D) 0.9

Q.39 Monoatomic, diatomic and triatomic gases whose initial volume and pressure are same, are compressed till their volume becomes half the initial volume.
(A) If the compression is adiabatic then monoatomic gas will have maximum final pressure.
(B) If the compression is adiabatic then triatomic gas will have maximum final pressure.
(C) If the compression is adiabatic then their final pressure will be same.
(D) If the compression is isothermal then their final pressure will be different.

Q.40 If heat is added at constant volume, 6300J of heat are required to raise the temperature of an ideal gas by 150K. If instead, heat is added at constant pressure, 8800 joules are required for the same temperature change. When the temperature of the gas changes by 300K, the internal energy of the gas changes by
(A) 5000J (B) 12600J (C) 17600J (D) 22600J

Q.41 Three processes form a thermodynamic cycle as shown on P-V diagram for an ideal gas. Process 1 → 2 takes place at constant temperature (300K). Process 2 → 3 takes place at constant volume. During this process 40J of heat leaves the system. Process 3 → 1 is adiabatic and temperature T_3 is 275K. Work done by the gas during the process 3 → 1 is



(A) -40J (B) -20J
(C) +40J (D) +20J

Q.42 When unit mass of water boils to become steam at 100°C, it absorbs Q amount of heat. The densities of water and steam at 100°C are ρ_1 and ρ_2 respectively and the atmospheric pressure is p_0. The increase in internal energy of the water is

(A) Q (B) $Q + p_0\left(\frac{1}{\rho_1} - \frac{1}{\rho_2}\right)$ (C) $Q + p_0\left(\frac{1}{\rho_2} - \frac{1}{\rho_1}\right)$ (D) $Q - p_0\left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right)$

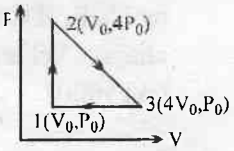
Q.43 A vertical cylinder with heat-conducting walls is closed at the bottom and is fitted with a smooth light piston. It contains one mole of an ideal gas. The temperature of the gas is always equal to the surrounding's temperature, T_0. The piston is moved up slowly to increase the volume of the gas η times. Which of the following is incorrect?
(A) Work done by the gas is $RT_0 \ln \eta$.
(B) Work done against the atmosphere is $RT_0(\eta - 1)$.
(C) There is no change in the internal energy of the gas.
(D) The final pressure of the gas is $\frac{1}{(\eta - 1)}$ times its initial pressure.

Q.44 When 2 gms of a gas are introduced into an evacuated flask kept at 25°C the pressure is found to be one atmosphere. If 3 gms of another gas added to the same flask the pressure becomes 1.5 atmospheres. The ratio of the molecular weights of these gases will be
(A) 1 : 3 (B) 3 : 1 (C) 2 : 3 (D) 3 : 2

Q.45 A polyatomic gas with six degrees of freedom does 25J of work when it is expanded at constant pressure. The heat given to the gas is
(A) 100J (B) 150J (C) 200J (D) 250J

Q.46 An ideal gas expands from volume V_1 to V_2. This may be achieved by either of the three processes: isobaric, isothermal and adiabatic. Let ΔU be the change in internal energy of the gas, Q be the quantity of heat added to the system and W be the work done by the system on the gas. Identify which of the following statements are true for ΔU?
(A) ΔU is least under adiabatic process.
(B) ΔU is greatest under adiabatic process.
(C) ΔU is greatest under the isobaric process.
(D) ΔU in isothermal process lies in-between the values obtained under isobaric and adiabatic processes.

Q.47 One mole of an ideal diatomic gas is taken through the cycle as shown in the figure.
$1 \rightarrow 2$: isochoric process
$2 \rightarrow 3$: straight line on P-V diagram
$3 \rightarrow 1$: isobaric process
The molecular speed of the gas in the states 1, 2 and 3 are in the ratio



(A) 1 : 2 : 2 (B) $1 : \sqrt{2} : \sqrt{2}$ (C) 1 : 1 : 1 (D) 1 : 2 : 4

Q.48 A closed vessel contains a mixture of two diatomic gases A and B. Molar mass of A is 16 times that of B and mass of gas A contained in the vessel is 2 times that of B. The following statements are given
(i) Average kinetic energy per molecule of A is equal to that of B.
(ii) Root mean square value of translational velocity of B is four times that of A.
(iii) Pressure exerted by B is eight times of that exerted by A.
(iv) Number of molecules of B in the cylinder is eight time that of A.
(A) (i), (ii) and (iii) are true
(B) (ii), (iii) and (iv) are true
(C) (i), (ii) and (iv) are true
(D) All are true

ANSWER KEY

Q.1	A	Q.2	A	Q.3	B, D	Q.4	B, C	Q.5	C
Q.6	D	Q.7	D	Q.8	A	Q.9	A	Q.10	D
Q.11	A	Q.12	D	Q.13	C	Q.14	D	Q.15	C
Q.16	D	Q.17	A	Q.18	C	Q.19	B	Q.20	A
Q.21	C	Q.22	A	Q.23	D	Q.24	A	Q.25	D
Q.26	C	Q.27	A	Q.28	A	Q.29	C	Q.30	B
Q.31	D	Q.32	D	Q.33	B, D	Q.34	B	Q.35	C, D
Q.36	B	Q.37	A	Q.38	A	Q.39	A	Q.40	B
Q.41	A	Q.42	B	Q.43	D	Q.44	A	Q.45	A
Q.46	A, C, D	Q.47	A	Q.48	D				

BANSALCLASSES

TARGET IIT JEE 2007

PHYSICAL CHEMISTRY

XII (ALL)

LIQUID SOLUTIONS

"A SPECIALLY DESIGNED KIT FOR LEARNING."

CONTENTS

THE KEY	⟶	Basic principles of subjects. An outline of the topics to be discussed in class lectures.
THE ATLAS	⟶	Basic layout of subject. A route map correlating different subtopics in coherent manner.
EXERCISE I	⟶	Introductory problems to get first hand experience of problem solving.
PROFICIENCY TEST	⟶	To check you newly acquired concepts.
EXERCISE II	⟶	A collection of good problems.
EXERCISE III	⟶	Test your objective skill.
EXERCISE IV	⟶	A collection of previous ten years JEE problems.

KEY CONCEPTS

Vapor Pressure. The pressure exerted by the vapors of a liquid which are in equilibrium with it at a given temperature.

Note: It depends only on temperature and on nature of the liquid. It does NOT depend on the surface area

Raoult's Law. The equilibrium vapor pressure of a volatile component is linearly proportional to the mole fraction of that compoent in liquid phase.

For non-volatile solutes : $P(\text{solution}) = x_{\text{solvent}}P^o$

or relative lowering of vapor pressure, $(P^o - P)/P^o = x_{\text{solute}}$.

A more useful form is $(P^o - P)/P = n/N$

where n = total number of moles of *all the free solute species* in the solution *finally* (i.e. at equilibrium).

Three cases arise.

(i) **Non-electrolyte** is dissolved e.g. glucose or urea. These molecules do not dissociate into ions. If 0.1 mol of urea is dissolved in 50 moles of water, then n/N = 0.1/50 simply.

(ii) **Strong electrolyte** is dissolved e.g. NaCl, $Ca(NO_3)_2$etc. These dissociate nearly completely into ions. If 0.1 mol of NaCl is dissolved in 50 moles of water, then n/N = 0.2/50 since NaCl dissociates completely in 0.1 mol Na^+ ions and 0.1 mol Cl^- ions. Similarly, for $Ca(NO_3)_2$, n/N = 0.3/50 if 0.1 mol of it dissociates completely into ions.

(iii) **Weak electrolyte** is dissolved e.g. HCOOH, CH_3NH_2 etc. In such cases, we should determine the *total* number of moles of all the solute species at equilibrium. e.g. if n_o moles of formic acid considered non-volatile here) are dissolved in N moles of solvent then,

$$\begin{array}{llll} HCOOH \Leftrightarrow & H^+ & + & COOH^- \\ n_o(1-\alpha) & n_o\alpha & & n_o\alpha \end{array}$$

Total number of moles at equilibrium $= n_o(1+\alpha)$. Hence, $n/N = n_o(1+\alpha)/N$.

Note : This factor, n (at equilibrium)/n(original) is referred to as **van't Hoff factor**.

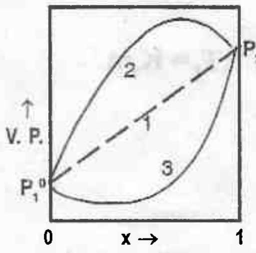
Ideal Solutions. The solutions which obey Raoult's Law are called ideal solution. For ideality :
(i) $\Delta H_{mix} = 0$, (ii) $\Delta V_{mix} = 0$ as well for liquid-liquid solutions.

Non ideal solution (Deviations From Raoult's Law)

Positive deviation. When the observed vapor pressure is *more than* that expected by Raoult's law.

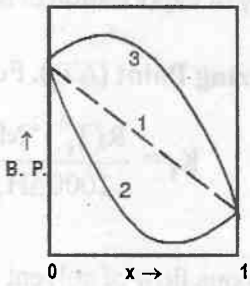
This is observed when $\Delta H_{mix} > 0$ i.e. energy is absorbed on mixing. Usually obtained by mixing of polar liquids with non-polar ones. e.g. cyclohexane and ethanol.

Negative deviation. When the observed vapor pressure is *less than* that expected by Raoult's law. This is observed when $\Delta H_{mix} < 0$ i.e. energy is released on mixing. Attractive forces between unlike molecules are greater than the forces of attraction between like molecules. e.g. chloroform and acetone. (Curve 3 in Fig. 1 and 2).



x is mole fraction of more volatile component (2)

Fig. 1



x is mole fraction of more volatile component (2)

Fig. 2

Azeotropic Solutions. During distillation, the mole fraction of more volatile component in vapor state is higher than that in liquid state. This makes distillation possible. However, there exist some solutions for particular compositions of which the mole fraction of components in liquis and vapor state is same. Thus, no advantage is derived by distilling such a mixture and it is termed as **azeotropic.**

Completely Immiscible Liquids : When they are distilled, they distil in the ratio of their vapor pressure at that temperature. e.g. When A and B are distilled wt ratio $\frac{w_B}{w_A}$ is given as $\frac{w_B}{w_A} = \frac{P_B^0 \cdot M_B}{P_A^0 \cdot M_A}$

Completely Miscibile Liquids. They can be handled by Raoult's Law i.e.

$$y_iP = x_iP_i^o$$

where P = Total pressure of vapors in equilibrium with the liquid solution,

P_i^o = vapor pressure of component *i* in pure state

y_i = mole fraction of ith component *in vapor state*, x_i = mole fraction of i^{th} component *in liquid state*

This most fundamental expression may be arranged in many useful forms. e.g. for binary solutions :

$$P = x_1(P_1^0 - P_2^0) + P_2^0$$

or

$$1/P = 1/P_2^0 + y_1(1/P_1^0 - 1/P_2^0)$$

Note : Vapor pressure of an ideal solution is always between P_1^0 and P_2^0 (Curve 1 in Fig. 1 and 2)

Bubble Point. When the first bubble of vapor appears in liquid solution.

Dew Point. When the first drop of liquid condenses from a mixture of vapors. OR when the last drop of liquid remains and rest of the liquid is completely vaporised.

Colligative Properties. The properties which depend only on the number of moles of solute (and not on their molecular weights or sizes) are referred to as colligative properties.

e.g. Lowring of vapor pressure, depression of freezing point, elevation of boiling point, osmotic pressure etc.

1. **Relative lowering of vapour Pressure.** $\frac{P^0 - P}{P^0} = \frac{n}{n+N} = \frac{w/m}{w/m + W/M} = x_{solute}$

2. **Elevation in Boiling Point, ΔT_b.** For dilute solutions, $\Delta T_b = K_b m$

where *m* is molality of the solution (i.e. total number of moles of all the solute particles per kg of solvent). K_b is ebullioscopic or boiling point elevation constant which is given by

$$K_b = \frac{R(T_b^0)^2 M_{solvent}}{1000 \Delta H_{vap}}$$

ΔH_{vap} is the enthalpy of vaporisation of solvent.

3. **Depression in freezing Point (ΔT_f).** For dilute solutions, $\mathbf{\Delta T_f = K_f m}$

where, $$K_f = \frac{R(T_f^0)^2 M_{solvent}}{1000 \Delta H_{fusion}}$$

Osmosis. Spontaneous flow of solvent molecules through a semipermeable membrane from a pure solvent to the solution (or from a dilute solution to a concentrated solution) is termed as osmosis.

Reverse Osmosis. If a pressure greater than the osmotic pressure is applied on the concentrated solution, the solvent starts to flow from concentrated solution to dilute solution (or pure solvent). This is reverse osmosis. One of its chief uses is desalination of sea water to get pure drinking water.

4. **Osmotic Pressure (π).** The hydrostatic pressure built up on the solution which just stops osmosis. Alternately, it may be defined as the pressure which must be applied to the concentrated solution in order to stop osmosis.

For dilute solutions $\quad \boldsymbol{\pi = cRT = h\rho g}$

where c is the total molar concentration of all the free species present in the solution, h is the height developed by the column of the concentrated solution and ρ is the density of the solution in the column. On the basis of osmotic pressure, the solutions can be classified in three classes.

Isotonic solutions. Two solutions having same osmotic pressures at same temperature. (This implies $c_1 = c_2$).

Hypertonic solution. When two solutions are being compared, then the solution with higher osmotic pressure is termed as hypertonic. The solution with lower osmotic pressure is termed as **hypotonic.**

Important. Osmotic pressures can be determined quite accurately, hence it is used in the determination of molecular weights of large proteins and similar substances.

Van't Hoff Factor (i)

Since colligative properties depends upon the number of particles of the solute, in some cases where the solute associates or dissociates in solution, abnormal results for molecules masses are obtained.

$$i = \frac{\textit{Observed colligative property(actual)}}{\textit{Theoretical colligative property}}$$

THE ATLAS

Liquid Solutions

1. Vapour Pressure
2. Raoult's law
   - (i) When volatile solute is added
     - (a) When solute and solvent; both are miscible
     - (b) When both are immiscible
   - (ii) When non-volatile solute is added.
3. Condensation of vapours of solution
4. Ideal and non-ideal solutions
5. Azeotropic mixtures

Colligative properties (C.P.)

1. Introduction
2. The various C.P.
   - (i) Lowering of V.P.
     - (a) Determination of molar masses
     - (b) It's measurement
   - (ii) Boiling point elevation
   - (iii) Depression in freezing point
   - (iv) Osmotic pressure
     - (a) Osmosis
     - (b) Reverse osmosis
     - (c) Isotonic solution
3. Van't Haff factor; Where the solute associates or dissociates in solution.

EXERCISE I

Raoult's law

Q.1 At 25°C, the vapour pressure of methyl alcohol is 96.0 torr. What is the mole fraction of CH_3OH in a solution in which the (partial) vapor pressure of CH_3OH is 23.0 torr at 25°C?

Q.2 The vapour pressure of pure liquid solvent A is 0.80 atm. When a nonvolatile substance B is added to the solvent its vapour pressure drops to 0.60 atm. What is the mole fraction of component B in the solution?

Q.3 The vapour pressure of pure water at 26°C is 25.21 torr. What is the vapour pressure of a solution which contains 20.0 glucose, $C_6H_{12}O_6$, in 70 g water?

Q.4 The vapour pressure of pure water at 25°C is 23.76 torr. The vapour pressure of a solution containing 5.40 g of a nonvolatile substance in 90.0 g water is 23.32 torr. Compute the molecular weight of the solute.

Raoult's law in combinaton with Dalton's law of P.P. and V.P. lowering

Q.5 The vapour pressure of ethanol and methanol are 44.5 mm and 88.7 mm Hg respectively. An ideal solution is prepared at the same temperature by mixing 60 g of ethanol with 40 g of methanol. Calculate total vapour pressure of the solution.

Q.6 Calculate the mole fraction of toluene in the vapour phase which is in equilibrium with a solution of benzene and toluene having a mole fraction of toluene 0.50. The vapour pressure of pure benzene is 119 torr; that of toluene is 37 torr at the same temperature.

Q.7 What is the composition of the vapour which is in equilibrium at 30°C with a benzene-toluene solution with a mole fraction of benzene of 0.40? With a mole fraction of benzene of 0.60?

$P_b^\circ = 119$ torr and $P_t^\circ = 37$ torr

Q.8 At 90°C, the vapour pressure of toluene is 400 torr and that of σ-xylene is 150 torr. What is the composition of the liquid mixture that boils at 90°C, when the pressure is 0.50 atm? What is the composition of vapour produced?

Q.9 Two liquids A and B form an ideal solution at temperature T. When the total vapour pressure above the solution is 400 torr, the mole fraction of A in the vapour phase is 0.40 and in the liquid phase 0.75. What are the vapour pressure of pure A and pure B at temperature T?

Q.10 Calculate the relative lowering in vapour pressure if 100 g of a nonvolatile solute (mol.wt.100) are dissolved in 432 g water.

Q.11 What weight of the non–volatile solute, urea needs to be dissolved in 100 g of water, in order to decrease the vapour pressure of water by 25%? What will be the molality of the solution?

Great [illegible] Nearin revision

Q.12 The vapour pressure of an aqueous solution of glucose is 750 mm Hg at 373 K. Calculate molality and mole fraction of solute.

Q.13 The vapour pressure of pure benzene at 25° C is 639.7 mm of Hg and the vapour pressure of a solution of a solute in C_6H_6 at the same temperature is 631.7 mm of Hg. Calculate molality of solution.

check

Q.14 The vapour pressure of pure benzene at a certain temperature is 640 mm of Hg. A nonvolatile nonelectrolyte solid weighing 2.175 g is added to 39.0 of benzene. The vapour pressure of the solution is 600 mm of Hg. What is molecular weight of solid substance?

Q.15 The vapour pressure of water is 17.54 mm Hg at 293 K. Calculate vapour pressure of 0.5 molal solution of a solute in it.

Q.16 Benzene and toluene form two ideal solution A and B at 313 K. Solution A (total pressure P_A) contains equal mole of toluene and benzene. Solution B contains equal masses of both (total pressure P_B). The vapour pressure of benzene and toluene are 160 and 60 mm Hg respectively at 313 K. Calculate the value of P_A/P_B.

Boiling point elevation and freezing point depression

Q.17 When 10.6 g of a nonvolatile substance is dissolved in 740 g of ether, its boiling point is raised 0.284°C. What is the molecular weight of the substance? Molal boiling point constant for ether is 2.11°C·kg/mol.

Q.18 A solution containing 3.24 of a nonvolatile nonelectrolyte and 200 g of water boils at 100.130°C at 1atm. What is the molecular weight of the solute? (K_b for water 0.513°C/m)

Q.19 The molecular weight of an organic compound is 58.0 g/mol. Compute the boiling point of a solution containing 24.0 g of the solute and 600 g of water, when the barometric pressure is such that pure water boils at 99.725°C.

Q.20 An aqueous solution of a nonvolatile solute boils at 100.17°C. At what temperature will this solution freeze? [K_f for water 1.86°C/m]

Q.21 Pure benzene freeze at 5.45°C. A solution containing 7.24 g of $C_2H_2Cl_4$ in 115.3 g of benzene was observed to freeze at 3.55°C. What is the molal freezing point constant of benzene?

Q.22 A solution containing 6.35 g of a nonelectrolyte dissolved in 500 g of water freezes at – 0.465°C. Determine the molecular weight of the solute.

Q.23 The freezing point of a solution containing 2.40 g of a compound in 60.0 g of benzene is 0.10°C lower than that of pure benzene. What is the molecular weight of the compound? (K_f is 5.12°C/m for benzene)

Q.24 The elements X and Y form compounds having molecular formula XY_2 and XY_4. When dissolved in 20 gm of benzene, 1 gm XY_2 lowers the freezing point by 2.3°, whereas 1 gm of XY_4 lowers the freezing point by 1.3°C. The molal depression constant for benzene is 5.1. Calculate the atomic masses of X and Y.

Q.25 Calculate the molal elevation constant, K_b for water and the boiling of 0.1 molal urea solution. Latent heat of vaporisation of water is 9.72 kcal mol^{-1} at 373.15 K.

Q.26 Calculate the amount of ice that will separate out of cooling a solution containing 50g of ethylene glycol in 200 g water to –9.3°C. (K_f for water = 1.86 K mol^{-1} kg)

Q.27 A solution of 0.643 g of an organic compound in 50ml of benzene (density ; 0.879 g/ml) lowers its freezing point from 5.51°C to 5.03°C. If K_f for benzene is 5.12 K, calculate the molecular weight of the compound.

Q.28 The cryoscopic constant for acetic acid is 3.6 K kg/mol. A solution of 1 g of a hydrocarbon in 100 g of acetic acid freezes at 16.14°C instead of the usual 16.60°C. The hydrocarbon contains 92.3% carbon. What is the molecular formula?

Osmotic pressure

Q.29 Find the freezing point of a glucose solution whose osmotic pressure at 25°C is found to be 30 atm. K_f(water) = 1.86kg.mol^{-1}.K.

Q.30 At 300 K, two solutions of glucose in water of concentration 0.01 M and 0.001 M are separated by semipermeable membrane. Pressure needs to be applied on which solution, to prevent osmosis? Calculate the magnitude of this applied pressure.

Q.31 At 10°C, the osmotic pressure of urea solution is 500 mm. The solution is diluted and the temperature is raised to 25°C, when the osmotic pressure is found to be105.3 mm. Determine extent of dilution.

Q.32 The osmotic pressure of blood is 7.65 atm at 37°C. How much glucose should be used per L for an intravenous injection that is to have the same osmotic pressure as blood?

Q.33 What would be the osmotic pressure at 17°C of an aqueous solution containing 1.75 g of sucrose ($C_{12}H_{22}O_{11}$) per 150 cm^3 of solution?

Q.34 A 250 mL water solution containing 48.0 g of sucrose, $C_{12}H_{22}O_{11}$, at 300 K is separated from pure water by means of a semipermeable membrane. What pressure must be applied above the solution in order to just prevent osmosis?

Q.35 A solution of crab hemocyanin, a pigmented protein extracted from crabs, was prepared by dissolving 0.750 g in 125 cm^3 of an aqueous medium. At 4°C an osmotic pressure rise of 2.6 mm of the solution was observed. The solution had a density of 1.00 g/cm^3. Determine the molecular weight of the protein.

Q.36 The osmotic pressure of a solution of a synthetic polyisobutylene in benzene was determined at 25°C. A sample containing 0.20 g of solute/100 cm^3 of solution developed a rise of 2.4 mm at osmotic equilibrium. The density of the solution was 0.88 g/cm^3. What is the molecular weight of the polyisobutylene?

Q.37 A 5% solution (w/v) of cane-sugar (Mol. weight = 342) is isotonic with 0.877%(w/v) of urea solution. Find molecular weight of urea.

Q.38 10 gm of solute A and 20 gm of solute B are both dissolved in 500 ml water. The solution has the same osmotic pressure as 6.67 gm of A and 30 gm of B dissolved in the same amount of water at the same temperature. What is the ratio of molar masses of A and B?

Van't Hoff factor & colligative properties

Q.39 A storage battery contains a solution of H_2SO_4 38% by weight. What will be the Van't Hoff factor if the $\Delta T_{f(\text{experiment})}$ in 29.08. [Given K_f = 1.86 mol^{-1} Kg]

Q.40 A certain mass of a substance, when dissolved in 100 g C_6H_6, lowers the freezing point by 1.28°C. The same mass of solute dissolved in 100g water lowers the freezing point by 1.40°C. If the substance has normal molecular weight in benzene and is completely ionized in water, into how many ions does it dissociate in water? K_f for H_2O and C_6H_6 are 1.86 and 5.12K kg mol^{-1}.

Q.41 2.0 g of benzoic acid dissolved in 25.0g of benzene shows a depression in freezing point equal to 1.62K. Molal depression constant (K_f) of benzene is 4.9 K.kg.mol^{-1}. What is the percentage association of the acid?

Q.42 A decimolar solution of potassium ferrocyanide is 50% dissociated at 300K. Calculate the osmotic pressure of the solution. (R=8.314 JK^{-1} mol^{-1})

Q.43 The freezing point of a solution containing 0.2 g of acetic acid in 20.0g of benzene is lowered by 0.45°C. Calculate the degree of association of acetic acid in benzene. (K_f for benzene = 5.12 K mol^{-1} kg)

Q.44 0.85 % aqueous solution of $NaNO_3$ is apparently 90% dissociated at 27°C. Calculate its osmotic pressure. (R= 0.082 l atm K^{-1} mol^{-1})

Q.45 A 1.2% solution (w/v) of NaCl is isotonic with 7.2% solution (w/v) of glucose. Calculate degree of ionization and Van't Hoff factor of NaCl.

PROFICIENCY TEST

Q.1 ***Fill in the blanks with appropriate items :***

1. Lowering of vapour pressure is ________ to the mole fraction of the solute.
2. The ratio of the value of any colligative property for NaCl solution to that of equimolal solution of sugar is nearly______.
3. Semipermeable membrane allows the passage of _________through it.
4. A binary solution which has same composition in liquid as well as vapour phase is called_______.
5. The molal elevation constant of solvent is also called_____.
6. The 0.1 M aqueous solution of acetic acid has boiling point _______ than that of 0.1 M aqueous solution of KCl.
7. For ideal solutions, the plot of total vapour pressure v/s composition is ______.
8. A solution of $CHCl_3$ and acetone shows_________deviation.
9. Gases which react with water are generally __________ soluble in it.
10. Assuming complete dissociation, Van't Hoff's factor for Na_2SO_4 is equal to ________.
11. The osmotic pressure of a solution _______ with increase in temperature.
12. Water will boil at 101.5°C at pressure of ________76 cm of Hg.
13. Osmotic pressure can be experimentally determined by ________ method.
14. $\pi - \frac{n_B}{V}RT$ is known as__________.
15. The molal elevation constant is the ratio of the elevation in boiling point to __________.

Q.2 ***True or False Statements :***

16. Relative lowering of vapour pressure is a colligative property.
17. Lowering of vapour pressure of a solution is equal to the mole fraction of the non-volatile solute present in it.
18. The components of an azeotropic solution can be separated by simple distillation.
19. Vapour pressure of a liquid depends on the size of the vessel.
20. Addition of non-volatile solute to water always lowers it vapour pressure.
21. Reverse osmosis is generally used to make saline water fit for domestic use.
22. A 6% solution of NaCl should be isotonic with 6% solution of sucrose.
23. A real solution obeys Raoult's law.
24. Boiling point is a characteristic temperature at which vapour pressure of the liquid becomes higher than the atmospheric pressure.
25. Molal depression constant is independent of the nature of solute as well as that of solvent.
26. The real solutions can exhibit ideal behaviour at high concentrations.
27. The osmotic pressure decreases on addition of solvent to the solution.
28. For urea the value of Vant's Hoff's factor 'i' is equal to 1.
29. The unit of k_b is kg K^{-1} mol^{-1}.
30. 0.1M solution of urea would be hypotonic with 0.1 M solution of NaCl.

EXERCISE II

Q.1 An aqueous solution containing 288 gm of a non-volatile compound having the stoichiometric composition $C_xH_{2x}O_x$ in 90 gm water boils at 101.24°C at 1.00 atmospheric pressure. What is the molecular formula?

$K_b(H_2O) = 0.512\ K\ mol^{-1}\ kg$

$T_b(H_2O) = 100°C$

Q.2 The degree of dissociation of $Ca(NO_3)_2$ in a dilute aqueous solution containing 7 gm of the salt per 100 gm of water at 100°C is 70%. If the vapour pressure of water at 100°C is 760 mm. Calculate the vapour pressure of the solution.

Q.3 The addition of 3 gm of substance to 100 gm CCl_4($M = 154\ gm\ mol^{-1}$) raises the boiling point of CCl_4 by 0.60°C of K_b (CCl_4) is 5.03 kg mol^{-1} K. Calculate

(a) the freezing point depression

(b) the relative lowering of vapour pressure

(c) the osmotic pressure at 298 K

(d) the molar mass of the substance

Given $K_f(CCl_4) = 31.8\ kg\ mol^{-1}K$ and ρ (density) of solution = 1.64 gm/cm^3

Q.4 A 10% solution of cane sugar has undergone partial inversion according to the reaction:

Sucrose + Water $\longrightarrow$ Glucose + Fructose. If the boiling point of solution is 100.27°C.

(a) What is the average mass of the dissolved materials?

(b) What fraction of the sugar has inverted? $K_b(H_2O) = 0.512\ K\ mol^{-1}\ kg$

Q.5 If 20 ml of ethanol (density = 0.7893 gm/ml) is mixed with 40 ml water (density = 0.9971 gms) at 25°C, the final solution has density of 0.9571 gm/ml. Calculate the percentage change in total volume of mixing. Also calculate the molality of alcohol in the final solution.

Q.6 Mixture of two liquids A and B is placed in cylinder containing piston. Piston is pulled out isothermally so that volume of liquid decreases but that of vapour increases. When negligibly small amount of liquid was remaining, the mole fraction of A in vapour is 0.4. Given P_A° =0.4 atm and P_3° = 1.2 atm at the experimental temperature. Calculate the total pressure at which the liquid has almost evaporated. (Assume ideal behaviour).

Q.7 1.5 g of a monobasic acid when dissolved in 150g of water lowers the freezing point by 0.165°C. 0.5 g of the same acid when titrated, after dissolution in water, requires 37.5 ml of N/10 alkali. Calculate the degree of dissociation of the acid (K_f for water = 1.86°C mol^{-1}).

Q.8 Sea water is found to contain 5.85% NaCl and 9.50% $MgCl_2$ by weight of solution. Calculate its normal boiling point assuming 80% ionisation for NaCl and 50% ionisation of $MgCl_2$ [$K_b(H_2O) = 0.51 kgmol^{-1}K$].

Q.9 The latent heat of fusion of ice is 80 calories per gram at 0^0C. What is the freezing point of a solution of KCl in water containing 7.45 grams of solute in 500 grams of water, assuming that the salt is dissociated to the extent of 95%?

Q.10 A complex is represented as $CoCl_3 \cdot xNH_3$. It's 0.1 molal solution in aq. solution shows $\Delta T_f = 0.558°C$. K_f for H_2O is 1.86 K mol^{-1}kg . Assuming 100% ionisation of complex and coordination no. of Co is six, calculate formula of complex.

Q.11 The molar volume of liquid benzene (density = 0.877 g ml^{-1}) increases by a factor of 2750 as it vaporizes at 20°C and that of liquid toluene (density = 0.867gml^{-1}) increases by a factor of 7720 at 20°C has a vapour pressure of 46.0 torr. Find the mole fraction of benzene in the vapour above the solution.

Q.12 At 100°C, benzene & toluene have vapour pressure of 1375 & 558 Torr respectively. Assuming these two form an ideal binary solution, calculate the composition of the solution that boils at 1 atm & 100°C. What is the composition of vapour issuing at these conditions?

Q.13 Calculate the boiling point of a solution containing 0.61g of benzoic acid in 50g of carbon disulphide assuming 84% dimerization of the acid. The boiling point and K_b of CS_2 are 46.2°C and 2.3 K kg mol^{-1}, respectively.

Q.14 At 25°C, 1 mol of A having a vapor pressure of 100torr and 1 mol of B having a vapor pressure of 300 torr were mixed. The vapor at equilibrium is removed, condensed and the condensate is heated back to 25°C. The vapors now formed are again removed, recondensed and analyzed. What is the mole fraction of A in this condensate?

Q.15 Phenol associates in benzene to a certain extent to form a dimer. A solution containing 20×10^{-3} kg phenol in 1 kg of benzene has its freezing point depressed by 0.69 K. Calculate the fraction of phenol that has dimerised. K_f for benzene = 5.12 kg mol^{-1}K.

Q.16 30 ml of CH_3OH (d = 0.7980 gm cm^{-3}) and 70 ml of H_2O (d=0.9984 gm cm^{-3}) are mixed at 25°C to form a solution of density 0.9575 gm cm^{-3}. Calculate the freezing point of the solution. $K_f(H_2O)$ is 1.86 kg mol^{-1} K. Also calculate its molarity.

Q.17 Dry air was drawn thorugh bulbs containing a solution of 40 grams of urea in 300 grams of water, then through bulbs containing pure water at the same temperature and finally through a tube in which pumice moistened with strong H_2SO_4 was kept. The water bulbs lost 0.0870 grams and the sulphuric acid tube gained 2.036 grams. Calculate the molecular weight of urea.

Q.18 Vapour pressure of C_6H_6 and C_7H_8 mixture at 50°C is given by **P (mm Hg) = 180 X_B + 90**, where X_B is the mole fraction of C_6H_6. A solution is prepared by mixing 936g benzene and 736g toluene and if the vapours over this solution are removed and condensed into liquid and again brought to the temperature of 50°C, what would be mole fraction of C_6H_6 in the vapour state?

Q.19 When the mixture of two liquids (water and nitrobenzene) boils at 372 K and the vapour pressure at this temperature are 97.7 kPa (H_2O) and 3.6 kPa ($C_6H_5NO_2$). Calculate the weight % of nitrobenzene in the vapour.

Q.20 The vapour pressure of a certain liquid is given by the equation:

$$\text{Log}_{10}P = 3.54595 - \frac{313.7}{T} + 1.40655 \log_{10} T$$ where P is the vapour pressure in mm and T = Kelvin Temperature. Determine the molar latent heat of vaporisation as a function of temperature. Calculate the its value at 80 K.

Q.21 The composition of vapour over a binary ideal solution is determined by the composition of the liquid. If X_A and Y_A are the mole fractions of A in the liquid and vapour, respectively, find the value of X_A for which $Y_A - X_A$ has a maximum. What is the value of the pressure at this composition in terms of P^0_A and P^0_B.

Q.22 The molar volume of liquid benzene (density = 0.877g ml^{-1}) increases by a factor of 2750 as it vaporises at 20°C while in equilibrium with liquid benzene. At 27°C when a non-volatile solute (that does not dissociate) is dissolved in 54.6 cm^3 of benzene vapour pressure of this solution, is found to be 98.88 mm Hg. Calculate the freezing point of the solution.
Given : *Enthalpy of vaporization of benzene(l) = 394.57 J/gm*
Molal depression constant for benzene = 5.0 K.kg. mol^{-1}.
Freezing point of benzene = 278.5 K.

Q.23 If the apparent degree of ionization of KCl (KCl = 74.5 gm mol^{-1}) in water at 290 K is 0.86. Calculate the mass of KCl which must be made up to 1 dm^3 of aqueous solution to the same osmotic pressure as the 4.0% solution of glucose at that temperature.

Q.24 An ideal solution was prepared by dissolving some amount of cane sugar (non–volatile) in 0.9 moles of water. The solution was then cooled just below its freezing temperature (271 K), where some ice get separated out. The remaining aqueous solution registered a vapour pressure of 700 torr at 373 K. Calculate the mass of ice separated out, if the molar heat of fusion of water is 6 kJ.

Q.25 The freezing point depression of a 0.109 M aq. solution of formic acid is –0.21°C. Calculate the equilibrium constant for the reaction,

$$HCOOH\,(aq) \rightleftharpoons H^+(aq) + HCOOH^-\,(aq)$$

K_f for water = 1.86 kg mol^{-1} K

Q.26 10 gm of NH_4Cl (mol. weight = 53.5) when dissolved in 1000 gm of water lowered the freezing point by 0.637°C. Calculate the degree of hydrolysis of the salt if its degree of dissociation of 0.75. The molal depression constant of water is 1.86 kg mol^{-1} K.

Q.27 The freezing point of 0.02 mol fraction solution of acetic acid (A) in benzene (B) is 277.4K. Acetic acid exists partly as a dimer $2A = A_2$. Calculate equilibrium constant for the dimerisation. Freezing point of benzene is 278.4 K and its heat of fusion ΔH_f is 10.042 kJ mol^{-1}.

Q.28 A saturated solution of a sparingly soluble salt, MCl_2 has a vapour pressure of 31.78 mm of Hg at 30°C, while pure water exerts a pressure of 31.82 mm of Hg at the same temperature. Calculate the solubility product of the compound at this temperature.

Q.29 The vapour pressure of two pure liquids, A and B that form an ideal solution are 300 and 800 torr respectively, at temperature T. A mixture of the vapour of A and B for which the mole fraction of A is 0.25 is slowly compressed at temperature T. Calculate
(a) the composition of the first drop of the condensate,
(b) the total pressure when this drop is formed,
(c) the composition of the solution whose normal boiling point is T,
(d) the pressure when only the last bubble of vapour remains, and
(e) the composition of the last bubble.

Q.30 Tritium, T (an isotope of H) combines with fluorine to form weak acid TF, which ionizes to give T^+. Tritium is radioactive and is a β–emitter. A freshly prepared aqueous solution of TF has pT (equivalent of pH) of 1.5 and freezes at –0.372°C. If 600ml of freshly prepared solution were allowed to stand for 24.8 years. Calculate (i) ionization constant of TF. (ii) Number of β–particles emitted.
(Given K_f for water = 1.86 kg mol K^{-1}, $t_{1/2}$ for tritium = 12.4 years)

EXERCISE III

Q.1 For an ideal binary liquid solution with $P_A^\circ > P_B^\circ$, which relation between X_A (mole fraction of A in liquid phase) and Y_A (mole fraction of A in vapour phase) is correct?

(A) $Y_A < Y_B$ (B) $X_A > X_B$ (C) $\frac{Y_A}{Y_B} > \frac{X_A}{X_B}$ (D) $\frac{Y_A}{Y_B} < \frac{X_A}{X_B}$

Q.2 Mole fraction of A vapours above the solution in mixture of A and B ($X_A = 0.4$) will be [Given : $P_A^\circ = 100$ mm Hg and $P_B^\circ = 200$ mm Hg]

(A) 0.4 (B) 0.8 (C) 0.25 (D) none of these

Q.3 The exact mathematical expression of Raoult's law is

(A) $\frac{P^0 - P_s}{P^0} = \frac{n}{N}$ (B) $\frac{P^0 - P_s}{P^0} = \frac{N}{n}$ (C) $\frac{P^0 - P_s}{P_s} = \frac{n}{N}$ (D) $\frac{P^0 - P_s}{P^0} = n \times N$

Q.4 A mixture contains 1 mole of volatile liquid A ($P_A^\circ = 100$ mm Hg) and 3 moles of volatille liquid B ($P_B^\circ = 80$ mm Hg). If solution behaves ideally, the total vapour pressure of the distillate is

(A) 85 mm Hg (B) 85.88 mm Hg (C) 90 mm Hg (D) 92 mm Hg

Q.5 Which of the following aqueous solution will show maximum vapour pressure at 300 K?

(A) 1 M NaCl (B) 1 M $CaCl_2$ (C) 1 M $AlCl_3$ (D) 1 M $C_{12}H_{22}O_{11}$

Q.6 The Van't Hoff factor for a dilute aqueous solution of glucose is

(A) zero (B) 1.0 (C) 1.5 (D) 2.0

Q.7 The correct relationship between the boiling points of very dilute solution oif $AlCl_3$ (T_1K) and $CaCl_2$ (T_2K) having the same molar concentration is

(A) $T_1 = T_2$ (B) $T_1 > T_2$ (C) $T_2 > T_1$ (D) $T_2 < T_1$

Q.8 A 0.001 molal solution of a complex $[MA_8]$ in water has the freezing point of –0.0054°C. Assuming 100% ionization of the complex salt and K_f for $H_2O = 1.86\ km^{-1}$, write the correct representation for the complex

(A) $[MA_8]$ (B) $[MA_7]A$ (C) $[MA_6]A_2$ (D) $[MA_5]A_3$

Q.9 The vapour pressure of a solution of a non-volatile electrolyte B in a solvent A is 95% of the vapour pressure of the solvent at the same temperature. If the molecular weight of the solvent is 0.3 times the molecular weight of solute, the weight ratio of the solvent and solute are

(A) 0.15 (B) 5.7 (C) 0.2 (D) 4.0

Q.10 At a given temperature, total vapour pressure in Torr of a mixture of volatile components A and B is given by

$$P_{Total} = 120 - 75\ X_B$$

hence, vapour pressure of pure A and B respectively (in Torr) are

(A) 120, 75 (B) 120, 195 (C) 120, 45 (D) 75, 45

Q.11 Assuming each salt to be 90 % dissociated, which of the following will have highest boiling point?

(A) Decimolar $Al_2(SO_4)_3$

(B) Decimolar $BaCl_2$

(C) Decimolar Na_2SO_4

(D) A solution obtained by mixing equal volumes of (B) and (C)

Q.12 The vapour pressure of a solvent decreased by 10 mm of Hg when a non-volatile solute was added to the solvent. The mole fraction of solute in solution is 0.2, what would be mole fraction of the solvent if decrease in vapour pressure is 20 mm of Hg

(A) 0.2 (B) 0.4 (C) 0.6 (D) 0.8

Q.13 Elevation of boiling point of 1 molar aqueous glucose solution (density = 1.2 g/ml) is

(A) K_b (B) 1.20 K_b (C) 1.02 K_b (D) 0.98 K_b

Q.14 What will be the molecular weight of $CaCl_2$ determined in its aq. solution experimentally from depression of freezing point?

(A) 111 (B) < 111 (C) > 111 (D) data insufficient

Q.15 1.0 molal aqueous solution of an electrolyte A_2B_3 is 60% ionised. The boiling point of the solution at 1 atm is $(K_{b(H_2O)} = 0.52 \text{ K kg mol}^{-1})$

(A) 274.76 K (B) 377 K (C) 376.4 K (D) 374.76 K

Q.16 Which of the following plots represents an ideal binary mixture?

(A) Plot of P_{total} v/s $1/X_B$ is linear (X_B = mole fraction of 'B' in liquid phase).

(B) Plot of P_{total} v/s Y_A is linear (Y_B = mole fraction of 'A' in vapour phase)

(C) Plot of $\frac{1}{P_{total}}$ v/s Y_A is linear

(D) Plot of $\frac{1}{P_{total}}$ v/s Y_B is non linear

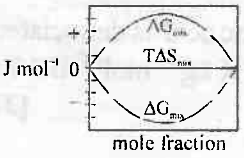
Q.17 Pressure over ideal binary liquid mixture containing 10 moles each of liquid A and B is gradually decreased isothermally. If P_A^o = 200 mm Hg and P_B^o = 100 mm Hg, find the pressure at which half of the liquid is converted into vapour.

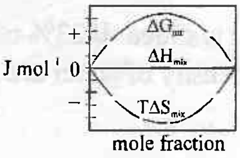
(A) 150 mm Hg (B) 166.5 mm Hg (C) 133 mm Hg (D) 141.4 mm Hg

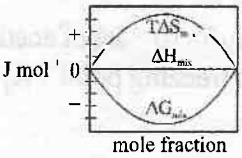
Q.18 The lowering of vapour pressure in a saturated aq. solution of salt AB is found to be 0.108 torr. If vapour pressure of pure solvent at the same temperature is 300 torr. Find the solubility product of salt AB

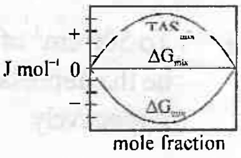
(A) 10^{-8} (B) 10^{-6} (C) 10^{-4} (D) 10^{-5}

Q.19 Which of the following represents correctly the changes in thermodynamic properties during the formation of 1 mol of an ideal binary solution.

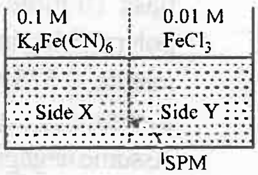
(A)


(B)


(C)


(D)


Q.20 $FeCl_3$ on reaction with $K_4[Fe(CN)_6]$ in aqueous solution gives blue colour. These are separated by a semipermeable membrane AB as shown. Due to osmosis there is



(A) blue colour formation in side X.

(B) blue colour formation in side Y.

(C) blue colour formation in both of the sides X and Y.

(D) no blue colour formation.

EXERCISE IV

OBJECTIVE

Q.1 The van't Hoff factor for 0.1 M $Ba(NO_3)_2$ solution is 2.74. The degree of dissociation is
(A) 91.3% (B) 87% (C) 100% (D) 74% **[JEE 1999]**

Q.2 In the depression of freezing point experiment, it is found that
(I) The vapour pressure of the solution is less than that of pure solvent.
(II) The vapour pressure of the solution is more than that of pure solvent.
(III) Only solute molecules solidify at the freezing point.
(IV) Only solvent molecules solidify at the freezing point.
(A) I, II (B) II, III (C) I, IV (D) I, II, III **[JEE 1999]**

Q.3 During depression of freezing point in a solution, the following are in equilibrium
(A) liquid solvent-solid solvent (B) liquid solvent-solid solute
(C) liquid solute-solid solute (D) liquid solute-solid solvent **[JEE 2003]**

Q.4 A 0.004 M solution of Na_2SO_4 is isotonic with a 0.010 M solution of glucose at same temperature. The apparent degree of dissociation of Na_2SO_4 is
(A) 25% (B) 50% (C) 75% (D) 85% **[JEE 2004]**

Q.5 The elevation in boiling point, when 13.44 g of freshly prepared $CuCl_2$ are added to one kilogram of water, is [Some useful data, K_b $(H_2O) = 0.52$ kg K mol^{-1}, mol. wt. of $CuCl_2 = 134.4$ gm]
(A) 0.05 (B) 0.1 (C) 0.16 (D) 0.21 **[JEE 2005]**

SUBJECTIVE

Q.6 A very small amount of a nonvolatile solute (that does not dissociate) is dissolved in 56.8 cm^3 of benzene (density 0.889 g cm^{-3}), At room temperature, vapour pressure of this solution is 98.88 mm Hg while that of benzene is 100 mm Hg. Find the molality of this solution. If the freezing temperature of this solution is 0.73 degree lower than that of benzene. What is the value of molal freezing point depression constant of benzene? **[JEE 1997]**

Q.7 A solution of a nonvolatile solute in water freezes at –0.30°C. The vapor pressure of pure water at 298K is 23.51mmHg and K_f for water is 1.86 degree/molal. Calculate the vapor pressure of this solution at 298K. **[JEE 1998]**

Q.8 To 500 cm^3 of water, 3×10^{-3} kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point ? K_f and density of water are 1.86 K kg^{-1} mol^{-1} and 0.997 g cm^{-3} respectively. **[JEE 2000]**

Q.9 The vapour pressure of two miscible liquids (A) and (B) are 300 and 500 mm of Hg respectively. In a flask 10 mole of (A) is mixed with 12 mole of (B). However, as soon as (B) is added, (A) starts polymerising into a completely insoluble solid. The polymerisation follows first-order kinetics. After 100 minute, 0.525 mole of a solute is dissolved which arrests the polymerisation completely. The final vapour pressure of the solution is 400 mm of Hg. Estimate the rate constant of the polymerisation reaction. Assume negligible volume change on mixing and polymerisation and ideal behaviour for the final solution. **[JEE 2001]**

Q.10 Match the boiling point with K_b for x, y and z, if molecular weight of x, y and z are same. **[JEE 2003]**

	b.pt.	K_b
x	100	0.68
y	27	0.53
z	253	0.98

Q.11 1.22 g of benzoic acid is dissolved in (i) 100 g acetone (K_b for acetone = 1.7) and (ii) 100 g benzene (K_b for benzene = 2.6). The elevation in boiling points T_b is 0.17°C and 0.13°C respectively.

(a) What are the molecular weights of benzoic acid in both the solutions?

(b) What do you deduce out of it in terms of structure of benzoic acid? **[JEE 2004]**

Q.12 72.5 g of phenol is dissolved in 1 kg of a solvent ($k_f = 14$) which leads to dimerization of phenol and freezing point is lowered by 7 kelvin. What percent of total phenol is present in dimeric form? **[JEE 2005]**

ANSWER

EXERCISE I

Q.1	0.24	Q.2	0.25	Q.3	24.5 torr	Q.4	57.24 g/mol
Q.5	66.13 mm Hg	Q.6	0.237	Q.7	0.682, 0.318; 0.829, 0.171		
Q.8	92 mol% toluene; 96.8 mol % toluene			Q.9	$P_A^\circ = 213.33$ torr, $P_B^\circ = 960.0$ torr		
Q.10	0.04	Q.11	111.1g, 18.52 molal			Q.12	0.741 m, 0.013
Q.13	0.162 m	Q.14	65.25	Q.15	17.38	Q.16	0.964
Q.17	106 g/mol	Q.18	64.0 g/mol	Q.19	100.079°C	Q.20	– 0.62°C
Q.21	5.08°C/m	Q.22	50.8 g/mol	Q.23	2050 g/mol	Q.24	x = 25.6, y = 42.6
Q.25	$K_b = 0.512$ kg mol K^{-1}, $T_b = 373.20$ K			Q.26	38.71 g	Q.27	156.06
Q.28	C_6H_6	Q.29	$T_f = -2.28$°C	Q.30	P = 0.2217 atm should be applied		
Q.31	$(V_{final} = 5.V_{original})$	Q.32	54.2 g	Q.33	0.81 atm	Q.34	13.8 atm
Q.35	5.4×10^5 g/mol	Q.36	2.4×10^5 g/mol			Q.37	59.99
Q.38	$M_A/M_B = 0.33$	Q.39	i = 2.5	Q.40	3 ions	Q.41	α = 99.2%
Q.42	7.482×10^5 Nm^{-2}	Q.43	94.5 %	Q.44	4.64 atm	Q.45	0.95; 1.95

PROFICIENCY TEST

1. proportional
2. 2 : 1
3. solvent molecules
4. azeotropic mixture
5. Ebullioscopic constant
6. lesser
7. straight line with slope ≠ 0
8. negative
9. more
10. 3
11. increases
12. greater than
13. Barkeley and Hartley's
14. Van't Hoff's solution equation
15. molality
16. T
17. F
18. F
19. F
20. T
21. T
22. F
23. F
24. F
25. F
26. F
27. T
28. T
29. F
30. T

EXERCISE II

Q.1 $C_{44}H_{88}O_{44}$ Q.2 746.24 mm/Hg

Q.3 (a) 3.79°C, (b) 0.018, (c) 4.65 atm, (d) 251.5 Q.4 (a) 210, (b) 64.1%

Q.5 % change in volume = 3.05, 8.604 m Q.6 0.66 atm Q.7 18.34%

Q.8 $T_b = 102.3°C$ Q.9 $T_f = -0.73°C$ Q.10 $[Co(NH_3)_5Cl]Cl_2$ Q.11 0.73

Q.12 $x_b = 0.2472,\ Y_b = 0.4473$ Q.13 46.33°C Q.14 $x_a'' = 0.1$

Q.15 $\alpha = 0.7333$ Q.16 –19.91°C, 7.63 M Q.17 M = 53.8

Q.18 0.93 Q.19 20.11 %

Q.20 ΔH_v at 80 K is 1659.1 calorie; $\Delta H_v = R\,[2.303 \times 313.7 + 1.40655T$

Q.21 $x_A = \left(\sqrt{P_A^0 P_B^0} - P_B^0\right)/(P_A^0 - P_B^0), P = \sqrt{P_A^0 P_B^0}$ Q.22 $T_f = 277.4K$ Q.23 8.9 gm

Q.24 12.54 Q.25 $K_a = 1.46\times10^{-4}$ Q.26 h = 0.082 Q.27 K = 3.36

Q.28 $4.9 \times 10^{-5}\ M^3$

Q.29 (a)0.47, (b) 565 torr, (c) x_A=0.08, x_B= 0.92, (d) 675 torr, (e) x'_A= 0.11, x'_B= 0.89

Q.30 (i) $K_a = 7.3 \times 10^{-3}$ (ii) 4.55×10^{22}

EXERCISE III

Q.1	C	Q.2	C	Q.3	C	Q.4	B	Q.5	D	Q.6	B	Q.7	B
Q.8	C	Q.9	B	Q.10	C	Q.11	A	Q.12	C	Q.13	D	Q.14	B
Q.15	D	Q.16	C	Q.17	D	Q.18	C	Q.19	C	Q.20	D		

EXERCISE IV

Q.1 B Q.2 C Q.3 A Q.4 C

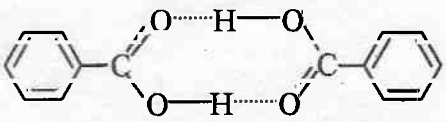
Q.5 C Q.6 0.1452, 5.028 K m^{-1}

Q.7 23.44 mm Hg Q.8 0.229 Q.9 1.0×10^{-4}

Q.10 $K_b(x) = 0.68,\ K_b(y) = 0.53,\ K_b(z) = 0.98$

Q.11 (a)122, (b) It means that benzoic acid remains as it is in acetone while it dimerises in benzene

as



Q.12 35% phenol is present in dimeric form

BANSALCLASSES

TARGET IIT JEE 2007

INORGANIC CHEMISTRY

XII (ALL)

QUESTION BANK ON

METALLURGY

ONLY ONE OPTION IS CORRECT.

Q.1 Formation of metallic copper from the sulphide ore in the normal thermo-metallurgical process essentially involves which one of the following reaction:

(A) $CuS + \frac{3}{2}O_2 \longrightarrow CuO + SO_2; \quad CuO + C \longrightarrow Cu + CO$

(B) $CuS + \frac{3}{2}O_2 \longrightarrow CuO + SO_2; \quad 2CuO + CuS \longrightarrow 3Cu + SO_2$

(C) $CuS + 2O_2 \longrightarrow CuSO_4; \quad CuSO_4 + CuS \longrightarrow 2Cu + 2SO_2$

(D) $CuS + \frac{3}{2}O_2 \longrightarrow CuO + SO_2; \quad CuO + CO \longrightarrow Cu + CO_2$

Q.2 $Ag_2S + NaCN + Zn \longrightarrow Ag$
This method of extraction of Ag by complex formation and then its displacement is called:
(A) Parke's method (B) McArthur-Forest method
(C) Serpeck method (D) Hall's method

Q.3 Calcination is the process of heating the ore:
(A) in inert gas (B) in the presence of air
(C) in the absence of air (D) in the presence of CaO and MgO

Q.4 Which of the following does not contain Mg:
(A) magnetite (B) magnesite (C) asbestos (D) carnallite

Q.5 Match the method of concentration of the ore in column I with the ore in column II and select the correct alternate:

	I		II
X	magnetic separation	(a)	Ag_2S
Y	froth floation	(b)	$FeCr_2O_4$
Z	gravity separation	(c)	$Al_2(SiO_3)_3$

	X	Y	Z		X	Y	Z
(A)	(a)	(b)	(c)	(B)	(b)	(a)	(c)
(C)	(c)	(a)	(b)	(D)	(b)	(c)	(a)

Q.6 Bessemerisation is carried out for
I : Fe, II : Cu, III : Al, IV : silver
(A) I, II (B) II, III (C) III, IV (D) I, III

Q.7 Refining of silver is done by:
(A) liquation (B) poling (C) cupellation (D) van Arkel method

Q.8 These are following extraction process of silver but not:
(A) as a side product in electrolytic refining of copper
(B) Parke's process in which Zn is used to extract silver by solvent extraction from molten lead
(C) by reaction of silver sulphide with KCN and then reaction of soluble complex with Zn
(D) by heating $Na[Ag(CN)_2]$

Q.9 Blister Cu is about:
(A) 60% Cu (B) 90% Cu (C) 98% Cu (D) 100% Cu

Q.10 Which one of the following is not a method of concentration of metals?
(A) gravity separation (B) froth floating process
(C) electromagnetic separation (D) smelting

Q.11 In which of the following isolations no reducing agent is required:
(A) iron from haematite (B) aluminium from bauxite
(C) mercury from cinnabar (D) zinc from zinc blende

Q.12 Chemical leaching is useful in the concentration of:
(A) copper pyrites (B) bauxite (C) galena (D) cassiterite

Q.13 The element which could be extracted by electrolytic reduction of its oxide dissolved in a high temperature melt is:
(A) sodium (B) magnesium (C) fluorine (D) aluminium

Q.14 Consider the following statements:
Roasting is carried out to :
(i) convert sulphide to oxide and sulphate
(ii) remove water of hydration
(iii) melt the ore
(iv) remove arsenic and sulphur impurities
Of these statements:
(A) (i), (ii) and (iii) are correct (B) (i) and (iv) are correct
(C) (i), (ii) and (iv) are correct (D) (ii), (iii) and (iv) are correct

Q.15 Iron obtained from blast furance is:
(A) wrought iron (B) cast iron (C) pig iron (D) steel

Q.16 Which of the following is not an ore:
(A) malacite (B) calamine (C) stellite (D) cerussite

Q.17 Which one of the following statements is not correct:
(A) Nickel forms $Ni(CO)_4$
(B) All the transition metals form monometallic carbonyls
(C) Carbonyls are formed by transition metals
(D) Transition metals form complexes

Q.18 In the extraction of nickel by Mond process, the metal is obtained by:
(A) electrochemical reduction (B) thermal decomposition
(C) chemical reduction by aluminium (D) reduction by carbon

Q.19 B_4C (boron carbide) is used except:
(A) to extract boron (B) as an abrasive for polishing
(C) for making bullet-proof clothing (D) for making diborane

Q.20 Boron can be obtained by various methods but not by:
(A) thermal decomposition of B_2H_6 (B) pyrolysis of BI_3 (Van Arkel)
(C) reducing BCl_3 with H_2 (D) electrolysis of fused BCl_3

Q.21 The correct statements are :
(A) generally the calcination and roasting is done in blast furance
(B) the sandy and rocky materials associated with ore are called matrix
(C) froth floatation process is suitable for sulphide ores
(D) substance that reacts with gangue to form fusible mass is called slag

Q.22 When copper is purified by electrorefining process, noble metals like Ag and Au are found in
(A) cathode mud (B) electrolytic solution (C) anode mud (D) over cathode or anode

Q.23 Formation of $Ni(CO)_4$ and subsequent its decomposition into Ni and CO (recycled) makes basis of Mond's process

$$Ni + 4CO \xrightarrow{T_1} Ni(CO)_4 \xrightarrow{T_2} Ni + 4CO$$

T_1 and T_2 are:
(A) 100°C, 50°C (B) 50°C, 100°C (C) 50°C, 230°C (D) 230°C, 50°C

Q.24 Match column (I) (process) with column (II) (electrolyte)

	(I) (process)		(II) (electrolyte)
(i)	Downs cell	(W)	fused $MgCl_2$
(ii)	Dow sea water process	(X)	fused $(Al_2O_3 + Na_3AlF_6)$
(iii)	Hall-Heroult	(Y)	fused KHF_2
(iv)	Moissan	(Z)	fused (40% NaCl + 60% $CaCl_2$)

Choose the correct alternate:

	(i)	(ii)	(iii)	(iv)		(i)	(ii)	(iii)	(iv)
(A)	Z	W	X	Y	(B)	X	Y	Z	W
(C)	W	Z	X	Y	(D)	X	Z	W	Y

Question No. 25 to 28 are based on following reactions:

(I) $FeCr_2O_4 + NaOH + air \longrightarrow (A) + Fe_2O_3$

(II) $(A) + (B) \longrightarrow Na_2Cr_2O_7$

(III) $Na_2Cr_2O_7 + X \xrightarrow{\Delta} Cr_2O_3$

(IV) $Cr_2O_3 + Y \xrightarrow{\Delta} Cr$

Q.25 Compounds (A) and (B) are:
(A) Na_2CrO_4, H_2SO_4 (B) $Na_2Cr_2O_7$, HCl
(C) Na_2CrO_5, H_2SO_4 (D) $Na_4[Fe(OH)_6]$, H_2SO_4

Q.26 (X) and (Y) are:
(A) C and Al (B) Al and C (C) C in both (D) Al in both

Q.27 Na_2CrO_4 and Fe_2O_3 are separated by
(A) dissolving in conc. H_2SO_4 (B) dissolving in NH_3
(C) dissolving in H_2O (D) dissolving in dil. HCl

Q.28 High temperature (> 1000°C) electrolytic reduction is necessary for isolating
(A) Al (B) Cu (C) C (D) F_2

Q.29 In froth-floatation process, palm oil functions as
(A) activator (B) frother (C) collector (D) agitator

Q.30 Collectors are the substances which help in attachment of an ore particle to air bubble in froth. A popular collector used industrially is
(A) sodium ethyl xanthate (B) sodium xenate
(C) sodium pyrophosphate (D) sodium nitroprusside

Q.31 Zone refining is based on the principle of
(A) fractional distillation (B) fractional crystallisation
(C) partition coefficient (D) chromatographic separation

Q.32 Which of the following species is (are) desirable products in extraction of copper but not in extraction of iron?
(A) $CaSiO_3$ (B) $FeSiO_3$ (C) SiO_2 (D) coke

Q.33 Poling is employed in refining of
(A) iron (B) copper (C) tin (D) lead

Q.34 Which of the following reaction(s) do(es) not occur in Bessemer's converter?
(A) $2Cu_2S + 5O_2 \longrightarrow 2CuSO_4 + 2CuO$ (B) $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2\uparrow$
(C) $2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$ (D) $FeO + SiO_2 \longrightarrow FeSiO_3$

Q.35 Dow's process
(A) involves purification of copper (B) involves extraction of magnesium
(C) gives metal chloride as product (D) gives pure metal as product
(E) results in evolution of CO

Q.36 In the cyanide process involving extraction of silver, zinc is used industrially as a(an)
(A) oxidising agent (B) reducing agent (C) solvent (D) solvating agent

Q.37 Carnallite does not contain
(A) K (B) Ca (C) Mg (D) Cl

Q.38 During initial treatment, preferential wetting of ore by oil and gangue by water takes place in
(A) Levigation (gravity separation) (B) Froth floatation
(C) Leaching (D) Bessemerisation

Q.39 Silica is added to roasted copper ores during extraction in order to remove
(A) cuprous sulphide (B) ferrous oxide (C) ferrous sulphide (D) cuprous oxide

Q.40 Addition of high proportions of manganese makes steel useful in making rails of railroads, because manganese
(A) gives hardness to steel (B) helps the formation of oxides of iron
(C) can remove oxygen and sulphur (D) can show highest oxidation state of +7

Q.41 Among the following statements, the incorrect one is
(A) calamine and siderite are carbonates (B) argentite and cuprite are oxide
(C) zinc blende and pyrites are sulphides (D) malachite and azurite are ores of copper

Q.42 In the commercial electrochemical process for aluminium extraction the electrolyte used is
(A) $Al(OH)_3$ in NaOH solution (B) an aqueous solution of $Al_2(SO_4)_3$
(C) a molten mixture of Al_2O_3 and Na_3AlF_6 (D) a molten mixture of AlO(OH) and $Al(OH)_3$

Q.43 Match List-I with List-II and select the correct answer using the codes given below the lists:

List-I	**List-II**
(a) van Arkel method	1. Manufacture of caustic soda
(b) Solvay process	2. Purification of titanium
(c) Cupellation	3. Manufacture of Na_2CO_3
(d) Poling	4. Purification of copper
	5. Refining of silver

Codes:

	A	B	C	D		A	B	C	D
(A)	2	1	3	4	(B)	4	3	2	5
(C)	2	3	5	4	(D)	5	1	3	4

Q.44 Blister copper is refined by stirring molten impure metal with green logs of wood because such a wood liberates hydrocarbon gases (like CH_4). This process X is called ______ and the metal contains impurities of Y is ______.
(A) X = cupellation, Y = CuO_2 (B) X = polling, Y = Cu_2O
(C) X = polling, Y = CuO (D) X = cupellation, Y = CuO

Q.45 Select the correct statement :
(A) Magnetite is an ore of manganese (B) Pyrolusite is an ore of lead
(C) Siderite is carbonate ore of iron (D) FeS_2 is rolled gold

Q.46 Three most occuring elements into the earth crust are
(A) O, Si, Al (B) Si, O, Fe (C) Fe, Ca, Al (D) Si, O, N

Q.47 An ore containing the impurity of $FeCrO_4$ is concentrated by
(A) magnetic-separation (B) gravity separation
(C) froth-floatation method (D) electrostatic method

Q.48 A piece of steel is heated until redness and then plugged into cold water or oil. This treatment of iron makes it
(A) soft and malleable (B) hard but not brittle (C) more brittle (D) hard and brittle

Q.49 Match the column:

List -I	Compound	List -II	Name
I	Pb_3O_4	(A)	red lead
II	$HgCl_2$	(B)	vermilion
III	Hg_2Cl_2	(C)	calomel
IV	HgS	(D)	corrosive sublimate

(A) I-A, II-B, III-C, IV-D
(B) I-A, II-D, III-B, IV-C
(C) I-A, II-D, III-C, IV-B
(D) I-C, II-B, III-D, IV-A

Q.50 In the extraction of aluminium
Process X : applied for red bauxite to remove iron oxide (chief impurity)
Process Y : (Serpeck's process) : applied for white bauxite to remove Z (chief impurity) then, process X and impurity Z are
(A) X = Hall and Herault's process and Y = SiO_2
(B) X = Baeyer's process and Y = SiO_2
(C) X = Serpeck's process and Y = iron oxide
(D) X = Baeyer's process and Y = iron oxide

Q.51 Which of the following statement(s) is / are incorrect?
(A) Liquation is applied when the metal has low melting point than that of impurities.
(B) Presence of carbon in steel makes it hard due to formation of Fe_3C called cementite.
(C) Less reactive metals like Hg, Pb and Cu are obtained by auto reduction of their sulphide or oxide ores.
(D) Amalgamation method of purification cannot be applied for Au and Ag.

Q.52 Si and Ge used for semiconductors are required to be of high purity and hence purified by
(A) zone-refining
(B) electrorefining
(C) Van-Arkel's process
(D) cupellation process

Q.53 In electrorefining of metals anode and cathode are taken as thick slab of impure metal and a strip of pure-metal respectively while the electrolyte is solution of a complex metal salt. This method cannot be applied for the refining of
(A) Copper
(B) Sodium
(C) Aluminium
(D) Zinc and Silver

Q.54 Correct statements is:
(A) Black jack is ZnS
(B) Sulphide ores are concentrated by floatation method
(C) Parke's process is based on distribution principle
(D) All are correct

Q.55 The metal for which, its property of formation of volatile complex is taken in account for its extraction is
(A) Cobalt
(B) Nickel
(C) Vanadium
(D) Iron

Q.56 Match List–I with List–II

List–I	Property	List–II	Element/compound
I	Explosive	A:	Cu
II	Self-reduction	B:	Fe_3O_4
III	Magnetic material	C:	$Cu(CH_3COO)_2.Cu(OH)_2$
IV	Verdigris	D:	$Pb(NO_3)_2$

(A) I–A, II–B, III–C, IV-D
(B) I–D, II–A, III–B, IV–C
(C) I–D, II–B, III–A, IV–C
(D) I–C, II–A, III–B, IV–D

Q.57 A metal has a high concentration into the earth crust and whose oxides cannot be reduced by carbon. The most suitable method for the extraction of such metal is
(A) Alumino thermite process
(B) Electrolysis process
(C) Van-Arkel's process
(D) Cupellation

Q.58 The process, which does not use a catalyst is
(A) Contact process (B) Thermite process (C) Ostwald's process (D) Haber's process

Q.59 Refractory materials are generally used in furnaces because
(A) they are chemically inert
(B) they can withstand high temperature
(C) they do not contain impurities
(D) they decrease melting point of ore

Q.60 % of silver in 'german silver' is
(A) 0 (B) 80 (C) 90 (D) 10

Q.61 Modern method of steel manufacturing is
(A) open hearth process (B) L.D. Process (C) Bessemerisation (D) Cupellation

Q.62 When an impurity in a metal has greater affinity for oxygen and is more easily oxidises than the metal itself. Then, the metal is refined by
(A) cupellation (B) zone-refining (C) polling (D) electrolytic process

Q.63 The chemical process of manufacturing of steel from its ore haematite involves
(A) oxidation
(B) reduction followed by oxidation
(C) oxidation followed by reduction
(D) oxidation followed by decomposition and reduction

Q.64 "Fool's gold" is
(A) iron pyrites (B) horn silver (C) copper pyrites (D) bronze

Q.65 During electrolytic reduction of alumina, two auxiliary electrolytes X and Y are added to increase the electrical conductance and lower the temperature of melt in order to making fused mixture very conducting. X and Y are
(A) cryolite and flourspar (B) cryolite and alum (C) alum and flourspar (D) flourspar and bauxite

Q.66 For extraction of sodium from NaCl, the electrolytic mixture NaCl + Na_3AlF_6 + $CaCl_2$ is used. During extraction process, only sodium is deposited on cathode but K and Ca do not because
(A) Na is more reactive than K and Ca
(B) Na is less reactive than K and Ca
(C) NaCl is less stable than Na_3AlF_6 and $CaCl_2$
(D) the discharge potential of Na^+ is less than that of K^+ and Ca^{2+} ions.

Q.67 A solution of Na_2SO_4 in water is electrolysed using inert electrodes. The products at cathode and anode are respectively
(A) O_2 ; H_2 (B) O_2 ; Na (C) H_2 ; O_2 (D) O_2 ; SO_2

Q.68 Which of the following statements is correct regarding the slag formation during the extraction of a metal like copper or iron.
(A) The slag is lighter and lower melting than the metal
(B) The slag is heavier and lower melting than the metal
(C) The slag is lighter and higher melting than the metal
(D) The slag is heavier and higher melting than the metal.

Q.69 Among the following groups of oxides, the group containing oxides that cannot be reduced by C to give the respective metal is
(A) CaO and K_2O (B) Fe_2O_3 and ZnO (C) Cu_2O and SnO_2 (D) PbO and Pb_3O_4

Q.70 The beneficiation of the sulphide ores is usually done by
(A) Electrolysis
(B) Smelting process
(C) Metal displacement method
(D) Froth flotation method

Q.71 In the alumino thermite process, Al acts as
(A) An oxidising agent (B) A flux (C) A reducing agent (D) A solder

Q.72 The process of the isolation of a metal by dissolving the ore in a suitable chemical reagent followed by precipitation of the metal by a more electropositive metal is called:
(A) hydrometallurgy (B) electrometallurgy (C) zone refining (D) electrorefining

Q.73 Carbon cannot be used in the reduction of Al_2O_3 because :
(A) it is an expensive proposition
(B) the enthalpy of formation of CO_2 is more than that of Al_2O_3
(C) pure carbon is not easily available
(D) the enthalpy of formation of Al_2O_3 is too high.

Q.74 Froth floatation process for concentration of ores is an illustration of the practical application of:
(A) Adsorption (B) Absorption (C) Coagulation (D) Sedimentation

Q.75 Which process of purification is represented by the following equation :

$$Ti\ (Impure) + 2I_2 \xrightarrow{250°C} TiI_4 \xrightarrow{1400°C} Ti\ (Pure) + 2I_2$$

(A) Cupellation (B) Poling (C) Van-Arkel Process (D) Zone refining

Q.76 Mercury is purified by:
(A) Passing through dilute HNO_3 (B) Distillation
(C) Distribution (D) Vapour phase refining

Q.77 Which of the following ore and metal are correctly matched:

	Ore	**Metal**
(A)	Carnallite	Zinc
(B)	Calamine	Titanium
(C)	Ilmenite	Magnesium
(D)	Chalcopyrite	Copper

Q.78 Which of the following metal is correctly matched with its ore:

	Metal	**Ore**
(A)	Zinc	Calamine
(B)	Tin	Azurite
(C)	Magnesium	Cassiterite
(D)	Silver	Ilmenite

Q.79 Which of the following employ(s) thermal decomposition of volatile iodide compounds?
(A) Thermite process (B) Hall's process (C) Van-Arkel's process (D) Mond's process

Q.80 The method of zone refining of metals is based on the principle of:
(A) Greater mobility of the pure metal than that of impurity.
(B) Higher melting point of the impurity than that of the pure metal.
(C) Greater noble character of the solid metal than that of the impurity
(D) Greater solubility of the impurity in the molten state than in the solid

Q.81 Railway wagon axles are made by heating iron rods embedded in charcoal powder. This process is known as:
(A) Sherardising (B) Annealing (C) Tempering (D) Case hardening

Q.82 In the extraction of copper from its sulphide are the metal is formed by the reduction of Cu_2O with:
(A) FeS (B) CO (C) Cu_2S (D) SO_2

Q.83 Carnallite on electrolysis gives:
(A) Ca and Cl_2 (B) Na and CO_2 (C) Al and Cl_2 (D) Mg and Cl_2

Q.84 Among the following statemetns, the incorrect one is:
(A) Calamine and siderite are carbonates (B) Argentite and cuperite are oxides
(C) Zinc blende and iron pyrites are sulphides (D) Malachite and azurite are ores of copper

Q.85 Match List I and II and select the correct answer using the codes given below the lists:

	List I		List II
I.	Cyanide process	(1)	Ultrapure Ge
II.	Floatation process	(2)	Dressing of HgS
III.	Electrolytic reduction	(3)	Extraction of Al
IV.	Zone refining	(4)	Extraction of Au

(A) I–(3), II–(1), III–(4), IV–(2) (B) I–(4), II–(2), III–(3), IV–(1)
(C) I–(3), II–(2), III–(4), IV–(1) (D) I–(4), II–(1), III–(3), IV–(2)

Q.86 The common method of extraction of metals from oxide ores is:
(A) Reduction with carbon (B) Reduction with hydrogen
(C) Reduction with aluminium (D) Electrolytic method

Question No. 87 to 100

Questions given below consist of two statements each printed as Assertion (A) and Reason (R); while answering these questions you are required to choose any one of the following four responses:
(A) if both (A) and (R) are true and (R) is the correct explanation of (A)
(B) if both (A) and (R) are true but (R) is not correct explanation of (A)
(C) if (A) is true but (R) is false
(D) if (A) is false and (R) is true

Q.87 **Assertion :** Sulphide ores are concentrated by froth floatation process.
Reason : Pine oil acts as a frothing agent in froth floatation process.

Q.88 **Assertion :** Platinum and gold occur in native state in nature.
Reason : Platinum and gold are noble metals.

Q.89 **Assertion :** Wolframite impurities are separated from cassiterite by electromagnetic separation.
Reason : Cassiterite being magnetic is attacted by the magnet and forms a separate heap.

Q.90 **Assertion :** In smelting, roasted ore is heated with powdered coke in presence of a flux.
Reason : Oxides are reduced to metals by C or CO. Impurities are removed as slag.

Q.91 **Assertion :** Al is used as a reducing agent in aluminothermy.
Reason : Al has a lower melting point than Fe, Cr and Mn.

Q.92 **Assertion :** Lead, tin and bismuth are purified by liquation method.
Reason : Lead, tin and bismuth have low m.p. as compared to impurities.

Q.93 **Assertion :** Wolframite impurity is separated from SnO_2 by magnetic separation
Reason : Tin stone is ferromagnetic, therefore attracted by magnet.

Q.94 **Assertion :** Titanium is purified by Van-Arkel method.
Reason : Ti reacts with I_2 to form TiI_4 which decomposes at 1700 K to give pure Ti.

Q.95 **Assertion :** CuO can be reduced by C, H_2 as well as CO
Reason : CuO is basic oxide.

Q.96 **Assertion :** Alkali metals can not be prepared by the electrolysis of their chlorides in aqueous solution
Reason : Reduction potentials of alkali metals cations is much lower than that of H^+.

Q.97 **Assertion :** Magnesium can be prepared by the electrolysis of aq. $MgCl_2$.
Reason : The reduction potential of Mg^{2+} is much lower than that of H^+.

Q.98 **Assertion :** Titanium can be purified by Van-Arkel process.
Reason : TiI_4 is a volatile, unstable compound.

Q.99 **Assertion :** Magnesia and quick lime are used as basic flux.
Reason : MgO and CaO can withstand very high temperatures.

Q.100 **Assertion :** Nickel is purified by the thermal decomposition of nickel tetracarbonyl.
Reason : Nickel is a transitional element.

ONE OR MORE THAN ONE OPTION MAY BE CORRECT

Q.1 Hoop's process of purification of aluminium involves formation of layers during electrolysis. It involves
(A) the three layers have same densities but different materials.
(B) the three layers have different densities
(C) the upper layer is of pure aluminium which acts as a cathode
(D) the bottom layer is of impure aluminium which acts as an anode and middle layer consists of cryolite and BaF_2.

Q.2 Metallurgical process of zinc involves roasting of zinc sulphide followed by reduction. Metallic zinc distills over as it is volatile and impurities like Cd, Pd and Fe gets condensed. The crude metal obtained is called spelter, which may be putified by
(A) electrolysis process (B) fractional distillation
(C) polling (D) heating with iodine

Q.3 Calcination and roasting processes of reduction of ores to their oxides are beneficial
(A) to convert ores into porous form so that their reduction becomes easier
(B) as volatile impurities like P, As, Sb, S are removed
(C) as organic impurities are removed.
(D) as the ores are converted into oxide form which makes the reduction easier

Q.4 In the extraction of copper, the reaction which takes place in Bessemer converter is
(A) $2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2\uparrow$ (B) $CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2\uparrow$
(C) $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2\uparrow$ (D) $2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$

Q.5 Extraction of silver from argentiferrous lead (Pb + Ag) involves
(A) distillation method (B) cupellation
(C) froth flotation method (D) treatment with NaCl

Q.6 In the manufacturing of metallic sodium by fused salt-electrolysis method (Down's process), small amount of $CaCl_2$ that added is known as auxiliary electrolyte and is used to
(A) improve the electrical conductance (B) decrease the melting point of NaCl
(C) stabilise the metallic sodium (D) increase the temperature of electrolysis

Q.7 Metal(s) which does/do not form amalgam is/are
(A) Fe (B) Pt (C) Zn (D) Au

Q.8 Auto reduction process is used in extraction of
(A) Cu (B) Hg (C) Al (D) Fe

Q.9 Zone refining is used for purification of
(A) Ge (B) Si (C) Ga (D) Se

Q.10 Which of the following process (es) are used for purification of Bauxite ore?
(A) Hall's process (B) Serpeck's process (C) Baeyer's process (D) Mond's process

Q.11 Metals which can be extracted by smelting process
(A) Pb (B) Fe (C) Zn (D) Mg

Q.12 Common impurities present in Bauxite are
(A) CuO (B) ZnO (C) Fe_2O_3 (D) SiO_2

Q.13 Which of the following reduction reactions are actually employed in commerical extraction of metals?
(A) $Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe$
(B) $Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$
(C) $2Na[Au(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + 2Au$
(D) $Cu_2S + Pb \rightarrow Cu + PbS\downarrow$

Q.14 Which of the following cannot be obtained by electrolytic reduction of their compounds in aqueous solution?
(A) Barium (B) Cadmium (C) Potassium (D) nickel

Q.15 Which of the following ores is(are) concentrated by froth floatation?
(A) haematite (B) galena (C) copper pyrite (D) azurite

Q.16 Which fo the following points is/are common between roasting and sintering?
(A) Both require heating of the ore.
(B) Both involve burning away of organic matter.
(C) Both the process cause partial fusion of ore, resulting in bigger lumps.
(D) Both are performed only for sulphide ores.

Q.17 Which of the following reaction(s) occur during calcination?
(A) $CaCO_3 \rightarrow CaO + CO_2$ (B) $4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$
(C) $2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$ (D) $CuS + CuSO_4 \rightarrow 2Cu\ 2SO_2$

Q.18 Roasting is usually performed in
(A) blast furnace (B) reverberatory furnace
(C) Bessemer's converter (D) electric furnace

Q.19 Which of the following is(are) sulphide ores?
(A) Argentite (B) Galena (C) Anglesite (D) Copper glance

Q.20 Which of the following is(are) regarded as iron ores?
(A) Haematite (B) Magnetite (C) Limonite (D) Copper pyrites

Q.21 Which of the following employ downward movement of ore due to gravity?
(A) Gravity separation (B) Froth floatation
(C) Blast furnace (D) Bessemer's coverter

Q.22 Calcium silicate slag formed in extraction of iron
(A) prevents the reoxidation of molten iron. (B) catalyses the combustion of carbon.
(C) reduces CO_2 toCO at the bottom of the furnace. (D) is used in cement industry.

Q.23 Amphoteric nature of aluminium is employed in which of the following process for extraction of aluminium?
(A) Baeyer's process (B) Hall's process
(C) Serpek's process (D) Dow's process

Q.24 Noble metal(s) which are commercially extracted by cyanide process is(are)
(A) copper (B) silver (C) gold (D) mercury

Q.25 Carbon reduction method is employed for commercial purification of
(A) haematite (B) cassiterite (C) iron pyrite (D) corundum

Q.26 The chief rection(s) occuring in blast furnace during extraction of iron from haematite is(are)
(A) $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$ (B) $FeO + SiO_2 \rightarrow FeSiO_3$
(C) $Fe_2O_3 + C \rightarrow 2Fe + 3CO$ (D) $CaO + SiO_2 \rightarrow CaSiO_3$

Q.27 Which of the following are true for electrolytic extraction of aluminium
(A) cathode material contains graphite (B) anode material contains graphite
(C) cathode reacts away forming CO_2 (D) anode reacts away forming CO_2

Q.28 During extraction of copper, it is obtained in the form of molten *matte*. Which of the following is **not true**?
(A) *matte* is further treated reverbratory furnace
(B) molten *matte* is electrolysed
(C) It is treated with a blast of air and sand
(D) It is dissolved in $CuSiF_6$ and crystallised.

Q.29 Which of the following ores is (are) concentrated industrially by froth floatation?
(A) Copper pyrites (B) Galena (C) Dolomite (D) Carnallite

Q.30 Which of the following is true for calcination of a metal ore?
(A) It makes the ore more porous
(B) The ore is heated to a temperature when fusion just begins
(C) Hydrated salts lose their water of crystallisation
(D) Impurities of S, As and Sb are removed in the form of their volatile oxides.

Q.31 The major role of fluorspar (CaF_2) which is added in small quantities in the electrolytic reduction of alumina dissolved in fused cryolite (Na_3AlF_6) is
(A) as a catalyst
(B) to make the fused mixture very conducting
(C) to lower the temperature of the melt
(D) to decrease the rate of oxidation of carbon at the anode.

Q.32 The difference(s) between roasting and calcination is (are)
(A) roasting is highly endothermic while calcination is not.
(B) partial fusion occurs in calcination but not in roasting.
(C) calcination is performed in limited supply of air but roasting employs excess air.
(D) combustion reactions occur in roasting but not in calcination.

Q.33 Leaching is used for the concentration of:
(A) Red bauxite (B) Haematite (C) Gold ore (D) Silver ore

ANSWER KEY

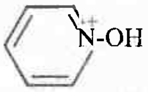
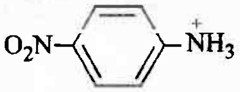
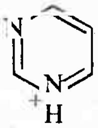
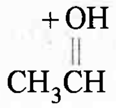
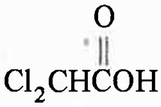
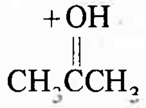
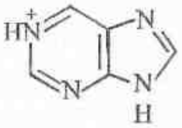
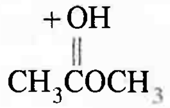
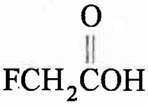
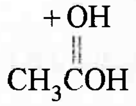
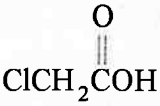
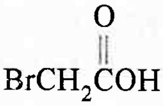
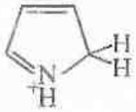
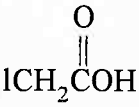
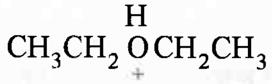
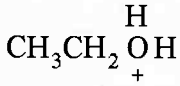
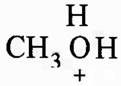
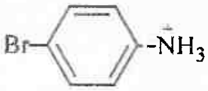
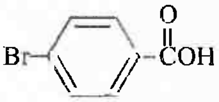
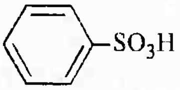
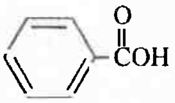
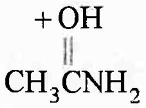
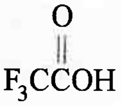
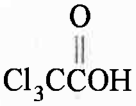
ONLY ONE OPTION IS CORRECT

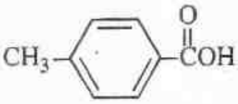
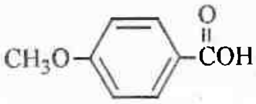
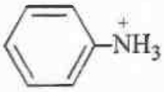
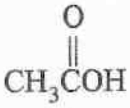
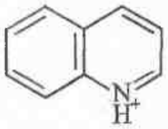
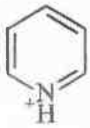
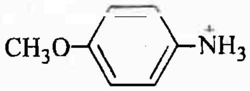
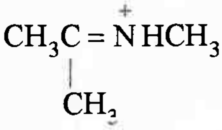
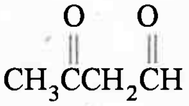
Q.1	B	Q.2	B	Q.3	C	Q.4	A	Q.5	B	Q.6	A	Q.7	C
Q.8	D	Q.9	C	Q.10	D	Q.11	C	Q.12	B	Q.13	D	Q.14	C
Q.15	C	Q.16	C	Q.17	B	Q.18	B	Q.19	D	Q.20	D	Q.21	B,C
Q.22	C	Q.23	C	Q.24	A	Q.25	A	Q.26	A	Q.27	C	Q.28	A
Q.29	B	Q.30	A	Q.31	B	Q.32	C	Q.33	B,C	Q.34	C	Q.35	B
Q.36	B	Q.37	B	Q.38	B	Q.39	B	Q.40	A	Q.41	B	Q.42	C
Q.43	C	Q.44	B	Q.45	C	Q.46	A	Q.47	A	Q.48	D	Q.49	C
Q.50	B	Q.51	D	Q.52	A	Q.53	B	Q.54	D	Q.55	B	Q.56	B
Q.57	B	Q.58	B	Q.59	B	Q.60	A	Q.61	B	Q.62	A	Q.63	B
Q.64	A	Q.65	A	Q.66	D	Q.67	C	Q.68	A	Q.69	A	Q.70	B
Q.71	C	Q.72	A	Q.73	D	Q.74	A	Q.75	C	Q.76	B	Q.77	D
Q.78	A	Q.79	C	Q.80	D	Q.81	D	Q.82	C	Q.83	D	Q.84	B
Q.85	B	Q.86	A	Q.87	B	Q.88	A	Q.89	C	Q.90	A	Q.91	B
Q.92	A	Q.93	C	Q.94	A	Q.95	B	Q.96	A	Q.97	D	Q.98	A
Q.99	B	Q.100	B										

ONE OR MORE THAN ONE OPTION MAY BE CORRECT

Q.1	B,C,D	Q.2	A,B	Q.3	A,B,C,D	Q.4	A,C,D
Q.5	A,B	Q.6	A,B	Q.7	A,B	Q.8	A,B
Q.9	A,B,C	Q.10	A,B,C	Q.11	A,B,C	Q.12	C,D
Q.13	B,C	Q.14	A,C	Q.15	B,C	Q.16	A,B
Q.17	A,C	Q.18	A,B	Q.19	A,B,D	Q.20	A,B,C
Q.21	A,C	Q.22	A,D	Q.23	A,B	Q.24	B,C
Q.25	A,B	Q.26	A,D	Q.27	B,D	Q.28	B,D
Q.29	A,B	Q.30	A,C	Q.31	B,C	Q.32	C,D
Q.33	A,C,D						

pK_a values

Compound	pK_a	Compound	pK_a
$CH_3C\equiv\overset{+}{N}H$	–10.1		0.79
HI	–10		1.0
HBr	–9		1.0
 $CH_3\overset{+OH}{\overset{\|}{C}}H$	–8	 $Cl_2CH\overset{O}{\overset{\|}{C}}OH$	1.3
 $CH_3\overset{+OH}{\overset{\|}{C}}CH_3$	–7.3	HSO_4^-	2.0
HCl	–7	H_3PO_4	2.1
$CH_3\overset{+}{S}H_2$	–6.8		2.5
 $CH_3\overset{+OH}{\overset{\|}{C}}OCH_3$	–6.5	 $FCH_2\overset{O}{\overset{\|}{C}}OH$	2.7
 $CH_3\overset{+OH}{\overset{\|}{C}}OH$	–6.1	 $ClCH_2\overset{O}{\overset{\|}{C}}OH$	2.8
H_2SO_4	–5	 $BrCH_2\overset{O}{\overset{\|}{C}}OH$	2.9
	–3.8	 $ICH_2\overset{O}{\overset{\|}{C}}OH$	3.2
 $CH_3CH_2\underset{+}{\overset{H}{O}}CH_2CH_3$	–3.6	HF	3.2
 $CH_3CH_2\underset{+}{\overset{H}{O}}H$	–2.4	HNO_2	3.4
 $CH_3\underset{+}{\overset{H}{O}}H$	–2.5		3.4
H_3O^+	–1.7	 $H\overset{O}{\overset{\|}{C}}OH$	3.8
HNO_3	–1.3		3.9
CH_3SO_3H	–1.2		4.0
	–0.60		4.2
 $CH_3\overset{+OH}{\overset{\|}{C}}NH_2$	0.0		
 $F_3C\overset{O}{\overset{\|}{C}}OH$	0.2		
 $Cl_3C\overset{O}{\overset{\|}{C}}OH$	0.64		

Compound	pK_a
	4.3
	4.5
	4.6
 $CH_3\overset{\overset{O}{\Vert}}{C}OH$	4.8
	4.9
	5.1
	5.2
	5.3
 $CH_3\underset{\overset{\vert}{CH_3}}{C}=\overset{+}{N}HCH_3$	5.5
 $CH_3\overset{\overset{O}{\Vert}}{C}CH_2\overset{\overset{O}{\Vert}}{C}H$	5.9
$HO\overset{+}{N}H_3$	6.0
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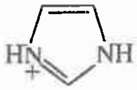	6.8
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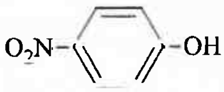	7.1
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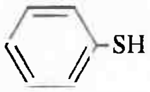
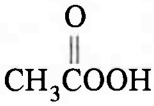
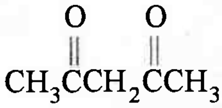
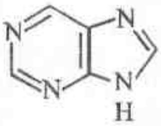
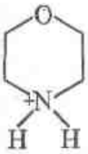
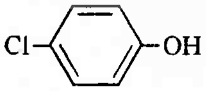
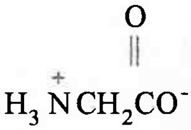
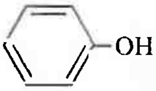
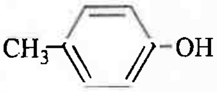
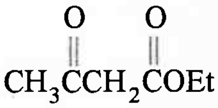
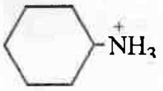
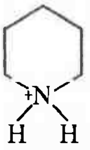
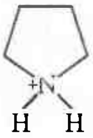
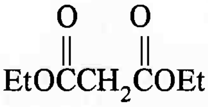
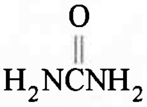
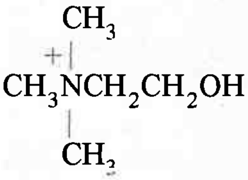
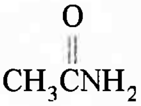
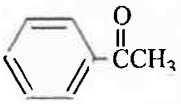
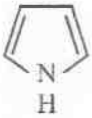
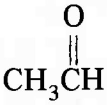
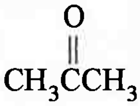
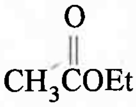
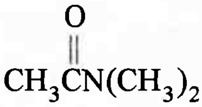
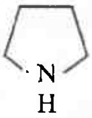
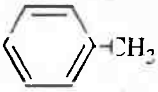
	7.8
	8.0

Compound	pK_a
$H_2N\overset{+}{N}H_3$	8.1
 $CH_3\overset{\overset{O}{\Vert}}{C}OOH$	8.2
$CH_3CH_2NO_2$	8.6
 $CH_3\overset{\overset{O}{\Vert}}{C}CH_2\overset{\overset{O}{\Vert}}{C}CH_3$	8.9
	8.9
$HC\equiv N$	9.1
	9.3
	9.4
$\overset{+}{N}H_4$	9.4
$HOCH_2CH_2\overset{+}{N}H_3$	9.5
 $H_3\overset{+}{N}CH_2\overset{\overset{O}{\Vert}}{C}O^-$	9.8
	10.0
	10.2
HCO_3^-	10.2
CH_3NO_2	10.2
	10.3
CH_3CH_2SH	10.5
$(CH_3)_3\overset{+}{N}H$	10.6
 $CH_3\overset{\overset{O}{\Vert}}{C}CH_2\overset{\overset{O}{\Vert}}{C}OEt$	10.7
$CH_3\overset{+}{N}H_3$	10.7

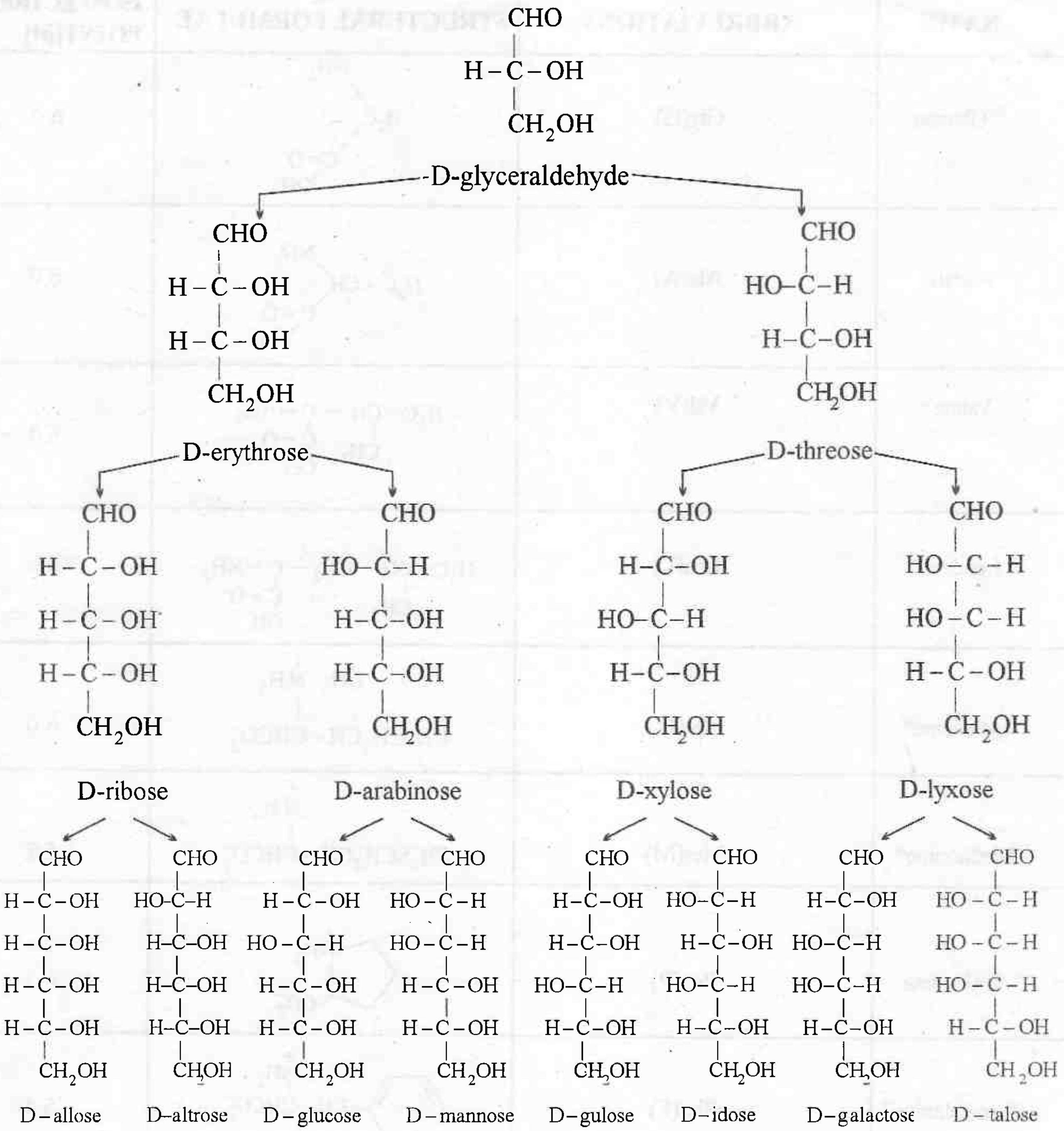
Compound	pK$_a$
	10.7
$(CH_3)_2\overset{+}{N}H_2$	10.7
$CH_3CH_2\overset{+}{N}H_3$	10.7
	11.1
	11.3
HPO_4^{2-}	12.3
CF_3CH_2OH	12.4
 $EtO\overset{O}{\overset{\parallel}{C}}CH_2\overset{O}{\overset{\parallel}{C}}OEt$	13.3
$HC\equiv CCH_2OH$	13.5
 $H_2N\overset{O}{\overset{\parallel}{C}}NH_2$	13.7
 $CH_3\overset{+}{N}(CH_3)_2CH_2CH_2OH$	13.9
	14.4
CH_3OH	15.5
H_2O	15.7
CH_3CH_2OH	16.0
 $CH_3\overset{O}{\overset{\parallel}{C}}NH_2$	16
	16.0
	~ 17

Compound	pK$_a$
 $CH_3\overset{O}{\overset{\parallel}{C}}H$	17
$(CH_3)_3COH$	18
 $CH_3\overset{O}{\overset{\parallel}{C}}CH_3$	20
 $CH_3\overset{O}{\overset{\parallel}{C}}OEt$	24.5
$HC\equiv CH$	25
$CH_3C{=}N$	25
 $CH_3\overset{O}{\overset{\parallel}{C}}N(CH_3)_2$	30
NH_3	36
	36
CH_3NH_2	40
	41
	43
$CH_2{=}CHCH_3$	43
$CH_2{=}CH_2$	44
	46
CH_4	50
CH_3CH_3	50

POINTS TO REMEMBER

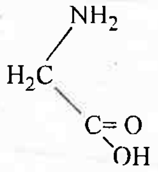
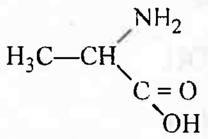
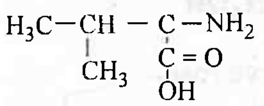
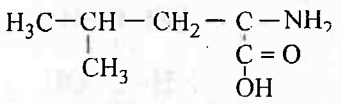
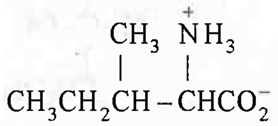
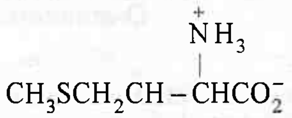
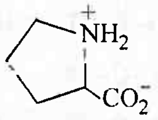
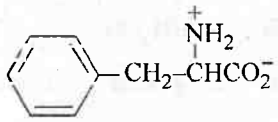
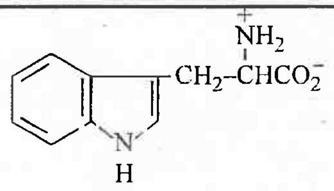
XII (A,B,C,D)

(2) The D–family aldoses

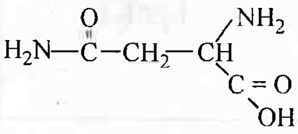
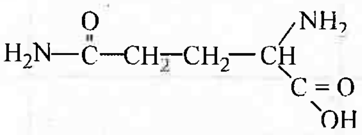
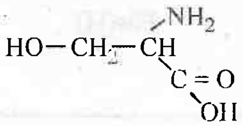


(3) LIST OF SOME VERY COMMON AMINO ACIDS FOUND IN PROTIENS

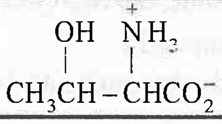
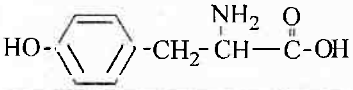
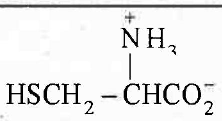
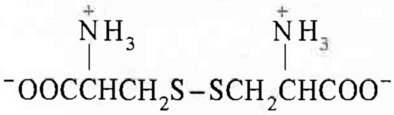
1. Neutral amino acids (with nonpolar side chains)

NAME	ABBREVIATIONS	STRUCTURAL FORMULAE	ISOELECTRIC POINT[pI]
@Glycine	Gly(G)		6.0
Alanine	Ala(A)		6.0
Valine*	Val(V)	 $H_3C-\underset{CH_3}{CH}-\underset{\underset{OH}{C=O}}{C}-NH_2$	6.0
Leucine*	Leu(L)	 $H_3C-\underset{CH_3}{CH}-CH_2-\underset{\underset{OH}{C=O}}{C}-NH_2$	6.0
Isoleucine*	Ile(I)	 $CH_3CH_2\overset{CH_3}{CH}-\overset{\overset{+}{N}H_3}{CH}CO_2^-$	6.0
Methionine*	Met(M)	 $CH_3SCH_2CH-\overset{\overset{+}{N}H_3}{CH}CO_2^-$	5.7
@@Proline	Pro(P)		6.3
Phenylalanine*	Phe(F)		5.5
Tryptophan*	Trp(W)		5.9

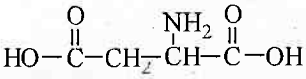
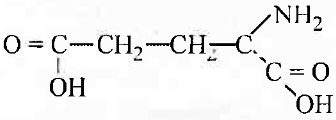
2. Neutral amino acids (with polar, but nonionized side chains)

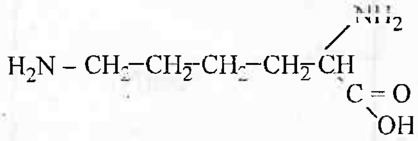
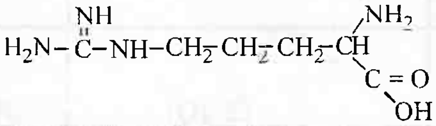
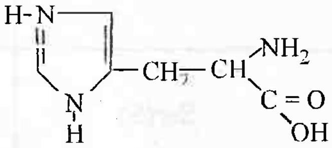
NAME	ABBREVIATIONS	STRUCTURAL FORMULAE	ISOELECTRIC POINT[pI]
Asparagine	Asn(N)		5.4
Glutamine	Gln(Q)		5.7
Serine	Ser(S)		5.7

3. Neutral amino acids (with polar, but nonionized side chains)

NAME	ABBREVIATIONS	STRUCTURAL FORMULAE	ISOELECTRIC POINT[pI]
Threonine*	Thr	 $\overset{OH}{\overset{\vert}{CH_3CH}}-\overset{\overset{+}{N}H_3}{\overset{\vert}{CHCO_2^-}}$	5.6
Tyrosine	Tyr(Y)		5.7
Cysteine	Cys	 $HSCH_2-\overset{\overset{+}{N}H_3}{\overset{\vert}{CHCO_2^-}}$	5.1
‡ Cystine	Cys–Cys	 $^-OOC\overset{\overset{+}{N}H_3}{\overset{\vert}{C}}HCH_2S-SCH_2\overset{\overset{+}{N}H_3}{\overset{\vert}{C}}HCOO^-$	

4. Acidic amino acids (side chain with carboxylic acid group)

NAME	ABBREVIATIONS	STRUCTURAL FORMULAE	ISOELECTRIC POINT[pI]
Aspartic acid	Asp(D)	 $HO-\overset{O}{\overset{\Vert}{C}}-CH_2-\overset{NH_2}{\overset{\vert}{CH}}-\overset{O}{\overset{\Vert}{C}}-OH$	2.8
Glutamic Acid	Glu(E)		3.2

5. Basic amino acids (side chain with nitrogenous basic group)			
NAME	**ABBREVIATIONS**	**STRUCTURAL FORMULAE**	**ISOELECTRIC POINT[pI]**
Lystine*	Lys(K)	 $H_2N-CH_2-CH_2-CH_2-CH_2-CH(NH_2)-C(=O)-OH$	9.7
Arginine*	Arg(R)	 $H_2N-C(=NH)-NH-CH_2-CH_2-CH_2-CH(NH_2)-C(=O)-OH$	10.8
Histidine*	His(H)		7.6

Note:

* Amino acids with an asterisk are essential amino acids, that must be supplemented through diet.

† At pH = 7, Asp and Glu have a net negative charge and exist as anions. At pH = 7, Lys and Arg have a net positive charge and exist as cations. Rest of the amino acids at this pH exist in the neutral form.

‡ Structurally, in cystine, the two cysteine molecules are joined through sulfur (disulfide linkage).

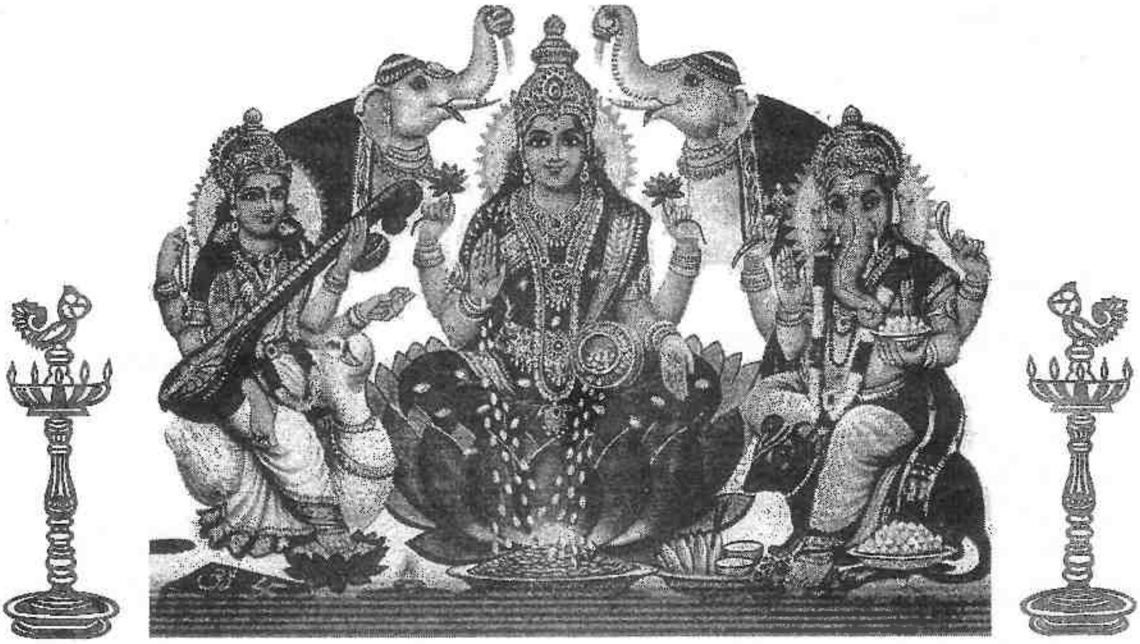
@@ Proline is an α-imino acid.

@ Except Glycine all other amino acids are optically active.

BANSAL CLASSES

CHEMISTRY

TARGET IIT JEE 2006
XIII (X,Y)



Wishing You & Your Family A Very Happy
& Prosperous Deepawali

QUESTION BANK ON

SALT ANALYSIS, CO-ORDINATION CHEMISTRY, CHEMICAL BONDING & PERIODICITY.

This Question Bank will be discussed just after the Deepawali vacation.

Q.1 The electron-affinity of N, O, S and Cl are such that
(A) $N < O < S < Cl$ (B) $O < N < Cl < S$ (C) $O \approx Cl < N \approx S$ (D) $O < S < Cl < N$

Q.2 The first, second and third ionisation potentials (E_1, E_2 and E_3) for an element are 7 eV, 12.5 eV and 42.3 eV respectively. The most stable oxidation state of the element will be
(A) +1 (B) +2 (C) +3 (D) +4

Q.3 The correct increasing order of electronegativity of C(sp^3), C (sp^2) and C(sp) atoms is
(A) C(sp^3) < C(sp^2) < C (sp) (B) C (sp) < C (sp^2) < C (sp^3)
(C) C (sp) = C (sp^2) = C (sp^3) (D) C (sp) = C (sp^2) < C (sp^3)

Q.4 A_2 and B_2 are two diatomic molecules with bond energies of A–A and B–B bonds as x and y respectively. If the bond energy of the molecule A–B formed up from A_2 and B_2 is z. Then, the resonance energy of molecules A–B will be
(A) $(\Delta E)_{A-B} = z - \sqrt{xy}$ (B) $(\Delta E)_{A-B} = x - y - z$ (C) $(\Delta E)_{A-B} - z - x + y$ (D) $(\Delta E)_{A-B} = \sqrt{xy} - z$

Q.5 Match the column

	FACT	**ELEMENT**
I	Most abundant metal	(A) Fr
II	An element of the highest atomic volume	(B) Fr
III	Natural radioactive element	(C) Fe
IV	Most abundant transition metal	(D) A*l*

(A) I-A, II-B, III-C, IV-D (B) I-D, II-B, III-A, IV-C
(C) I-B, II-A, III-C, IV-D (D) I-D, II-B, III-C, IV-A

Q.6 The electron affinity of inert gases are
(A) zero (B) 2 kJ /mole (C) 5 kJ/mole (D) 9 kJ/mole

Q.7 Astatine is a radioactive halogen. It is a solid at room temperature because
(A) of greater Van der Waal's force of attraction between large atoms of astatine
(B) of less Van der Waal's force of attraction between large atoms of astatine
(C) of less Van der Waal's force of attraction between small atoms of astatine
(D) it shows non-metallic characters

Q.8 Fluorine has the highest electronegativity among the ns^2np^5 group on the Pauling's Scale, but the electron affinity of fluorine is less than that of chlorine because
(A) fluorine being the first member of the family, behaves in an unusual manner
(B) the atomic number of fluorine is less than that of chlorine
(C) chlorine can accommodate an electron better than fluorine by utilising its vacant 3d-orbitals
(D) small size, high electron density and an increased electron repulsion makes addition of an electron to fluorine less favourable than that in the case of chlorine.

Q,9 The correct sequence of elements in the decreasing order of their first ionisation energy is
(A) Na > Mg > Al > Si (B) Mg > Na > Al > Si
(C) Al > Mg > Na > Si (D) Si > Mg > Al > Na

Q.10 An element I shows + 1 as well as –1 oxidation states. The correct oder of radii of I^-, I and I^+ species is
(A) $I^+ < I < I^-$ (B) $I^- = I^+ < I^-$ (C) $I^- < I < I^+$ (D) $I^- > I^+ = I$

Q.11 The most widely used and accepted for electronegativity is "Pauling's scale". This scale is based on
(A) bond energy data
(B) bond length data
(C) force of attraction between nucleus and valence electrons
(D) hydration energy of ionic molecules

Q.12 Which of the following is the correct order of increasing radius of species (atom / ion)?
(A) $Mg < Na^+ < F^- < Al$ (B) $Na^+ < Al < Mg < F^-$
(C) $Na^+ < F^- < Al < Mg$ (D) $Na^+ < F^- < Mg < Al$

Q.13 Which of the following electronic configurations represents a sudden large jump between the values of second and third ionisation energies of an element?
(A) $1s^2 2s^2 2p^3$ (B) $1s^2 2s^2 2p^6 3s^2 3p^1$
(C) $1s^2 2s^2 2p^6 3s^2 3p^3$ (D) $1s^2 2s^2 2p^6 3s^2$

Q.14 The bond angle of H–O–H in water is about 105°, the P-character of the hybrid orbitals will be
(A) 75% (B) 79.5% (C) 81% (D) 71%

Q.15 Fluorine does not form oxyacids unlike other halogens because
(A) it is the most electronegative atom and thus it cannot show positive oxidation states
(B) it is the most electron affinitive
(C) it has the highest ionisation potential among halogens.
(D) it shows variable oxidation states

Q.16 The electron-affinity of elements decreases down the group, but chlorine is more electron-affinitive than fluorine. This is because of
(A) small radius of fluorine and high density (B) small radius of chlorine and high density
(C) large radius of chlorine and high density (D) small radius of fluorine and low density

Q.17 The modern periodic table is given by
(A) Bohr (B) Moseley (C) Mendeleev (D) Dobereiner

Q.18 If x, y and z are electronegativity, ionisation potential and electron-affinity respectively. Then the electron affinity (z) in the terms of electronegativity (x) and ionisation potential (y) will be
(A) $z = \frac{x+y}{z}$ (B) $z = \frac{x-y}{z}$ (C) $z = \frac{x^2+y^2}{2}$ (D) $z = 2x-y$

Q.19 Which of the following statements is not true about the long form of modern periodic table?
(A) it reflects the sequence of filling of electrons in order of sub-energy levels s, p, d and f
(B) it helps to predict the stable valency states of the elements.
(C) it reflects trends in physical and chemical properties of the elements
(D) it helps to predict the relative ionicity of the bond between any two elements.

Q.20 The correct order of electron affinity of B, C, N and O is
(A) $O > C > N > B$ (B) $B < N > C > O$ (C) $O > C > B > N$ (D) $O < B > C > N$

Q.21 The transition elements (d-block elements) show variable oxidation states because
(A) of the presence of ns, np and nd electrons.
(B) the energy difference between (n–1)d and ns electrons is very less, thus (n–1)d electrons also behave like valence electrons.
(C) of the presence of ns and nd orbitals
(D) of the presence of electrons in np and nd orbitals

Q.22 Match the column

	SCIENTIST		**PERIODIC TABLE**
(I)	Duma	(a)	Octave rule
(II)	Newland	(b)	Atomic volume curve
(III)	Lother Meyer	(c)	Homologous series
(IV)	Dobereiner	(d)	Triad rule

The correct option is
(A) I-(a), II-(b), III-(c), IV-(d) (B) I-(c), II-(a), III-(b), IV-(d)
(C) I-(c), II-(a), III-(d), IV-(b) (D) I-(d), II-(b), III-(a), IV-(c)

Q.23 Nitrogen and phosphorous belong to the same group in the periodic table and yet the later forms H_3PO_3, H_3PO_4, $(HPO_3)_n$, $H_4P_2O_7$ and the former forms only HNO_3, HNO_2 and HNO_4 i.e. former forms less number of oxy-acids. This is because
(A) N is much more electronegative than P
(B) N atom is smaller in size compared to P-atom.
(C) N atom does not have d-orbitals in its valence shell but P has
(D) N has a lower affinity for H than P

Q.24 Be and Mg have zero values of electron affinity because
(A) their 2s and 3s-orbitals are fully occupied
(B) their first ionisation-energies are very small
(C) their electronegativity are very high.
(D) their electron-affinity are very high in Mg^{2+} and Be^{2+} states

Q.25 The statement which is not correct for periodic classification of elements is
(A) the properties of elements are a periodic function of their atomic numbers
(B) non-metallic elements are less in number than metallic elements
(C) the first ionisation energies of elements along a period do not vary in a regular manner with increase in atomic number
(D) electronegativity and electron affinity increase across the period

Q.26 The correct order of covalent, Van der Waal's and crystal radii is
(A) $r_{\text{covalent}} < r_{\text{crystal}} < r_{\text{Van der Waal}}$ (B) $r_{\text{covalent}} < r_{\text{Van der Waal}} < r_{\text{crystal}}$
(C) $r_{\text{crystal}} < r_{\text{covalent}} < r_{\text{Van der Waal}}$ (D) $r_{\text{crystal}} < r_{\text{Van der Waal}} < r_{\text{covalent}}$

Q.27 The first ionisation energy of elements increases across the period. The first ionisation energy of nitrogen and oxygen will be respectively
(A) 13.6 eV, 14.6 eV (B) 14.6eV , 13.6 eV (C) 13.6 eV, 13.6 eV (D) 14.6 eV , 14.6 eV

Q.28 The correct order (s) of stability of oxidation state(s) for Ge, Sn and Pb is / are
(A) $Ge^{4+} < Sn^{4+} < Pb^{4+}$ (B) $Ge^{2+} < Sn^{2+} < Pb^{2+}$
(C) $Pb^{2+} < Sn^{2+} < Ge^{2+}$ (D) $Pb^{4+} < Sn^{4+} < Ge^{4+}$

Q.29 Which of the following pairs is chemically similar?
(A) Zr – Hf (B) Cu – Ag (C) Fe – Au (D) Hf – La

Q.30 Three elements X, Y and Z have atomic numbers 19, 37 and 55 respectively. Then, the correct statement(s) is /are:
(A) their ionisation potential would increase with increasing atomic numbers
(B) Y would have an ionisation potential between those of X and Z
(C) Y would have the highest ionisation potential
(D) Z would have the highest ionisation potential

Q.31 The correct order of the first ionisation potential is
(A) Ne > Cl > P > S > Al > Mg (B) Ne > Cl > P > S > Mg > Al
(C) Ne > Cl > S = P > Mg > Al (D) Ne > Cl < S > P < Al > Mg

Q.32 The ionic radii of N^{3-}, O^{2-}, F^-. Na^+ follows the order
(A) $N^{3-} > O^{2-} > F^- > Na^+$ (B) $N^{3-} > Na^+ > O^{2-} > F^-$
(C) $Na^+ > O^{2-} > N^{3-} > F^-$ (D) $O^{2-} = F^- = N^{3-} = Na^+$

Q.33 Which is the correct order of ionisation energies?
(A) $F^- > F > Cl^- > Cl$ (B) $F > F^- > Cl > Cl^-$
(C) $F > F^- > Cl^- > Cl$ (D) $F^- > F > Cl > Cl^-$

Q.34 The radioactive element which was discovered by Madam Curie and the name of which is based on her country is
(A) uranium (B) radium (C) polonium (D) neptunium

Q.35 An increase in both atomic and ionic radii with atomic number occurs in any group of the periodic table and in accordance with this the ionic radii of Ti (IV) and Zr (IV) ions are 0.68 Å and 0.74 Å respectively; but for Hf (IV) ion, the ionic radius is 0.75 Å, which is almost the same as that for Zr(IV) ion. This is due to
(A) greater degree of covalency in compounds of Hf^{4+}
(B) lanthanide contraction
(C) actinide contraction
(D) difference in co-ordination number of Zn^{4+} and Hf^{4+} in their compounds

Q.36 In general, the configuration of lanthanides is $(n-2)f^{1-14}(n-1)s^2p^6d^{0-1}ns^2$. It has been observed that, with increase in atomic number of lanthanides, there is a decrease in ionic radii from La (1.22 Å) to Lu (0.99 Å). The reason for decrease in ionic radii is an increase in
(A) electronegative character
(B) valency electrons and number of shells
(C) atomic and ionic volumes
(D) nuclear attraction for valence electrons leading to inward shrinking of shell.

Q.37 Molecular sizes of ICl and Br_2 are nearly same but boiling point of ICl is about 40°C higher than Br_2. Because
(A) I – Cl is weaker than Br – Br bond
(B) ionisation energy of Br atom is less than I atom
(C) ICl is a polar whereas Br_2 is a non-polar molecule
(D) ICl is non-polar whereas Br_2 is polar

Q.38 The correct order of Cl–O bond lengths in ClO^-, ClO_2^-, ClO_3^- and ClO_4^- is
(A) $ClO_4^- < ClO_3^- < ClO_2^- < ClO^-$ (B) $ClO_4^- = ClO_3^- = ClO_2^- = ClO^-$
(C) $ClO^- < ClO_2^- < ClO_3^- < ClO_4^-$ (D) $ClO_3^- < ClO_4^- < ClO_2^- < ClO^-$

Q.39 S–O, B–O and P–O bond order in PO_4^{3-}, SO_4^{2-} and BO_3^{3-} ions follows the order of
(A) $SO_4^{2-} > BO_3^{3-} > PO_4^{3-}$ (B) $SO_4^{2-} = BO_3^{3-} = PO_4^{3-}$
(C) $SO_4^{2-} > PO_4^{3-} > BO_3^{3-}$ (D) $BO_3^{3-} > PO_4^{3-} > SO_4^{2-}$

Q.40 The correct order of viscosity of alcohol, ethylene glycol and glycerol is
(A) alcohol > glycol > glycerol (B) glycerol > glycol > alcohol
(C) glycol > glycerol > alcohol (D) alcohol > glycerol > glycol

Q.41 The electronic configurations of four elements are
L : $1s^2 2s^2 2p^4$ Q : $1s^2 2s^2 2p^6 3s^2 3p^5$
P : $1s^2 2s^2 2p^6 3s^1$ R : $1s^2 2s^2 2p^6 3s^2$
the formulae of ionic compounds that could be formed between them are
(A) L_2P, RL, PQ, R_2Q (B) LP, RL, PQ, RQ
(C) P_2L, RL, PQ, RQ_2 (D) LP, R_2L, P_2Q, RQ

Q.42 The PCl_5 molecule has a trigonal bipyramidal structure because P atom is in sp^3d-hybrid state. The orbitals used by P atom for bonding are
(A) $d_{z^2}, s, p_x, p_y, p_z, d_{x^2-y^2}$ (B) s, p_x, p_y, p_z, d_{yz}
(C) $s, p_x, p_y, p_z, d_{z^2}$ (D) s, p_x, p_y, p_z, d_{xy}

Q.43 The hybrid states of carbon in diamond, graphite, acetylene and benzene respectively are
(A) sp^2, sp, sp^3, sp^2 (B) sp, sp^2, sp^3, sp^2 (C) sp^3, sp^2, sp, sp^2 (D) sp^2, sp^3, sp, sp^2

Q.44 The ratio of σ to π bonds in mesitylene is
(A) 3 (B) 7 (C) 5 (D) 6

Q.45 The order of energies of sp, sp^2 and sp^3-hybrid orbitals is (for the same principal quantum number of s and p orbitals)
(A) $sp < sp^2 < sp^3$ (B) $sp^3 < sp^2 < sp$ (C) $sp = sp^2 = sp^3$ (D) $sp^3 < sp < sp^2$

Q.46 The observed dipole-moment of HCl is found to be 1.303 D (Debye). This shows that HCl has 17% ionic and 83% covalent characters. If H–Cl bond-distance is 1.26 Å and charges on H and Cl ions are +e and –e respectively. The calculated dipole moment will be
(A) 1.303 D (B) 6.05 D (C) 3.303 D (D) 5.602 D

Q.47 The species whose excited states are same as ground states:
(A) N, O (B) F, O (C) N, F (D) O, Cl

Q.48 The compound that having 3c–2e bonds is
(A) $AlCl_3$ (B) Al_2Cl_6 (C) B_2H_6 (D) BF_3

Q.49 Aceto-acetic ester is an unsaturated hydroxyl compound because of the fact that ordinary ester is an equilibrium mixture of keto and enolic forms. The percentage of keto and enolic forms of aceto-acetic ester at equilibrium is
(A) 92.1% keto form + 7.9% enolic form (B) 92.5% enolic form + 7.5% keto form
(C) 50% keto form + 50% enolic form (D) 70% keto form + 30% enolic form

Q.50 A sigma bond is formed up on the overlapping of
(A) hybrid atomic orbitals (B) unhybrid atomic orbitals
(C) molecular orbitals (D) non-bonding orbitals

Q.51 The concept of hybridisation was given by
(A) Pauling (B) Mulliken (C) Hund (D) Ingold

Q.52 Formal charge of an atom is defined an (FC = formal charge, VE = number of valence electrons in free atom, BE = bonding electrons, LPE = lone pair electrons)

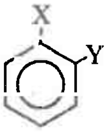
(A) $FC = VE - BE - LPE$ (B) $FC = \frac{1}{2} VE - BE - LPE$

(C) $FC = VE - \frac{1}{2} BE - LPE$ (D) $FC = VE - BE - \frac{1}{2} LPE$

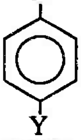
Q.53 In a molecule AB_x, the central atom makes $\angle B-A-B = 105°$, the s-character in the hybrid state of A will be
(A) 11–12% (B) 20–21% (C) 31–32% (D) 50–51%

Q.54 Valence bond theory was given by Heitler and London and modified by ____________
(A) Pauling and Slater (B) Heitler and Pauling
(C) Pauling and Mulliken (D) Pauling and Hund

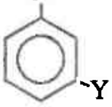
Q.55 The ortho, para and meta products of benzene are shown

I


(ortho)

II


(para)

III


(meta)

the correct order of the dipole moments of the above species will be
(A) I > II > III (B) II > I > III (C) III > II > I (D) I > III > II

Q.56 The keto form of acetone has 9 sigma (σ), 1 pi bond (π) and 2 lone pairs of electrons, the number σ, π bonds and lone pair of electrons in its enol form will be
(A) $9\sigma, 2\pi, 1\ell p$ (B) $9\sigma, 1\pi, 2\ell p$ (C) $8\sigma, 3\pi, 1\ell p$ (D) $8\sigma, 2\pi, 2\ell p$

Q.57 The correct increasing order of molecules in accordance with number of lone pair of electrons on central-atoms is
(A) $XeF_2 < H_2O < NH_3$ (B) $XeF_2 < NH_3 > H_2O$
(C) $NH_3 < H_2O < XeF_2$ (D) $H_2O = XeF_2 = NH_3$

Q.58 The correct order of bond-strengths of bonds formed by different types of overlapping is
(A) 1s-1s > 1s-2s > 2s-2s > 2s-2p (B) 1s-1s < 1s-2s < 2s-2s < 2s-2p
(C) 1s-2s < 1s-1s < 2s-2p < 2s-2s (D) 2s-2p < 2s-2s < 1s-1s < 1s-2s

Q.59 The most suitable method of separation of ortho and para-nitrophenols mixed in the ratio of 1:1 is
(A) distillation (B) crystallisation
(C) chromatographic method (D) colour spectrum and spectroscopic methods

Q.60 The dielectric constant(D) for water is about 80, this indicates that
(A) the force of attraction between ions(charges) increases 80 times in water
(B) the force of attraction between ions(charges) decreases 80 times in water
(C) bond length in the compounds increases 80 times in water
(D) bond-energy is not affected in water

Q.61 A diatomic molecule has a dipole moment of 1.2 D. If its bond-length is 1.0 Å. The fraction of an electronic charge q exists on each atom is
(A) 22% e (B) 28% e (C) 25% e (D) 29% e

Q.62 The correct increasing order of carbon-carbon bond lengths in benzene, ethane, ethene, acetylene and graphite is
(A) benzene < ethane < ethene < acetylene < graphite
(B) acetylene < ethene < benzene < graphite < ethane
(C) acetylene < ethene < graphite < benzene < ethane
(D) benzene < graphite < acetylene < ethene < ethane

Q.63 Which of the following sets of species is iso–steres?
(A) NH_3 and NH_4^+ (B) NH_4^+ and CH_4 (C) CH_4 and H_2O (D) NH_3 and CH_4

Q.64 Carbon with oxygen forms three types of oxides i.e. carbon mono-oxide(CO), carbon-dioxide(CO_2) and carbon suboxide(C_3O_2). The exact structure of C_3O_2 will be

(A) $C=O \rightarrow C=C=\underset{\cdot\cdot}{\ddot{O}}$ (B) $\underset{\cdot\cdot}{\ddot{O}}=C=C=C=\underset{\cdot\cdot}{\ddot{O}}$

(C) $\underset{\cdot\cdot}{\ddot{O}}=C=\ddot{O}\rightarrow C=\underset{\cdot\cdot}{\ddot{O}}$ (D) $O \rightarrow O=C=C=\ddot{C}:$

Q.65 Which of the following carbon (represented with *) is in sp^3 hybrid state?

(A) $(CH_3)_3\overset{*}{C}OH$ (B) $CH_3\overset{*}{C}OCH_3$ (C) $CH_3\overset{*}{C}OOH$ (D) $CH_3\overset{*}{C}OCl$

Q.66 The number of σ and π bonds in dicyanogen $(CN)_2$ are
(A) $2\sigma + 3\pi$ (B) $3\sigma + 2\pi$ (C) $3\sigma + 4\pi$ (D) $4\sigma + 3\pi$

Q.67 Graphite is the most stable allotrope of carbon, which has a hexagonal structure in which carbon atoms are in sp^2 hybrid state. It forms several layers, 3.14 Å away from each other. Such layers provide the property of lubricant. The force that acts between the layers of graphite is
(A) hydrogen bond (B) Van der Waal's force
(C) covalent force (D) dipole-dipole attraction

Q.68 The hybrid state of B-atom in boron-hydride is sp^2, while in its dimer it has sp^3 hybrid state because
(A) one of the empty orbitals of boron takes part in hybridisation
(B) overlapping between s and p-orbitals of H and B forms a π bond
(C) B_2H_6 is an electron rich compound
(D) B_2H_6 is less stable than BH_3

Q.69 Tri-iodide ion has a linear symmetry with bond-angle of 180°. In the structure of I_3^- ion
(A) I_2 acts as a lewis acid while I^- as a lewis base
(B) I_2 acts as a lewis base and I^- as a lewis acid
(C) both I_2 and I^- as a lewis bases
(D) both I_2 and I^- as a lewis acids

Q.70 The bond-order of C-O bond and charge at O-atoms for CO_3^{2-} (carbonate ion) are
(A) 1.25, e/3 (B) 1.25, 3e/2 (C) 1.33, 2e/3 (D) 1.33, e/3

Q.71 In the methane molecule and diamond, the tetra-valencies of carbon atoms are projected at angles of 109°28'. This was the first proposed by the first Noble prize Winner in Chemistry, that is
(A) Kekule (B) Van't-Hoff and Le-Bel
(C) Lewis (D) Pauling

Q.72 Dipole moment is an important method of structure determination of molecules. It helps to determine polarity, charge, % covalent and ionic characters of molecules. The formula used to determine % ionic character of the compound is : (μ = dipole moment)

(A) % ionic character = $\frac{\mu_{cal}}{\mu_{obs}} \times 100$ (B) % ionic character = $\frac{\mu_{obs}}{\mu_{cal}} \times 100$

(C) % ionic character = $\frac{\mu_{obs} - \mu_{cal}}{\mu_{obs}} \times 100$ (D) % ionic character = $\frac{\mu_{cal} - \mu_{obs}}{\mu_{cal}} \times 100$

Q.73 Molecular orbital theory was proposed by
(A) Pauling-Slater (B) Mulliken-Hund (C) Gilepsy-Pauling (D) Sidgwick-Sugden

Q.74 The newly discovered allotrope of carbon that having a football like structure is
(A) C_{60}; Fulleзene (B) C_{60}; Fluorine (C) C_{60}; Fullerene (D) C_{120}; Allene

Q.75 Bond-order of Be_2 and C_2 respectively are
(A) 0, 2 (B) 2, 2 (C) 2, 0 (D) 1, 1

Q.76 The species which are iso-electronic as well as iso-structurals are called
(A) isomers (B) isodiaphers (C) iso-steres (D) bio-steres

Q.77 If E_{HR}, E_1, E_2 and E_3 are the energies of hybrid resonance, most stable resonating structure, the least stable resonating structure and the moderate stable resonating structure, then the resonance energy of the molecule will be
(A) $E_{HR} - E_1$ (B) $E_{HR} - E_2$ (C) $E_{HR} - E_3$ (D) $E_3 - E_1$

Q.78 In the test of Hg_2^{2+} ions, the black ppt. are formed on addition of NH_4OH is due to the formation of
(A) $Hg + Hg(NH_2)Cl$ (B) $Hg_2^{2+} + Hg(NH_2)Cl$
(C) $Hg^{2+} + Hg^+$ (D) $Hg + Hg^+$

Q.79 Which of the following is not a preliminary test used to detect ions?
(A) borax bead test (B) flame test (C) brown ring test (D) cobalt nitrate test

Q.80 $K_4[Fe(CN)_6]$ is used in the detection of
(A) Fe^{2+} (B) Fe^{3+} (C) Cu^{2+} (D) Zn^{2+}

Q.81 The gas(es) evolve in the test of NO_2^- ion is/are
(A) NO_2 (B) NO (C) N_2O (D) N_2O_3

Q.82 An aqueous solution of $FeSO_4$, $Al_2(SO_4)_3$ and chrome alum is heated with excess of Na_2O_2 and filtered. The substances obtained are
(A) a colourless filtrate and a green residue (B) a yellow filtrate and a green residue
(C) a yellow filtrate and a blue residue (D) a green filtrate and a white residue

Q.83 Which of the following complex is formed when excess of KCN is added to aqueous solution of copper sulphate?
(A) $Cu(CN)_2$ (B) $K_4[Cu(CN)_4]$ (C) $K[Cu(CN)_2]$ (D) $K_3[Cu(CN)_4]$

Q.84 Which one of the following compounds on reaction with NaOH and Na_2O_2 gives yellow colour?
(A) $Cr(OH)_3$ (B) $Zn(OH)_2$ (C) $Al(OH)_3$ (D) $Fe(OH)_3$

Q.85 Br^- ion is identified using conc. H_2SO_4. During addition of conc. H_2SO_4 to test-tube containing 1-2 ml of given mixture, a brownish-red gas which gives fumes in air is evolved. This gas contains
(A) Br_2 (B) HBr (C) HBr + Br_2 (D) HBr + HI

Q.86 A white sodium salt dissolves readily in water to give a solution, which is neutral to litmus. When silver nitrate solution is added to this solution, a white precipitate is formed which does not dissolve in dilute HNO_3. The acidic radical would be
(A) CO_3^{2-} (B) Cl^- (C) SO_3^{2-} (D) Br^-

Q.87 $X(aq) \xrightarrow{K_2CrO_4} Y$ (insoluble in acetic acid). X must give ____________ colour in flame test
(A) crimson red (B) dark blue (C) apple green (D) golden yellow

Q.88 $X + NH_3 + KOH \longrightarrow Y$ (Brown ppt.), X and Y are respectively
(A) Nessler's reagent, iodide of Millon's base (B) Iodide of Millon's base, Nessler's reagent
(C) Iodide of Millon's base, prussian blue (D) Nessler's reagent, golden spangles

Q.89 Sometimes, yellow turbidity appears on passing H_2S gas even in the absence of II group radicals. This is because of
(A) sometimes III group radicals are precipitated as their sulphates
(B) IV group radicals are precipated as sulphides
(C) the oxidation of H_2S gas by some acid radicals
(D) III group radicals are precipitated as hydroxides

Q.90 Which of the following cannot give iodometric titration?
(A) Fe^{3+} or Cu^{2+} (B) Cu^{2+} and Ag^+ (C) Pb^{2+} or Ag^+ (D) Ag^+ and Pb^{2+}

Q.91 $(MgCl_2 + NH_4OH)$ mixture is used for quantitative estimation of
(A) PO_4^{3-} (B) SO_4^{2-} (C) AsO_4^{3-} (D) BO_3^{3-}

Q.92 The number of geometrical isomers of octahedral complex $[Co(OX)(PMe_3)_2NH_3]Cl$ is
(A) 2 (B) 3 (C) 4 (D) 5

Q.93 $K_4[Fe(CN)_6] + 6H_2SO_4 + 6H_2O \longrightarrow X(gas)\uparrow$; gas X is
(A) N_2 (B) CO (C) H_2 (D) NH_3

Q.94 For a complex ion $[Cu(NH_3)_4]^{2+}$
(A) stability constant is $[Cu^{2+}][NH_4^+]/[Cu(NH_3)_4]^{2+}$
(B) stability constant is $[Cu(NH_3)_4]^{2+}/[Cu^{2+}][NH_3]^4$
(C) stability is more if instability constant is higher
(D) stability is less if stability constant is higher

Q.95 The complex, which can be reduced easily is
(A) $V(CO)_6$ (B) $Cr(CO)_6$ (C) $Fe(CO)_5$ (D) $Ni(CO)_4$

Q.96 The complex ion(s) which is/are coloured but NOT due to d-d transitions

(A) CrO_4^{2-} (B) $[Cu(NH_3)_4]^{2+}$ (C) $[CoF_6]^{3-}$ (D) $[Ti(H_2O)_6]^{3+}$

Q.97 Complex/complex ion X is the most stable amongst following, then X must be

(A) $Fe(CO)_5$ (B) $[Fe(CN)_6]^{3+}$ (C) $[Fe(C_2O_4)_3]^{3-}$ (D) $[Fe(H_2O)_6]^{3+}$

Q.98 In a square-planar complex, central metal ion is in dsp^2 hybrid state and involves the hybridization of ________

(A) s, p_x, p_y, d_{xy} orbitals (B) s, p_x, p_y, $d_{x^2-y^2}$ orbitals

(C) s, p_x, p_y, d_{yz} orbitals (D) s, p_y, p_z, $d_{x^2-y^2}$ orbitals

Q.99 A complex has a cobalt ion as central metal ion and 5, 1 and 2 molecules/atoms of NH_3, NO_2 and Cl as ligands. One mole of this compound gives three moles of ions in aqueous solution and reacts with two moles of $AgNO_3$ to give 2 moles of AgCl. The exact formula of the said complex is

(A) $[Co(NH_3)_4(NO_2)Cl]Cl(NH_3)$ (B) $[Co(NH_3)_3Cl_3]$

(C) $[Co(NH_3)_5(NO_2)]Cl_2$ (D) $[Co(NH_3)_4Cl_2]NO_2$

Q.100 Which of the following statement(s) is/are correct about metal carbonyls?

(A) the oxidation state of a metal in carbonyls is zero

(B) the secondary carbonyls are obtained from photo decomposition

(C) metal carbonyls are single bonded species

(D) dπ - pπ overlapping is observed in carbonyls

Q.101 Among the following, which is not a π-bonded organometallic compound?

(A) $K[PtCl_3(\eta^6\text{–}C_2H_4)]$ (B) $Fe(\eta^5\text{–}C_5H_5)_2$

(C) $Cr(\eta^6\text{–}C_6H_6)_2$ (D) $(CH_3)_4Sn$

Q.102 The complex which involves outer-orbital hybridization of central metal ion is

(A) $[Zn(NH_3)_6]^{2+}$ (B) $[Cr(NH_3)_6]^{3+}$ (C) $[V(NH_3)_6]^{3+}$ (D) $[Co(NH_3)_6]^{3+}$

Q.103 Ligands in the complex Lithium tetrahydroaluminate is/are

(A) H_3O^+ (B) H^- (C) both H^+ and H^- (D) H

Q.104 The compound, which is used in the treatment of lead poisoning is

(A) EDTA (B) RMgX (C) $(C_6H_6)_2Cr$ (D) $(C_6H_6)_2V$

Q.105 The lowest energy d-d transitions in Cr(III) complexes vary in order of

(A) $[CrCl_6]^{3-} < [Cr(H_2O)_6]^{3-} < [Cr(en)_3]^{3+} < [Cr(CN)_6]^{3-}$

(B) $[CrCl_6]^{3-} < [Cr(en)_3]^{3+} < [Cr(H_2O)_6]^{3-} < [Cr(CN)_6]^{3-}$

(C) $[Cr(CN)_6]^{3-} < [CrCl_6]^{3-} < [Cr(H_2O)_6]^{3+} < [Cr(en)_3]^{3+}$

(D) $[Cr(H_2O)_6]^{3+} < [Cr(en)_3]^{3+} < [CrCl_6]^{3-} < [Cr(CN)_6]^{3-}$

Q.106 The number of σ and π bonds in $(NC)_2C_2M(CO)_3(C_2H_5)$ are

(A) 19σ, 11π (B) 11σ, 19π (C) 19σ, 19π (D) 11σ, 11π

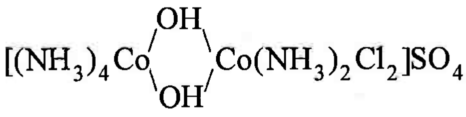
Q.107 Which of the following statement(s) is/are correct about stability of chelates?

(A) as the number of rings in complex increases, stability of complex (chelate) also increases

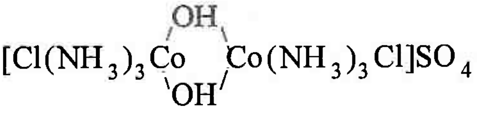
(B) a chelate having five membered rings is more stable if it contains double bonds

(C) a chelate having six membered ring is more stable if it does not contain double bonds

(D) chelating ligands are atleast bidentate ligands

Q.108 

$[(NH_3)_4Co(OH)_2Co(NH_3)_2Cl_2]SO_4$

and 

$[Cl(NH_3)_3Co(OH)_2Co(NH_3)_3Cl]SO_4$

are

(A) ligand isomers (B) co-ordinate-position isomers

(C) ionisation isomers (D) co-ordinate isomers

Q.109 The octahedral complex which cannot show geometrical isomerism (A and B are monodentate ligands) is
(A) $[MA_2B_4]$ (B) $[MA_4B_2]$ (C) $[MA_3B_3]$ (D) $[MA_5B]$

Q.110 The complex/complex ion, which shows optical activity is
(A) $[Cr(H_2O)_4Cl_2]^+$ (B) $[Co(H_2O)_2(NH_3)_2Cl_2]^+$
(C) $[Co(NH_3)_6]^{3+}$ (D) $[Co(CN)_5NC]$

Q.111 Two complexes $V(C_6H_6)_2$ and $Cr(C_6H_6)_2$ are readily oxidized to their respective cations in the presence of air. The number of unpaired electrons, in them respectively are
(A) 0, 1 (B) 1, 0 (C) 1, 1 (D) 0, 0

Q.112 The existance of two different coloured complexes of $[Co(NH_3)_4Cl_2]$ is due to
(A) ionization isomerism (B) linkage isomerism
(C) geometrical isomerism (D) co-ordination isomerism

Q.113 A metal carbonyl is formulated as $M(CO)_x$ (where M = central metal atom and x = number of carbonyl groups), the metal is bonded to
(A) oxygen (B) carbon (C) C–O partial bond (D) C–O double bond

Q.114 The most common co-ordination numbers of metal atoms/ions in complexes are
(A) 2 and 4 (B) 4 and 6 (C) 6 and 8 (D) 2 and 6

Q.115 Complex $K[Ag(CN)_2]$ is used in silver plating instead of $AgNO_3$ because
(A) Ag^+ ions are completely removed from solution
(B) this layer of Ag is formed on Cu
(C) large potential difference is required
(D) less availability of Ag^+ ions because Cu^+ cannot displace Ag^+ from $[Ag(CN)_2]^-$ ions

Q.116 M–L bonds in carbonyl posses
(A) only σ character (B) only π character
(C) both σ and π characters (D) none of these

Q.117 The correct IUPAC name of $H_4[Pt(CN)_6]$ is
(A) hexacyanoplatinic (II) acid (B) hexacyanoplatinic (III) acid
(C) hexacyanoplatinic (IV) acid (D) hydrogen platinum hexacyano

Q.118 The complex, which is used in the treatment of cancer is
(A) cis-$[PtCl_2(NH_3)_2]$ (B) trans-$[PtCl_2(NH_3)_2]$
(C) $[PtCl_4]^{2-}$ (D) trans-$[PtCl_2(NH_3)_2]^{2-}$

Q.119 The colours, spectra and magnetic properties of complexes could be explained on basis of crystal field theory (CFT) proposed by
(A) Werner (B) Bathe (C) Pauling (D) Zeise

Q.120 The correct order of energies of d-orbitals of metal ion in a square planar complex is
(A) $dxy = dyz = dxz = dx^2 - y^2 = dz^2$ (B) $dx^2 - y^2 - dz^2 > dxy = dyz = dxz$
(C) $dx^2 - y^2 > dz^2 = dxy = dyz > dxz$ (D) $dx^2 - y^2 > dxy > dz^2 > dxz = dyz$

ANSWER KEY

Q.1	A	Q.2	B	Q.3	A	Q.4	A
Q.5	B	Q.6	A	Q.7	A	Q.8	D
Q.9	D	Q.10	A	Q.11	A	Q.12	B
Q.13	D	Q.14	B	Q.15	A	Q.16	A
Q.17	A	Q.18	D	Q.19	B	Q.20	C
Q.21	B	Q.22	B	Q.23	C	Q.24	A
Q.25	C	Q.26	A	Q.27	B	Q.28	B,D
Q.29	A	Q.30	A	Q.31	B	Q.32	A
Q.33	A	Q.34	C	Q.35	B	Q.36	D
Q.37	C	Q.38	A	Q.39	C	Q.40	B
Q.41	C	Q.42	C	Q.43	C	Q.44	B
Q.45	A	Q.46	B	Q.47	A	Q.48	C
Q.49	A	Q.50	A	Q.51	A	Q.52	C
Q.53	B	Q.54	A	Q.55	D	Q.56	B
Q.57	C	Q.58	A	Q.59	A	Q.60	B
Q.61	C	Q.62	B	Q.63	B	Q.64	B
Q.65	A	Q.66	C	Q.67	B	Q.68	A
Q.69	A	Q.70	C	Q.71	B	Q.72	B
Q.73	B	Q.74	C	Q.75	A	Q.76	C
Q.77	A	Q.78	A	Q.79	C	Q.80	B,C,D
Q.81	A,B	Q.82	B	Q.83	D	Q.84	A
Q.85	C	Q.86	B	Q.87	C	Q.88	A
Q.89	C	Q.90	A	Q.91	A,C	Q.92	C
Q.93	B	Q.94	B	Q.95	A	Q.96	A
Q.97	C	Q.98	B	Q.99	C	Q.100	A,B,D
Q.101	D	Q.102	A	Q.103	B	Q.104	A
Q.105	C	Q.106	A	Q.107	A,D	Q.108	B
Q.109	D	Q.110	B	Q.111	B	Q.112	C
Q.113	B	Q.114	B	Q.115	D	Q.116	C
Q.117	A	Q.118	A	Q.119	B	Q.120	D

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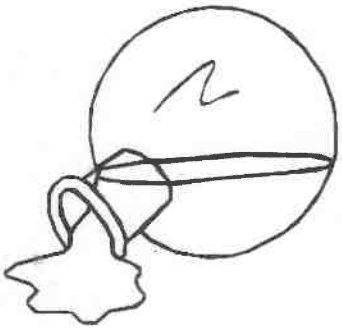

QUALITATIVE ANALYSIS

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Concept Building Exercise 16.1

1. **When a white powder (A) is strongly heated, it gives off a colorless, odorless gas (B) which turns lime water milky (C) and then colorless giving a solution (D). The solid residue (E) is yellow when hot but turns white on cooling. Identify the compounds A, B, C, D and E. Write the chemical equation for the reactions.**

Ans. White powder (A) gives colorless, odorless gas which changes lime water milky, hence the compound (A) is a carbonate of any cation, but residue 'E' which is left on heating (A) is yellow when hot and white when cooled. Therefore (E) must be ZnO. Thus the compound (A) is $ZnCO_3$.

2. **A well known orange crystalline compound (A) when burnt imparts violet colour of flame. (A) on treating with (B) and concentrated. H_2SO_4 gives red gas (C) which gives red yellow solution (D) with alkaline water (D) on treating with acetic acid and lead acetate gives yellow precipitate (E). (B) sublimes on heating. Also on heating (B) with NaOH, gas (F) is formed which gives white fumes with HCl. What are (A) to (F) ?**

Ans. (1) (B) sublimes on heating & gives gas (F) with NaOH which forms white fumes with HCl so (B) is NH_4Cl

(2) (A) reacts with (B) & concentrated H_2SO_4 to give reddish brown gas [CrO_2Cl_2) i.e (C)] and thus (A) is $K_2Cr_2O_7$.

(i)K_2CrO_7(A) + $4NH_4Cl$ (B, red) + $3H_2SO_4 \longrightarrow K_2SO_4$ + $2CrO_2Cl_2$ (red, C)+ $2(NH_4)_2SO_4$ + $3H_2O$

(ii) $CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4$ (D, Yellow solution) + 2NaCl + $2H_2O$

(iii) $Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow PbCrO_4$ (Yellow precipitate, E)+ $2CH_3COONa$

(iv) NH_4Cl (s) $\xrightarrow{\Delta}$ NH_4Cl(g) (Sublimation)

(v) $NH_4Cl + NaOH \xrightarrow{\Delta} NaCl + NH_3 + H_2O$

(vi) NH_3 (F) + HCl $\longrightarrow$ NH_4Cl (white fumes)

3. **A unknown inorganic compound (X) gave the following reactions : (i) on heating 'X' gave a residue, oxygen and oxide of nitrogen. (ii) Addition of acetic acid and $K_2Cr_2O_7$ to its aqueous solution give a yellow precipitate. (iii) Addition of NaOH to its aqueous solution first forms a white precipitate, dissolve in the excess of the reagent. Identify the compound (X) and write balanced equation for step (i), (ii) & (iii).**

Ans. (i) $Pb(NO_3)_2 \xrightarrow{\Delta} 2PbO + 4NO_2 + O_2$ (X)

(ii) $Pb(NO_3)_2 + 2\,CH_2COOH \longrightarrow Pb\,(CH_3COO)_2 + 2HNO_3$

$2\,Pb\,(CH_3COO_2)_2 + K_2Cr_2O_7 + H_2O \longrightarrow$

$2PbCrO_4\downarrow$ (yellow) + $2CH_3COOK + 2CH_3COOH$

(iii) $Pb(NO_3)_2 + 2NaOH \rightarrow Pb(OH)_2\downarrow$ (White) + $2NaNO_3$

$Pb(OH)_2 + 2NaOH \longrightarrow Na_2PbO_2 + 2H_2O$

Concept Testing Exercise 16.1

1 A mixture when rubbed with organic acid smells like vinegar. It contains :
(a) sulphite (b) nitrate (c) nitrite (d) acetate

2 Soda extract is prepared by
(a) fusing soda and mixture and then extracting with water
(b) dissolving $NaHCO_3$ and mixture in dil. HCl
(c) boiling Na_2CO_3 and mixture in dil. HCl
(d) boiling Na_2CO_3 and mixture in distilled water

3 For the tests of halides, the soda extract is acidified with
(a) dil. H_2SO_4(b) dil. HNO_3 (c) dil. HCl (d) any of the three

4 Which of the following gives green colour to the flame?
(a) $CaCO_3$ (b) NaCl (c) $Sr(NO_3)_2$ (d) $BaCl_2$

5 A white solid is first heated with dilute H_2SO_4 and then with concentrated H_2SO_4. No action is observed in either case. The solid contains :
(a) Sulphide (b) Sulphite
(c) sulphate (d) thiosulphate

6 Which of the following do not respond to borax bead test?
(a) Nickel salts (b) Copper salts
(c) Cobalt salts (d) Aluminium salts

7 An aqueous solution of $FeSO_4.Al_2(SO_4)_3$ and chrome alum is heated with excess of Na_2O_2 and filtered. The materials obtained are
(a) a colourless filtrate and a green residue
(b) a yellow filtrate and a green residue
(c) a yellow filtrate and a brown residue
(d) a green filtrate and a brown residue

8 The salt used for performing 'bead test' in qualitative inorganic analysis is
(a) $K_2SO_4{\cdot}Al_2(SO_4)_3{\cdot}24H_2O$(b) $FeSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$
(c) $Na(NH_4)HPO_4{\cdot}4H_2O$ (d) $CaSO_4{\cdot}2H_2O$

9 The compound formed in the borax bead test of Cu^{2+} ion in oxidising flame is
(a) Cu (b) $CuBO_2$ (c) $Cu(BO_2)_2$ (d) None of these

10 In borax based test which compound is formed?
(a) Orthoborate (b) Metaborate
(c) Double oxide (d) Tetraborate

11 Potassium chromate solution is added to an aqueous solution of a metal chloride. The precipitate thus obtained are insoluble in acetic acid. These are subjected to flame test the colour of the flame is
(a) Lilac (b) Apple green
(c) Crimson red (d) Golden yellow

12 Which of the following statements is correct
(a) manganese salts give a violet borax bead test in reducing flame
(b) from a mixed precipitate of AgCl and AgI, ammonia solution dissolves only AgCl
(c) ferric ions give a deep green precipitate, on adding potassium ferrocyanide solution
(d) on boiling the solution having K^+, Ca^{2+} and HCO_3^- ions we get a precipitate of $K_2Ca(CO_3)_2$

13 A red solid insoluble in water. However, it becomes soluble, if some KI is added to water. Heating the red solid in a test tube, results in liberation of some violet coloured fumes and droplets of a metal appear on cooler part of the test tube. The red solid is
(a) Pb_3O_4 (b) HgI_2 (c) HgO (d) $(NH_4)_2Cr_2O_7$

Concept Building Exercise 16.2

1 **A mixture of three gases A, B and C is passed first into acidified $K_2Cr_2O_7$ solution when A is absorbed turning the solution green. The remainder of the gas is passed through excess of lime water which turns milky resulting in the absorption of B. The residual gas C is absorbed by alkaline pyrogallol solution. However the original mixture does not turn lead acetate paper black. Identify A, B & C. Give equations for the reactions involved.**

Ans. (A) , (B) & (C) are SO_2 , CO_2 & O_2 respectively.

$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr(SO_4)_3 + H_2O$

$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3\downarrow + H_2O$

2 **A white substance (A) on heating with excess of dil HCl gave an offensive smelling gas (B) and a solution (C). Solution (C) on treatment with aqueous NH_3 did not give any precipitate but on treatment with NaOH solution gave a precipitate (D) which dissolves in excess of NaOH solution. (A) on strong heating in air gave a strong smelling gas (E) and a solid (F). Solid (F) dissolved completely in HCl and the solution gave a precipitate with $BaCl_2$, in acid solution. Identify A to F and write balanced chemical equations for various reactions involved.**

Ans. Solution C gives precipitate with NaOH solution which is slouble in excess of NaOH solution hence the cation should be of the amphoteric metal like Zn or Al. Again solid F is soluble in HCl and gives white precipitate with $BaCl_2$. Therefore anion must be SO_4^{2-} ion.

Now the A gives offensive smelling gas hence the A may be ZnS or Al_2S_3. But Al_2S_3 on heating in air does not form $Al_2(SO_4)_3$.

$\underset{(A)}{ZnS} + 2HCl \longrightarrow \underset{(C)}{ZnCl_2} + \underset{(B)}{H_2S}\uparrow$, $\underset{(C)}{ZnCl_2} + 2NaOH \rightarrow \underset{(D)}{Zn(OH)_2}\downarrow + 2NaCl$

$Zn(OH)_2 + 2NaOH \longrightarrow Na_2ZnO_2 + 2H_2O$ $\quad$ $\underset{(A)}{2\,ZnS} + 3O_2 \longrightarrow \underset{(F)}{2ZnO} + \underset{(E)}{2SO_2}$

$ZnS\,(A) + 2O_2 \longrightarrow ZnSO_4\,(F)$ $\quad$ $ZnSO_4 + BaCl_2 \longrightarrow BaSO_4\downarrow + ZnCl_2$

3 **An inorganic compound (A), transparent like glass is a strong reducing agent. Its hydrolysis in water gives a white turbidity (B). Aqueous solution of (A) gives white precipitate (C) with NaOH (aqueous) which is soluble in excess NaOH. (A) reduces auric chloride to produce purple of cassias. (A) also reduces I_2 and gives chromyl chloride test. Identify (A) -(C). Give equations for the reactions involved.**

Ans. (1) Since (A) gives chromyl chloride test & thus, it has Cl^-

(2) Since (A) is strong reducing agent So (A) is $SnCl_2$

(i) $SnCl_2 + H_2O \longrightarrow Sn(OH)_2 + 2NaCl$

white transparent $\quad$ (B)

solid (A) $\quad$ white turbidity

(ii). $\underset{(A)}{SnCl_2} + 2NaOH \longrightarrow \underset{(C)}{Sn(OH)_2} + 2NaCl$

$Sn(OH)_2 + 2NaOH \longrightarrow Na_2SnO_2 + 2H_2O$

soluble

(iii) $3SnCl + 2AuCl_3 \longrightarrow 3SnCl_4 + 2Au$ (purple of cassius)

(iv) $SnCl_2 + 2HCl + I_2 \longrightarrow SnCl_4 + 2HI$

Concept Testing Exercise 16.2

1 The acidic solution of a salt produces blue colour with KI starch solution. The salt may be
(a) sulphite (b) bromide (c) nitrite (d) chloride

2 Sulphite on treatment with dil. H_2SO_4 liberates a gas which
(a) turns lead acetate paper black (b) burns with blue flame
(c) smells like vinegar (d) turns acidified $K_2Cr_2O_7$ paper green

3 In the ring test for nitrates, the ring formed is due to
(a) $FeSO_4 \cdot NO$ (b) $FeSO_4 \cdot NO_2$ (c) $Fe(NO_3)_3$ (d) $Fe_2(SO_4)_3 \cdot NO$

4 When a mixture containing phosphate is heated with conc. HNO_3 and ammonium molybdate solution, a canary yellow precipitate is formed. The formula of the yellow precipitate is
(a) $(NH_4)_3PO_4$ (b) $(NH_4)_3PO_4 \cdot 12MoO_4$ (c) $(NH_4)_3PO_4 \cdot 12MoO_3$ (d) $(NH_4)_3PO_4 \cdot (NH_4)_2 \cdot MoO_4$

5 The colour developed when sodium sulphide is added to sodium nitroprusside is
(a) violet (b) yellow (c) red (d) black

6 A gas is evolved which burns with blue flame when the mixture is heated with conc. H_2SO_4. The mixture contains
(a) carbonate (b) oxalate (c) nitrate (d) nitrite

7 On heating a mixture of NaCl, $Kr_2Cr_2O_7$ and conc. H_2SO_4 which of the following is formed?
(a) $CrCl_3$ (b) CrO_2Cl_2 (c) Cl_2 (d) $NaClO_2$

8 The basic radical which is tested by the reagent which is also used for the test of phosphate is
(a) Cd^{2+} (b) Sn^{2+} (c) Sb^{3+} (d) As^{3+}

9 Manganese salt + PbO_2 + conc. HNO_3 → The solution acquires purple colour. The colour is due to
(a) $HMnO_4$ (b) a lead salt (c) $Mn(NO_3)_2$ (d) H_2MnO_4

10 Cobalt salt + KNO_2 + CH_3COOH → yellow ppt. The yellow precipitate is
(a) potassium cobaltonitrite (b) potassium cobalt nitrite
(c) cobalt nitrite (d) cobalt nitrate

11 All ammonium salts liberate ammonia when
(a) heated (b) heated with caustic soda
(c) heated with H_2SO_4 (d) heated with $NaNO_2$

12 Ethyl borate burns with
(a) yellow flame (b) green flame (c) blue flame (d) crimson flame

13 The brown ring test is performed for the qualitative detection of
(a) bromides (b) iodides (c) nitrates (d) phosphates

14 The metal ion which is precipitated when H_2S is passed with HCl
(a) Zn^{2+} (b) Ni^{2+} (c) Cd^{2+} (d) Mn^{2+}

15 When H_2S gas is passed in a metal sulphate solution in presence of NH_4OH, a white precipitate is produced. The metal is identified as
(a) Zn (b) Fe (c) Pb (d) Hg

Concept Testing Exercise 16.3

1 Mercurous chloride turns black on treatment with ammonium hydroxide. This is due to the formation of
(a) $Hg(NH_2)Cl$ (b) $Hg_2Cl_2 \cdot NH_4OH$ (c) Hg and $HgNH_2Cl$ (d) $HgCl_2 \cdot NH_4OH$

2 A light yellow precipitate is formed in the second group of the qualitative analysis on passing H_2S even when no radical of second group is present. This is due to the presence of ..... in the mixture
(a) phosphate (b) acetate (c) oxalate (d) nitrate

3 An organic precipitate in the second group is given by
(a) Sb^{3+} (b) Sn^{2+} (c) Hg^{2+} (d) As^{3+}

4 A precipitate of which of the following would be obtained when HCl is added to a solution of stannous sulphide (SnS) in yellow ammonium sulphide :
(a) SnS (b) SnS_2 (c) $(NH_4)_2SnS_2$ (d) Sn_2S_3

5 Ferric ion forms a prussian blue coloured precipitate with $K_4[Fe(CN)_6]$ due to the formation of
(a) $K_4Fe(CN)_6$ (b) $Fe_4[Fe(CN)_6]_3$ (c) $Fe(OH)_3$ (d) $KFe[Fe(CN)_6]$

6 The group reagent for the V group radicals is
(a) $(NH_4)_2CO_3$ (b) $(NH_4)_2SO_4$ (c) NH_4Cl (d) $(NH_4)_2C_2O_4$

7 The sulphides of which one of the following groups of elements are soluble in yellow ammonium sulphide
(a) As, Sb and Sn (b) As, Cd and Sn (c) Cd, Cu and Bi (d) Hg, Cu and Cd

8 When dimethyl glyoxime solution is added to an aqueous solution of nickel (II) chloride followed by ammonium hydroxide
(a) no precipitate is obtained (b) a blue coloured ppt. is obtained
(c) a red coloured ppt. is obtained (d) a black coloured ppt. is obtained

9 In IV group analysis NH_4OH is added before passing H_2S gas because
(a) the sulphides of IV group are insoluble in NH_4OH
(b) the sulphides of other metals are soluble in NH_4OH
(c) the concentration of S^{2-} ions is high enough to precipitate the sulphides of IV group
(d) the sulphides of second group are soluble in NH_4OH

10 In qualitative analysis Cd is under
(a) I group (b) II group (c) III group (d) IV group

11 When H_2S gas is passed through the HCl containing aqueous solution of $CuCl_2$, $HgCl_2$, $BiCl_3$ and $CoCl_2$, it does not precipitate out
(a) CuS (b) HgS (c) Bi_2S_3 (d) CoS

12 Mark the correct statement
(a) I group basic radicals precipitate as chlorides (b) IV group basic radicals precipitate as sulphides
(c) V group basic radicals precipitate as carbonates (d) All the above statements are correct

13 When H_2S is passed through Hg_2^{2+}, we get
(a) HgS (b) HgS + Hg_2S (c) HgS + Hg (d) Hg_2S

14 How do we differentiate between Fe^{3+} and Cr^{3+} in group III?
(a) By adding excess of NH_4OH solution (b) By increasing NH_4^+ ion concentration
(c) By decreasing OH^- ion concentration (d) Both (b) and (c)

15 In Nessler's reagent for detection of ammonia, the active species is
(a) Hg_2Cl_2 (b) Hg^{2+} (c) Hg_2I_2 (d) HgI_4^{2-}

16 Precipitation of IV group cations takes place when H_2S passed is
(a) less ionised (b) highly ionised (c) not ionised (d) none of these

Multiple Correct Questions

1 A substance (A) is red in colour on heating in dry test tube it turns violet. On further heating reddish brown fumes are seen to evolve. Droplets of colourless transparent liquid are seen on upper inner part of test tube. A black residue is also observed. (A) could be
(a) $CoBr_2 \cdot 6H_2O$ (b) $Na_4[Fe(CN)_5NOS]$
(c) $[Fe(SCN)_3(OH_2)_3]$ (d) $Co(NO_3)_2 \cdot 6H_2O$

2. Which of the following on heating will produce a gas that turns white I_2O_5 dark when passed over
(a) $NaHSO_3$ (b) $Na_2C_2O_4$
(c) $(HCOO)_2$ (d) $CuSO_4$

3. A substance (P) on heating liberates gas(es) [Q]. [Q] when pass through aqueous $AgNO_3$ produces a white ppt. P could be
(a) KCl (b) $CaOCl_2$ (c) NH_4Cl (d) NH_4CN

4. Which of the following solids produces a reddish brown gas on heating. The colour of gas is intensified by adding any reducing agent
(a) NH_4NO_3 (b) $Al(NO_3)_3$ (c) $Pb(NO_3)_2$ (d) $NaNO_2$
(e) $(NH_4)_2Cr_2O_7$ (f) $CoBr_3$ (g) AuBr (h) $SnBr_2$

5. A substance (A) produces Lilac flame test on heating, the gas liberated burns with a blue flame. The substance could be
(a) K_2CO_3 (b) HCOOK
(c) $K_2C_2O_4$ (d) $KHC_2O_4 \cdot H_2SO_4$

6. As a mixture is tested by a flame test an orangish (light red) flame is seen as the substance is heated in a dry test tube. A colourless odorless gas evolved that turn lime water milky and finally colourless. The original mixture could be
(a) $Na_2CO_3 + SiO_2$ (b) $CaCO_3 + SiO_2$
(c) $NaCl + SrCO_3$ (d) $CaCl_2 + CuCl$

7. A substance (A) when heated after borax bead has been dipped in solution produces a bluish bead. When this bead is dipped in another solution (B) and heated in non luminous flame. The bead turns green. (A) and (B) could have been
(a) $Co(NO_3)_2$, $ZnSO_4$ (b) $CuSO_4$, KNO_3
(c) $Cr(ON)_3$, KNO_3 (d) $ZnCl_2$, $CoSO_4$

8. When borax bead is dipped in solution (A) and heated certain colour was seen. When it is redipped in (B) and heated (green) colour was observed. (A) and (B) could have been
(a) $MnSO_4$, $KMnO_4$ (b) $CrCl_3$, KCl
(c) $ZnCl_2$, $Co(NO_3)_2$ (d) $Co(NO_3)_2$, $ZnCl_2$
(e) $Co(NO_3)_2$, $FeCl_3$ (f) $Fe(SO_4)_3$, $Co(NO_3)_2$

9. A substance (A) on acidification produces brisk effervescence. The gas evolved is collected in a chamber. When burning Mg is introduced in the chamber, it continuous to burn although some what dimly. When this chamber suddenly opened a mild explosion is observed. Original compound could be
(a) CH_3COONa (b) Na_2S
(c) Na_2SO_3 (d) Trona : $Na_2CO_3 \cdot NaHCO_3$

10. A substance (A) releases brisk effervescence on acidification. The gas evolved is colourless. It turns blue litmus red, lime water milky and finally colourless. It also decolourises acidified $KMnO_4$. The original substance (A) could have been
(a) $NaCl + Na_2SO_3$ (b) $NaNO_2 + CaCO_3$
(c) $HgS + Pb(NO_3)_2$ (d) $CaSO_4 + MgSO_3$

11. Aqueous solution (A) and (B) produce brown ppt. when mixed. They could be
(a) $Pb(NO_3)_2$, NaCl (b) $CaOCl_2$, $Pb(ClO_4)_2$
(c) NaOCl, Ferric alum (d) Na_2S, $Na_2[Fe(CN)_5NO]$
(e) acidified $FeSO_4$, $NaNO_2$

12. Heating (P) with (Q) releases dark red fumes. (P) and (Q) could be
(a) $HgCl_2 + CrO_3$, conc. H_2SO_4
(b) conc. H_2SO_4, $MgBr_2$ (c) $Sn(NO_3)_2$, conc. H_2SO_4
(d) $CaCl_2 + K_2Cr_2O_7$, conc. H_2SO_4

13. Add a little $Na_2S_2O_3$ to (A), a white ppt is obtained which dissolves in excess hypo to produce a colourless solution. A could have been
(a) $AgNO_3$ (b) $CuCl_2$
(c) $Mn(NO_3)_2$ (d) $Pb(OAc)_2$

14. Two solids (A) and (B) are red and violet respectively. When mixed together and heated they form a white solid (C). (C) dissolves in water to produce colourless solution. This solution decolourises acidified $KMnO_4$. (A) and (B) could be
(a) Pb_3O_4, $KMnO_4$ (b) Pb_3O_4, I_2
(c) P (Red), I_2 (d) P (red), CrO_5
(e) P (red), S_8

15. Addition of a solution (L) to (M) produces a white turbidity/ppt. (L) and (M) could be
(a) $[Ag(NH_3)_2]^+Cl^-$, dil. HNO_3
(b) $[Ag(NH_3)_2]^+Cl^-$, $AgNO_3$ (aq.)
(c) $[Ag(NH_3)_2]^+Cl^-$, $Na_2S_2O_3$
(d) $[Ag(NH_3)_2]^+Cl^-$, Na_2S
(e) $[Ag(NH_3)_2]^+Cl^-$, conc. H_2SO_4

16. Which of the following can dissolve AgI
(a) conc. HCl (b) NH_3 (aq.)
(c) hot dil. HNO_3 (d) NaS_2O_3 (aq.)

17. A substance (A) produces a silvery mirror on adding another substance (B). (A) and (B) could be
(a) $AgNO_3$, glucose (b) $Ag(NH_3)_2^+$, $N_2H_5HSO_3$
(c) $Ag(NH_3)_2^+$, NH_2OH (d) CH_3COOAg, NH_2OH

18. A substance (P) dissolves in hot dil. HNO_3 although it fails to dissolve in distilled water. The solution when treated with aq. Na_2CO_3 produces a yellowish white ppt. Addition of dil. HNO_3 dissolved this ppt giving back the original solution. To this solution is added (P) and allowed to stand. After 10 minutes aq. Na_2CO_3 was again added to the solution. A reddish ppt was obtained. (P) could have been
(a) Ag (b) $AgNO_3$ (c) $Hg(N_3)_2$
(d) $Hg(NO_3)_2$ (e) Hg

19. A given solution (A) produces a black ppt on passing H_2S. The ppt when boiled with powder turns white. The original solution could have been
(a) $AgNO_2$ (b) $Hg_2(NO_3)_2$ (c) $Hg(NO_3)_2$ (d) $Pb(NO_3)_2$

20. A yellow solution produces a yellow ppt on adding excess KI. However when excess $AgNO_3$ was added a red ppt. was obtained. Original solution could have been
(a) Na_2CrO_4 (b) $[Ag(NH_3)_2]_2CrO_4$
(c) $FeCl_3$ (d) $AgNO_3$ (e) $Hg_2(OAc)_2$

21. Which of the following reagent will dissolve zinc hydroxide leaving $Fe(OH)_3$ uneffected
(a) NaOH (b) HCl (c) CH_3COOH
(d) NH_3 (e) NH_4Cl

EXERCISE - 1

1. A colorless water soluble solid X on heating gives equimolar quantities of Y and Z. Y gives dense white fumes HCl and Z does so with NH_3. Y gives brown precipitate with Nessler's reagent and Z gives white precipitate with nitrates of Ag^+, Pb^{2+} and Hg^+. What is X ?

2. A metal chloride (A) gives white precipitate (B) in presence of aq. NH_3 and $(NH_4)_3PO_4$. B on heating gives C and a pungent smell gas (D) which turns red litmus blue. Identify A to D and give reactions.

3. An aqueous solution of salt (A) gives a white crystalline precipitate (B) with NaCl solution. The filtrate gives a black precipitate (C) when H_2S is passed into it. Compound (B) dissolves in hot water and the solution gives yellow precipitate (D) on treatment with sodium iodide and cooling. The compound (A) does not give any gas with dilute HCl but liberates a reddish brown gas on heating. Identify the compounds (A) to (D) and give an equation for the liberation of the reddish brown gas.

4. A white compound (A) when heated with dil. HCl gave on offensive smelling gas (B) and a solution (C). The residual solution (C) did not give any precipitate with AQ NH3 but a definite precipitate (D) was obtained with NaOH which however dissolves in excess of reagent. (A) When heated strongly in air gave another offensive smelling gas (E) and a solid (F). F dissolved completely in HCl and gave white precipitate with $BaCl_2$. Identify (A) to (F) and explain the reaction.

5. A salt of tin (A) gives a basic chloride when dissolved in excess of water. The salt (A) gives grey mass with another substance (D) which on heating gives corrosive sublimate and another compound (B) which is a fuming liquid and fumes more in moist air. Salt of (A) gives blue coloured precipitate (C) with acidified $(NH_4)_2MoO_4$. Identify (A), (B) and (C) and explain the reactions.

6. An inorganic sodium salt (A) gives two colorless gases (B) and (C) leaving a residue (D). B turns white copper sulphate blue, while C turns lime water milky and then colorless. The residual solid (D) when heated strongly gives substance (E) and (F). E gives white precipitate with $BaCl_2$ F when treated with dil. HCl gives a gas (G), which when passed through a solution of SO_2 gives a yellow precipitate due to (H). Identify A to H with proper reasoning.

8. An unknown inorganic compound (X) loses its water of crystallization on heating and its aqueous solution gives the following tests.
   (i) It gives white turbidity with dil HCl
   (ii) It decolorizes a solution of iodine in K I
   (iii) It gives a white ppt with $AgNO_3$ solution which turns black on standing. Identify compound (X) and give chemical equation for the reaction at step (i) , (ii) & (iii).

9. A metal chloride (X) shows the following reactions:—
   (i) When H_2S is passed in acidified aqueous solution of (X) a black precipitate is obtained.
   (ii) The precipitate obtained in step (i) is not soluble in yellow ammonium sulphide.
   (iii) When a solution of stannous chloride is added to an aqueous solution of X, a white precipitate is obtained which turns grey on addition of more stannous chloride.
   (iv) When an aqueous solution of KI is added to an aqueous solution of (X) a red precipitate is obtained which dissolved on addition of excess of KI. Identify X and write down equations for the reactions at step i, ii, iii & iv.

10. A solution of white solid (A) insoluble in water and soluble in conc.HCl on exposure to air gradually turns green. The compound (A) also dissolves in NH_3 to give a colourless solution. But on keeping in air the solution turns dark blue. The ammonical solution of compound (A) forms a red explosive compound with acetylene. Identify , (A) and explain the reactions.

11. An aqueous solution of an inorganic compound (X) gives the following reactions.
    (i) With an aqueous solution of barium chloride a precipitate insoluble in dilute HCl is obtained.
    (ii) Addition of KI gives a brown precipitate which turns white, on addition of excess of hypo
    (iii) With an aqueous solution of $K_4[Fe(CN)_6]$; a chocolate coloured precipitate is obtained. Identify X and give equation for i, ii and iii observations.

12. A certain compound (X) is used in laboratory for analysis. Its aqueous solution gives the following reactions.
    (i) On addition to a copper sulphate solution, a brown precipitate is obtained which turns white

on addition of excess of $Na_2S_2O_3$.

(ii) On addition of Ag^+ ion solution a Yellow curdy precipitate is obtained which is insoluble in aq. NH_3.

(iii) Identify (X) and give reactions at step (i) and (ii).

13. Identify the inorganic salt a whose aqueous solution gives following reactions.

(i) Yellow precipitate with $AgNO_3$ solution, soluble in dil HNO_3

(ii) White precipitate with aq. NH_3 and also with NaOH solution. However the precipitate dissolves in excess of aq. NH_3 and NaOH respectively.

14. A compound X does not give N_2 on heating. Its aqueous solution when heated with caustic soda liberate a gas Y which turns red litmus blue. Heating of alkaline solution of X is continued to expel the gas Y completely. However residual solution again liberates the gas Y when heated with zinc powder. Identify X and Y.

15. A white coloured inorganic salt gives following reactions.

(i) When exposed to H_2S becomes black

(ii) It is decomposed by dil HCl evolving a gas with effervescence, the gas turns lime water milky

(iii) When heated strongly to about 450°C it decomposes to give three gases and leaves a red coloured residue used by housewives. Identify compound X and the four gases evolved during reactions.

16. A well known orange crystalline compound (A) When burnt imparts violet colour to flame when heated with compound (B) in presence of concentrated H_2SO_4 if evolves a red gas C which when passed through alkaline solution of lead acetate gives yellow precipitate of (D). Compound (B) sublimes on heating when B is heated with NaOH, it evolves gas E which fumes with HCl. Identify A to E.

17. An aqueous solution of a gas (X) gives the following reactions.

(i) It decoularises an acidified $K_2Cr_2O_7$ solution.

(ii) On boiling with H_2O_2, cooling it and then adding an aqueous solution of $BaCl_2$, a precipitate insoluble in dil. HCl is obtained.

(iii) On passing H_2S in the solution of gas X in water, a white turbidity is obtained. Identify (X) give equation for steps (i) , (ii) & (iii).

18. A mineral popularly known as apatite is used to prepare a fertilizer, which provides phosphorus element to soil.

(i) The fertilizer is obtained by treating apatite with H_2SO_4

(ii) When heated with silica and coke , it yields white phosphorus and calcium silicate. Suggest formula for apatite and explain the reactions *(i)* and *(ii)*.

EXERCISE-2

1. Two species (A) and (B) exist in equilibrium at pH of about 4 and can be interconverted by changing the pH, (A) dominating at pH 7. Acidified solution of (B) is orange, and on adding H_2O_2 it forms deep blue colour due to the formation of compound (C), this blue colour fades away gradually. Further acidified solution of (B) on reaction with NaCl gives orange red fumes due to the formation of (D). Identify (A), (B), (C), & (D).

2. A salt reacts with NaOH to form a green colored precipitate (X) which is soluble in excess of NaOH. (X) on heating gives a green powder (Y). (Y) on fusion with NaOH in air gives a yellow colored solution (Z). Identify the compound X, Y & Z.

3. Three black powders A, B, C are kept in three dishes. A dissolves in dil H_2SO_4 to give blue solution. Moistened with HCl, A gives a green color in flame test. B does not dissolve in dil HCl but when boiled with concentrated HCl, dissolves giving chlorine. This solution with H_2S in ammonical solution produces a flesh colored precipitate C does not dissolve in HCl but when heated with KNO_3, burns away evolving a gas which turns lime water milky. What are A, B& C ?

4. An aqueous solution of salt (A) gives a white crystalline precipitate (B) with NaCl solution. The filtrate gives a black precipitate (C) when H_2S gas is passed into it. Compound (B) gives precipitate (D) with NaI solution on boiling and cooling. The compound (A) does not give any gas with dil HCl but liberates a reddish brown gas on heating. Identify the compounds A, B, C and D. Write the chemical equations for various reactions involved.

5. A black coloured compound (A) fails to dissolve in dil. H_2SO_4. On heating in air, it gives a gas (B) and a solid (E). (B) gives a white turbidity (D) on passing in a solution of an acid (C). Gas (B) when passed over a solid (I) produces a gas (J). Passing (J) in the blue aqueous solution of (E) gives a precipitate (F) soluble in aq. ammonia, giving a colorless solution (K). The solution turns blue on exposure to air, forming (L). No reaction occurs, however, on passing (B) in (E) directly. To this solution, on addition of acetic acid and aq $K_4[Fe(CN)_6]$, a chocolate precipitate (H) is obtained. On addition of an aqueous solution of $BaCl_2$ to an aqueous solution of (E) a white precipitate insoluble in HNO_3 is obtained. Identify (A) to (K).
6. (A) Gives a blue solution in H_2O. On passing H_2S, a black precipitate (B) is formed which is soluble in HNO_3. On addition of NaOH, the solution gives blue precipitate (C) which becomes black on boiling in NaOH. On passing ammonia into solution of (A) in water, a deep blue precipitate is formed, which dissolves in excess of NH_3 giving deep blue colorations (D). Treatment of KCN with aqueous solution of (A) gives a yellow precipitate (E) which dissolves in excess of KCN giving a colourless solution.
7. A white solid (A) loses on heating one sixth of its weight and becomes a yellow solid (B), (B) on heating in air gains weight & gives a red solid (C). (C) is partly soluble in dil HNO_3 leaving a brown residue (D). (A) is soluble in dil HNO_3 giving effervescence to give a solution (E). (E) reacts with NaOH followed by Cl_2 water to give (D). (A) does not appreciably dissolves in dil HCl or H_2SO_4. Identify (A) to (E).
8. A solution of white solid (A) gave white precipitate (B) with water. On treatment with HCl, the precipitate B produced A. The solution of A gives black precipitate (C) on reacting with sodium stannite and NaOH. The Compound A gives a colorless gas (D) with concentrated H_2SO_4. The gas is soluble in water and its aqueous solution produce white precipitate with $Hg_2(NO_3)_2$ but no precipitate with $Hg(NO_3)_2$. Identify (A) to (D) and write the chemical reactions involved.
9. Compound (A) is greenish solid which gives the following tests : (i) Addition of $BaCl_2$ solution to a solution of (A) results in the formation of a white precipitate (B) which is insoluble in dilute HCl. (ii) On heating water vapours and two oxides of sulphur (C) & (D) are liberated, leaving a red brown residue (E). (iii) Compound (E) dissolves in warm concentrated HCl to give a yellow solution (F). (iv) With H_2S gas, the solution (F) yields a yellow white precipitate. (G) which when filtered leaves a greenish filtrate (H). Identify the compounds A to H.
10. A metallic chloride (A) does not respond to chromyl chloride test. However (A) gives a white precipitate with limited amount of another metal chloride (B) and grey precipitate with excess amount of (B). (A) when treated with KI gives a scarlet red precipitate which dissolves in excess of KI forming an important reagent (C) used in qualitative analysis. Identify (A), (B) and (C). Write all reactions.
11. A pale yellow inorganic compound (A) is insoluble in mineral acid but is soluble in aqueous NH_3 forming (B). It also dissolves in $Na_2S_2O_3$ solution and forms (C). On boiling an aqueous solution of (C), a black precipitate. (D) is obtained. When (D) is dissolved in HNO_3 and HCl is added, a white precipitate. (E) is obtained. (A) on heating with concentrated H_2SO_4 and MnO_2 yields brown fumes. Identify (A) to (E).
12. An aqueous solution of a compound (X) when treated with $BaCl_2$ solution gives a white precipitate in soluble in concentrated HCl. Another sample of (X) gives first white precipitate with NaOH which is soluble in excess of NaOH solution. The solution of (X) does not give the precipitate on passing H_2S gas. (X) produces violet flame test and gives a blue solid when heated in charcoal cavity with a drop of $CO(NO_3)_2$. Identify the compound (X) and give necessary reactions.
13. An aqueous solution of salt (A) gives white crystalline precipitate. (B) with NaCl solution. The filtrate gives a black precipitate. (C) when H_2S is passed in it. Compound (B) is dissolved in hot water and the solution gives a yellow ppt. (D) on treating with NaI and cooling. The compound (A) does not give any gas with dil HCl but liberated reddish brown gas on heating. Identify the compound (A), (B), (C) & (D).
14. A mixture of two white substances is soluble in water. This solution gives brown colour gas on passing chlorine gas. Another sample of solution gives white precipitate with $BaCl_2$ which is soluble in concentrated HCl. The original solution of the mixture gives white precipitate with large excess of NaOH solution whose suspension is used as an antacid. After filtering off this precipitate, the filtrate was boiled with excess NaOH. This solution gave a yellowish precipitate on adding $NaClO_4$. Identify the mixture.
15. An unknown inorganic compound (A) gave the following reactions :
    (i) The compound (A) on heating gave a residue, oxygen and an oxide of nitrogen.
    (ii) An aqueous solution of the compound (A) on addition of tap water gave a turbidity which did not dissolve in nitric acid.
    (iii) The turbidity dissolved in aq. NH_3 solution

16. An orange coloured solid (A) is soluble in water and gives a gas (B) and green coloured solid (C) on heating. The compound (A) gives a gas (D) when reacts with NaOH and solution turns yellow. The gas (D) turns red litmus blue. Identify the compounds (A) to (D) and explain the reaction.

17. A white solid (A) is insoluble in water but soluble in concentrated HCl. It turns green gradually on keeping in air. Solid (A) gives a colourless solution with ammonia. But on keeping in air the solution becomes dark blue in colour. The ammonical solution of solid (A) forms a red explosive compound with acetylene. What is white solid (A). Give the equations of the reactions.

18. A compound (X) on heating with an excess of NaOH solution gives a gas (Y) which gives white fumes on exposure to HCl. Heating is continued to expel the gas completely. The resultant alkaline solution again liberates the same gas Y when heated with Zn powder. However, the compound (X) when heated alone does not give nitrogen. Identify the compounds X and Y.

19. A colorless crystalline solid (A) turns our skin black. It gives two gases (B) and (C) on heating (950°C) along with a residue (D). The gas (B) is soluble in water to give a compound (E). The residue (D) is soluble in (E). The solid (A) gives brown precipitate with NaOH.(A) produces silver mirror with glucose solution. The solid (A) also gives white precipitate with KCN which is soluble in excess of KCN. Identify the compound (A).

20. Mg burns in air to form two compounds (A) and (B). (A) is sparingly soluble in water and the resulting solution is weakly basic. (B) dissolves in water to form (C) and gas (D). Gas (D) with dilute HNO$_3$ gives (E), with percentage composition 35% nitrogen 5 % hydrogen. (E) on heating gives gas (F) which behave as an oxidising agent too. Explain the reaction sequence.

21. A green compound (A) gives black residue (B) on reacting with ammonium sulphide which is soluble in aqua regia. Its solution in aqua regia again gives compound (A). This solution on treatment with KCN and the resulting solution on treatment with NaOH and Br$_2$ water followed by heating gives a black residue. Identify the compounds (A), (B) and (C) and explain the reactions involved.

22. The aqueous solution of a inorganic compound (X) yielded a white precipitate when treated with dil HNO$_3$ and AgNO$_3$. Another sample of the solution of (X) when treated with NaOH gave a white precipitate first which dissolved in excess of NaOH yielding a colorless solution. When H$_2$S gas was passed through that solution a white precipitate was obtained. Identify the compound (X) and give the reactions.

1. Compound A is a light green solid. It gives the following tests :
   (i) It dissolves in dil H$_2$SO$_4$. No gas is produced.

EXERCISE-3(a)

   (ii) A drop of KMnO$_4$ is added to the above solution. The pink colour disappears.
   (iii) Compound A is heated strongly, gases B & C with pungent smell, come out. A brown residue D is left behind.
   (iv) The gas mixture B & C is passed into a dichromate solution. The solution turns green.
   (v) The green solution from step (iv) Gives a white ppt E with a solution of barium nitrate.
   (vi) Residue D from step (iii) is heated on charcoal in a reducing flame. It gives a magnetic substance. Name the compounds A, B, C, O & E. **[IIT — 80]**

2. An unknown solid mixture contains one or two of the following : CaCO$_3$, BaCl$_2$, AgNO$_3$, Na$_2$SO$_4$, ZnSO$_4$ and NaOH. The mixture is completely soluble in water and the solution gives pink colour with phenolphthalein. When 0.1N HCl solution is gradually added to the above solution, a precipitate is produced which dissolves with further addition of the acid, what is / are present in the solid ? Give equations to explain the appearance of the precipitate and its dissolution. **[IIT — 81]**

3. When 16.8 g. of white solid (X) was heated 4.4 g of acid gas (A) that turned lime water milky was driven off together with 1.8 g. of a gas (B) which condensed to a colorless liquid. The solid that remained (Y) dissolved in water to give an alkaline solution, which with excess of BaCl$_2$, solution gave a white precipitate (Z). The precipitate efflorescence with acid giving of CO$_2$ gas. Identify the compounds A, B & Y and write the chemical equations for the thermal decomposition of X. **[IIT — 84]**

4. A compound (A) is greenish crystalline salt, which gave the following results.
   (i) Addition of BaCl$_2$ solution to the solution of (A) results in the formation of a white precipitated (B), which is insoluble in dil HCl.

(ii) On heating (A), water vapors and two oxides of sulphur (C) & (D) are liberated leaving a red brown residue (E).

(iii) (E) dissolves in warm concentrated HCl to give a yellow solution (F).

(iv) With H_2S, the solution (F) yields a pale yellow precipitate (C) which when filtered, l eaves a greenish filtrate (H).

(v) Solution (F) with treatment of thiocyanate ion gives blood red colored compound (I). Identify the substances from (A) to (D). **[IIT — 88]**

5. A mixture of two salts was treated as follows : **[IIT — 87]**

(i) The mixture was heated with MnO_2 & concentrated H_2SO_4, when yellowish green gas was liberated.

(ii) The mixture on heating with NaOH solution gave a gas turned red litmus blue.

(iii) Its solution in water gave blue precipitate with potassium ferricyanide and red coloration with ammonium thiocyanate.

(iv) The mixture was boiled with KOH and the liberated gas was bubbled through on alkaline solution of K_2HgI_4 to give brown precipitate. Identify the two salts. **[IIT 87, REE 88, REE 89]**

6. A hydrated metallic salt (A), light green in color, on careful heating give a white anhydrous (B). (B) is soluble in water and its aqueous solution reacts with No to give a dark brown compound (C). (B) on heating gives a brown residue (D) and a mixture of two gases (E) & (F). The gaseous mixture when passed through acidified permanganate, discharges the pink color and when passed through $BaCl_2$ solution gives a white precipitate. Identify (A) to (F). **[IIT — 88]**

7. When 20.02 g. of a white solid (X) is heated, 4.4g of an acid gas (A) and 1.8g. of a neutral gas (B) are evolute leaving behind a solid residue (Y) of weight 13.8 g. (A) turns lime water milky and (B) condenses into a liquid which changes anhydrous $CuSO_4$ blue. The aqueous solution of (Y) is alkaline to litmus and give 19.7 g of white precipitate (Z) with $BaCl_2$, (Z) gives carbon dioxide with an acid. Identify (A), (B), (X), (Y) and (Z). **[IIT — 89]**

8. The gas liberated on heating a mixture of two salts with NaOH, give a reddish brown precipitate with an alkaline solution of K_2HgI_4. The aqueous solution of the mixture on treatment with $BaCl_2$ gives a white precipitate which is sparingly soluble in concentrated HCl. On heating the mixture with $K_2Cr_2O_7$ and concentrated H_2SO_4, red vapors (A) are produced. The aqueous solution of the mixture gives a deep blue coloration (B) with potassium ferricyanide solution. Identify the radicals. **[IIT — 91]**

9. A light bluish green crystalline solid responds the following tests :

(i) Its aqueous solution gives brown precipitate or color with alkaline K_2HgI_4 solution.

(ii) Its aqueous solution gives blue color with $K_3Fe(CN)_6$ solution.

(iii) Its solution in HCl gives white precipitate with $BaCl_2$ solution. Identify the ions present and suggest formula of compound. **[IIT — 92]**

10. An orange solid (A) on heating gives a green residue (B), a colourless gas (C) and water vapor. The dry gas (C) on passing over heated Mg gave a white solid (D). (D) on reaction with water gave a gas (E) which formed dense white fumes with HCl. Identify (A) to (E) giving reactions. **[IIT — 93]**

11. (A) is binary compound of a univalent metal. 1.422 g of (A) reacts completely with 0.321g. of sulphur in an evacuated and sealed tube to give 1.743 g of a white crystalline solid (B) that formed a hydrated double salt (C) with $Al_2(SO_4)_3$. Identify (A), (B) & (C). **[IIT — 94]**

12. When gas (A) is passed through dry KOH at low temperature, a deep red colored compound (B) and a gas (C) are obtained. The gas (A) on reaction with but—2—ene followed by treatment with $Zn \mid H_2O$ yields acetaldehyde. Identify (A) , (B) & (C). **[IIT — 94]**

13. Calcium burns in nitrogen to produce a white powder which dissolves in sufficient water to produce a gas (A) and an alkaline solution. The solution on exposure to air produces a thin solid layer of (B) on the surface. Identify the compounds (A) and (B). **[IIT — 96]**

14. Gradual addition of KI solution to $Bi(NO_3)_3$ solution initially produces a dark brown precipitate which dissolves in excess of KI to give a clear yellow solution. Write equations for the above reactions. **[IIT — 96]**

15. A colourless inorganic salt [A] decomposes completely at about 250°C to give only two products , (B) and (C) leaving no residue. the oxide (C) is a liquid at room temp. and neutral to moist litmus paper while the gas (B) is a neutral oxide. While phosphorus burns in excess of (B) to produce a strong white dehydrating agent. Write balanced equations for the following reactions involved in the above process.

[IIT — 96]

16. Sodium nitroprusside when added to an alkaline solution of sulphide ions produces purple coloration due to the formation of : [IIT — 95]
(A) $Na_4[Fe(CN)_5NOS]$ (B) $Na_3[Fe(CN)_5NOS]$ (C) $Na_2[Fe(H_2O)_5NOS]$ (D) $Na[Fe(H_2O)_5NOS]$

17. Which of the following anions is not easily removed from aqueous solutions by precipitation ?
(A) Cl^- (B) SO_4^{2-} (C) NO_3^- (D) CO_3^{-2} [IIT — 95]

18. An aqueous solution contains the following ions Hg_2^{2+}, Hg^{2+}, Pb^{+2} & Cd^{2+}. The addition of dil. HCl (6N) precipitates. [IIT — 95]
(A) Hg_2Cl_2 only (B) Hg_2Cl_2 & $PbCl_2$ (C) $PbCl_2$ only (D) $PbCl_2$ & $HgCl_2$

19. Which one of the following pairs of substances, when mixed produces chlorine gas on heating. [IIT 95]
(A) HCl (Conc.) & $KMnO_4$ (B) NaCl & H_2SO_4 (Conc.) (C) NaCl & MnO_2 (D) NaCl & HNO_3 (Conc.)

20. A scarlet compound 'A' is treated with concentrated HNO_3 to give a chocolate brown precipitate 'B'. The precipitate is filtered and the filtrate is neutralised with NaOH. Addition of KI to the resulting solution gives a yellow precipitate 'C'. The precipitate B on warming with concentrated HNO_3 in the presence of $Mn(NO_3)_2$ produces a pink, coloured solution due to the formation of 'D'. Identify 'A', 'B', 'C' & 'D'. Write the reaction sequence. [IIT — 95]

21. (i) An aqueous solution of white coloured compound (A) on reaction with HCl gives a white precipitate of compound (B).
(ii) (B) becomes soluble in chlorine water with formation of (C).
(iii) (C) reacts with KI to give a precipitate which becomes soluble in excess of it forming a compound (D). Compound (D) is used for detecting ammonium salt.
(iv) (B) and (C) both on treatment with $SnCl_2$ give a grey precipitate of (E).
(v) When conc. H_2SO_4 is added slowly into a mixture of cold solution of (A) and $FeSO_4$ a brown ring of compound (F) is formed. Identify (A) to (F). [IIT — 97]

1. An unknown inorganic compound (X) gave the following reactions
(i) The compound (X) on heating gave a residue, oxygen and oxide of nitrogen.

EXERCISE - 3(b)

(ii) An aqueous solution of compound (X) on addition to tap water gave a turbidity which did not dissolve in HNO_3.
(iii) The turbidity dissolved in aq. NH_3. Identify the compound (X) and give equations for the reactions (i), (ii) & (iii). [REE — 85]

2. An unknown inorganic compound (X) loses its water of crystallisation. On heating and its aqueous solution gives the following reactions : [REE — 86]
(i) It gives a white turbidity with dilute HCl solution.
(ii) It decolorises a solution of iodine in KI.
(iii) It gives a white precipitate with $AgNO_3$ solution, which turns black on standing.
Identify compound (X) and give chemical equations for the reactions at step (i), (ii) & (iii).

3. A certain inorganic compound (A) on heating loses water of crystallisation. On further heating a blackish brown powder (B) and two oxides of sulphur (C & D) are obtained. The powder (B) on boiling with HCl gives a yellow solution (E). When H_2S is passed in (E) a white turbidity (F) and an apple green solution (G) is obtained. The solution (E) on treatment with thiocyanate ion gives blood red compound (H). Identify (A) to (H). [REE—86]

4. Identify (A), (B), (C) & (D) and give their chemical formulae :
(i) $(A) + NaOH \xrightarrow{heat} NaCl + NH_3 + H_2O$ (ii) $NH_3 + CO_2 + H_2O \longrightarrow (B)$
(iii) $(B) + NaCl \longrightarrow (C) + NH_4Cl$ (iv) $(C) \xrightarrow{heat} Na_2CO_3 + H_2O + (D)$ [REE — 86]

5. A black coloured compound (A) on reaction with dilute H_2SO_4 gives a gas (B) which on passing in a solution of an acid (C) gives a white turbidity (D). Gas (B) when passed in an acidified solution of a compound (E) gives a precipitate (F) soluble in dilute HNO_3. After boiling this solution when an excess

of aq. NH_3 is added , a blue coloured compound (G) is formed. To this solution on addition of acetic acid and aqueous $K_4Fe(CN)_6$ a chocolate precipitate (H) is obtained. On addition of an aqueous solution of $BaCl_2$ to an aqueous solution of (E) , a white precipitate insoluble in HNO_3 is obtained. Identify from (A) to (H). **[REE — 87]**

6. On the basis of following reaction , Identify (A) , (B) , (C) & (D) and write down their chemical formulae?

(i) (A) aqueous + Zn $\xrightarrow{\text{heat}}$ (B) gas (ii) (A) aqueous + (C) $\xrightarrow{\text{heat}}$ PH_3 **[REE — 87]**

(iii) (A) aqueous + NH_4Cl $\xrightarrow{\text{heat}}$ (D) gas

7. An aqueous solution of inorganic compound (X) gives following reactions : **[REE — 89]**
   (i) With an aqueous solution of $BaCl_2$ a precipitate insoluble in dilute HCl is obtained.
   (ii) Addition of excess of KI gives a brown precipitate which turns white on addition of excess of hypo
   (iii) With an aqueous solution of $K_4Fe(CN)_6$ a chocolate coloured precipitate is obtained.
   Identify (X) and give equations for the reaction for (i) , (ii) & (iii) observations.
8. An inorganic compound (X) gives brick red flame on performing the flame test. This also give the following tests : **[REE — 89]**
   (i) Smell of chlorine when placed in moist air.
   (ii) If KI & CH_3COOH are added to its suspension in water , a brown colour is obtained.
   Identify (X) and write down equations for reactions at step (i) & (ii).
9. A compound (X) imparts a golden yellow flame and shows the following reactions : **[REE — 90]**
   (i) Zn powder when boiled with a conc. aqueous solution of (X) dissolves and hydrogen is evolved.
   (ii) When an aqueous solution of (X) is added to an aqueous solution of stannous chloride , a white precipitate is obtained first which dissolves in excess of solution of (X).
   Identify (X) and write equations at step (i) & (ii).
10. A certain metal (A) is boiled in dilute HNO_3 to give a salt (B) and an oxide of nitrogen (C). An aqueous solution of (B) with brine gives a precipitate (D) which is soluble in aq. NH_3. On adding aqueous solution of (B) to hypo solution, a white precipitate (E) is obtained. (E) turns black on standing. Identify (A) to (E). **[REE — 90]**
11. An aqueous solution of a gas (X) gives the following reactions : **[REE — 90]**
    (i) It decolourises an acidified $K_2Cr_2O_7$ solution.
    (ii) On boiling it with H_2O_2 , cooling it & then adding an aqueous solution of $BaCl_2$ a precipitate insoluble in dilute HCl is obtained.
    (iii) On passing H_2S in the solution a white turbidity is obtained.
    Identify (X) and give equations for the reactions at steps (i) , (ii) & (iii).
12. A metal chloride (X) shows the following reactions : **[REE — 91]**
    (i) When H_2S is passed in an acidified aqueous solution of (X) a black precipitate is obtained.
    (ii) The precipitate obtained in step (i) is not soluble in yellow ammonium sulphide.
    (iii) When a solution of stannous chloride is added to an aqueous solution of (X) , a white precipitate is obtained which turns grey on addition of more of stannous chloride.
    (iv) When an aqueous solution of KI is added to an aqueous solution of (X), a red precipitate is obtained which dissolves on addition of excess of KI.
    Identify (X) and write down the equations for the reactions at steps (i), (iii) & (iv)
13. An aqueous solution of a gas (X) shows the following reactions :
    (i) It turns red litmus blue.
    (ii) When added in excess to a $CuSO_4$ solution , a deep blue colour is obtained.
    (iii) On addition of $FeCl_3$ solution a brown precipitate soluble in dilute HNO_3 is obtained.
    Identify (X) and give equations for the reactions at step (ii) & (iii). **[REE — 91]**
14. A certain compound (X) is used in laboratory for analysis. Its aqueous solution gave the following reactions :

(i) On addition to $CuSO_4$ solution , a brown precipitate is obtained which turns white on addition of excess of $Na_2S_2O_3$ solution.

(ii) On addition to Ag+ ion solution a yellow curdy precipitate is obtained which is insoluble in aq. NH_3.

Identify (X) giving reactions. **[REE — 91]**

15. A certain salt (X) gives the following tests : **[REE — 92]**

(i) Its aqueous solution is alkaline to litmus.

(ii) On strongly heating it swells to give glassy material.

(iii) When conc. H_2SO_4 is added to a hot conc. solution of (X) , white crystals of weak acid separate out.

Identify (X) and write down the chemical equations for reactions at steps (i), (ii) & (iii).

16. A certain compound (X) shows the following reactions : **[REE — 92]**

(i) When KI is added to an aqueous suspension of (X) containing acetic acid , iodine is liberated.

(ii) When CO_2 is passes through an aqueous suspension of (X) the turbidity transforms to a precipitate.

(iii) When a part of (X) in water is heated with ethyl alcohol , a product of anaesthetic use is obtained.

Identify (X) and write down chemical equations for reaction at step (i), (ii) & (iii).

17. An aqueous solution of an inorganic compound (X) shows the following reactions **[REE — 93]**

(i) It decolorizes an acidified $KMnO_4$ solution accompanied with evolution of oxygen.

(ii) It liberates I_2 from acidified KI solution.

(iii) It gives brown precipitate with alkaline $KMnO_4$ solution with evolution of O_2.

(iv) It removes black stains from old oil painting.

Identify (X) and give chemical reactions for the steps (i) to (iv).

18. Two solid laboratory reagents (A) & (B) give following reactions :

Compound (A) :

(i) On strongly heating it gives two oxides of sulphur.

(ii) On adding aqueous NaOH solution to its aqueous solution , a dirty green precipitate is obtained which starts turning brown on exposure to air.

Compound (B) :

(i) It imparts green colour to flame.

(ii) Its solution doesn't give precipitate on passing H_2S.

(iii) When it is heated with $K_2Cr_2O_7$ & conc. H_2SO_4 , a red gas is evolved. The gas when passed in aqueous NaOH solution turns it yellow.

Identify (A) & (B) and give chemical reactions. **[REE — 93]**

19. Identify (A) to (D) in following steps and give chemical equations : **[REE — 93]**

(i) A white amorphous powder (A) on heating yields a colorless, non—combustible gas (B) and a solid (C).

(ii) The gas (B) turns lime water milky but the milkiness disappears with the continuous passage of the gas.

(iii) Compound (C) dissolves in dilute acid gives a white precipitate on addition of $K_4[Fe(CN)_6]$ solution.

(iv) The solution of (A) gives a white precipitate (D) on the addition of excess of aq. NH_3 and passing H_2S.

20. (i) A black mineral (A) on heating in presence of air gives a gas (B). **[REE — 94]**

(ii) The mineral (A) on reaction with dil. H_2SO_4 gives a gas (C) & solution of a compound (D)

(iii) On passing gas (C) into an aqueous solution of (B) a white turbidity is obtained.

(iv) The aqueous solution of compound (D) on reaction with potassium ferricyanide gives a blue compound (E). Identify (A) to (E) and give chemical equations for reactions at steps (i) to (iv)

21. An inorganic lewis acid (X) shows the following reactions
    - (i) It fumes in moist air.
    - (ii) The intensity of fumes increases when a rod dipped in aq. NH_3 is brought near it.
    - (iii) An acidic solution of (X) on addition of NH_4Cl & aq. NH_3 gives a precipitate which dissolves in NaOH solution.
    - (iv) An acidic solution of (X) does not give precipitate with H_2S.

    Identify (X) and give chemical equations. **[REE — 94]**

22. The certain inorganic compound (X) shows the following reactions :
    - (i) On passing H_2S through an acidified solution of (X) a brown precipitate is obtained.
    - (ii) The precipitate obtained at step (i) dissolves in excess of yellow ammonium sulphide.
    - (iii) On adding an aqueous solution of NaOH to a solution of (X) , first a white precipitate is obtained which dissolves in excess of NaOH.
    - (iv) The aqueous solution of (X) reduces $FeCl_3$.

    Identify (X) cation and give chemical equations. **[REE — 94]**

23. (i) An inorganic iodide (A) on heating with a solution of KOH gives a gas (B) and the solution of a compound (C).
    - (ii) The gas (B) on ignition in air gives a element (D) and water.
    - (iii) $CuSO_4$ is finally reduced to the metal on passing (B) through its solution.
    - (iv) A precipitate of compound (E) is formed on reaction of (C) with $CuSO_4$ solution. Identify (A) to (E) and give chemical equation. **[REE — 94]**

24. (i) An inorganic compound (A) is formed on passing a gas (B) through a conc. liquor containing Na_2S and sodium sulphite.
    - (ii) On adding (A) into a dilute solution of silver nitrate a white precipitate appears which quickly changes into a black coloured compound (C).
    - (iii) On adding two or three drops of $FeCl_3$ into the excess of solution (A) a violet coloured compound (D) is formed. This colour disappears quickly.
    - (iv) On adding a solution of (A) into the solution of cupric chloride , a white precipitate is first formed which dissolves on adding excess of (A) forming a compound (E).

    Identify (A) to (E) and give chemical equations for the reaction at steps (i) to (iv). **[REE — 96]**

25. (i) A black coloured compound (B) is formed on passing H_2S through the solution of a compound (A) in aq. NH_3.
    - (ii) (B) on treatment with HCl and potassium chlorate gives (A).
    - (iii) (A) on treatment with KCN gives a buff coloured precipitate which dissolves in excess of this reagent forming a compound (C).
    - (iv) The compound (C) is changed into a compound (D) when its aqueous solution is boiled
    - (v) The solution of (A) was treated with excess of $NaHCO_3$ & then with bromine water. On cooling & shaking for some time , a green colour of compound (E) is formed. No change is observed on heating.

    Identify (A) to (E) and give chemical equations. **[REE — 96]**

26. (i) A blue coloured compound (A) on heating gives two product (B) & (C). **[REE — 97]**
    - (ii) A metal (D) is deposited on passing hydrogen through heated (B).
    - (iii) The solution of (B) in HCl on treatment with the $[Fe(CN)_6]$ gives a chocolate brown coloured precipitate of compound (E).
    - (iv) (C) turns lime water milky which disappears on continuous passage of (C) forming a compound (F). Identify (A) to (F) and give chemical equations for the reactions at step (i) to (iv).

BANSALCLASSES

TARGET IIT JEE 2007

INORGANIC CHEMISTRY

XIII (XYZ)

S-BLOCK ELEMENTS

GROUP -I & II

OXIDES

Sodium Oxide (Na_2O):

Preparation :

(i) It is obtained by burning sodium at 180°C in a limited supply of air or oxygen and distilling off the excess of sodium in vacuum.

$$2Na + \frac{1}{2}O_2 \xrightarrow{180°} Na_2O$$

(ii) By heating sodium peroxide, nitrate or nitrate with sodium.

$Na_2O_2 + 2Na \longrightarrow 2Na_2O$

$2NaNO_3 + 10Na \longrightarrow 6Na_2O + N_2$

$2NaNO_2 + 6Na \longrightarrow 4Na_2O + N_2$

Properties :

(i) It is white amorphous mass.

(ii) It decomposes at 400°C into sodium peroxide and sodium

$$2Na_2O \xrightarrow{400°C} Na_2O_2 + 2Na$$

(iii) It dissolve violently in water, yielding caustic soda.

$$Na_2O + H_2O \longrightarrow 2NaOH$$

Sodium Peroxides (Na_2O_2):

Preparation: It is formed by heating the metal in excess of air or oxygen at 300°, which is free from moisture and CO_2.

$$2Na + O_2 \longrightarrow Na_2O_2$$

Properties:

(i) It is a pale yellow solid, becoming white in air from the formation of a film of NaOH and Na_2CO_3.

(ii) In cold water (~0°C) produces H_2O_2 but at room temperature produces O_2. In ice-cold mineral acids also produces H_2O_2.

$$Na_2O_2 + 2H_2O \xrightarrow{\sim 0°C} 2NaOH + H_2O_2$$

$$2Na_2O_2 + 2H_2O \xrightarrow{25°C} 4NaOH + O_2$$

$$Na_2O_2 + H_2SO_4 \xrightarrow{\sim 0°C} Na_2SO_4 + H_2O_2$$

(iii) It reacts with CO_2, giving sodium carbonate and oxygen and hence its use for purifying air in a confined space e.g. submarine, ill-ventilated room,

$$2Na_2O_2 + 2CO_2 \longrightarrow 2Na_2CO_3 + O_2$$

(iv) It is an oxidising agent and oxidises charcoal, CO, NH_3, SO_2.

$3Na_2O_2 + 2C \longrightarrow 2Na_2CO_3 + 2Na$ [deposition of metallic Na]

$CO + Na_2O_2 \longrightarrow Na_2CO_3$

$SO_2 + Na_2O_2 \longrightarrow Na_2SO_4$

$2NH_3 + 3Na_2O_2 \longrightarrow 6NaOH + N_2$

(v) It contains peroxide ion $[-O-O-]^{-2}$

Uses:

(i) For preparing H_2O_2, O_2

(ii) Oxygenating the air in submarines

(iii) Oxidising agent in the laboratory.

Oxides of Potassium:

	K_2O,	K_2O_2,	K_2O_3,	KO_2	and	KO_3
Colours:	White	White	Red	Bright Yellow		Orange Solid

Preparation:

(i) $2KNO_3 + 10K \xrightarrow{\text{heating}} 6K_2O + N_2$

** $\underset{\text{(White)}}{K_2O} \xrightarrow{\text{heating}} \underset{\text{(Yellow)}}{K_2O}$

** $K_2O + H_2O \longrightarrow 2KOH$

(ii) $2K + O_2 \xrightarrow[\text{air at 300°C}]{\text{Controlled}} K_2O_2$ [Props: Similar with Na_2O_2]

(iii) Passage of O_2 through a blue solution of K in liquid NH_3 yields oxides K_2O_2 (white), K_2O_3 (red) and KO_2 (deep yellow) i.e

$$\text{K in liq. } NH_3 \xrightarrow{O_2} \underset{\text{white}}{K_2O_2} \longrightarrow \underset{\text{red}}{K_2O_3} \longrightarrow \underset{\text{yellow}}{KO_2}$$

** KO_2 reacts with H_2O and produces H_2O_2 and O_2 both

$$2KO_2 + 2H_2O \longrightarrow 2KOH + H_2O_2 + O_2$$

KO_3 : $\underset{\text{(Dry powdered)}}{KOH} + O_3 \text{ (ozonised oxygen)} \xrightarrow{-10°\text{to}-15°C} \underset{\text{(orange solid)}}{KO_3}$

Magnesium Oxide (MgO):

It is also called magnesia and obtained by heating natural magnesite.

$$MgCO_3 \longrightarrow MgO + CO_2$$

Properties:

(i) It is white powder.

(ii) It's m.p. is 2850°C. Hence used in manufacture of refractory bricks for furances.

(iii) It is very slightly soluble in water imparting alkaline reaction.

Calcium Oxide (CaO):

It is commonly called as quick lime or lime and made by decomposing lime stone at a high temperature about 1000°C.

$$CaCO_3 \longrightarrow CaO + CO_2 + 42000 \text{ cal}$$

Properties:

(i) It is white amorphous powder of m.p. 2570°C.

(ii) It emits intense light (lime light), when heated in oxygen-hydrogen flame.

(iii) It is an basic oxide and combines with some acidic oxide e.g.

$$CaO + SiO_2 \longrightarrow CaSiO_3$$
$$CaO + CO_2 \longrightarrow CaCO_3$$

(iv) It combines with water to produce slaked lime.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

Magnesium Peroxide (MgO_2) and Calcium Peroxide (CaO_2):

These are obtained by passing H_2O_2 in a suspension of $Mg(OH)_2$ and $Ca(OH)_2$.

Uses: MgO_2 is used as an antiseptic in tooth paste and as a bleaching agent.

HYDROXIDES

Sodium Hydroxides:

Preparation:

(i) Electrolysis of Brine :

$NaCl \rightleftharpoons Na^+ + Cl^-$

At anode : $2Cl^- \longrightarrow Cl_2 + 2e$

At cathode : $H^+ + e^- \longrightarrow H$

(ii) Caustication of Na_2CO_3 (Gossage's method):

$$\underset{\text{(suspension)}}{Na_2CO_3 + Ca(OH)_2} \rightleftharpoons 2NaOH + CaCO_3\downarrow$$

Since the $K_{sp}(CaCO_3) < K_{sp}(Ca(OH)_2)$, the reaction shifts towards right.

Properties:

(i) It is white crystalline, deliquescent, highly corrosive solid.

(ii) It is stable towards heat.

(iii) It's aqueous solution alkaline in nature and soapy in touch.

(iv) $NH_4Cl + NaOH \longrightarrow NaCl + NH_3\uparrow + H_2O$

$$FeCl_3 + 3NaOH \longrightarrow \underset{\text{Brown ppt}}{Fe(OH)_3\downarrow} + 3NaCl$$

$$ZnCl_2 + 2NaOH \longrightarrow Zn(OH)_2\downarrow + 2NaCl$$

$$Zn(OH)_2\downarrow + 2NaOH \xrightarrow{\text{Excess}} \underset{\text{soluble}}{Na_2ZnO_2} + 2H_2O$$ [Same with $AlCl_3$, $SnCl_2$, $PbCl_2$]

(v) Acidic and amphoteric oxides gets dissolved easily e.g.

$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$

$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$

(vi) Aluminium and Zn metal gives H_2 from NaOH

$2Al + 2NaOH + 2H_2O \longrightarrow 3H_2 + 2NaAlO_2$

(vii) Several non metals such as P, S, Cl etc. yield a hydride instead of hydrogen.e.g.

$4P + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$ (Disproportionation reaction)

Potassium Hydroxide:

Preparation: Electrolysis of KCl aqueous solution.

Properties: Same as NaOH

**(a) It is stronger base compared to NaOH.

(b) Solubility in water is more compared to NaOH.

(c) In alcohol, NaOH is sparingly soluble but KOH is highly soluble.

(d) As a reagent KOH is less frequently used but in absorption of CO_2, KOH is preferably used compared to NaOH. Because $KHCO_3$ formed is soluble whereas $NaHCO_3$ is insoluble and may therefore choke the tubes of apparatus used.

Magnesium Hydroxide: It occurs in nature as the mineral brucite.

Preparation: It can be prepared by adding caustic soda solution to a solution of Mg-sulphate or chloride solution.

$$Mg^{+2} + 2NaOH \longrightarrow Na_2SO_4 + Mg(OH)_2$$

Properties:

(i) It can be dried at temperature upto 100°C only otherwise it breaks into its oxide at higher temperature.

$Mg(OH)_2 \longrightarrow MgO + H_2O$

(ii) It is slightly soluble in water imparting alkalinity.

(iii) It dissolves in NH_4Cl solution

$$Mg(OH)_2 + 2NH_4Cl \longrightarrow MgCl_2 + 2NH_4OH$$

** Thus, $Mg(OH)_2$ is not therefore precipitated from a solution of Mg^{+2} ions by NH_4OH in presence of excess of NH_4Cl.

Calcium Hydroxide:

Preparation: By spraying water on quicklime

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

Properties:

(i) It is sparingly soluble in water.

(ii) It's solubility in hot water is less than that of cold water. Hence solubility decreases with increase in temperature.

(iii) It readily absorbs CO_2 as used as a test for the gas.

(iv) It is used as a mortar.
[Mortar is a mixture of slaked lime (1 Part) and sand (3 Parts) made into paste with water.]

CARBONATES

Sodium Carbonate:

Preparation:

(i) Leblanc Process:

$$NaCl + H_2SO_4\ (conc.) \xrightarrow{\text{mild heating}} NaHSO_4 + HCl$$

$$NaCl + NaHSO_4 \xrightarrow[\text{heated}]{\text{Strongly}} \underset{\text{(Salt Cake)}}{Na_2SO_4} + HCl$$

$$Na_2SO_4 + 4C \longrightarrow Na_2S + 4CO\uparrow$$

$$Na_2S + CaCO_3 \longrightarrow Na_2CO_3 + CaS$$

(ii) Solvay Process:

$$NH_3 + H_2O + CO_2 \longrightarrow NH_4HCO_3$$

$$NaCl + NH_4HCO_3 \longrightarrow NaHCO_3 + NH_4Cl$$

$$2NaHCO_3 \xrightarrow{150^\circ C} Na_2CO_3 + H_2O + CO_2$$

Properties:

(i) Anhydrous Na_2CO_3 is called as soda ash, which does not decompose on heating but melts at 852 °C.

(ii) It forms number of hydrates.

$Na_2CO_3.\ H_2O \longrightarrow$ Crystal carbonate $\longleftarrow Na_2CO_3$ + moisture in air

$Na_2CO_3.\ 7H_2O \longrightarrow$ ———

$Na_2CO_3.10H_2O \longrightarrow$ Washing soda

(iii) Na_2CO_3 absorbs CO_2 yielding sparingly soluble sodium bicarbonate which can be calcined at 250° to get pure sodium carbonate.

$$Na_2CO_3 + H_2O + CO_2 \underset{250^\circ C}{\rightleftharpoons} 2NaHCO_3$$

(iv) It dissolved in acid with effervescence of CO_2 and causticised by lime to give caustic soda.

$$Na_2CO_3 + HCl \longrightarrow 2NaCl + H_2O + CO_2$$

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow 2NaOH + CaCO_3$$

Uses: It is widely used in glass making as smelter.

Potassium Carbonate:

By leblance process, it can be prepared but by solvay process it cannot be prepared because $KHCO_3$ is soluble in water.

Properties: It resembles with Na_2CO_3, m.p. is 900°C but a mixture of Na_2CO_3 and K_2CO_3 melts at 712°C.

Uses: It is used in glass manufacturing.

Calcium Carbonate:

It occurs in nature as marble, limestone, chalk, coral, calcite etc. It is prepared by dissolving marble or limestone in HCl and removing iron and aluminium present, by precipitating with NH_3 and then adding $(NH_4)_2CO_3$ to the solution.

$$CaCl_2 + (NH_4)_2CO_3 \longrightarrow CaCO_3 + 2NH_4Cl$$

Properties:

(i) It dissociates above 1000°C as follows:

$$CaCO_3 \longrightarrow CaO + CO_2$$

(ii) It dissolves in water containing CO_2 forming $Ca(HCO_3)_2$ but is precipitated from the solution by boiling.

$$CaCO_3 + H_2O + CO_2 \underset{\text{boiling}}{\rightleftharpoons} Ca(HCO_3)_2$$

Magnesium Carbonate:

It occurs in nature as magnesite, isomorphous with calcite. It is obtained as a white precipitated by adding sodium bicarbonate to a solution of a magnesium salt; but only basic carbonate, called magnesia alba, having the approximate composition $MgCO_3$, $Mg(OH)_2$, $3H_2O$ is precipitated.

Properties: Same with $CaCO_3$.

BICARBONATES

Sodium bicarbonates:

Preparation: By absorption of CO_2 in Na_2CO_3 solution.

$$Na_2CO_3 + H_2O + CO_2 \underset{> 100°C}{\rightleftharpoons} \underset{\text{sparingly soluble}}{2NaHCO_3}$$

Uses: It is used in medicine and as baking powder.

Potassium bicarbonates:

Preparation: Same as $NaHCO_3$

Properties: Same with $NaHCO_3$

But It is more alkaline and more soluble in water compared to $NaHCO_3$.

Magnesium bicarbonate:

$$MgCO_3 + CO_2 + H_2O \underset{\text{boil i g}}{\rightleftharpoons} Mg(HCO_3)_2$$

Calcium bicarbonate:

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca(HCO_3)_2$$

CHLORIDES

Sodium Chloride: Prepared from brine containing 25% NaCl.

Properties:

(i) It is nonhygroscopic but the presence of $MgCl_2$ in common salt renders it hygroscopic.

(ii) It is used to prepare freezing mixture in laboratory [Ice-common salt mixture is called freezing mixture and temperature goes down to –23°C.]

(iii) For melting ice and snow on road.

Potassium Chloride: It is also occurs in nature as sylvyne (KCl) or carnalite ($2KCl$, $MgCl_2$, $6H_2O$)

Uses: It is used as fertiliser.

Magnesium Chloride:

Preparation: By dissolving $MgCO_3$ in dil. HCl

$$MgCO_3 + 2HCl \longrightarrow MgCl_2 + H_2O + CO_2$$

Properties:

(i) It crystallises as hexahydrate. $MgCl_2 . 6H_2O$

(ii) It is deliquescent solid.

(iii) This hydrate undergoes hydrolysis as follows:

$$MgCl_2\cdot 6H_2O \longrightarrow Mg(OH)Cl + HCl + 5H_2O$$
$$Mg(OH)Cl \longrightarrow MgO + HCl$$

** Hence, Anh. $MgCl_2$ cannot be prepared by heating this hydrate.

** Because of this formation of HCl. Sea water cannot be used in marine boilers which corrodes the iron body.

(iv) Anhydrous $MgCl_2$ can be prepared by heating a double salt like. $MgCl_2 . NH_4Cl . 6H_2O$ as follows:

$$MgCl_2 . NH_4Cl . 6H_2O \xrightarrow[\Delta]{-H_2O} MgCl_2 . NH_4Cl \xrightarrow[\Delta]{\text{strong}} MgCl_2 + NH_3 + HCl$$

Sorel Cement: It is a mixture of MgO and $MgCl_2$ (paste like) which set to hard mass on standing. This is used in dental filling, flooring etc.

Calcium Chloride:

(i) It is the by-product in solvay process.

(ii) It may also be prepared by dissolving the carbonate in HCl

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$$

Properties:

(i) It is deliquescent crystals.

(ii) It gets hydrolysed like $MgCl_2$ hence anhydrous $CaCl_2$ cannot be prepared.

$$CaCl_2 + H_2O \rightleftharpoons CaO + 2HCl$$

Hence, anh $CaCl_2$ is prepared by heating $CaCl_2 . 6H_2O$ in a current of HCl (dry)

(iii) Anh. $CaCl_2$ is used in drying gases and organic compounds but not NH_3 or alcohol due to the formation of $CaCl_2 . 8NH_3$ and $CaCl_2 . 4C_2H_5OH$.

SULPHATES

Sodium Sulphate:

Preparation:

It is formed in the 1st step of leblanc process by heating common salt with sulphuric acid.

$$2NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2HCl$$

Thus the salt cake formed is crystallised out from its aqueous solution as $Na_2SO_4 . 10H_2O$. This called as Glauber's salt.

** One interesting feature of the solubility of glauber's salt is; when crystallised at below 32.4°C, then $Na_2SO_4 . 10H_2O$ is obtained but above 32.4°C, Na_2SO_4 (anh.) comes out.

Properties: It is reduced to Na_2S when fused with carbon.

$$Na_2SO_4 + 4C \longrightarrow Na_2S + 4CO$$

Uses: It is used in medicine.

Potassium Sulphate:

It occurs in stassfurt potash beds as schonite K_2SO_4, $MgSO_4$, $6H_2O$ and Kainite, KCl, $MgSO_4$, $3H_2O$ from which it is obtained by solution in water and crystallisation. It separates from the solution as anh, crystals whereas Na_2SO_4 comes as decahydrate.

Uses: It is used to prepare alumn.

Magnesium Sulphate:

Preparation:

(i) It is obtained by dissolving kieserite. $MgSO_4.H_2O$ in boiling water and then crystallising the solution as a hepta hydrate. i.e. $MgSO_4.7H_2O$. It is called as Epsom salt.

(ii) It is also obtained by dissolving magnesite in hot dil. H_2SO_4.

$$MgCO_3 + H_2SO_4 \longrightarrow MgSO_4 + H_2O + CO_2$$

(iii) or by dissolving dolomite ($CaCO_3, MgCO_3$) in hot dil. H_2SO_4 and removing the insoluble $CaSO_4$ by filtration.

(iv) It is isomorphous with $FeSO_4.7H_2O$, $ZnSO_4.7H_2O$

Calcium Sulphate: It occurs as anhydrite $CaSO_4$ and as the dihydrate $CaSO_4.2H_2O$, gypsum, alabaster or satin-spar.

Properties:

(i)

$$\begin{tikzcd}
\text{Gypsum } (CaSO_4.2H_2O) \arrow[r, shift left, "120^\circ C"] & 2CaSO_4.H_2O \text{ (Plaster of paris)} \arrow[l, shift left, "+H_2O"] \arrow[d, "200^\circ C"] \\
& \text{(anhydrous)}CaSO_4. \\ & \text{Dead burnt. plaster}
\end{tikzcd}$$

(ii) Solubility of $CaSO_4$ at first increases upto a certain point and then decreases with rise of temperature.

(iii) Plaster paris is used in mould making due to its porous body.

BANSALCLASSES

TARGET IIT JEE 2007

INORGANIC CHEMISTRY

XII (ALL)

QUESTION BANK ON

'S-BLOCK ELMENTS

S-BLOCK ELEMENTS

Q.1 Cs^+ ions impart violet colour to Bunsen flame. This is due to the fact that the emitted radiations are of
(A) high energy (B) lower frequencies (C) longer wave-lengths (D) zero wave number

Q.2 The compound(s) of alkaline earth metals, which are amphoteric in nature is/are
(A) BeO (B) MgO (C) $Be(OH)_2$ (D) $Mg(OH)_2$

Q.3 An alkaline earth metal (M) gives a salt with chlorine, which is ~~in~~soluble in water at room temperature ~~but soluble in boiling water~~. It also forms an insoluble sulphate whose mixture with a sulphide of a transition metal is called 'lithopone' -a white pigment. Metal M is [$BaSO_4 + ZnS$]
(A) Ca (B) Mg (C) Ba (D) Sr

Q.4 The reaction of an element A with water produces combustible gas B and an aqueous solution of C. When another substance D reacts with this solution C also produces the same gas B. D also produces the same gas even on reaction with dilute H_2SO_4 at room temperature. Element A imparts golden yellow colour to Bunsen flame. Then, A, B, C and D may be identified as
(A) Na, H_2, NaOH and Zn (B) K, H_2, KOH and Zn
(C) K, H_2, NaOH and Zn (D) Ca, H_2, $CaCOH_2$ and Zn

increases down the group

Q.5 The hydroxide of alkaline earth metal, which has the lowest value of solubility product (K_{sp}) at normal temperature (25°C) is
(A) $Ca(OH)_2$ (B) $Mg(OH)_2$ (C) $Sr(OH)_2$ (D) $Be(OH)_2$

Q.6 The correct statement is/are
(A) $BeCl_2$ is a covalent compound (B) $BeCl_2$ is an electron deficient molecule
(C) $BeCl_2$ can form dimer (D) the hybrid state of Be in $BeCl_2$ is sp^2

Be & Mg hydroxide insoluble

Q.7 (Yellow ppt) $T \xleftarrow{[K_2CrO_4/CH_3COOH]} X \xrightarrow{dil.HCl} Y$(Yellow ppt) + Z↑ (pungent smelling gas)
If X gives green flame test. Then, X is
(A) $MgSO_4$ (B) BaS_2O_3 (C) $CuSO_4$ (D) PbS_2O_3

Q.8 Which of the following carbonate of alkali metals has the least thermal stability?
(A) Li_2CO_3 (B) K_2CO_3 (C) Cs_2CO_3 (D) Na_2CO_3

Q.9 The 'milk of magnesia' used as an antacid is chemically
(A) $Mg(OH)_2$ (B) MgO (C) $MgCl_2$ (D) MgO + $MgCl_2$

Q.10 The alkali metals which form normal oxide, peroxide as well as super oxides are
(A) Na, Li (B) K, Li (C) Li, Cs (D) K, Rb

Q.11 The pair of compounds, which cannot exist together in a solution is
(A) $NaHCO_3$ and NaOH (B) Na_2CO_3 and NaOH
(C) $NaHCO_3$ and Na_2CO_3 (D) $NaHCO_3$ and H_2O

Q.12 $Mg_2C_3 + H_2O \longrightarrow X$ (organic compound). Compound X is
(A) C_2H_2 (B) CH_4 (C) propyne (D) ethene

Q.13 The hydration energy of Mg^{2+} is
(A) more than that of Mg^{3+} ion (B) more than that of Na^+ ion
(C) more than that of Al^{3+} ion (D) more than that of Be^{2+} ion

Q.14 The golden yellow colour associated with NaCl to Bunsen flame can be explained on the basis of
(A) low ionisation potential of sodium (B) emission spectrum
(C) photosensitivity of sodium (D) sublimation of metallic sodium of yellow vapours

Q.15 Solution of sodium metal in liquid ammonia is a strong reducing agent due to presence of
(A) solvated sodium ions (B) solvated hydrogen ions
(C) sodium atoms or sodium hydroxide (D) solvated electrons

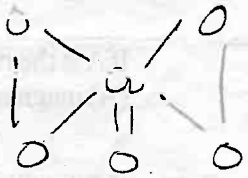
Q.16 Which of the property of alkali metals is not listed correctly?
(A) the least electronegative metal : Cs (B) a natural radioactive metal : Fr
(C) the alkali metal with lowest density : K (D) the heaviest alkali metal : Cs
(Li) ✓

Q.17 The salt which finds uses in qualitative inorganic analysis is
(A) $CuSO_4 \cdot 5H_2O$ or $ZnSO_4 \cdot 5H_2O$ (B) $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
(C) $Na(NH_4)HPO_4 \cdot 4H_2O$ → microcosmic salt (D) $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$
↳ we can identify cations

Q.18 Fire extinguishers contain
(A) conc. H_2SO_4 solution (B) H_2SO_4 and $NaHCO_3$ solutions → CO_2
(C) $NaHCO_3$ solution (D) $CaCO_3$ solution

Q.19 $CsBr_3$ contains
(A) Cs–Br covalent bonds (B) Cs^{3+} and Br^- ions
(C) Cs^+ and Br_3^- ions (D) Cs^{3+} and Br_3^{3-} ions

Q.20 KO_2 finds use in oxygen cylinders used for space and submarines. The fact(s) related to such use of KO_2 is/are
(A) it produces O_2 (B) it produces O_3
(C) it absorbs CO_2 (D) it absorbs both CO and CO_2



Q.21 The compound(s) which have –O–O– bond(s) is/are
(A) BaO_2 (B) Na_2O_2 (C) CrO_5 (ionic) (D) Fe_2O_3

Q.22 $Na + Al_2O_3 \xrightarrow{\text{High temperature}} X; \xrightarrow[\text{water}]{CO_2\text{ in}} Y$; compound Y is
(A) $NaAlO_2$ (B) $NaHCO_3$ (C) Na_2CO_3 (D) Na_2O_2

Q.23 The correct order of second ionisation potentials (IP) of Ca, Ba and K is
(A) K > Ca > Ba (B) Ba > Ca > K (C) K > Ba > Ca (D) K = Ba = Ca

Q.24 EDTA is used in the estimation of
(A) Mg^{2+} ions (B) Ca^{2+} ions
(C) both Ca^{2+} and Mg^{2+} ions (D) Mg^{2+} ions but not Ca^{2+} ions

Q.25 Highly pure dilute solution of sodium in ammonia
(A) shows blue colouration due to solvated electrons
(B) shows electrical conductivity due to both solvated electrons as well as solvated sodium ions
(C) shows red colouration due to solvated electrons but a bad conductor of electricity
(D) produces hydrogen gas or carbonate

Q.26 aq. NaOH + P_4 (white) $\longrightarrow PH_3$ + X; compound X is
(A) NaH_2PO_2 (B) $NaHPO_4$ (C) Na_2CO_3 (D) $NaHCO_3$

Q.27 The correct order of solubility is
✓
(A) $CaCO_3 < KHCO_3 < NaHCO_3$ (B) $KHCO_3 < CaCO_3 < NaHCO_3$
(C) $NaHCO_3 < CaCO_3 < KHCO_3$ (D) $CaCO_3 < NaHCO_3 < KHCO_3$

Q.28 The complex formation tendency of alkaline earth metals decreases down the group because
✓
(A) atomic size increases (B) availability of empty d and f-orbitals increases
(C) nuclear charge to volume ratio increases (D) all the above

Q.29 The alkaline earth metals, which do not impart any colour to Bunsen flame are
✓
(A) Be and Mg (B) Mg and Ca (C) Be and Ca (D) Be and Ba

Burnt ($CaSO_4$) anhy. (Gypsum) → ($CaSO_4 \cdot \frac{1}{2}H_2O$)

POP

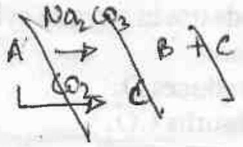
Q.30 $Y \xleftarrow{\Delta, 205°C} CaSO_4 \cdot 2H_2O \xrightarrow{\Delta, 120°C} X$. X and Y are respectively
(A) plaster of paris, dead burnt plaster (B) dead burnt plaster, plaster of paris
(C) CaO and plaster of paris (D) plaster of paris, mixture of gases

Q.31 A metal M readily forms water soluble sulphate, and water insoluble hydroxide $M(OH)_2$. Its oxide MO is amphoteric, hard and having high melting point. The alkaline earth metal M must be
(A) Mg (B) Be (C) Ca (D) Sr

Q.32 When K_2O is added to water, the solution becomes basic in nature because it contains a significant concentration of
(A) K^+ (B) O^{2-} (C) OH^- (D) O_2^{2-}

Q.33

$$\begin{tikzcd}
\text{(White ppt) D} & \text{A} \arrow[l, "Na_2CO_3"'] \arrow[r, "K_2CrO_4", "\text{(in acetic acid)}"'] \arrow[d, "\text{dil. } H_2SO_4"'] & \text{B(Yellow ppt)} \\
 & \text{C(White ppt)} &
\end{tikzcd}$$



If A is the metallic salt, then the white ppt. of D must be of
(A) magnesium oxide (B) red lead (C) barium carbonate (D) calcium carbonate

Q.34 (Milky Cloud) $C \xleftarrow{CO_2} A + Na_2CO_3 \longrightarrow B + C$
The chemical formulae of A and B are
(A) NaOH and $Ca(OH)_2$ (B) $Ca(OH)_2$ and NaOH
(C) NaOH and CaO (D) CaO and $Ca(OH)_2$

Q.35 An aqueous solution of an halogen salt of potassium reacts with same halogen X_2 to give KX_3, a brown coloured solution, in which halogen exists as X_3^- ion, X_2 as a Lewis acid and X^- as a Lewis base, halogen X is
(A) chlorine (B) bromine (C) iodine (D) fluorine

Q.36 The correct order of basic-strength of oxides of alkaline earth metals is
(A) BeO > MgO > CaO > SrO (B) SrO > CaO > MgO > BeO
(C) BeO > CaO > MgO > SrO (D) SrO > MgO > CaO > BeO

Q.37 Which of the following compounds are paramagnetic in nature?
(A) KO_2 (B) K_2O_2 (C) Na_2O_2 (D) RbO_2

Q.38 The order of stability of chlorides of alkali metals is
(A) LiCl > NaCl > KCl < CsCl (B) LiCl > NaCl > KCl > CsCl
(C) NaCl > KCl > CsCl > LiCl (D) LiCl > NaCl > CsCl > KCl

Q.39 $NaOH(Solid) + CO \xrightarrow{200°C} X$; product X is
(A) $NaHCO_3$ (B) $NaHCO_2$ (C) HCOONa (D) H_2CO_3

Q.40 $X \xrightarrow{N_2,\Delta} Y \xrightarrow{H_2O} Z(\text{colourless gas}) \xrightarrow[CuSO_4]{} T(\text{blue colour})$

Then, substances Y and T are

(A) $Y = Mg_3N_2$ and $T = CuSO_4{\cdot}5H_2O$ (B) $Y = Mg_3N_2$ and $T = CuSO_4{\cdot}4NH_3$

(C) $Y = Mg(NO_3)_2$ and $T = CuO$ (D) $Y = MgO$ and $T = CuSO_4{\cdot}4NH_3$

Q.41 Weakest base among KOH, NaOH, $Ca(OH)_2$ and $Zn(OH)_2$ is

(A) $Ca(OH)_2$ (B) KOH (C) NaOH (D) $Zn(OH)_2$

Q.42 If X and Y are the second ionisation potentials of alkali and alkaline earth metals of same period, then

(A) $X > Y$ (B) $X < Y$ (C) $X = Y$ (D) $X << Y$

Q.43 The aqueous solutions of lithium salts are poor conductor of electricity rather than other alkali metals because of

(A) high ionisation energy

(B) high electronegativity

(C) lower ability of Li^+ ions to polarize water molecules

(D) higher degree of hydration of Li^+ ions

Q.44 Sodium metal is highly reactive and cannot be stored under

(A) toluene (B) kerosene oil (C) alcohol (D) benzene

Q.45 Which of the following substance(s) is/are used in laboratory for drying purposes?

(A) anhydrous P_2O_5 (B) graphite (C) anhydrous $CaCl_2$ (D) Na_3PO_4

Q.46 Nitrogen dioxide cannot be prepared by heating

(A) KNO_3 (B) $AgNO_3$ (C) $Pb(NO_3)_2$ (D) $Cu(NO_3)_2$

Q.47 In $LiAlH_4$, metal Al is present in

(A) anionic part (B) cationic part

(C) in both anionic and cationic part (D) neither in cationic nor in anionic part

Q.48 $X \xrightarrow{CoCl_2} CaCl_2 + Y\uparrow$; the effective ingredient of X is

(A) OCl^- (B) Cl^- (C) OCl^+ (D) OCl_2^-

Q.49 Which one of the following fluoride of alkali metals has the highest lattice energy?

(A) LiF (B) CsF (C) NaF (D) KF

Q.50 Crown ethers and cryptands form

(A) complexes with alkali metals

(B) salts of alkali metals

(C) hydroxides of alkali metals used for inorganic quantitative analysis

(D) organic salts of alkali metals

Q.51 White heavy precipitates are formed when $BaCl_2$ is added to a clear solution of compound A. Precipitates are insoluble in dilute HCl. Then, the compound A is

(A) a bicarbonate (B) a carbonate (C) a sulphate (D) a chloride

Q.52 Among $MgCl_2$, RbCl, $BeCl_2$ and LiCl, the compounds with the highest and the lowest % of ionic characters are

(A) $MgCl_2$ and $BeCl_2$ (B) RbCl and $BeCl_2$ (C) $BeCl_2$ and $MgCl_2$ (D) RbCl and LiCl

Q.53 $X + C + Cl_2 \xrightarrow[\text{of about 1000 K}]{\text{High temperature}} Y + CO$; $Y + 2H_2O \rightarrow Z + 2HCl$

Compound Y is found in polymeric chain structure and is an electron deficient molecule. Y must be

(A) BeO (B) $BeCl_2$ (C) $Be(OH)_2$ (D) $BeO \cdot Be(OH)_2$

Q.54 The correct order of degree of hydration of M^+ ions of alkali metals is

(A) $Li^+ < K^+ < Na^+ < Rb^+ < Cs^+$ (B) $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$

(C) $Cs^+ < Rb^+ < K^+ < Na^+ < Li^+$ (D) $Cs^+ < Rb^+ < Na^+ < K^+ < Li^+$

Q.55 $BeCl_2 + LiAlH_4 \longrightarrow X + LiCl + AlCl_3$

(A) X is LiH (B) X is BeH_2

(C) X is $BeCl_2 \cdot 2H_2O$ (D) none

Q.56 The order of thermal stability of carbonates of IIA group is

(A) $BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3$ (B) $MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$

(C) $CaCO_3 > SrCO_3 > BaCO_3 > MgCO_3$ (D) $MgCO_3 = CaCO_3 > SrCO_3 = BaCO_3$

Q.57 A pair of substances which gives the same products on reaction with water is

(A) Mg and MgO (B) Sr and SrO (C) Ca and CaH_2 (D) Be and BeO

Q.58 Na_2SO_4 is water soluble but $BaSO_4$ is insoluble because

(A) the hydration energy of Na_2SO_4 is higher than that of its lattice energy

(B) the hydration energy of Na_2SO_4 is less than that of its lattice energy

(C) the hydration energy of $BaSO_4$ is less than that of its lattice energy

(D) the hydration energy of $BaSO_4$ is higher than that of its lattice energy

Q.59 Which of the following is not a anomalous property of lithium?

(A) Hydrated lithium ion is the largest among alkali metals

(B) The melting and boiling points of lithium are comparatively high

(C) Lithium is softer than that of other alkali metals

(D) The ionisation potential and electronegativity of lithium are higher than those of other alkali metals

Q.60 The incorrect statement(s) is/are

(A) Mg cannot form complexes

(B) Be can form complexes due to a very small atomic size

(C) the first ionisation potential of Be is higher than that of Mg

(D) Mg forms an alkaline hydroxide while Be forms amphoteric oxides

Q.61 The commercial method of preparation of potassium by reduction of molten KCl with metallic sodium at 850°C is based on the fact that

(A) potassium is solid and sodium distils off at 850 °C

(B) potassium being more volatile and distils off thus shifting the reaction forward

(C) sodium is more reactive than potassium at 850 °C

(D) sodium has less affinity to chloride ions in the presence of potassium ion

Q.62 $Be_2C + {}^{2}H_2O \longrightarrow BeO + X$ $2Be(OH)_2 + CH_4$

$CaC_2 + H_2O \longrightarrow Ca(OH)_2 + Y$; then X and Y are respectively

(A) CH_4, CH_4 (B) CH_4, C_2H_6 (C) CH_4, C_2H_2 (D) C_2H_2, CH_4

Q.63 Which of the following statements are false?

(A) $BeCl_2$ is a linear molecule in the vapour state but it is polymeric in the solid state

(B) Calcium hydride is called hydrolith.

(C) Carbides of both Be and Ca react with water to form acetylene

(D) Oxides of both Be and Ca are amphoteric.

Refer no C-family

Q.64 Which of the following are ionic carbides?
(A) CaC_2 (B) Al_4C_3 (C) SiC (D) Be_2C

Q.65 Which of the following groups of elements have chemical properties that are most similar
(A) Na, K, Ca (B) Mg, Sr, Ba (C) Be, Al, Ca (D) Be, Ra, Cs

Q.66 $MgBr_2$ and MgI_2 are soluble in acetone because of
(A) Their ionic nature (B) Their coordinate nature
(C) Their metallic nature (D) Their covalent nature

Q.67 Which of the following is not the characteristic of barium?
(A) It emits electrons on exposure to light
(B) It is a silvery white metal
(C) It forms $Ba(NO_3)_2$ which is used in preparation of green fire
(D) Its ionization potential is lower than radium.

Question No. 68 to 74

Questions given below consist of two statements each printed as Assertion (A) and Reason (R); while answering these questions you are required to choose any one of the following four responses:
(A) if both (A) and (R) are true and (R) is the correct explanation of (A)
(B) if both (A) and (R) are true but (R) is not correct explanation of (A)
(C) if (A) is true but (R) is false
(D) if (A) is false and (R) is true

Q.68 **Assertion :** Beryllium does not impart any characteristic colour to the bunsen flame.
Reason : Due to its very high ionization energy, beryllium requires a large amount of energy for exciation of the electrons.

Q.69 **Assertion :** In fused state, calcium chloride cannot be used to dry alcohol or NH_3.
Reason : $CaCl_2$ is not a good desiccant.

Q.70 **Assertion :** Best diagonal relationship is shown between Be and Al.
Reason : Ionization energy of Be is almost the same as that of Al.

Q.71 **Assertion :** Beryllium halides dissolve in organic solvents.
Reason : Beryllium halides are ionic in character.

Q.72 **Assertion :** $BeCl_2$ fumes in moist air.
Reason : $BeCl_2$ reacts with moisture to form HCl gas.

Q.73 **Assertion :** Calcium carbide on hydrolysis gives methane.
Reason : Calcium carbide contains C_2^{2-} anion.

Q.74 **Assertion :** When CO_2 is passed through lime water, it first turns milky and then the solution becomes clear when the passage of CO_2 is continued.
Reason : The milkiness is due to the formation of insoluble $CaCO_3$ which then changes to soluble $Ca(HCO_3)_2$ when excess of CO_2 is present.

Q.75 **Assertion :** $MgCO_3$ is soluble in water when a current of CO_2 is passed.
Reason : The solubility of $MgCO_3$ is due to the formation of $Mg(HCO_3)_2$.

ANSWER KEY

Q.1	A	Q.2	A,C	Q.3	C	Q.4	A	Q.5	D
Q.6	A,B,C	Q.7	B	Q.8	A	Q.9	A	Q.10	D
Q.11	A	Q.12	C	Q.13	B	Q.14	A B	Q.15	D
Q.16	C	Q.17	C	Q.18	B	Q.19	C	Q.20	A,C
Q.21	A,B,C	Q.22	C	Q.23	A	Q.24	C	Q.25	A,B
Q.26	A	Q.27	D	Q.28	A	Q.29	A	Q.30	A
Q.31	B	Q.32	C	Q.33	C	Q.34	B	Q.35	C
Q.36	B	Q.37	A,D	Q.38	C	Q.39	C	Q.40	B
Q.41	D	Q.42	A	Q.43	D	Q.44	C	Q.45	A,C
Q.46	A	Q.47	A	Q.48	A	Q.49	A	Q.50	A
Q.51	C	Q.52	B	Q.53	B	Q.54	C	Q.55	B
Q.56	A	Q.57	C	Q.58	A,C	Q.59	C	Q.60	A
Q.61	B	Q.62	C	Q.63	C,D	Q.64	A,B,D	Q.65	B
Q.66	D	Q.67	A	Q.68	A	Q.69	C	Q.70	A
Q.71	C	Q.72	A	Q.73	D	Q.74	A	Q.75	A

Be & Mg hydroxide - insoluble

all fluorides are 〃 except BeF_2.

(11) Conjugate acid base pair exist in a soln

$6Na + Al_2O_3 \rightarrow 3Na_2O + Al$

$Na_2O + H_2O \rightarrow NaOH$

$2NaOH \xrightarrow[+CO_2]{} Na_2CO_3 + H_2O$

(38) $I-I \xrightarrow{I^{\ominus}} I_3^{\ominus}$

L.A. C.B.

BANSALCLASSES

TARGET IIT JEE 2007

INORGANIC CHEMISTRY

XII (ALL)

QUESTION BANK ON

Salt Analysis

QUESTION BANK ON SALT ANALYSIS

There are 100 questions in this question bank.

Select the correct alternative : (Only one is correct)

Q.1 In the precipitation of the iron group in qualitative analysis, ammonium chloride is added before adding ammonium hydroxide to
(A) decrease concentration of OH^- ions. (B) prevent interference by phosphate ions.
(C) increase concentration of Cl^- ions. (D) increase concentration of NH_4^+ ions.

Q.2 A salt gives violet vapours when treated with conc. H_2SO_4, it contains
(A) Cl^- (B) I^- (C) Br^- (D) NO_3^-

$H_2SO_4 \to$ O.A
$I^- \xrightarrow[ox]{} I_2$
↓ violet vapour

Q.3 The acidic solution of a salt produced a deep blue colour with starch iodide solution. The salt may be
(A) chloride (B) nitrite (C) acetate (D) bromide

$Hg_2^{2+}, Ag^+, Pb^{2+}, Ba^{2+}$ ppt CrO_4^{2-}

Q.4 When a mixture of solid NaCl, solid $K_2Cr_2O_7$ is heated with conc. H_2SO_4, orange red vapours are obtained. These are of the compound
(A) chromous chloride (B) chromyl chloride
(C) chromic chloride (D) chromic sulphate

CrO_2Cl_2 covalent
chlorides [illegible] give the test.

Chromyl chloride test
Vapours + aq NaOH → yellow soln chromate → add Pb → PbCrO4 obtained → confirms

Q.5 Which of the following pairs of ions would be expected to form precipitate when dilute solution are mixed?
(A) Na^+, SO_4^{2-} (B) NH_4^+, CO_3^{2-} (C) Na^+, S_2^{2-} [✓ (D) Fe^{3+}, PO_4^{3-}]

Q.6 Nessler's reagent is
(A) K_2HgI_4 (B) K_2HgI_4 + KOH (C) K_2HgI_2 + KOH (D) K_2HgI_4 + KI

hydrolyzed

Q.7 When bismuth chloride is poured into a large volume of water the white precipitate produced is
(A) $Bi(OH)_3$. (B) Bi_2O_3 (C) BiOCl (D) Bi_2OCl_3

Q.8 Ferric ion forms a prussian blue coloured ppt. due to
(A) $K_4[Fe(CN)_6]$ (B) $Fe_4[Fe(CN)_6]_3$ (C) $KMnO_4$ (D) $Fe(OH)_3$

↓ colour ↓ ppt

Q.9 A mixture, on heating with conc. H_2SO_4 and MnO_2, librates brown vapour of
[✓ (A) Br_2] (B) NO_2 (C) HBr (D) I_2

Q.10 Which one of the following can be used in place of NH_4Cl for the identification of the third group radicals?
(A) NH_4NO_3 (B) $(NH_4)_2SO_4$ (C) $(NH_4)_2S$ (D) $(NH_4)_2CO_3$

Q.11 At the occasion of marriage, the fire works are used, which of the following gives green flame?
(A) Ba (B) K (C) Be (D) Na

Q.12 Nitrate is confirmed by ring test. The brown colour of the ring is due to formation of
(A) ferrous nitrite (B) nitroso ferrous sulphate
(C) ferrous nitrate (D) $FeSO_4NO_2$

amphoteric nature

Q.13 $Fe(OH)_3$ can be separated from $Al(OH)_3$ by addition of
(A) dil. HCl (B) NaCl solution (C) NaOH solution (D) NH_4Cl and NH_4OH

Q.14 If NaOH is added to an aqueous solution of zinc ions a white ppt appears and on adding excess NaOH, the ppt dissolves. In this solution zinc exist in the
(A) cationic part (B) anionic part
(C) both in cationic and anionic parts (D) there is no zinc ion in the solution

(B) → amphoteric nature

Q.15 Mark the compound which is soluble in hot water.
(A) Lead chloride (B) Mercurous chloride (C) Stronsium sulphate (D) Silver chloride

a

Q.16 Colour of nickel chloride solution is
(A) pink (B) black (C) colourless (D) green

Fe^{2+}, Ni^{2+}, Cr^{3+} [illegible] → Green

Q.17 Sometimes yellow turbidity appears while passing H_2S gas even in the absence of II group radicals. This is because of
(A) sulphur is present in the mixture as impurity.
(B) IV group radicals are precipitated as sulphides.
(C) the oxidation of H_2S gas by some acid radicals.
(D) III group radicals are precipitated as hydroxides.

This is the reason why CdS in Group II A is still confirmed even though it stands out with its yellow colour.

Q.18 The ion that cannot be precipitated by H_2S and HCl is
(A) Pb^{2+} (B) Cu^{2+} (C) Ag^+ (D) Ni^{2+}

Q.19 In V group, $(NH_4)_2CO_3$ is added to precipitate out the carbonates. We do not add Na_2CO_3 because
(A) $CaCO_3$ is soluble in Na_2CO_3.
(B) Na_2CO_3 increases the solubility of V group carbonate.
(C) $MgCO_3$ will be precipitated out in V group.
(D) None of these

Q.20 Distinguishing reagent between silver and lead salts is
(A) H_2S gas (B) dil HCl solution followed by warming
(C) NH_4Cl (solid) + NH_4OH solution (D) NH_4Cl (solid) + $(NH_4)_2CO_3$ solution

Q.21 Which of the following cations is detected by the flame test?
(A) NH_4 (B) K^+ (C) Mg^{2+} (D) Al^{3+}

Q.22 Which one among the following pairs of ions cannot be separated by H_2S in dilute HCl?
(A) Bi^{3+}, Sn^{4+} (B) Al^{3+}, Hg^{2+} (C) Zn^{2+}, Cu^{2+} (D) Ni^{2+}, Cu^{2+}

Q.23 A metal salt solution gives a yellow ppt with silver nitrate. The ppt dissolves in dil. nitric acid as well as in ammonium hydroxide. The solution contains
(A) bromide (B) iodide (C) phosphate (D) chromate

confirmatory test for phosphate, arsenate → red.

Q.24 A metal salt solution forms a yellow ppt with potassium chromate in acetic acid, a white ppt with dilute sulphuric acid, but gives no ppt with sodium chloride or iodide, it is :
(A) lead carbonate (B) basic lead carbonate
(C) barium nitrate (D) strontium nitrate

confirmatory test for AgCl → in Group I

Q.25 Which is soluble in NH_4OH?
(A) $PbCl_2$ (B) AgCl (C) $PbSO_4$ (D) $CaCO_3$

Q.26 Which of the following combines with Fe(II) ions to form a brown complex
(A) N_2O (B) NO (C) N_2O_3 (D) N_2O_4

Q.27 Nessler's reagent is used to detect
(A) CrO_4^{2-} (B) PO_4^{3-} (C) MnO_4^- (D) NH_4^+ — Standard test for NH_3/NH_4

Q.28 Prussian blue is formed when
(A) ferrous sulphate reacts with $FeCl_3$.
(B) ferric sulphate reacts with $K_4[Fe(CN)_6]$. → std
(C) Ammonium sulphate reacts with $FeCl_3$
(D) ferrous ammonium sulphate reacts with $FeCl_3$

Q.29 What product is formed by mixing the solution of $K_4[Fe(CN)_6]$ with the solution of $FeCl_3$?
(A) Ferro-ferricyanide (B) Ferri-ferrocyanide (C) Ferri-ferricyanide (D) None of these

Q.30 Which of the following will not give positive chromyl chloride test?
(A) Copper chloride, $CuCl_2$
(B) Mercuric chloride, $HgCl_2$ → covalent (B)
(C) Zinc chloride, $ZnCl_2$
(D) Anillinium chloride, $C_6H_5NH_3Cl$ ↓ organic but ionic

Q.31 A blue colouration is not obtained when
(A) ammonium hydroxide dissolves in copper sulphate. tetraammine complex
(B) copper sulphate solution reacts with $K_4[Fe(CN)_6]$. → ✗✗
(C) ferric chloride reacts with sodium ferrocyanide. blue ppt
(D) anhydrous white $CuSO_4$ is dissolved in water. blue

Q.32 AgCl dissolves in ammonia solution giving
(A) Ag^+, NH_4^+ and Cl^-
(B) $Ag(NH_3)^+$ and Cl^-
(C) $Ag_2(NH_3)^{2-}$ and Cl^-
(D) $Ag(NH_3)_2^+$ and Cl^-

~~ccc~~S ~(D) obvious...

Q.33 A white crystalline substance dissolves in water. On passing H_2S gas in this solution, a black ppt is obtained. The black ppt dissolves completely in hot HNO_3. On adding a few drops of conc. H_2SO_4, a white ppt is obtained. This ppt is that of
(A) $BaSO_4$ (B) $SrSO_4$ (C) $PbSO_4$ (D) $CdSO_4$

if soln is $HgCl_2$ → conf test for both $SnCl_2$ & $HgCl_2$

Q.34 When excess of $SnCl_2$ is added to a solution of $HgCl_2$, a white ppt turning grey is obtained. The grey colour is due to the formation of
(A) Hg_2Cl_2 (B) $SnCl_4$ (C) Sn (D) Hg

→ white Hg_2Cl_2 + Hg ↳ black ↓ grey

if soln is group I ppt, Hg_2Cl_2 will be obtained

??(Q.35) Of the following sulphides which one is insoluble in dil. acids but soluble in alkalies.
(A) PbS (B) CdS (C) FeS (D) As_2S_3

Chloroform test for I^- | Br^-
Q.36 When chlorine water is added to an aqueous solution of potassium halide in presence of chloroform, a violet colour is obtained. On adding more of chlorine water, the violet colour disappears, and a colourless solution is obtained. This test confirms the presence of the following in aqueous solution
(A) Iodide (B) Bromide (C) Chloride (D) Iodide and bromide

Any will do
Violet → I_2
Red → Br_2

Hence → HNO_3 ✗ NO_3 → Barium

Q.37 An aqueous solution of colourless metal sulphate M, gives a white ppt, with NH_4OH. This was soluble in excess of NH_4OH. On passing H_2S through this solution a white ppt is formed. The metal M in the salt is
(A) Ca (B) Ba (C) Al (D) Zn

Thermal decomp^n

Q.38 When $AgNO_3$ is strongly heated, the products formed are
(A) NO and NO_2 (B) NO_2 and O_2 (C) NO_2 and N_2O (D) NO and O_2

Q.39 AgCl is soluble in
(A) Aqua regia (B) H_2SO_4 (C) dil. HCl (D) aq. NH_3

Q.40 A substance on treatment with dil. H_2SO_4 liberates a colourless gas which produces (i) turbidity with baryta water and (ii) turns acidified dichromate solution green. The reaction indicates the presence of
(A) CO_3^{2-} (B) S^{2-} (C) SO_3^{2-} (D) NO_2^-

Q.41 When copper nitrate is strongly heated, it is converted into
(A) Cu metal (B) cupric oxide (C) cuprous oxide (D) copper nitrate

Q.42 A white solid is first heated with dil H_2SO_4 and then with conc. H_2SO_4. No action was observed in either case. The solid salt contains
(A) sulphide (B) sulphite (C) thiosulphate (D) sulphate

Q.43 A pale green crystalline metal salt of M dissolves freely in water. On standing it gives a brown ppt on addition of aqueous NaOH. The metal salt solution also gives a black ppt on bubbling H_2S in basic medium. An aqueous solution of the metal salt decolourizes the pink colour of the permanganate solution. The metal in the metal salt solution is
(A) copper (B) aluminium (C) lead (D) iron

shows
variable
O.S.
c Id
↓
bo.
hydro

Q.44 On the addition of a solution containing CrO_4^{2-} ions to the solution of Ba^{2+}, Sr^{2+} and Ca^{2+} ions, the ppt obtained first will be of
(A) $CaCrO_4$ (B) $SrCrO_4$ (C) $BaCrO_4$ (D) a mixture of all the three

Q.45 Turnbull's blue is a compound
(A) ferricyanide (B) ferro ferricyanide (C) ferrous cyanide (D) ferriferrocyanide

Q.46 Sodium borate on reaction with conc. H_2SO_4 and C_2H_5OH gives a compound A which burns with a green edged flame. The compound A is
(A) $H_2B_4O_7$ (B) $(C_2H_5)_2B_4O_7$ (C) H_3BO_3 (D) $(C_2H_5)_3BO_3$

Q.47 When $K_2Cr_2O_7$ crystals are heated with conc. HCl, the gas evolved is
(A) O_2 (B) Cl_2 (C) CrO_2Cl_2 (D) HCl

A kind of prep.
for chromyl
chloride;
Ref. wikipedia...

Q.48 Which is most soluble in water?
(A) AgCl (B) AgBr (C) AgI (D) AgF

(-)(-) = +
AgF is
soluble

Q.49 On passing H_2S gas in II group sometimes the solution turns milky. It indicates the presence of
(A) oxidising agent (B) acidic salt (C) thiosulphate (D) reducing agent.

$S^{2-} \rightarrow S^0$

$[Ni(dmg)_2]$ → complex coloured...

Q.50 Dimethyl glyoxime in a suitable solvent was refluxed for 10 minutes with pure pieces of nickel sheet, it will result in
(A) Red ppt (B) Blue ppt. (C) Yellow ppt. (D) No ppt.

??

Q.51 A mixture of chlorides of copper, cadmium, chromium, iron and aluminium was dissolved in water acidified with HCl and hydrogen sulphide gas was passed for sufficient time. It was filtered, boiled and a few drops of nitric acid were added while boiling. To this solution ammonium chloride and sodium hydroxide were added in excess and filtered. The filtrate shall give test for
(A) sodium and iron (B) sodium, chromium and aluminium
(C) aluminium and iron (D) sodium, iron, cadmium and aluminium

Q.52 A metal is brunt in air and the ash on moistening smells of ammonia. The metal is
(A) Na (B) Fe (C) Mg (D) Al

Li_3N & Mg_3N_2 formed; hydrolysis makes NH_3...

Q.53 Solution of chemical compound X reacts with $AgNO_3$ solution to form a white ppt. Y which dissolves in NH_4OH to give a complex Z. When Z is treated with dil. HNO_3, Y reappears. The chemical compound X can be
(A) NaCl (B) CH_3Cl (C) NaBr (D) NaI

Q.54 A white ppt obtained in a analysis of a mixture becomes black on treatment with NH_4OH. It may be
(A) $PbCl_2$ (B) AgCl (C) $HgCl_2$ (D) Hg_2Cl_2

Q.55 A salt on treatment with dil. HCl gives a pungent smelling gas and a yellow precipitate. The salt gives green flame when tested. The solution gives a yellow precipitate with potassium chromate. The salt is:
(A) $NiSO_4$ (B) BaS_2O_3 (C) PbS_2O_3 (D) $CuSO_4$

one of The most insoluble things on earth...

Q.56 Which compound does not dissolve in hot dilute HNO_3?
(A) HgS (B) PbS (C) CuS (D) CdS

$Fe^{2+} \to Fe^{3+}$
Brown residue due to Fe(OH) hydroxide

Q.57 An aqueous solution of $FeSO_4$, $Al_2(SO_4)_3$ and chrome alum is heated with excess of Na_2O_2 and filtered. The materials obtained are:
(A) a colourless filtrate and a green residue. (B) a yellow filtrate and a green residue.
(C) a yellow filtrate and a brown residue. (D) a green filtrate and a brown residue.

Cr^{3+} oxi. to Cr^{+6}

Q.58 Which of the following compound on reaction with NaOH and Na_2O_2 gives yellow colour?
(A) $Cr(OH)_3$ (B) $Zn(OH)_2$ (C) $Al(OH)_3$ (D) None of these

Q.59 CrO_3 dissolves in aqueous NaOH to give:
(A) $Cr_2O_7^{2-}$ (B) CrO_4^{2-} (C) $Cr(OH)_3$ (D) $Cr(OH)_2$

(B) amphoteric...

Q.60 Which of the following cannot give iodometric titration?
(A) Fe^{3+} (B) Cu^{2+} (C) Pb^{2+} (D) Ag^+

Q.61 Which of the following is not efflorescent?
(A) Hydrated Na_2CO_3 (B) Hydrated $CuSO_4$
(C) NaOH (D) All of these

Q.62 An aqueous solution of a substance gives a white ppt. on treatment with dil. HCl, which dissolves on heating. When hydrogen sulphide is passed through the hot acidic solution, a black ppt. is obtained. The substance is a
(A) Hg^{2+} salt (B) Cu^{2+} salt (C) Ag^{+} salt (D) Pb^{2+} salt

Q.63 Which of the following does not react with AgCl? → $[Ag(NH_3)_2]Cl$
(A) Na_2CO_3 (B) $NaNO_3$ (C) NH_4OH (D) $Na_2S_2O_3$
Not oxagents

Q.64 Which one of the following does not produce metallic sulphide with H_2S?
(A) $ZnCl_2$ (B) $CdCl_2$ (C) $CoCl_2$ (D) $CuCl_2$

Q.65 Which of the following statement is correct?
(A) Fe^{2-} gives brown colour with ammonium thiocyanate.
(B) Fe^{2+} gives blue precipitate with potassium ferricyanide.
(C) Fe^{3+} gives brown colour with potassium ferricyanide.
(D) Fe^{3+} gives red colour with potassium ferrocyanide.

Q.66 Which metal salt gives a violet coloured bead in the borax bead test?
✓ (A) Fe^{2+} (B) Ni^{2+} (C) Co^{2+} (D) Mn^{2+}

Q.67 Which of the following gives a precipitate with $Pb(NO_3)_2$ but not with $Ba(NO_3)_2$?
✓ (A) Sodium chloride (B) Sodium acetate
(C) Sodium nitrate (D) Sodium hydrogen phosphate

Q.68 Which of the following is soluble in yellow ammonium sulphide?
✓ (A) CuS (B) CdS (C) SnS (D) PbS

Q.69 A chloride dissolves appreciably in cold water. When placed on a platinum wire in Bunsen flame no distinctive colour is noticed, the cation would be:
✓ (A) Mg^{2+} (B) Ba^{2+} (C) Pb^{2+} (D) Ca^{2+}

Q.70 A white salt is readily soluble in water and gives a colourless solution with a pH of about 9. The salt could be: $CaCO_3$ insoluble
✓ (A) NH_4NO_3 (B) CH_3COONa (C) CH_3COONH_4 (D) $CaCO_3$

Q.71 An element (X) forms compounds of the formula XCl_3, X_2O_5 and Ca_3X_2, but does not form XCl_5. Which of the following is the element X?
✓ (A) B (B) Al (C) N (D) P
NBr_3 | NI_3

Q.72 A white sodium salt dissolves readily in water to give a solution which is neutral to litmus. When silver nitrate solution is added to the solution, a white precipitate is obtained which does not dissolve in dil. HNO_3. The anion could be:
✓ (A) CO_3^{2-} (B) Cl^- (C) SO_4^{2-} (D) S^{2-}

Q.73 A mixture of two salts is not water soluble but dissolves completely in dil HCl to form a colourless solution. The mixture could be:
(A) $AgNO_3$ and KBr (B) $BaCO_3$ and ZnS (C) $FeCl_3$ and $CaCO_3$ (D) $Mn(NO_3)_2$ and $MgSO_4$

(A) AgNO3 soluble, KBr ionic (B) — — (C) → soluble (D) soluble

Q.74 Three separate samples of a solution of a single salt gave these results. One formed a white precipitate with excess of ammonia solution, one formed a white precipitate with dil NaCl solution and one formed a black precipitate with H_2S. The salt could be:
(A) $AgNO_3$ (B) $Pb(NO_3)_2$ (C) $Hg(NO_3)_2$ (D) $MnSO_4$

Q.75 Which one of the following ionic species will impart colour to an aqueous solution?
(A) Ti^{4+} (B) Cu^{+} (C) Zn^{2+} (D) Cr^{3+}

(D)

Q.76 When a substance A reacts with water it produces a combustible gas B and a solution of substance C in water. When another substance D reacts with this solution of C, it also produces the same gas B on warming but D can produce gas B on reaction with dilute sulphuric acid at room temperature. A imparts a deep golden yellow colour a smokeless flame to Bunsen burner. A, B, C and D respectively are:
(A) Na, H_2, NaOH, Zn (B) K, H_2, KOH, Al
(C) Ca, H_2, $Ca(OH)_2$, Sn (D) CaC_2, C_2H_2, $Ca(OH)_2$, Fe

Q.77 Which is not dissolved by dil HCl?
(A) ZnS (B) MnS (C) $BaSO_3$ (D) $BaSO_4$

Q.78 The brown ring test for NO_2^- and NO_3^- is due to the formation of complex ion with formula:
(A) $[Fe(H_2O)_6]^{2+}$ (B) $[Fe(NO)(CN)_5]^{2-}$
(C) $[Fe(H_2O)_5(NO)]^{2+}$ (D) $[Fe(H_2O)(NO)_5]^{2+}$

Q.79 In Nessler's reagents, the ion present is:
(A) HgI^{2-} (B) HgI_4^{2-} (C) Hg^{+} (D) Hg^{2+}

Q.80 The cations present in slightly acidic solution are Fe^{3+}, Zn^{2+} and Cu^{2+}. The reagent which when added in excess to this solution would identify and separte Fe^{3+} in one step is:
(A) 2 M HCl (B) 6 M NH_3 (C) 6 M NaOH (D) H_2S gas

A → [illegible]
B → complex [illegible]
C → Fe(OH)
D → Fe/Zn both

Q.81 Which of the following leaves no residue on heating?
(A) $Pb(NO_3)_2$ (B) NH_4NO_3 (C) $Cu(NO_3)_2$ (D) $NaNO_3$

Q.82 When I_2 is passed through KCl, KF, KBr :
(A) Cl_2 and Br_2 are evolved (B) Cl_2 is evolved
(C) Cl_2, F_2 and Br_2 are evolved (D) None of these

disp oxn does happen in aqs sol

Q.83 In the separation of Cu^{2+} and Cd^{2+} in 2nd group qualitative analysis of cations tetrammine copper (II) sulphate and tetrammine cadmium (II) sulphate react with KCN to form the corresponding cyano complexes. Which one of the following pairs of the complexes and their relative stability enables the separation of Cu^{2+} and Cd^{2+}?
(A) $K_3[Cu(CN)_4]$ more stable and $K_2[Cd(CN)_4]$ less stable.
(B) $K_2[Cu(CN)_4]$ less stable and $K_2[Cd(CN)_4]$ more stable.
(C) $K_2[Cu(CN)_4]$ more stable and $K_2[Cd(CN)_4]$ less stable.
(D) $K_3[Cu(CN)_4]$ less stable and $K_2[Cd(CN)_4]$ more stable.

(A)
H_2S add
CdS

Q.84 Which one has the minimum solubility product?
(A) AgCl (B) $AlCl_3$ (C) $BaCl_2$ (D) NH_4Cl

(A)

Q.85 Which of the following sulphate is insoluble in water?
(A) $CuSO_4$ (B) $CdSO_4$ (C) $PbSO_4$ (D) $Bi_2(SO_4)_3$

Q.86 A metal X on heating in nitrogen gas gives Y. Y on treatment with H_2O gives a colourless gas which when passed through $CuSO_4$ solution gives a blue colour Y is:
(A) $Mg(NO_3)_2$ (B) Mg_3N_2 (C) NH_3 (D) MgO

Q.87 Which of the following gives blood red colour with KCNS?
(A) Cu^{2+} (B) Fe^{3+} (C) Al^{3+} (D) Zn^{2+}

Q.88 Which of the following is insoluble in excess of NaOH?
(A) $Al(OH)_3$ (B) $Cr(OH)_3$ (C) $Fe(OH)_3$ (D) $Zn(OH)_2$

Q.89 In the borax bead test of Co^{2+}, the blue colour of bead is due to the formation of:
(A) B_2O_3 (B) Co_3B_2 (C) $Co(BO_2)_2$ (D) CoO

Q.90 Mercurous ion is represented as:
(A) Hg_2^{2+} (B) Hg^{2+} (C) $Hg + Hg^{2+}$ (D) Hg_2^+

Q.91 The metal ion which is precipitated when H_2S is passed with HCl:
(A) Zn^{2+} (B) Ni^{2+} (C) Cd^{2+} (D) Mn^{2+}

Q.92 Which of the following is not a preliminary test used to detect ions:
(A) borax bead test (B) flame test (C) brown ring test (D) cobalt nitrate test

Q.93 Which one of the following metal sulphides has maximum solubility in water?
(A) HgS, $K_{sp} = 10^{-54}$ (B) CdS, $K_{sp} = 10^{-30}$ (C) FeS, $K_{sp} = 10^{-20}$ (D) ZnS, $K_{sp} = 10^{-22}$

Q.94 The compound formed in the borax bead test of Cu^{2+} ion in oxidising flame is:
(A) Cu (B) $CuBO_2$ (C) $Cu(BO_2)_2$ (D) None of these

Q.95 A gas 'X' is passed through water to form a saturated solution. The aqueous solution on treatment with $AgNO_3$ gives a white precipitate. The saturated aqueous solution also dissolves magnesium ribbon with evolution of a colourless gas Y. Identify X and Y:
(A) $X = CO_2$, $Y = Cl_2$ (B) $X = Cl_2$, $Y = CO_2$
(C) $X = Cl_2$, $Y = H_2$ (D) $X = H_2$, $Y = Cl_2$

Q.96 Read of the following statements and choose the correct code w.r.t true(T) and false(F).
(I) manganese salts give a violet borax bead test in reducing flame
(II) from a mixed precipitate of AgCl and AgI, ammonia solution dissolves only AgCl
(III) ferric ions give a deep green precipitate, on adding potassium ferrocyanide solution
(IV) on boiling the solution having K^+, Ca^{2+} and HCO_3 we get a precipitate of $K_2Ca(CO_3)_2$
(A) TTFF (B) FTFT (C) FTFF (D) TTFT

Q.97 Identify the correct order of solubility of Na_2S, CuS and ZnS in aqueous medium is:
(A) CuS > ZnS > Na_2S (B) ZnS > Na_2S > CuS
(C) Na_2S > CuS > ZnS (D) Na_2S > ZnS > CuS

Q.98 When H_2S gas is passed through the HCl containing aqueous solution of $CuCl_2$, $HgCl_2$, $BiCl_3$ and $CoCl_2$, it does not precipitate out:
(A) CuS (B) HgS (C) Bi_2S_3 (D) CoS

Q.99 Mark the correct statement:
(A) I group basic radicals precipitate as chlorides
(B) IV group basic radicals precipitates as sulphides.
(C) V group basic radicals precipitates as carbonates.
(D) All the above statement are correct.

Q.100 Potassium chromate solution is added to an aqueous solution of a metal chloride. The precipitate thus obtained are insoluble in acetic acid. These are subjected to flame test, the colour of the flame is:
(A) Lilac (B) Apple green (C) Crimson red (D) Golden yellow

ANSWER KEY

Q.1	A	Q.2	B	Q.3	B	Q.4	B
Q.5	D	Q.6	B	Q.7	C	Q.8	B
Q.9	A	Q.10	C	Q.11	A	Q.12	B
Q.13	C	Q.14	B	Q.15	A	Q.16	D
Q.17	C	Q.18	D	Q.19	D	Q.20	B
Q.21	B	Q.22	A	Q.23	C	Q.24	C
Q.25	B	Q.26	B	Q.27	D	Q.28	B
Q.29	B	Q.30	B	Q.31	B	Q.32	D
Q.33	C	Q.34	D	Q.35	D	Q.36	A
Q.37	D	Q.38	B	Q.39	D	Q.40	C
Q.41	B	Q.42	D	Q.43	D	Q.44	C
Q.45	B	Q.46	D	Q.47	C	Q.48	D
Q.49	A	Q.50	D	Q.51	B	Q.52	C
Q.53	A	Q.54	D	Q.55	B	Q.56	A
Q.57	C	Q.58	A	Q.59	B	Q.60	A, B
Q.61	C	Q.62	D	Q.63	B	Q.64	A, C
Q.65	B, C	Q.66	D	Q.67	A	Q.68	C
Q.69	A	Q.70	B	Q.71	C	Q.72	B
Q.73	B	Q.74	B	Q.75	D	Q.76	A
Q.77	D	Q.78	C	Q.79	B	Q.80	B
Q.81	B	Q.82	D	Q.83	A	Q.84	A
Q.85	C	Q.86	B	Q.87	B	Q.88	C
Q.89	C	Q.90	A	Q.91	C	Q.92	C
Q.93	C	Q.94	C	Q.95	C	Q.96	C
Q.97	D	Q.98	D	Q.99	D	Q.100	B

Q.53 $Fe^{3+} \xrightarrow{SCN^-(\text{excess})} \text{blood red(A)} \xrightarrow{F^-(\text{excess})} \text{colourless(B)}$

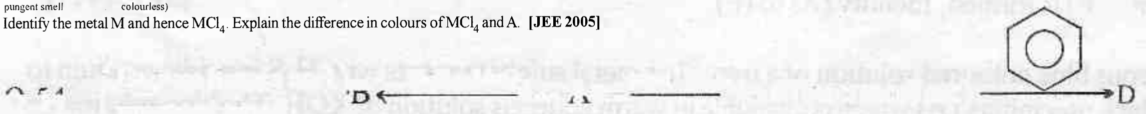
Identify A and B
(a) Write IUPAC name of A and B
(b) Find out spin only magnetic moment of B **[JEE 2005]**

Q.54 $\left(\begin{array}{l}\text{Brown fumes and}\\ \text{pungent smell}\end{array}\right) \xleftarrow{} \xrightarrow{NaBr+MnO_2} \wedge \xrightarrow{\text{conc.}HNO_3} \text{C(intermediate)} \longrightarrow$ CH_3 (Explosive product)

Find A, B, C and D. Also write equations A to B and A to C. **[JEE 2005]**

Q.55 $\underset{\substack{\text{white fumes having}\\ \text{pungent smell}}}{(B)} \xleftarrow{\text{Moist air}} \underset{\substack{(M = \text{transition element}\\ \text{colourless)}}}{MCl_4} \xrightarrow{Zn} \underset{\text{(purple colour)}}{(A)}$

Identify the metal M and hence MCl_4. Explain the difference in colours of MCl_4 and A. **[JEE 2005]**



BANSALCLASSES

TARGET IIT JEE 2007

INORGANIC CHEMISTRY

XII (ALL)

SOLUTION OF SALT ANALYSIS

CONTENTS

EXERCISE - I
EXERCISE - II

ANSWERS (SALT ANALYSIS)

EXERCISE–I

Q.1 X is $HgCl_2$

Q.2 X is $Na_2S_2O_3.5H_2O$

Q.3 $\underset{(X)}{ZnCl_2} + 2AgNO_3 \rightarrow \underset{\text{White}}{2AgCl\downarrow} + Zn(NO_3)_2$

$ZnCl_2 + 2NaOH \rightarrow \underset{\text{White}}{Zn(OH)_2\downarrow} + 2NaCl$

$Zn(OH)_2 + 2NaOH \rightarrow \underset{\text{Colourless sol}^n}{Na_2ZnO_2} + 2H_2O$

$Na_2ZnO_2 + H_2S \rightarrow \underset{\text{White}}{ZnS\downarrow} \, 2NaOH$

Q.4 $\underset{(X)}{NH_4NO_3} + NaOH \rightarrow NaNO_3 + \underset{(Y)}{NH_3\uparrow} + H_2O$

$NH_3 + HCl \rightarrow \underset{\text{White fumes}}{NH_4Cl}$

$NaNO_3 + 8H \xrightarrow[NaOH]{Zn} NaOH + 2H_2O + NH_3\uparrow$

Q.5 $\underset{(A)}{(NH_4)_2Cr_2O_7} \rightarrow \underset{(B)}{N_2} + \underset{(C)\text{green}}{Cr_2O_3} + 4H_2O$

$(NH_4)_2Cr_2O_7 + 2NaOH \rightarrow \underset{\text{yellow solution}}{Na_2CrO_4} + \underset{(D)}{2NH_3} + 2H_2O$

Hence the compound A is $(NH_4)_2Cr_2O_7$.

Q.6 (A) gives turbidity with top water (which contains Cl^-) & it is insoluble in HNO_3, but it is soluble in NH_4OH. Hence the compound is $AgNO_3$.

(i) $2AgNO_3 \xrightarrow{\Delta} 2Ag + 2NO_2\uparrow + O_2\uparrow$

(ii) $AgNO_3 + Cl^- \rightarrow AgCl\downarrow + NO_3^-$

(iii) $AgCl + 2NH_4OH \rightarrow [Ag(NH_3)_2]Cl + 2H_2O$

Q.7 $2Br^- + Cl_2 \rightarrow 2Cl^- + \underset{\text{brown}}{Br_2}$

$SO_4^{2-} + BaCl_2 \rightarrow \underset{\text{white}}{BaSO_4\downarrow} + 2Cl^-$

$Mg^{2+} + 2NaOH \rightarrow Mg(OH)_2 + 2Na^+$

Therefore mixture consists K_2SO_4 and $MgBr_2$.

Q.8 A gives white precipitate (B) with $NaCl$ which is soluble in hot water and ths, (B) may be $PbCl_2$. So (A) contains Pb^{2+} ions. (2) (A) liberates reddish brown gas on heating and thus, it should have NO_3^- ios, (3) So, (A) is $Pb(NO_3)_2$.

(i) $Pb(NO_3)_2 + 2NaCl \rightarrow \underset{(B)}{PbCl_2} + 2NaNO_3$

(ii) $PbCl_2 + H_2S \rightarrow \underset{\text{(C) black ppt.}}{PbS} + 2HCl$

(iii) $\underset{(B)}{PbCl_2} + 2NaI \rightarrow \underset{\text{yellow ppt. (D)}}{PbI_2} + 2NaCl$

(iv) $Pb(NO_3)_2 \rightarrow PbO + 2NO_2 + ½ O_2$

Q.9 $Al_2(SO_4)_3 + 3BaCl_2 \rightarrow 2AlCl_3 + \underset{\text{white}}{3BaSO_4} \downarrow$

$Al_2(SO_4)_3 + 6NaOH \rightarrow \underset{\text{white}}{2Al(OH)_3} + 3Na_2SO_4$

$Al(OH)_3 + NaOH \rightarrow \underset{\text{soluble}}{NaAlO_2} + 2H_2O$

Compound (X) gives white precipitate with $BaCl_2$ which is insoluble in concentrated *HCl* hence the anion of (*X*) must be SO_4^{2-} ion. Because the cation gives white precipitate with *NaOH* which is soluble in excess of *NaOH*, therefore cation of compound (*X*) may be Zn^{2+} or Al^{3+} ion. But Zn^{2+} cannot be cation of the compound (*X*).

Q.10 (i) $Pb(NO_3)_2 \xrightarrow{\Delta} 2PbO + 4NO_2 + O_2$

(ii) $Pb(NO_3)_2 + K_2Cr_2O_7 \xrightarrow{CH_3COOH} PbCrO_4 \downarrow$

(iii) $Pb(NO_3)_2 + 2NaOH \rightarrow \underset{\text{White}}{Pb(OH)_2} \downarrow 2NaNO_3$

$Pb(OH)_2 + \underset{\text{(excess)}}{2NaOH} \rightarrow \underset{\text{soluble}}{Na_2[Pb(OH)_4]}$

le in

Q.11 A metallic chloride when does not respond test for *C* (Chromyl chloride test) may be $HgCl_2$.

(i) $\underset{(A)}{2HgCl_2} + \underset{(B)}{SnCl_2} \rightarrow SnCl_4 + \underset{\text{white}}{Hg_2Cl_2}$

$Hg_2Cl_2 + SnCl_2 \rightarrow SnCl_4 + \underset{\text{Grey}}{2Hg}$

(ii) $HgCl_2 + 2KI \rightarrow HgI_2 + 2KCl$

$\underset{\text{Excess}}{2KI} + HgI_2 \longrightarrow \underset{\text{(C) scarlet red}}{K_2HgI_4}$

Q.12 $\underset{(A)}{FeSO_4} + BaCl_2 \rightarrow \underset{\text{white (B)}}{BaSO_4} \downarrow + FeCl_2$

white precipitate of (*B*) is insoluble in dil. *HCl* hence in compound (*A*) SO_4^{-2} ion is present.

$(A)\ FeSO_4.7H_2O \rightarrow FeSO_4 + 7H_2O$

$2FeSO_4 \rightarrow \underset{\substack{(E) \\ \text{Red brown}}}{Fe_2O_3} + \underset{(C)}{SO_2} \uparrow + \underset{(D)}{SO_3} \uparrow$

So (*A*)

ios, (3)

$Fe_2O_3 + 6HCl \rightarrow \underset{\text{yellow solu}^n}{2FeCl_3} + 3H_2O$

$2FeCl_3 + H_2S \rightarrow 2FeCl_2 + 2HCl + S \downarrow$

Q.13 $\underset{(A)}{BiCl_3} + H_2O \rightarrow \underset{(B)}{BiOCl} + 2HCl$

$\underset{(B)}{BiOCl} + 2HCl \rightarrow \underset{(A)}{BiCl_3} + H_2O$

$2BiCl_3 + 3Na_2SnO_2 + 6NaOH \rightarrow \underset{\text{Black (C)}}{2Bi\downarrow} + 3Na_2SnO_3 + 6NaCl + 3H_2O$

$2BiCl_3 + 3H_2SO_4 \rightarrow \underset{(D)}{Bi_2(SO_4)_3} + 6HCl$

$Hg_2(NO_3)_2 + 2HCl \rightarrow \underset{\text{White}}{Hg_2Cl_2} + 2HNO_3$

Q.14 Solution C gives ppt. with $NaOH$ solution which is soluble in excess of $NaOH$ solution hence the cation should be of the amphoteric metal like Zn or Al.

A gain solid F is soluble in HCl and gives white precipitate with $BaCl_2$. Therefore anion must be SO_4^{2-} ion. Now the A gives offensive smelling gas hence hence the A may be ZnS or Al_2S_3. But Al_2S_3 on heating in air des not form $Al_2(SO_4)_3$. . Chemical reactions are as follows :

$\underset{(A)}{ZnS} + 2HCl \rightarrow \underset{(C)}{ZnCl_2} + \underset{(B)}{H_2S\uparrow}$

$\underset{(C)}{ZnCl_2} + 2NaOH \rightarrow \underset{(D)}{Zn(OH)_2\downarrow} + 2NaCl$

$Zn(OH)_2 + 2NaOH \rightarrow Na_2ZnO_2 + 2H_2O$

$\underset{(A)}{2ZnS} + 3O_2 \rightarrow \underset{(F)}{2ZnO} + \underset{(E)}{2SO_2}$

$\underset{(A)}{ZnS} + 2O_2 \rightarrow ZnSO_4(F)$

$ZnSO_4 + BaCl_2 \rightarrow BaSO_4\downarrow + ZnCL_2$

Q.15 $\underset{\text{blue sol}}{CuSO_4(A)} \xrightarrow{H_2S} \underset{\text{black (B)}}{CuS} \xrightarrow{HNO_3} \underset{\text{soluble}}{Cu(NO_3)_2} \xrightarrow{NaOH} \underset{\text{blue ppt.(C)}}{Cu(OH)_2}$

$\xrightarrow{NH_3} [Cu(NH_3)_4]SO_4$ (D) (deep blue solution)

$\xrightarrow{KCN} \underset{\text{yellow ppt. (E)}}{CuCN} \xrightarrow{KCN} \underset{\text{colourless}}{K_2[Cu(CN)_4]}$

Q.16 $X.\ Y(A : \text{mixture}) \xrightarrow{H_2O}$ solution $\xrightarrow{\text{phenolphthalein}}$ pink

$\Rightarrow$ as A is basic $\xrightarrow{dil.\ HCl}$ ppt. $\Rightarrow$ A is basic i.e. either of X and Y is a base it means X (or Y) is $NaOH$ since precipitate dissolve by further $\xrightarrow{\text{further addition of } HCl}$ ppt. dissolves

$\Rightarrow$ Zn salt $\Rightarrow$ Y is $ZnSO_4$ (or X)

$ZnSO_4 + NaOH \rightarrow Na_2ZnO_2 \xrightarrow{HCl} Zn(OH)_2\downarrow \xrightarrow{HCl} ZnCl_2$ ppt. soluble.

Q.17 A : $CuO \xrightarrow{H_2SO_4} CuSO_4(blue) \xrightarrow{\text{Flame test}}$ green colour

B : $MnO_2 \xrightarrow{\text{conc. HCl}} MnCl_2 + Cl_2 \xrightarrow[NH_4^+]{H_2S} MnS$ (flesh colour)

C : Carbon powder : $C \xrightarrow{KNO_3} CO_2 \xrightarrow{\text{Lime water}}$ milky

Q.18 Metal salt gives green coloured precipitate with $NaOH$ hence the precipitate will be of $Cr(OH)_3$. It is also soluble in $NaOH$ to form sodium chromite. It is also confirmed by the fact that $Cr(OH)_3$ gives Cr_2O_3 (green powder) which on fusion with $NaOH$ in air to form sodium chromate which is yellow in colour.

$$Cr^{3+} + 3NaOH \rightarrow \underset{(X)}{Cr(OH)_3} + 3Na^+$$

$$2Cr(OH)_3 + NaOH \rightarrow \underset{\text{Sodium chromite}}{NaCrO_2} + 2H_2O$$

$$2Cr(OH)_3 \xrightarrow{\Delta} \underset{\text{green}}{Cr_2O_3} + 3H_2O$$

$$2Cr_2O_3 + 8NaOH + 3O_2 \rightarrow \underset{(Z)}{4Na_2CrO_4} + 4H_2O$$

Q.19 $$\underset{\substack{\text{Chromate}\\\text{(yellow)}}}{2CrO_4^{2-}} + 2H^+ \underset{alkali}{\overset{acid}{\Leftrightarrow}} \underset{\substack{\text{Dichromate}\\\text{(orange) (B)}}}{Cr_2O_7^{2-}} + H_2O$$

$$\underset{(B)}{Cr_2O_7^{2-}} + 2H + 4H_2O_2 \rightarrow \underset{\text{(C) blue colour}}{2CrO_5} + 5H_2O$$

Blue colour fades away gradually due to decomposition of CrO_5 into Cr^{3+} ions and oxygen. Acidified solution of : $B + NaCl \rightarrow CrO_2Cl_2$ (Chromyl chloride). (*D*) Orange red fumes.

Q.20 White powder (*A*) gives colourless, odorless gas shich changes lime water mily hance the compound (*A*) is a carbonate of any cation, but residue '*E*' which is left on heating (*A*) is yellow when hot and white wen cooled. Therefore (*E*) must be *ZnO*. Thus the compound (*A*) is $ZnCO_3$. The reactions are as follows :

$$\underset{(A)}{ZnCO_3} \xrightarrow{\text{heat}} \underset{(E)}{ZnO} + \underset{(B)}{CO_2} \uparrow$$

$$\underset{(B)}{CO_2} + \underset{\text{Lime water}}{Ca(OH)_2} \longrightarrow \underset{\text{White ppt. (C)}}{CaCO_3 \downarrow} + H_2O$$

$$\underset{(C)}{CaCO_3} + H_2O + \underset{(B)}{CO_2} \rightarrow \underset{(D)}{Ca(HCO_3)_2}$$

EXERCISE–II

(Asked in REE)

01.(I) Step (ii) suggest *X* to be a compound of *Ag* as it gives tubidity with tap water which contains Cl^-. Since the turbidity is soluble in NH_4OH .

(II) *X* may be $AgNO_3$ since it gives oxides of Nitrogen.

Reactions : $2AgNO_3 \rightarrow \underset{\text{residue}}{2Ag} + 2NO_2 + O_2$

$$\underset{(X)}{AgNO_3} + \underset{\text{tap}}{Cl^-} \rightarrow \underset{\text{water Turbidity}}{AgCl} + NO_3^-$$

$$AgCl + 2NH_4OH \rightarrow \underset{\text{soluble}}{Ag(NH_3)_2Cl} + 2H_2O$$

02.(I) Step (ii) suggest that X may be hypo as it decolorizes solution of I_2 and also loses water of crystallization.

(II) X is $Na_2S_2O_3.5H_2O$ i.e. : hypo

$Na_2S_2O_3.5H_2O \rightarrow Na_2S_2O_3 + 5H_2O$

$\underset{(X)}{Na_2S_2O_3} + 2HCl \xrightarrow{\Delta} 2NaCl + SO_2 + \underset{\text{Turbidity}}{S} + H_2O$

$\underset{(X)}{2Na_2S_2O_3} + I_2 \rightarrow Na_2S_4O_6 + 2NaI$

$\underset{(X)}{Na_2S_2O_3} + 2AgNO_3 \rightarrow \underset{\text{white ppt.}}{Ag_2S_2O_3} + 2NaNO_3$

$Ag_2S_2O_3 + H_2O \xrightarrow[\text{on standing}]{} \underset{\text{Black}}{Ag_2S} + H_2SO_4$

03. (A) on heating gives two oxides of S and thus it is $FeSO_4 . 7H_2O$.

1. $\underset{(A)}{FeSO_4 . 7H_2O} \xrightarrow{\Delta} FeSO_4 + 7H_2O$

2. $2FeSO_4 \xrightarrow{\Delta} \underset{(B)}{Fe_2O_3} + \underset{(C)}{SO_2} + \underset{(D)}{SO_3}$

3. $Fe_2O_3 + 6HCl \longrightarrow \underset{\text{(E) yellow}}{2FeCl_3} + 3H_2O$

4. $2FeCl_3 + H_2S \longrightarrow \underset{(G)}{FeCl_2} + 2HCl + \underset{\text{Turbidity (F)}}{S}$

$\underset{(E)}{Fe^{3+}} + 3CNS^- \longrightarrow Fe(CNS)_3$ (blood Red colour)

04. (i) $\underset{(A)}{NH_4Cl} + NaOH \xrightarrow{\Delta} NH_3 + NaCl + H_2O$

(ii) $NH_3 + CO_2 + H_2O \longrightarrow NH_4HCO_3$ (B)

(iii) $NH_4HCO_3 + NaCl \longrightarrow \underset{(C)}{NaHCO_3} + NH_4Cl$

(iv) $2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$ (D)

05. (1) The black coloured compound may be FeS because it reacts with dil. H_2SO_4 to produce H_2S.

$\underset{(A)}{FeS} + H_2SO_4 \longrightarrow FeSO_4 + \underset{(B)}{H_2S}$

(2) Gas H_2S on passing through HNO_3 gives turbidity of S .

$\underset{(B)}{H_2S} + \underset{(C)}{2HNO_3} \longrightarrow 2NO_2 + 2H_2O + \underset{(D)}{S}$

(3) (E) is $CuSO_4$ because it gives white precipitate of $BaSO_4$ with $BaCl_2$ & blue color with NH_4OH .

$\underset{(E)}{CuSO_4} + BaCl_2 \longrightarrow CuCl_2 + \underset{\text{white}}{BaSO_4}$

(4) Gas (B) i.e. H_2S gives black precipitate with $CuSO_4$.

$\underset{(E)}{CuSO_4} + H_2S \longrightarrow \underset{\text{(F) black}}{CuS} + H_2SO_4$

(5) Compound F (CuS) gives $Cu(NO_3)_2$ with HNO_3 which on treating with NH_4OH gives blue colour .

$\underset{(F)}{CuS} + 2HNO_3 \longrightarrow Cu(NO_3)_2 + H_2S$

$Cu(NO_3)_2 + 4NH_4OH \longrightarrow \underset{\text{(G) blue}}{[Cu(NH_3)_4](NO_3)_2} + 4H_2O$

(6) (G) on acidifying with CH_3COOH and then treating with $K_4Fe(CN)_6$ gives chocolate coloured precipitate of $Cu_2[Fe(CN)_6]$.

$[Cu(NH_3)_4].(NO_3)_2 + 4CH_3COOH \longrightarrow Cu(NO_3)_2 + 4CH_3COONH_4$
$2Cu(NO_3)_2 + K_4Fe(CN)_6 \longrightarrow Cu_2[Fe(CN)_6] + 4KNO_3$.

06. (i) (A) is an alkali and the reaction is , $\underset{(A)}{2NaOH} + Zn \xrightarrow{\Delta} Na_2ZnO_2 + \underset{(B)}{H_2}$.

(ii) (A) is NaOH and (C) is phosphorous . The reaction is ,

$\underset{(A)}{3NaOH} + 3H_2O + P_4 \xrightarrow{\Delta} PH_3 + 3NaH_2PO_2$

(iii) (D) is NH_3 gas and the reaction is , $\underset{(A)}{NaOH} + \underset{(D)}{NH_4Cl} \xrightarrow{\Delta} \underset{gas}{NH_3} + NaCl + H_2O$

07. It is clear from point (iv) that (X) is H_2O_2 .
$Ti(SO_4)_2 + 2H_2O + \underset{(X)}{H_2O_2} \longrightarrow \underset{\text{pertitanic acid (yellow)}}{H_2TiO_4} + 2H_2SO_4$
(i) $2K_2MnO_4 + 2H_2O \longrightarrow 2MnO_2 + O_2 + 4KOH$.
(ii) $\underset{(X)}{H_2O_2} + Cl_2 \longrightarrow 2HCl + O_2$
(iii) $H_2O_2 + 2KI + H_2SO_4 \longrightarrow Fe_2SO_4 + 2H_2O + I_2\uparrow$

08. (i) Step 1 suggest that the compound (X) contains SO_4^{2-} radical .
(ii) Step 3 suggest that the compound (X) contains Cu^{2+} radical .
(iii) Hence the salt is $CuSO_4$.
(i) $CuSO_4 + BaCl_2 \longrightarrow \underset{\substack{\text{white ppt.}\\\text{(insoluble in HCl)}}}{BaSO_4} + CuCl_2$.
(ii) $\underset{(X)}{2CuSO_4} + 4KI \longrightarrow 2CuI_2 + 2K_2SO_4$
$\underset{\text{(unstable)}}{CuI_2} \longrightarrow Cu_2I_2 + I_2$
$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$
(iii) $\underset{(X)}{2CuSO_4} + K_4Fe(CN)_6 \longrightarrow \underset{\text{chocolate coloured ppt.}}{Cu_2[Fe(CN)_6]} + 2K_2SO_4$

09. (i) (X) gives brick red flame test so it contains Ca^{2+} ;
(ii) (X) gives smell of Cl_2 in moist air so (X) is $CaOCl_2$.
$\underset{(X)}{CaOCl_2} + \underset{\text{(moist air)}}{CO_2} \longrightarrow CaCO_3 + Cl_2$
or $\underset{(X)}{CaOCl_2} + H_2O \longrightarrow Ca(OH)_2 + Cl_2$
(iii) With KI & CH_3COOH , it reacts as follows ,
$CaOCl_2 + 2KI + 2CH_3COOH \longrightarrow Ca(CH_3COO)_2 + I_2 + 2KCl + H_2O$

10. (i) (X) imparts golden yellow flame and so contain Na^+ .
(ii) Step 2 suggest that (X) is NaOH because it reacts with Zn to give H_2 .
$Zn + \underset{(X)}{2NaOH} \longrightarrow Na_2ZnO_2 + H_2$
(iii) (X) is also justified by step 3 reactions .
$\underset{(X)}{2NaOH} + SnCl_2 \longrightarrow \underset{\text{white ppt.}}{Sn(OH)_2} + 2NaCl$
$Sn(OH)_2 + \underset{\text{(X)excess}}{2NaOH} \longrightarrow \underset{\text{soluble}}{Na_2SnO_2} + 2H_2O$

itate

11. (i) The compound (B) reacts with NaCl to give white ppt. (D) soluble in NH_4OH to (D) is AgCl .
(ii) Thus (B) must contain Ag^+ ion .
(iii) (B) is obtained from (A) and dil. HNO_3, so (B) is $AgNO_3$ and (A) is Ag .

$$\underset{(A)}{3\,Ag} + 4\,HNO_3 \longrightarrow \underset{(B)}{3\,AgNO_3} + \underset{(C)}{NO} + 2\,H_2O$$

$$\underset{(B)}{AgNO_3} + NaCl \longrightarrow \underset{(D)}{AgCl} + NaNO_3$$

$$\underset{(D)}{AgCl} + 2\,NH_4OH \longrightarrow \underset{\text{soluble}}{Ag(NH_3)_2Cl} + 2\,H_2O$$

$$2\,AgNO_3 + Na_2S_2O_3 \longrightarrow \underset{\text{(E) white}}{Ag_2S_2O_3} + 2\,NaNO_3\ .$$

$$Ag_2S_2O_3 \longrightarrow \underset{\text{(E) black}}{Ag_2S} + SO_3$$

12. (X) decolourizes $K_2Cr_2O_7$ solution hence it should be reducing agent .
(i) $K_2Cr_2O_7 + H_2SO_4 + 3\,SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$

$Cr_2O_7^{2-} + 2\,H^+ + 3\,SO_2 \longrightarrow 2\,Cr^{3+} + 3\,SO_4^{2-} + H_2O$

(ii) $SO_2 + H_2O_2 \longrightarrow H_2SO_4$

$H_2SO_4 + BaCl_2 \longrightarrow BaSO_4\downarrow + 2\,HCl$

or $SO_2 + H_2O_2 + BaCl_2 \longrightarrow BaSO_4\downarrow + 2\,HCl$

(iii) $SO_2 + 2\,H_2S \longrightarrow 3\,S\downarrow + 2\,H_2O$. [X] is SO_2 .

13. (1) (X) gives black ppt. in acid medium & thus it may be $HgCl_2$, $PbCl_2$, $CuCl_2$ or $SnCl_2$.
(2) Black ppt. are insoluble in yellow ammonium sulphide & thus it is not $SnCl_2$.
(3) Step 3 & 4 suggest that (X) is $HgCl_2$.

(i) $$\underset{(X)}{HgCl_2} + H_2S \longrightarrow \underset{\text{black ppt.}}{HgS} + 2\,HCl$$

(ii) $$\underset{(X)}{2\,HgCl_2} + SnCl_2 \longrightarrow SnCl_4 + \underset{\text{white ppt.}}{Hg_2Cl_2}\ .$$

$$Hg_2Cl_2 + SnCl_2 \longrightarrow SnCl_4 + \underset{\text{grey ppt.}}{2\,Hg}$$

(iii) $$\underset{(X)}{HgCl_2} + 2\,KI \longrightarrow \underset{\text{red ppt.}}{HgI_2} + 2\,KCl$$

$$HgI_2 + 2\,KI \longrightarrow K_2HgI_4$$

14.(i) Aqueous solution of gas (X) turns red litmus blue , the solution is alkaline in nature. So the gas may be NH_3.
(ii) With $CuSO_4$, NH_4OH gives deep blue coloured $Cu(NH_3)_4SO_4$.
i.e. $$CuSO_4 + 4\,NH_4OH \longrightarrow \underset{\text{(deep blue complex)}}{[Cu(NH_3)_4]SO_4} + H_2O$$

(iii) $$FeCl_3 + 3\,NH_4OH \longrightarrow \underset{\text{(brown ppt.)}}{Fe(OH)_3} + 3\,NH_4Cl$$

The brown ppt. of $Fe(OH)_3$ form soluble $Fe(NO_3)_3$ with dil. HNO_3 .

$$Fe(OH)_3 + 3\,HNO_3 \longrightarrow \underset{\text{(soluble)}}{Fe(NO_3)_3} + 3\,H_2O$$

Hence X is NH_3 .

15. (1)(X) give yellow ppt. insoluble in NH_4OH with Ag^+ and so contain I^- ions .
(2)Step (a) suggest it to be KI .

(i) $$Cu^{2+} + 5I^- \longrightarrow \underbrace{\underset{\text{white ppt}}{Cu_2I_2} + \underset{\text{brown}}{I_3^-}}_{\text{Brown ppt.}}$$

$$I_3^- + 2S_2O_3^{2-} \longrightarrow 3I^- + S_4O_6^{2-}$$

(ii) $Ag^+ + KI \longrightarrow AgI + K^+$
(X) yellow ppt.

16. (i) $Na_2B_4O_7 + 7\,H_2O \longrightarrow 2\,NaOH + 4\,H_3BO_3$
(X)

(ii) $Na_2B_4O_7 \,.\, 10\,H_2O \xrightarrow{\Delta} Na_2B_4O_7 + 10\,H_2O$

(iii) $Na_2B_4O_7 \xrightarrow{\Delta} 2\,NaBO_2 + B_2O_3$
glassy mass

(iii) $Na_2B_4O_7 + H_2SO_4 + 5\,H_2O \longrightarrow Na_2SO_4 + 4\,H_3BO_3$ (weak acid)

17. (i) $CaOCl_2 + 2KI + 2CH_3COOH \longrightarrow Ca(CH_3COO)_2 + I_2 + 2KCl + H_2O$
(X)

(ii) $CaOCl_2\,(aq.) + CO_2 \longrightarrow CaCO_3 + Cl_2$
Turbid white ppt.

(iii) $CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$
(X)

$C_2H_5OH + Cl_2 \longrightarrow CH_3CHO + 2\,HCl$
$CH_3CHO + 3\,Cl_2 \longrightarrow CCl_3CHO + 3\,HCl$
$2\,Ca(OH)_2 + 2\,CCl_3CHO \longrightarrow 2\,CHCl_3 + (HCOO)_2\,Ca$
(i), (ii) & (iii) suggest that X is bleaching powder.

18. (i) (X) removes black stains from old oil painting so (X) is H_2O_2.

(ii) $5\,H_2O_2 + 2\,KMnO_4 + 3\,H_2SO_4 \longrightarrow K_2SO_4 + 2\,MnSO_4 + 8\,H_2O + 5\,O_2$
(X)

(iii) $3\,H_2O_2 + 2\,KMnO_4 \longrightarrow 2\,MnO_2 + 2\,KOH + 3\,O_2 + 2\,H_2O$
(X)

(iv) $4\,H_2O_2 + PbS \longrightarrow PbSO_4 + 4\,H_2O$
black white

19. Compound A :

(i) (A) gives on heating two oxides of S and so (A) is $FeSO_4 \,.\, 7\,H_2O$

$FeSO_4 \,.\, 7\,H_2O \xrightarrow{\Delta} FeSO_4 + 7\,H_2O$
(A)

$2\,FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2 + SO_3$
$FeSO_4 + 2\,NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4$
$Fe^{2+} \xrightarrow[\text{alkali medium}]{\text{oxidation}} Fe^{3+} + e^-$

Compound B :

(i) (B) gives green colour flame and thus it contains Ba^{+2} ion as it also does not give ppt. with H_2S

(ii) (B) on heating with $K_2Cr_2O_7$ & H_2SO_4 conc. gives red gas i.e. chromyl chloride and thus (B) also have Cl^- ion.

(iii) Thus (B) is $BaCl_2$.

$2\,BaCl_2 + K_2Cr_2O_7 + 3\,H_2SO_4 \longrightarrow K_2SO_4 + 2\,Cr_2O_2Cl_2 + 2\,BaSO_4 + 3\,H_2O$
Red gas

$CrO_2Cl_2 + 4\,NaOH \longrightarrow Na_2CrO_4 + 2\,NaCl + 2\,H_2O$
yellow solⁿ

NH₃.

20. (i) $\underset{(A)}{ZnCO_3} \longrightarrow \underset{(C)}{ZnO} + \underset{(B)}{CO_2} \uparrow$(Non combustible gas)

(ii) $CO_2 + \underset{\text{lime water}}{Ca(OH)_2} \longrightarrow CaCO_3 + H_2O$

(iii) $CaCO_3 + \underset{\text{excess}}{CO_2} + H_2O \longrightarrow Ca(HCO_3)_2$

$ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$

(iv) $2ZnCl_2 + K_4[Fe(CN)_6] \longrightarrow \underset{\text{white}}{Zn_2[Fe(CN)_6]} + 4KCl$

(v) $ZnCO_3 + 2HCl \longrightarrow ZnCl_2 + H_2O + CO_2$

(vi) $ZnCl_2 + H_2S \xrightarrow{NH_4OH} \underset{\text{white(D)}}{ZnS} + 2HCl$

21. (i) $\underset{(A)}{4FeS} + 7O_2 \longrightarrow \underset{(B)}{4SO_2} + 2\,Fe_2O_3$

(ii) $\underset{(A)}{FeS} + H_2SO_4 \longrightarrow \underset{(D)}{FeSO_4} + \underset{(C)}{H_2S}$

(iii) $\underset{(C)}{2H_2S} + \underset{(B)}{SO_2(aq)} \longrightarrow 2H_2O + \underset{\text{turbidity}}{3S}$

(iv) $3FeSO_4 + 2K_3[Fe(CN)_6] \longrightarrow \underset{\text{blue colour(E)}}{Fe_3[Fe(CN)_6]_2} + 3K_2SO_4$

22. X is anhydrous $AlCl_3$,a lewis acid

(i) $AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl$ (fumes)

(ii) $HCl + NH_4OH \longrightarrow \underset{\text{white fumes}}{NH_4Cl} + H_2O$

(iii) $AlCl_3 + 3NaOH \longrightarrow 3NH_4Cl + Al(OH)_3$ (white ppt.)

$Al(OH)_3 + NaOH \longrightarrow \underset{\text{(soluble)}}{NaAlO_2} + 2\,H_2O$

(iv) $AlCl_3 + H_2S \longrightarrow$ No ppt. in acidic medium

23. X is Sn^{2+}

(i) $Sn^{2+} + H_2S \longrightarrow SnS + 2H^+$

(ii) $SnS + (NH_4)_2S \longrightarrow$ soluble

(iii) $Sn^{2+} + 2NaOH \longrightarrow \underset{\text{(white ppt)}}{Sn(OH)_2} + 2Na^+$

(iv) $Sn(OH)_2 + 2NaOH \longrightarrow \underset{\text{(soluble)}}{Na_2SnO_2} + 2H_2O$

(v) $Sn^{2+} + 2FeCl_3 \longrightarrow Sn^{4+} + 2FeCl_2$

24. Inorganic compound (A) is PH_4I

(i) $\underset{(A)}{PH_4I} + KOH \longrightarrow \underset{(B)}{PH_3} + \underset{(C)}{KI} + H_2O$

(ii) $\underset{(B)}{2PH_3} + 4O_2 \longrightarrow \underset{(D)}{P_2O_5} + 3H_2O$

(iii) $3CuSO_4 + 2PH_3 \longrightarrow Cu_3P_2 + 3H_2SO_4$

(iv) $2Cu^{2+} + 5I^- \longrightarrow \underbrace{\underset{\text{white}}{Cu_2I_2 \downarrow} + \underset{\text{brown}}{I_3^-}}_{\text{Brown ppt.}}$

25. The reactions indicate that the compound (A) is sodium thiosulphate. It is formed in step (i) by passing gas (B) which is either I_2 or SO_2.

(i) $Na_2S + Na_2SO_3 + \underset{(B)}{I_2} \longrightarrow Na_2S_2O_3 + 2NaI$

or $2Na_2S + Na_2SO_3 + 3SO_2 \longrightarrow 3Na_2S_2O_3$

(ii) $2AgNO_3 + Na_2S_2O_3 \longrightarrow \underset{\text{(White ppt)}}{Ag_2S_2O_3} + 2NaNO_3$

$Ag_2S_2O_3 + H_2O \longrightarrow \underset{\text{(C) black}}{Ag_2S} + H_2SO_4$

(iii) $S_2O_3^{2-} + Fe^{3+} \longrightarrow \underset{\text{(D) violet}}{[Fe^{3+}(S_2O_3)_2]^-}$

$[Fe(S_2O_3)_2]^- + Fe^{3+} \longrightarrow 2Fe^{2+} + S_4O_6^{2-}$

(iv) $2Cu^{2+} + 3S_2O_3^{2-} \longrightarrow \underset{\text{white ppt.}}{Cu_2S_2O_3\downarrow} + S_4O_6^{2-}$

$\underset{\text{white ppt.}}{3Cu_2S_2O_3\downarrow} + \underset{\text{(excess)}}{2Na_2S_2O_3} \longrightarrow \underset{\text{(E) soluble complex}}{Na_4[Cu_6(S_2O_3)_5]}$

26. A = $CoCl_2$, B = CoS, C = $K_4[Co(CN)_6]$, D = $K_3[Co(CN)_6]$, E = Na_3 $[Co(CO_3)_3]$

27. A = $CuCO_3$, B = CuO, C = CO_2, D = Cu, E = $Cu_2[Fe(CN)_6]$, F = $Ca(HCO_3)_2$.

28. The ors is chromite $FeOCr_2O_3$.

(i) $4FeO.\ Cr_2O_3 + 8Na_2CO_3 + 7O_2 \xrightarrow{\text{Lime}} \underset{(B)}{2Fe_2O_3} + \underset{(C)}{8Na_2CrO_4}$

(ii) $\underset{(B)}{Fe_2O_3} + 6HCl \longrightarrow 2FeCl_3 + 3H_2O$

$4FeCl_3 + 3K_4Fe(CN)_6 \longrightarrow \underset{\text{(D) Prussian blue}}{Fe[Fe(CN)_6]_3} + 12\ KCl$

(iii) $2Na_2CrO_4 + H_2SO_4 \longrightarrow \underset{(E)}{Na_2Cr_2O_7} + Na_2SO_4 + H_2O$

(iv) $Na_2Cr_2O_7 + 2KCl \longrightarrow \underset{\text{(F) orange red}}{K_2Cr_2O_7} + 2NaCl$

(v) $K_2Cr_2O_7 + 4H_2SO_4 + 3H_2C_2O_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 6CO_2 + 7H_2O$

$Cr_2(SO_4)_3 + 6K_2C_2O_4 \longrightarrow \underset{\text{(G) Blue crystal}}{2K_3[Cr_2(C_2O_4)_3]} + 3K_2SO_4$

29. A = $CuSO_4.\ H_2O$, B = $CuSO_4$, C = CuO, D = SO_3 , E = Ag , F = NO_2

30.(i) $FeSO_4$ + dil $H_2SO_4 \longrightarrow$ no gas

(ii) $10FeSO_4 + 8H_2SO_4 + 2KMnO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$

(iii) $FeSO_4 \longrightarrow Fe_2O_3 + SO_2\uparrow + SO_3\uparrow$

(iv) $K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$

(v) $Cr_2(SO_4)_3 + 3Ba(NO_3)_2 \longrightarrow \underset{\text{white}}{3BaSO_4} + 2Cr\ (NO_3)_3$

(vi) $Fe_2O_3 + 3C \longrightarrow 2\ Fe + 3CO\uparrow$

31. $ZnSO_4 + 4NaOH \longrightarrow Na_2ZnO_2 + Na_2SO_4 + 2H_2O$

$Na_2ZnO_2 + 2HCl \longrightarrow Zn(OH)_2\downarrow + 2NaCl$

$Zn(OH)_2 + 2HCl \longrightarrow ZnCl_2 + 2H_2O$

Hence the mixture contains NaOH & $ZnSO_4$

32. $2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$

168g.(X) (Y)   18g.(B)   44g.(A)

Since 16g. of $NaHCO_3$ gives 44 g. of CO_2 & 18g. of H_2O

∴ 16.8g. of $NaHCO_3$ gives 4.4g. of CO_2 (A) & 1.8g. of H_2O(B).

Now , $CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 \downarrow + H_2O$

$H_2O(g) \longrightarrow H_2O(l)$

$Na_2CO_3 + 2H_2O \longrightarrow 2NaOH + H_2CO_3$

Alkaline solution

$BaCl_2 + H_2CO_3 \longrightarrow BaCO_3 \downarrow + 2HCl$

white (Z)

$BaCO_3 + H_2SO_4 \longrightarrow BaSO_4 + H_2O + CO_2\uparrow$

A = CO_2 , B = H_2O , & Y = Na_2CO_3

33. $2NH_4Cl + MnO_2 + 2H_2SO_4 \xrightarrow{\Delta} MnSO_4 + Cl_2 + 2H_2O + (NH_4)_2SO_4$

$NH_4Cl + NaOH \xrightarrow{\Delta} NH_3 \uparrow + H_2O$

turns red litmus to blue

$2\,FeCl_2 + 2K_3Fe(CN)_6 \longrightarrow Fe_3[Fe(CN)_6]_2 + 6KCl$

blue colour

$Fe^{2+} \xrightarrow{\text{oxidation in aqueous solution}} Fe^{3+}$

$Fe^{3+} + 3SCN \longrightarrow Fe\,(SCN)_3$

Blood red colour

It is a mixture of $FeCl_2$ and NH_4Cl.

34.(i) $FeSO_4 + BaCl_2 \longrightarrow FeCl_2 + BaSO_4$

(A)   white ppt. (B)

(ii) $FeSO_4.7H_2O \xrightarrow{\Delta} FeSO_4 + 7H_2O$

$2FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2 + SO_3$

(E)   (C)   (D)

brown residue

(iii) $Fe_2O_3 + 6HCl \longrightarrow 2FeCl_3 + 3H_2O$

(E)   (F) yellow solution

(iv) $2\,FeCl_3 + H_2S \longrightarrow 2FeCl_2 + 2HCl + S\downarrow$

(H)   (G)

(v) $FeCl_3 + 3NH_4SCN \longrightarrow Fe(SCN)_3 + 3NH_4Cl$

(I)

35.(i) $FeSO_4\,.\,7\,H_2O \xrightarrow{\Delta} FeSO_4 + 7\,H_2O$

(A)   (B)

$2\,FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2 + SO_3$

(B)   (D)   (E)   (F)

Brown

(ii) (B) is soluble in water and reacts with NO give brown compound.

$FeSO_4(aq.) + NO \longrightarrow FeSO_4.NO.$

Brown ring (C)

(iii) Gaseous mixture decolorises acidified $KMnO_4$

$5SO_2 + 2KMnO_4 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$

(iv) $SO_3 + H_2O \longrightarrow H_2SO_4$

$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HCl$

white ppt.

36. $X \longrightarrow A + B + Y$

20.02g. 4.4g. 1.8g. 13.8g.

The above data reveals that $\underset{(X)}{2MHCO_3} \longrightarrow \underset{(A)}{CO_2} + \underset{(B)}{H_2O} + \underset{(Y)}{M_2CO_3}$

4.4g. CO_2 is obtained by 20.02g. $MHCO_3$

4.4g. CO_2 is obtained by 200.2g. $MHCO_3$.

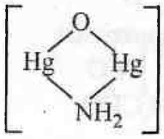
Molecular weight of $MHCO_3$ is $\frac{200.2}{2}=100.1$

$\therefore$ Atomic weight of M = 39.1

Thus metal is potassium.

$\underset{(X)}{2\,KHCO_3} \longrightarrow \underset{(A)}{CO_2} + \underset{(B)}{H_2O} + \underset{(Y)}{K_2CO_3}$

37. (i) $NH_4^+ + NaOH \longrightarrow NH_3 + Na^+ + H_2O$

$2K_2HgI_4 + 3NaOH + NH_3 \longrightarrow$  $I + 4KI + 2H_2O + 3NaI$

brown

(ii) $SO_4^{2-} + BaCl_2 \longrightarrow BaSO_4 + 2Cl^-$

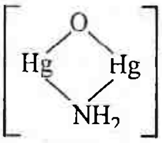
(iii) $4Cl^{2-} + K_2Cr_2O_7 + 3H_2SO_4 \longrightarrow 2CrO_2Cl_2 + K_2SO_4 + 3H_2O + 2SO_4^{2-}$

(iv) $3Fe^{+2} + 2K_3Fe(CN)_6 \longrightarrow Fe_3[Fe(CN)_6]_2 + 6K^+$

(B) blue

38. $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O \longrightarrow Fe^{2+} + SO_4^{2-} + 2NH_4^{2+} + SO^{2-} + 6H_2O$

Mohr salt

$3NaOH + NH_3 + 2K_2HgI_4 \longrightarrow$  $I + 4KI + 3NaI + 2H_2O$

$3Fe^{2+} + 2K_3Fe(CN)_6 \longrightarrow Fe_3[Fe(CN)_6]_2 + 6K^+$

Blue

$SO_4^{2-} + BaCl_2 \longrightarrow BaSO_4 + 2Cl^-$

White ppt.

39. $\underset{(A)}{(NH_4)_2Cr_2O_7} \xrightarrow{\Delta} \underset{(C)}{N_2} + \underset{\text{green (B)}}{Cr_2O_3} + 4H_2O$

$N_2 + 3Mg \xrightarrow{\Delta} \underset{(D)}{Mg_3N_2}$

$\underset{(D)}{Mg_3N_2} + 6H_2O \longrightarrow 3Mg(OH)_2 + \underset{(E)}{2NH_3}$

$\underset{(E)}{NH_3} + HCl \longrightarrow \underset{\text{(White fumes)}}{NH_4Cl}$

40. (i) (B) forms double salt with $Al_2(SO_4)_3$ and thus, may be K_2SO_4.

(ii) $(A) + S \longrightarrow (B)\ K_2SO_4$

$\therefore$ 1.743 g K_2SO_4 is obtained by 1.422g.A

$\therefore$ 174 g K_2SO_4 is obtained by $\frac{1.422 x 174}{1.743}=142\ g.A.$

$\therefore$ 174 g. K_2SO_4 requires 32g.S.

$\therefore$ 1.743 g K_2SO_4 requires $\frac{32x1.743}{174}=0.321g.S.$

Thus, given data confirms that (B) is K_2SO_4.

Now $2(A) + S \longrightarrow K_2SO_4$

(A potassium salt)

M.wt. of (A) x 2 = 142

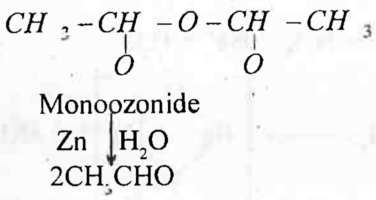
$\therefore$ M.wt. of (A) = 71

Since (A) is pot. salt : .M.wt. of left component = 71 - 39 = 32.

Thus salt is KO_2.

$$\underset{(A)}{2KO_2} + S \longrightarrow \underset{(B)}{K_2SO_4} \xrightarrow{Al_2(SO_4)_3} \underset{Aq.\ (C)}{K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\,H_2O}$$

41. (i) $O_3 + CH_3-CH=CH-CH_3 \longrightarrow$



$$CH_3-\underset{\underset{O}{|}}{CH}-O-\underset{\underset{O}{|}}{CH}-CH_3$$

Monoozonide

$\downarrow$ Zn H_2O

$2CH_3CHO$

(ii) $\underset{(A)}{5O_3} + 2KOH \longrightarrow \underset{\text{Potassium Ozonide}}{2KO_3} + H_2O(g) + \underset{(C)}{5\,O_2}$

42. $\underset{(A)}{Pb_3O_4} + 4HNO_3 \longrightarrow \underset{(B)}{PbO_2} + Pb\,(NO_3)_2 + 2H_2O$

$\underset{(C)}{Pb(NO_3)_2 + 2H_2O} \xrightarrow{2KI} PbI_2 + 2KNO_3$

$\underset{(B)}{PbO_2} \xrightarrow[+4HNO_3]{2Mn(NO_3)} \underset{\text{(pink colour)}}{HMnO_4} + 4\,Pb\,(NO_3)_3 + 2H_2O$

43. $A \rightarrow NH_3$ $B \rightarrow CaCO_3$

44. $Bi(NO_3)_3 + 3KI \longrightarrow \underset{\text{Black}}{BiI_3\downarrow} + 3KNO_3$

$BiI_3 + \underset{\text{(excess)}}{KI} \longrightarrow \underset{\text{orange complex}}{K[BiI_4]}$

45. $A = NH_4NO_3$; $B = N_2O$ & $C = H_2O$

$NH_4NO_3 \longrightarrow N_2O + 2H_2O$

$P_4 + 10N_2O \longrightarrow \underset{(D)}{P_4O_{10}} + 10N_2$

46. (A) $Hg_2(NO_3)_2$ (B) Hg_2Cl_2 (C) $HgCl_2$ (D) K_2HgI_4 (E) Hg (F) $[Fe(H_2O)_5(NO)]^{2+}$

47. Metal ion, Cu^{2+}

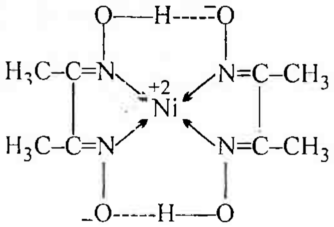
$Cu^{2+}\,(aq) + H_2S\,(aq) \longrightarrow \underset{(A)}{CuS} + 2H^+$

$2Cu^{2+} + 4I^-\,(aq) \longrightarrow \underset{(B)}{Cu_2I_2} + I_2$

48. $A = MnSO_4$, $B = Na_2MnO_4$, $C = NaMnO_4$, $D = MnO_2$, $E = HMnO_4$, $F = BaSO_4$

49. $A = NaHSO_3$, $B = Na_2SO_3$, $C = Na_2S_2O_3$, $D = Na_2S_4O_6$

50. A = HgI_2, B = KI, C = HgS, D = Hg

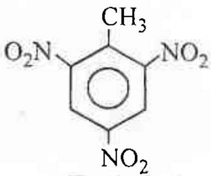
51. 

hybridisation – dsp^2, M.M = 0, Diamagnetic

52. $A_1 = CuCO_3.Cu(OH)_2$ (malachite)
$A_2 = Cu_2S$ (copper glance)
S = CuO
P = Cu_2I_2
G = $SO_2\uparrow$

53. A = $[Fe(SCN)(H_2O)_5]^{2+}$, M.M. = $\sqrt{35}$
Pentaaquathiocyanato-S-iron (III) ion
B = $[FeF_6]^{3-}$, M.M. = $\sqrt{35}$
hexaflouroferrate (III) ion

54. A = conc. H_2SO_4 B = Br_2 C = NO_2^+ D =



(T.N.T.)

(Explosive)

55. A –$[Ti(H_2O)_6]^{3+}$
B –HCl
MCl_4–$TiCl_4$
Purple colour of $[Ti(H_2O)_6]^{3+}$ is due to d–d transition.

$O)]^{2+}$

BANSALCLASSES

TARGET IIT JEE 2007

PHYSICAL CHEMISTRY

XII (ALL)

SOLID STATES

" A SPECIALLY DESIGNED KIT FOR LEARNING."

CONTENTS

THE KEY	⟶	Basic principles of subjects. An outline of the topics to be discussed in class lectures.
THE ATLAS	⟶	Basic layout of subject. A route map correlating different subtopics in coherent manner
EXERCISE I	⟶	Introductory problems to get first hand experience of problem solving.
PROFICIENCY TEST	⟶	To check you newly acquired concepts.
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EXERCISE III	⟶	Test your objective skill.
EXERCISE IV	⟶	A collection of previous ten years JEE problems.

THE KEY

Crystalline solids:

Crystalline solids are those whose atom, molecules or ions have an ordered arrangement extending over a **Long Range.** example-(Rock salt, NaCl).

Amorphous solids:

Amorphous solids are those whose constitutent particles are randomly arrange and have no ordered long range structure. example: Rubber, Glass ect.

TYPES OF CRYSTALLINE SOLIDS:

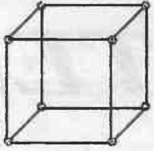
Type of Solid	**Intermolecular forces**	**Properties**	**Examples**
Ionic	Ion-Ion forces	Brittle, hard high Melting	NaCl, KCl, $MgCl_2$
Molecular	Dispersion forces/Dipole-Dipole /H-bond	Soft, low melting non-conducting	H_2O, Br_2, CO_2, CH_4
Covalent network	Covalent bonds	Hard: High melting	C-Diamond SiO_2
Metallic	Metallic bonds	Variable hardness and melting point conducting	Na, Zn, Cu, Fe

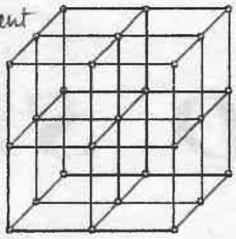
TYPES OF UNIT CELL:

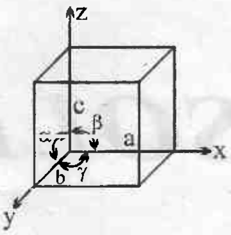
Collection of lattice points, whose repetition produce whole lattice is called a unit cell. The whole lattice can be considered to be made by repetion of unit cell.

2) Crystal is formed when unit cell is repeated in three dimensions...

(4) lattice points:- Location of constituent Particles in a unit cell..





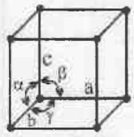


1. Unit Cell:

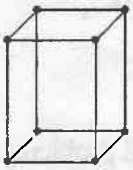
(1) Smallest part of a crystal that can represent the picture of entire crystal.

Space (3) lattice. Collection of array of points Showing constituent Particles arrang. of a crystal in 3 D.

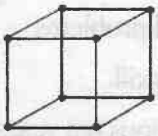
Crystal Systems		**Bravais Lattice**	**Unit Cell Parameters**	
			Intercepts	**Crystal Angles**
1	Cubic	Primitive, Face Centered, Body Centered	a = b = c	$\alpha = \beta = \gamma = 90°$
2	Orthorhombic	Primitive, Face Centered, Body Centered, End Centered	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$
3	Rhombohedral	Primitive	a = b = c	$\alpha = \beta = \gamma \neq 90°$
4	Monoclinic	Primitive, End Centered	$a \neq b \neq c$	$\alpha = \gamma = 90°, \beta \neq 90°$
5	Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$
6	Tetragonal	Primitive, Body Centered	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$
7	Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$



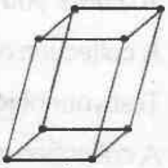
Simple Cubic
a = b = c
$\alpha = \beta = \gamma = 90°$



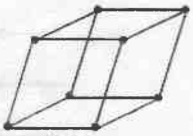
Tetragonal
$a = b \neq c$
$\alpha = \beta = \gamma = 90°$



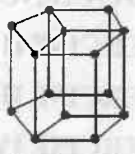
Orthorhombic
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$



Monoclinic
$a \neq b \neq c$
$\alpha = \gamma = 90°, \beta \neq 90°$



Triclinic
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$



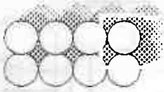
Hexagonal Primitive
$a = b \neq c$
$\alpha = \beta = 90°, \gamma = 120°$

There are 4 ways in which c.p. are arrenged in ~~[illegible]~~ unit cell.—

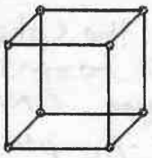
(1) [illegible] at the corners of the cube....

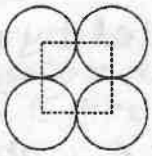
1.1 Primitive or simple cubic (PS/SC) unit cell: Spheres in one layer sitting directly on top of those in previous layer, so that all layers are identical. Each sphere is touched by six other, hence coordination number is 6. 52% of available space occupied by spheres.

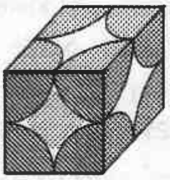
Example: Polonium crystallises in simple cubic arrangement.



(1) Atoms are only at their corners. Of the cells..







Z = 1 ; C.N. = 6

1.2 Body Centered cubic (BCC) unit cell: Spheres in one layer sit in the depression made by first layer in a-b-a-b manner. Coordination number is 8, and 68% of available space is occupied by atoms.

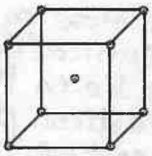
Example: Iron, sodium and 14 other metal crystallises in this manner.

Coordination no. :- No. of nearest neighbours that an atom has in a unit cell...

SCC → 6 ; BCC → 8 ; FCC → 12

HCP & CCP ; FCC has 12

(2) P/S unit cell + One atom located at the centre of the cubic cell.



Z = 2 ; C.N. = 8

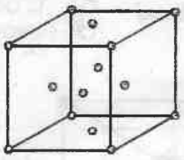
HCP AB AB

CCP ABC ABC

1.3 Face centered cubic (FCC) unit cell:

Examples : Al, Ni, Fe, Pd all solid noble gases etc.

(3) Atoms are at the corners, plus centre of each face of cube....



Z = 4 : C.N. = 12

(4) end centred cubic unit cell :- doesn't exist in nature.

2. Density of cubic crystals:

Apart from corners, choose any two opp. faces & place face atom at their faces...

TYPE OF PACKING:

3. Closest packing of atoms: This is the most efficient way of packing 74% of available space is occupied by spheres and coordination number is 12.

(i) ***Hexagonal close pack (A-B-A-B) type packing :*** Each layer has hexagonal arrangement of touching sphere and 3rd layer is similar (exactly on top) of first layer.

(ii) ***Cubic close pack (A-B-C-A-B-C):*** AB layers are similar to HCP arrangement but third layer is offset from both A and B layers. The fourth layer is exactly on top of first layer.

Bravais Lattice

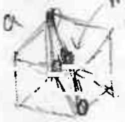
Total 14 Bravais lattice exist in nature, out of (7×4) = 28 possible....

(2) Atomic Radius

(a) PS/SC.

$r = a/2$.

(b) BCC

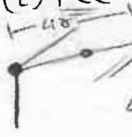


m.p. of hypotenuse = $\sqrt{3}a$.

Body atoms touch along hypo. not corner.

$4r = \sqrt{3}a$ i.e. $r = \frac{\sqrt{3}a}{4}$

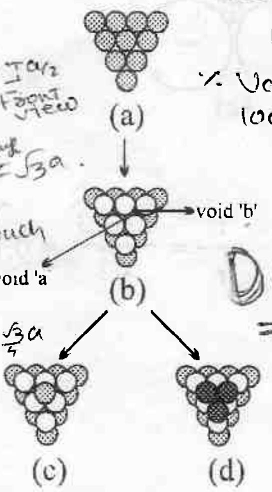
(c) FCC



Touch on face

$4r = \sqrt{2}a$

$r = a/2\sqrt{2}$



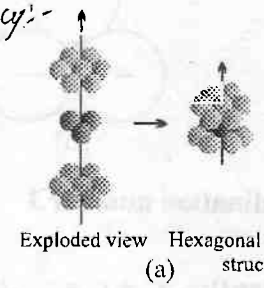
Packing efficiency :- 100 PF.

% Vacant space 100 − 100 PF = 100(1 − PF)

Density $= \frac{ZM}{N_a a^3}$

$\frac{M}{N_a}$ = mass of 1 atom

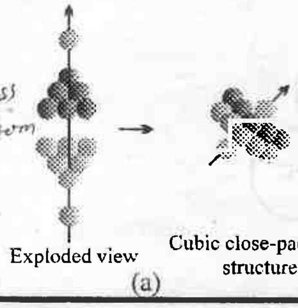
Z = eff no. of atoms.



Exploded view

Hexagonal close-packed structure

(a)



Exploded view

Cubic close-packed structure

(a)

Analysis of Cubic Sys

(1) Eff. no. of atoms in a unit cell.

(a) Simple | Primitive cubic cell $8 \times 1/8 = 1$.

(b) $8 \times 1/8 + 1 = 2$ BCC

(c) $8 \times 1/8 + 6 \times 1/2 = 4$ FCC

(3) Packing fraction

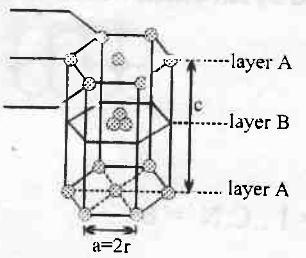
Fraction of total volume of unit cell occupied by eff. no. of atoms :-

(a) $1 \times \frac{4}{3} \pi a^3/8 = \pi/8$

(b) $2 \times \frac{3a^3\sqrt{3}}{a^3}$

(a) $1 \times \frac{4/3 \pi a^3/8}{a^3} = 0.5236$

Hexagonal primitive unit cell



Close packings are of 4 types

		Type	Geometry	C.N.C
Hexagonal	CP	ABAB	Hexagonal	12
Cubic	CP	ABCABC	FCC	12
Square	SCP	AAA	Simple cubic cell	6
Triangular	TCP	AAA	Rombohedral	8

H.C.P. :- generated by placing the sphere of III layer in such a way that it forms tetrahedral void with II & III layer. C.NO. =)12.

C.C.P. :- generates FCC & is obtained by placing the spheres of III layer on the octahedral voids of I & II layer. C.NO=12.

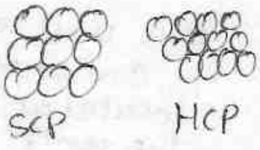
S.C.P. generates simple cubic unit cell...

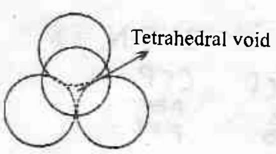
Square close packing forms cubical voids. All voids lie in the same vertical plane. This is least eff. cp C.NO=6

C.V. present at intersection of body diagonal.

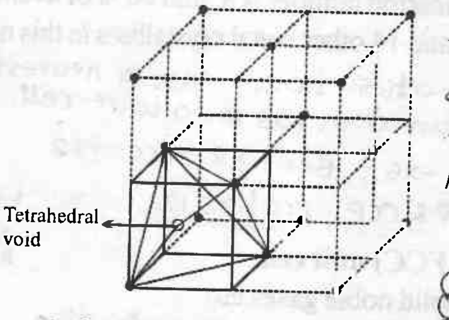
4. Types of voids

4.1 Tetrahedral void

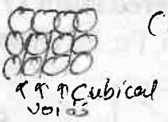




TCP - Generates by Tetrahedral unit cell.

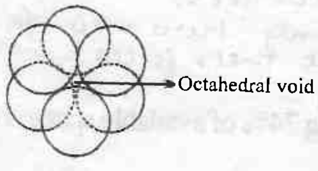


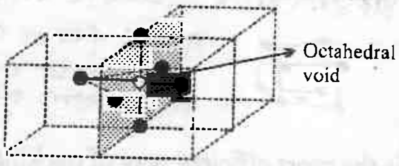
Number of tetrahedral voids per FCC unit cell



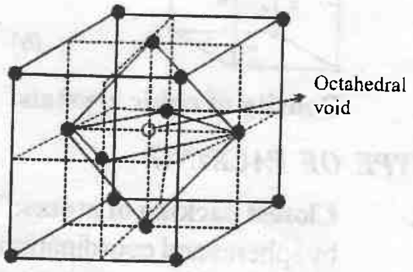
4.2 Octahedral void

TCP forms triangular voids and voids are formed along a vertical line. C.NO. = 8 (6+1+1)





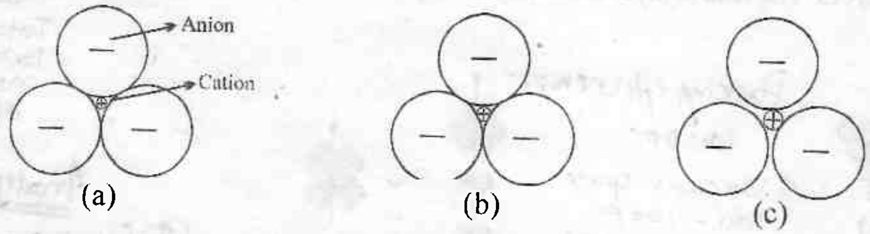
An octahedral void at the centre of an edge in a FCC unit cell.



An octahedral void at the body centered position in FCC unit cell

T.C.P. :-

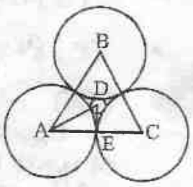
5. Radius ratio



(a) (b) (c)

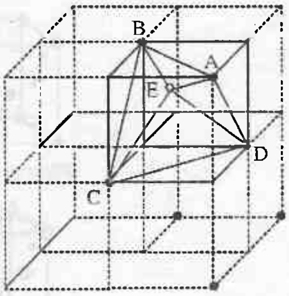
5.1 Radius ratio for co-ordination number 3

(Triangular Arrangement): $r^+ + r^- = \frac{2}{3}\sqrt{3}\,r^-$; $\frac{r^+}{r^-} = \frac{2-\sqrt{3}}{\sqrt{3}} = 0.155$



5.2 Radius ratio for coordination number 4

(Tetrahedral arrangement): $r^+ + r = \frac{\sqrt{3}a}{4}$; $4r^- = \sqrt{2}\,a = \frac{\sqrt{3}}{\sqrt{2}} r^-$

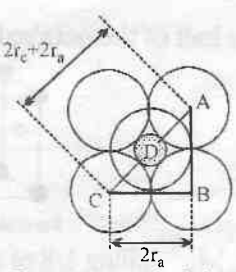


$$\frac{r^+}{r^-} = \frac{\sqrt{3}-\sqrt{2}}{\sqrt{2}} = 0.225$$

5.3 Radius ratio for coordination number 6: $r^+ + r = \sqrt{2}\, r^-$

(Octahedral Arrangement) or $\frac{r^+}{r^-} = \sqrt{2} - 1 = 0.414$

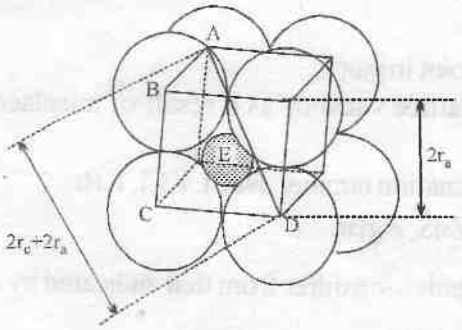
Radius ratio for coordination number 4
(Square plannar arrangement)



Top view of octahedral arrangement

5.4 Radius ratio for coordination number 8 : $r^+ + r^- = \frac{\sqrt{3}}{2} a$

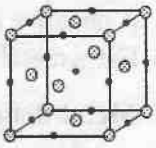
(Body centered cubic crystal) $r^+ + r^- = \sqrt{3}\, r^-$



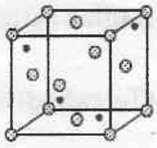
$$\frac{r^+}{r^-} = \sqrt{3} - 1 = 0.732$$

6. Types of ionic structures

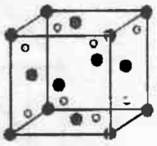
6.1 Rock salt structure: (NaCl) Larger atom formic ccp arrangement and smaller atom filling all octahedral voids.



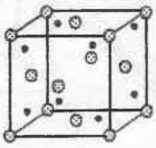
Rock salt structure


Zinc blende structure

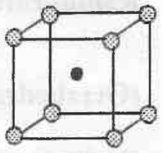
6.2 **Zinc blende (sphalerite) structure:**(ZnS) Larger atom formic ccp arrangement and smaller atom filling half of alternate tetrahedral voids


Fluorite structure

6.3 **Fluorite structure:**(CaF_2) Ca^{2+} forming ccp arrangement and F^- filling all tetrahedral voids.


Antifluorite structure

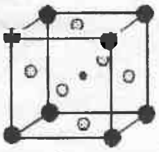
6.4 **Antifluorite structure :**(Li_2O) O^{2-} ion forming ccp and Li^+ taking all tetrahedral voids.


Cesium chloride structure

6.5 **Cesium halide structure:** (CsCl) Cl^- at the corners of cube and Cs^+ in the center

6.6 **Corundum Structure:** (Al_2O_3) O^{2-} forming hcp and Al^{3+} filling 2/3 octahedral voids.

6.7 **Rutile structure:** (TiO_2) O^{2-} forming hcp while Ti^{4+} ions occupy half of the octahedral voids.


Pervoskite structure

6.8 **Pervoskite structure:**($CaTiO_3$) Ca^{2+} in the corner of cube O^{2-} at the face center and Ti^{4+} at the centre of cube.

6.9 **Spinel and inverse spinel structure:** ($MgAl_2O_4$)O^{2-} forming fcc, Mg^{2+} filling 1/8 of tetrahedral voids and Al^{3+} taking half of octahedral voids.In an inverse spinel structure, O^{2-} ion form FCC lattice, A^{2+} ions occupy 1/8 of the tetrahedral voids and trivalent cation occupies 1/8 of the tetrahedral voids and 1/4 of the octahedral voids.

7. **Crystal defects:**

Point defects: When ions or atoms do not hold the theoretical position, this is called point defect. Point defects are of two types:

(I) ***Stoichiometric defects***:

(a) **Schottky defect:** Due to missing of ions from lattice point in pairs.

(b) **Frenkel defect:** It is caused due to the creation of lattice vacancy as a result of misplaced ion in interstitial site.

✶ Schottky defect common in ionic solid with high coordination number. NaCl, KCl, KBr

✶ Frenkel defect :- Solid with low coordination number ZnS, AgBr.

(II) ***Non-Stoichiometric defects***: Ratio of positive and negative ion differ from that indicated by chemical formula.

✶ **Metal-excess defect :**

(a) A negative ion replaced by electron. (F-centre)

(b) Extra metal ion present in lattice and electron also present in interstitial site.

✶ **Metal-deficiency defect caused by :** Cation missing from lattice point, electroneutrality maintained by metal ions with higher oxidation state as $Fe_{0.94}$°O.

THE ATLAS

TYPES OF SOLIDS

Crystalline Solids

Crystalline solids have long range order i.e. the constituent particles are arranged in a regular fashion and this symmetrical arrangement extends throughout the crystal length.

Amorphous Solids

Lattice - Unit Cells

(i) A unit cell is the smallest repeating structural unit the crystalline solid. Bravais has predicted that there are only 14 unit cells that exists in nature.

(ii)The relation between the edge length (a) and the radius of atom (r) forming lattice are as follows. PC :$a=2r$, BCC: $\sqrt{3}a=4$;FCC:$\sqrt{2}a=4r$& HP:$a=2r$ height(c) $=4r\sqrt{\frac{2}{3}}$

Packing fraction and density determination

(i) The ratio of volume occupied by the effective atoms to the volume of the unit cell is called packing fraction. Its values for various unit cells are PC = 0.52, BCC = 0.68, FCC & HP = 0.74.

(ii)Density (ρ) of cubic crystal is calculated using the relation $\rho = \frac{n\times M}{N_{AV}\times a^3}$ where

n=number of effective atoms, M=Atomic mass,N_{AV}=Avogadro's number and a= Edge length.

Type of void and radius ratio rule

(i) Tetrahedral & octahedral voids are present only inclosest packed structures. The effective number of octahedral voids in a unit cell is equal to the effective number of atoms in the unit cell & effective number of tetrahedral voids is equal to double the number of effective atoms in the unit cell.

(ii)The sum of radius of the atom of host lattice (r_h) and the radius of atom occupying void($r_{f(t)}$or $r_{f(o)}$) is given by

For octahedral void, $r_h+r_{f(o)}=\frac{a}{2}$ & for tetrahedral void,$r_h+r_{f(t)}=\frac{\sqrt{3}a}{4}$

(iii)Limiting radius is defined as the minimum ratio of cation to anion radius. It is defined when cation is in contact with anions and anions are also in contact with each other.

(iv)Radius ratio depends on the co-ordination number. The limiting radius ratio for the various co-ordination numbers are

C.N.3 : 0.155, C.N.4 (Tetrahedral) : 0.225, C.N.4(Square planar) : 0.414, C.N.6 (Octahedral) : 0.414, C.N.8 (BCC) : 0.732, C.N.12 (Ideal FCC) : 1

Defects in Solids

Ionic lattice has 2 major defects. Schottky defect occurs due to the cation-anion pair vacancy, which decreases the density of crystal. Frenkel defect occurs when an ion leaves its lattice site and fits into an interstitial space. Due to Frenkel defect, density of crystal remains unaffected.

EXERCISE I

Formula of ionic solid from unit cell description

Q.1 A cubic solid is made up of two elements A and B. Atoms B are at the corners of the cube and A at the body centre. What is the formula of compound.

Q.2 A compound alloy of gold and copper crystallizes in a cubic lattice in which gold occupy that lattice point at corners of the cube and copper atom occupy the centres of each of the cube faces. What is the formula of this compound.

Q.3 A cubic solid is made by atoms A forming close pack arrangement, B occupying one. Fourth of tetrahedral void and C occupying half of the octahedral voids. What is the formula of compound.

Q.4 What is the percent by mass of titanium in rutile, a mineral that contain Titanium and oxygen, if structure can be described as a closet packed array of oxide ions, with titanium in one half of the octahedral holes. What is the oxidation number of titanium?

Q.5 Spinel is a important class of oxides consisting of two types of metal ions with the oxide ions arranged in CCP pattern. The normal spinel has one-eight of the tetrahedral holes occupied by one type of metal ion and one half of the octahedral hole occupied by another type of metal ion. Such a spinel is formed by Zn^{2+}, Al^{3+} and O^{2-}, with Zn^{2+} in the tetrahedral holes. Give the formulae of spinel.

Edge length, density and number of atoms per unit cell

Q.6 KF crystallizes in the NaCl type structure. If the radius of K^+ ions 132 pm and that of F^- ion is 135 pm, what is the shortest K–F distance? What is the edge length of the unit cell? What is the closet K–K distance?

Q.7 A closed packed structure of uniform spheres has the edge length of 534 pm. Calculate the radius of sphere, if it exist in
(a) simple cubic lattice (b) BCC lattice (c) FCC lattice

Q.8 Calculate the density of diamond from the fact that it has face centered cubic structure with two atoms per lattice point and unit cell edge length of 3.569 Å.

Q.9 An element crystallizes into a structure which may be described by a cubic type of unit cell having one atom on each corner of the cube and two atoms on one of its body diagonals. If the volume of this unit cell is 24×10^{-24} cm^3 and density of element is 7.2 g cm^{-3}, calculate the number of atoms present in 200 g of element.

Q.10 Silver has an atomic radius of 144 pm and the density of silver is 10.6 g cm^{-3}. To which type of cubic crystal, silver belongs?

Q.11 AgCl has the same structure as that of NaCl. The edge length of unit cell of AgCl is found to be 555 pm and the density of AgCl is 5.561 g cm^{-3}. Find the percentage of sites that are unoccupied.

Q.12 Xenon crystallises in the face-centred cubic lattice and the edge of the unit cell is 620 pm. What is the nearest neighbour distance and what is the radius of xenon atom?

Q.13 The two ions A^+ and B^- have radii 88 and 200 pm respectively. In the closed packed crystal of compound AB, predict the co-ordination number of A^+.

Q.14 CsCl has the bcc arrangement and its unit cell edge length is 400 pm. Calculate the interionic distance in CsCl.

Q.15 Gold crystallizes in a face centered cubic lattice. If the length of the edge of the unit cell is 407 pm, calculate the density of gold as well as its atomic radius assuming it to be spherical. Atomic mass of gold = 197 amu.

Q.16 The density of KBr is 2.75 g cm^{-3}. The length of the edge of the unit cell is 654 pm. Show that KBr has face centered cubic structure.
($N = 6.023 \times 10^{23}$ mol^{-1}, At. mass : K = 39, Br = 80)

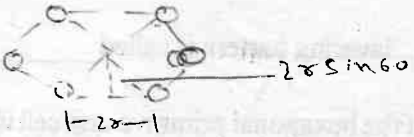
Q.17 An element crystallizes in a structure having FCC unit cell of an edge 200 pm. Calculate the density, if 200 g of this element contains 24×10^{23} atoms.

Q.18 The effective radius of the iron atom is 1.42 Å. It has rock salt like structure. Calculate its density (Fe = 56 amu)

Q.19 A crystal of lead(II) sulphide has NaCl structure. In this crystal the shortest distance between Pb^{+2} ion and S^{2-} ion is 297 pm. What is the length of the edge of the unit cell in lead sulphide? Also calculate the unit cell volume.

Q.20 If the length of the body diagonal for CsCl which crystallises into a cubic structure with Cl^- ions at the corners and Cs^+ ions at the centre of the unit cells is 7 Å and the radius of the Cs^+ ion is 1.69 Å, what is the radii of Cl^- ion?

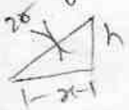
AB AB ~~closed~~ type packing (HCP)



Volume of unit cell = base area × height

Base area = $6 \times \frac{\sqrt{3}}{4}(2r)^2 = 6\sqrt{3}r^2$

Height = 2 × Distance bt. two closest packed layers = $2 \times 2r \times \sqrt{2/3} = 4r\sqrt{\frac{2}{3}}$



$\frac{r}{x} = \cos 30^\circ = \frac{\sqrt{3}}{2}$ $x = \frac{2r}{\sqrt{3}}$

; $h^2 = (2r)^2 - x^2 = 8r^2/3$.

Volume of unit cell = area × height = $24\sqrt{2}r^3$

Eff. No. of atoms per unit cell : $12 \times 1/6$ (corners) + $2 \times 1/2$ (face centred) + 3 in the body = 6.

Volume of 6 spheres = $6 \times 4/3\pi r^3 = 8\pi r^3$

Packing fraction = $\frac{8\pi r^3}{24\sqrt{2}r^3} = 0.74$

PROFICIENCY TEST

1. Crystalline solids are isotropic.

2. Rhombohedral, triclinic and hexagonal are the unit cells, which have only primitive arrangement possible.

3. Rank of FCC and HP units cells are same.

4. The minimum void fraction for any unit cell in any shape having only one type of atom and all voids unfilled is 0.26.

5. Packing fraction of a lattice structure depends on the radius of the atom crystallizing in it.

6. The location of tetrahedral voids in FCC unit cell are the centers of 8 minicubes forming a large cube.

7. Effective number of octahedral voids in a unit cell is equal to the effective number of atoms in the unit cell.

8. Radius ratio for co-ordination number 4 having tetrahedral and square planar geometry is same.

9. The radius ratio value for co-ordination number 4 having square planar geometry and co-ordination number 6 having octahedral geometry is same.

10. A metallic element crystallises into a lattice containing a sequence of layers of AB AB AB .... Any packing of spheres leaves out voids in the lattice 26% percent by volume of this lattice is empty space.

11. The relation between edge length (a) and radius of atom (r) for BCC lattice is________.

12. The relation between edge length (a) and radius of atom (r) for FCC lattice is________

13. ABCABC......layering pattern is called ________ packing, found in _______ lattice.

14. ABABAB.....layering pattern is called _______ packing , found in _______ lattice.

15. Height (c) of the hexagonal primitive unit cell in terms of radius of atom (r) is________.

16. Anions would be in contact with each other only if the cation to anion radius for a given co-ordination number is_______.

17. The number of tetrahedral voids in hexagonal primitive unit cell is________.

18. The limiting radius for co-ordination number 8 is_________.

19. For cesium chloride structure, the interionic distance (in terms of edge length, a) is equal to _______.

20. Density of a crystal ___due to Schottky defect and _____due to Frankel defect.

EXERCISE II

Q.1 Iron has body centered cubic lattice structure. The edge length of the unit cell is found to be 286 pm. What is the radius of an iron atom?

Q.2 Cesium chloride forms a body centered cubic lattice. Cesium and chloride ions are in contact along the body diagonal of the unit cell. The length of the side of the unit cell is 412 pm and Cl^- ion has a radius of 181 pm. Calculate the radius of Cs^+ ion.

Q.3 In a cubic closed packed structure of mixed oxides the lattice is made up of oxide ions, one eighth of tetrahedral voids are occupied by divalent ions (A^{2+}) while one half of the octahedral voids occupied trivalent ions (B^{3+}). What is the formula of the oxide?

Q.4 A solid A^+ and B^- had NaCl type closed packed structure. If the anion has a radius of 250 pm, what should be the ideal radius of the cation? Can a cation C^+ having a radius of 180 pm be slipped into the tetrahedral site of the crystal of A^+B^-? Give reasons for your answer.

Q.5 Calculate the value of Avogadro's number from the following data:
Density of NaCl = 2.165 cm^{-3}
Distance between Na^+ and Cl^- in NaCl = 281 pm.

Q.6 If the radius of Mg^{2+} ion, Cs^+ ion, O^{2-} ion, S^{2-} ion and Cl^- ion are 0.65 Å, 1.69 Å, 1.40 Å, 1.84 Å, and 1.81 Å respectively. Calculate the co-ordination numbers of the cations in the crystals of MgS, MgO and CsCl.

Q.7 Iron occurs as bcc as well as fcc unit cell. If the effective radius of an atom of iron is 124 pm. Compute the density of iron in both these structures.

Q.8 KCl crystallizes in the same type of lattice as does NaCl. Given that $\frac{r_{Na^+}}{r_{Cl^-}} = 0.5$ and $\frac{r_{Na^+}}{r_{K^+}} = 0.7$ Calculate:
(a) The ratio of the sides of unit cell for KCl to that for NaCl and
(b) The ratio of densities of NaCl to that for KCl.

Q.9 An element A (Atomic weight = 100) having bcc structure has unit cell edge length 400 pm. Calculate the density of A and number of unit cells and number of atoms in 10 gm of A.

Q.10 Prove that the void space percentage in zinc blende structure is 25%.

Q.11 A unit cell of sodium chloride has four formula units. The edge of length of the unit cell is 0.564 nm. What is the density of sodium chloride.

Q.12 In a cubic crystal of CsCl (density = 3.97 gm/cm^3) the eight corners are occupied by Cl^- ions with Cs^+ ions at the centre. Calculate the distance between the neighbouring Cs^+ and Cl^- ions.

Q.13 KF has NaCl structure. What is the distance between K^+ and F^- in KF if density of KF is 2.48 gm/cm^3.

Q.14 The composition of a sample of wustite is $Fe_{0.93}O_{1.0}$. What percentage of iron is present in the form of Fe(III)?

Q.15 $BaTiO_3$ crystallizes in the prevoskite structure. This structure may be described as a cubic lattice with barium ions occupying the corner of the unit cell, oxide ions occupying the face-centers and titanium ion occupying the center of the unit cell.

(a) If titanium is described as occupying holes in BaO lattice, what type of holes does it occupy?

(b) What fraction of this type hole does it occupy?

Q.16 Rbl crystallizes in bcc structure in which each Rb^+ is surrounded by eight iodide ions each of radius 2.17 A. Find the length of one side of RbI unit cell.

Q.17 If NaCl is dopped with 10^{-3} mol % $SrCl_2$, what is the numbers of cation vacancies?

Q.18 Find the size of largest sphere that will fit in octahedral void in an ideal FCC crystal as a function of atomic radius 'r'. The insertion of this sphere into void does not distort the FCC lattice. Calculate the packing fraction of FCC lattice when all the octahedral voids are filled by this sphere.

Q.19 A cubic unit cell contains manganese ions at the corners and fluoride ions at the center of each edge.

(a) What is the empirical formula of the compound?

(b) What is the co-ordination number of the Mn ion?

(c) Calculate the edge length of the unit cell, if the radius of Mn ion is 0.65 Å and that of F^- ion is 1.36 Å.

Q.20 NaH crystallizes in the same structure as that of NaCl. The edge length of the cubic unit cell of NaH is 4.88 Å.

(a) Calculate the ionic radius of H^-, provided the ionic radius of Na^+ is 0.95 Å.

(b) Calculate the density of NaH.

Q.21 Metallic gold crystallises in fcc lattice. The length of the cubic unit cell is a = 4.07 Å.

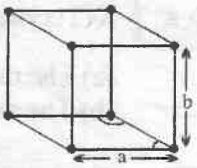
(a) What is the closest distance between gold atoms.

(b) How many "nearest neighbours" does each gold atom have at the distance calculated in (a).

(c) What is the density of gold?

(d) Prove that the packing fraction of gold is 0.74.

Q.22 Ice crystallizes in a hexagonal lattice. At the low temperature at which the structure was determined, the lattice constants were a = 4.53 Å, and b = 7.60 Å(see figure). How many molecules are contained in a unit cell? [density (ice) = 0.92 gm/cm^3)]



Q.23 Using the data given below, find the type of cubic lattice to which the crystal belongs.

	Fe	V	Pd
a in pm	286	301	388
ρ in gm cm^{-3}	7.86	5.96	12.16

Q.24 Potassium crystallizes in a body-centered cubic lattice with edge length, a = 5.2 Å.

(a) What is the distance between nearest neighbours?

(b) What is the distance between next-nearest neighbours?

(c) How many nearest neighbours does each K atom have?

(d) How many next-nearest neighbours does each K atom have?

(e) What is the calculated density of crystalline potassium?

Q.25 Prove that void space in fluorite structure per unit volume of unit cell is 0.251.

Q.26 A compound formed by elements X & Y, Crystallizes in a cubic structure, where X is at the corners of the cube and Y is at six face centers. What is the formula of the compound? If side length is 5Å, estimate the density of the solid assuming atomic weight of X and Y as 60 and 90 respectively.

Q.27 The metal nickel crystallizes in a face centred cubic structure. Its density is 8.9 gm/cm^3. Calculate
(a) the length of the edge of the unit cell.
(b) the radius of the nickel atom. [Atomic weight of Ni = 58.89]

Q.28 The olivine series of minerals consists of crystals in which Fe and Mg ions may substitute for each other causing substitutional impurity defect without changing the volume of the unit cell. In olivine series of minerals, oxide ion exist as FCC with Si^{4+} occupying $\frac{1}{4}$ th of octahedral voids and divalent ions occupying $\frac{1}{4}$ th of tetrahedral voids. The density of forsterite (magnesium silicate) is 3.21 g/cc and that of fayalite (ferrous silicate)is 4.34 g/cc. Find the formula of forsterite and fayalite minerals and the percentage of fayalite in an olivine with a density of 3.88 g/cc.

Q.29 The mineral hawleyite, one form of CdS, crystallizes in one of the cubic lattices, with edge length 5.87Å. The density of hawleyite is 4.63 g cm^{-3}.
(i) In which cubic lattice does hawleyite crystallize?
(ii) Find the Schottky defect in g cm^{-3}.

Q.30 A strong current of trivalent gaseous boron passed through a germanium crystal decreases the density of the crystal due to part replacement of germanium by boron and due to interstitial vacancies created by missing Ge atoms. In one such experiment, one gram of germanium is taken and the boron atoms are found to be 150 ppm by weight, when the density of the Ge crystal decreases by 4%. Calculate the percentage of missing vacancies due to germanium, which are filled up by boron atoms.
Atomic wt. Ge = 72.6, B = 11

EXERCISE III

Q.1 A solid has a structure in which W atoms are located at the corners of a cubic lattice, O atom at the centre of the edges and Na atom at centre of the cubic. The formula for the compound is
(A) $NaWO_2$ (B) $NaWO_3$ (C) Na_2WO_3 (D) $NaWO_4$

Q.2 The density of CaF_2 (fluorite structure) is 3.18 g/cm^3. The length of the side of the unit cell is
(A) 253 pm (B) 344 pm (C) 546 pm (D) 273 pm

Q.3 Which of the following statements is correct in the rock-salt structure of an ionic compounds?
(A) coordination number of cation is four whereas that of anion is six.
(B) coordination number of cation is six whereas that of anion is four.
(C) coordination number of each cation and anion is four.
(D) coordination number of each cation and anion is six.

Q.4 The coordination number of cation and anion in Fluorite CaF_2 and CsCl are respectively
(A) 8:4 and 6:3 (B) 6:3 and 4:4 (C) 8:4 and 8:8 (D) 4:2 and 2:4

Q.5 The interstitial hole is called tetrahedral because
(A) It is formed by four spheres.
(B) Partly same and partly different.
(C) It is formed by four spheres the centres of which form a regular tetrahedron.
(D) None of the above three.

Q.6 The tetrahedral voids formed by ccp arrangement of Cl^- ions in rock salt structure are
(A) Occupied by Na^+ ions (B) Occupied by Cl^- ions
(C) Occupied by either Na^+ or Cl^- ions (D) Vacant

Q.7 The number of nearest neighbours around each particle in a face-centred cubic lattice is
(A) 4 (B) 6 (C) 8 (D) 12

Q.8 If the anions (A) form hexagonal closest packing and cations (C) occupy only 2/3 octahedral voids in it, then the general formula of the compound is
(A) CA (B) CA_2 (C) C_2A_3 (D) C_3A_2

Q.9 A solid is formed and it has three types of atoms X, Y, Z. X forms a FCC lattice with Y atoms occupying all the tetrahedral voids and Z atoms occupying half the octrahedral voids. The formula of the solid is:
(A) X_2Y_4Z (B) XY_2Z_4 (C) X_4Y_2Z (D) X_4YZ_2

Q.10 The intermetallic compound LiAg crystallizes in cubic lattice in which both lithium and silver have coordination number of eight. The crystal class is
(A) Simple cubic (B) Body centred cubic (C) Face centred cubic (D) None

Q.11 A compound XY crystallizes in BCC lattice with unit cell edge lenght of 480 pm. If the radius of Y^- is 225 pm, then the radius of X^+ is
(A) 127.5 pm (B) 190.68 pm (C) 225 pm (D) 255 pm

Q.12 The mass of a unit cell of CsCl corresponds to
(A) 1 Cs^+ and 1 Cl^- (B) 1 Cs^+ and 6 Cl^- (C) 4 Cs^+ and 4 Cl^- (D) 8 Cs^+ and 1 Cl^-

Q.13 In the closest packing of atoms A (radius : r_a), the radius of atom B that can be fitted into tetrahedral voids is
(A) $0.155\ r_a$ (B) $0.225\ r_a$ (C) $0.414\ r_a$ (D) $0.732\ r_a$

Q.14 Which one of the following schemes of ordering closed packed sheets of equal sized spheres do not generate close packed lattice.
(A) ABCABC (B) ABACABAC (C) ABBAABBA (D) ABCBCABCBC

Q.15 An ionic compound AB has ZnS type structure. If the radius A^+ is 22.5 pm, then the ideal radius of B^- would be
(A) 54.35 pm (B) 100 pm (C) 145.16 pm (D) none of these

Q.16 NH_4Cl crystallizes in a body-centered cubic type lattice with a unit cell edge length of 387 pm. The distance between the oppositively charged ions in the lattice is
(A) 335.1 pm (B) 83.77 pm (C) 274.46 pm (D) 137.23 pm

Q.17 $r_{Na^+} = 95$ pm and $r_{Cl^-} = 181$ pm in NaCl (rock salt) structure. What is the shortest distance between Na^+ ions?
(A) 778.3 pm (B) 276 pm (C) 195.7 pm (D) 390.3 pm

Q.18 In diamond, carbon atom occupy FCC lattice points as well as alternate tetrahedral voids. If edge length of the unit cell is 356 pm, then radius of carbon atom is
(A) 77.07 pm (B) 154.14 pm (C) 251.7 pm (D) 89 pm

Q.19 Which of the following will show schottky defect
(A) CaF_2 (B) ZnS (C) AgCl (D) CsCl

Q.20 Give the correct order of initials **T** (true) or **F** (false) for following statements.
I. In an anti-fluorite structure anions form FCC lattice and cations occupy all tetrahedral voids.
II. If the radius of cations and anions are 0.2 Å and 0.95 Å then coordinate number of cation in the crystal is 4.
III An atom/ion is transferred from a lattice site to an interstitial position in Frenkel defect.
IV. Density of crystal always increases due to substitutinal impurity defect.
(A) TFFF (B) FTTF (C) TFFT (D) TFTF

EXERCISE IV

Q.1 The edge length of unit cell of a metal having molecular weight 75 g/mol is 5 Å which crystallizes in cubic lattice. If the density is 2 g/cc then find the radius of metal atom. ($N_A = 6 \times 10^{23}$). Give the answer in pm. **[JEE 2006]**

Q.2 An element crystallises in FCC lattice having edge length 400 pm. Calculate the maximum diameter which can be placed in interstital sites without disturbing the structure. **[JEE 2005]**

Q.3 Which of the following FCC structure contains cations in alternate tetrahedral voids?
(A) NaCl (B) ZnS (C) Na_2O (D) CaF_2 **[JEE 2005]**

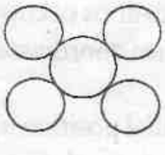
Q.4(i) AB crystallizes in a rock salt structure with A : B = 1 : 1. The shortest distance between A and B is $Y^{1/3}$ nm. The formula mass of AB is 6.023 Y amu where Y is any arbitrary constant. Find the density in kg m^{-3}.

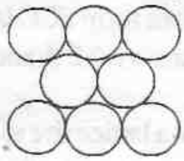
(ii) If measured density is 20 kg m^{-3}. Identify the type of point defect. **[JEE–2004]**

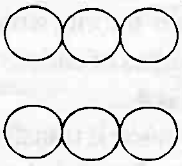
Q.5 Marbles of diameter 10 mm each are to be arranged on a flat surface so that their centres lie within the area enclosed by four lines of length each 40 mm. Sketch the arrangement that will give the maximum number of marbles per unit area, that can be enclosed in this manner and deduce the expression to calculate it. **[JEE–2003]**

Q.6 A substance A_xB_y crystallises in a FCC lattice in which atoms "A" occupy each corner of the cube and atoms "B" occupy the centres of each face of the cube. Identify the correct composition of the substance A_xB_y.
(A) AB_3 (B) A_4B_3
(C) A_3B (D) composition cannot be specified **[JEE-2002]**

Q.7 The figures given below show the location of atoms in three crystallographic planes in FCC lattice. Draw the unit cell for the corresponding structure and identify these planes in your diagram. **[JEE-2000]**







Q.8 In a solid "AB" having NaCl structure "A" atoms occupy the corners of the cubic unit cell. If all the face-centred atoms along one of the axes are removed, then the resultant stoichiometry of the solid is
(A) AB_2 (B) A_2B (C) A_4B_3 (D) A_3B_4 **[JEE-2000]**

Q.9 In any ionic solid [MX] with schottky defects, the number of positive and negative ions are same. **[T/F]** **[JEE-2000]**

Q.10 The coordination number of a metal crystallising in a hcp structure is **[JEE-2000]**
(A) 12 (B) 4 (C) 8 (D) 6

Q.11 A metal cryatallises into two cubic phases, FCC and BCC whose unit cell lengths are 3.5 and 3.0 Å respectively. Calculate the ratio of densities of FCC and BCC. **[JEE-1999]**

Q.12 Which of the following statements are correct :
(A) The coordination number of each type of ion in CsCl is 8.
(B) A metal that crystallises in BCC structure has a coordination number 12.
(C) A unit cell of an ionic crystal shares some of its ions with other unit cells
(D) The length of the unit cell in NaCl is 552 pm.
[r_{Na^+} = 95 pm ; r_{Cl^-} = 181 pm] **[JEE-1998]**

Q.13 In the sodium chloride structure, each Na^+ ion is surrounded by six Cl^- nearest neighbours and _____ Na^+ ions next nearest neighbours. **[JEE-1997]**

Q.14 A unit cell of sodium chloride has four formula units. The edge length of the unit cell is 0.564 nm. What is the density of sod. chloride. **[JEE-1997]**

Q.15 Chromium crystallises with bcc lattice. The unit cell length is 287 pm. Calculate atomic rad. What would be the density of chromium. **[JEE-1997]**

ANSWER KEY

EXERCISE I

Q.1	A-B	Q.2	$AuCu_3$	Q.3	$A_4B_2C_2$	Q.4	59.95%, +4
Q.5	$ZnAl_2O_4$	Q.6	267 pm, 534 pm, 378 pm			Q.7	267 pm, 231.2 pm, 188.8 pm
Q.8	3.5 g cm^{-3}	Q.9	3.472×10^{24} atoms			Q.10	FCC
Q.11	0.24%	Q.12	438.5 pm, 219.25 pm			Q.13	6
Q.14	346.4 pm	Q.15	19.4g/cm^3 , 143.9 pm			Q.17	41.67 g cm^{-3}
Q.18	5.74 g cm^{-3}	Q.19	$a = 5.94\times10^{-8}$cm, $V=2.096\times10^{-22}$ cm^{-3}			Q.20	1.81Å

PROFICIENCY TEST

1.	F	2.	T	3.	F	4.	T
5.	F	6.	T	7.	T	8.	F
9.	T	10.	T	11.	$\sqrt{3}\,a = 4r$	12.	$\sqrt{2}\,a = 4r]$
13.	cubic close, FCC			14.	hexagonal close, HP		
15.	$c = 4r\sqrt{\frac{2}{3}}$	16.	least or minimum			17.	12
18.	0.732	19.	$\frac{\sqrt{3}a}{2}$	20.	decreases, remains constant		

EXERCISE II

Q.1	123.84 pm	Q.2	175.8 pm	Q.3	AB_2O_4	Q.4	103.4 pm, No
Q.5	6.01×10^{23}	Q.6	4, 6, 8	Q.7	7.887 g/cc , 8.59 gm/cm^3		
Q.8	**(a)** 1.143, **(b)** 1.172						
Q.9	5.188 gm/cm^3, 6.023×10^{22} atoms of A, 3.0115×10^{22} unit cells						
Q.11	2.16 gm/cm^3	Q.12	3.57 Å	Q.13	2.685 Å	Q.14	15.053
Q.15	**(a)** octahedral, **(b)** 1/4			Q.16	4.34 Å		
Q.17	6.02×10^{18} mol^{-1}			Q.18	0.414 r, 79.3%		
Q.19	(a) MnF_3, (b) 6, (c) 4.02Å			Q.20	(a) 1.49 Å, (b) 1.37 g/cm^3		

Q.21	**(a)** 2.88 Å, **(b)** 12 , **(c)** 19.4 g/cc	Q.22	4 molecules of H_2O
Q.23	for Fe is bcc, for V is bcc, for Pd is face centered		
Q.24	(a) 4.5 Å, (b) 5.2 Å, (c) 8, (d) 6, (e) 0.92 g/cm^3	Q.26	XY_3, 4.38 g/cm^3
Q.27	**(a)** 3.52 Å,**(b)** 1.24 Å	Q.28	Mg_2SiO_4, Fe_2SiO_4, 59%
Q.29	(i) 3.90, (ii) 0.120 g/cc	Q.30	2.376%

EXERCISE III

Q.1	B	Q.2	C	Q.3	D	Q.4	C	Q.5	C	Q.6	D	Q.7	D
Q.8	C	Q.9	A	Q.10	B	Q.11	B	Q.12	A	Q.13	B	Q.14	C
Q.15	B	Q.16	A	Q.17	D	Q.18	A	Q.19	D	Q.20	D		

EXERCISE IV

Q.1	216.5 pm	Q.2	117.1 pm	Q.3	B

Q.4 (i) = 5 kg m^{-3}

(ii) There is huge difference in theoretically calculated density and observed density. It is only possible if some foreign species occupies interstitial space i.e. substitution defect.

Q.5 Discuss

Q.6	A	Q.7	Discuss	Q.8	D	Q.9	True	Q.10	A
Q.11	1.259	Q.12	A, C, D	Q.13	12	Q.14	2.165 g/cm^3		

Q.15 (i)124.27 pm, (ii) 7.30 g/cm^3

BANSAL CLASSES

TARGET IIT JEE 2007

PHYSICAL CHEMISTRY

XII (ALL)

THERMODYNAMICS

" A SPECIALLY DESIGNED KIT FOR LEARNING."

CONTENTS

THE KEY	⟶	Basic principles of subjects. An outline of the topics to be discussed in class lectures.
EXERCISE I	⟶	Introductory problems to get first hand experience of problem solving.
PROFICIENCY TEST	⟶	To check you newly acquired basic concepts.
EXERCISE II	⟶	A collection of good problems.
EXERCISE III	⟶	Test your objective skill.
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THE KEY

The subject of ***Thermodynamics*** deals basically with the interaction of one body with another in terms of quantities of heat & work. It may be *defined* as the branch of science which deals with energy changes associated with various physical & chemical processes. The entire formulation of thermodynamics is based on a few (Three) fundamental laws which have been established on the basis of human experience of the experimental behaviour of macroscopic aggregates of matter collected over a long period of time. ***Thermochemistry*** is the branch of physical chemistry which deals with the thermal or heat changes caused by chemical reactions. It is based on first law of thermodynamics. There are two laws of thermochemistry:

(a) Lavoisier & Laplace law (b) Hess's law.

TERMS & CONVENTIONS

A number of terms & conventions are used in thermodynamics.

A ***System*** is defined as that part of the universe which is at the moment under investigation.

Universe less the system is defined as ***Surroundings***. The actual or imaginary surface that separates the system from the surroundings is called the ***Boundary***.

TYPES OF SYSTEMS:

A system is said to be ***Isolated*** if it cannot exchange matter and energy with the surroundings (coffee in a thermos flask).

A system is said to be ***Closed*** if it can exchange energy but not matter. Coffee in a closed stainless steel flask is an example. A system is said to be ***Open*** if it can exchange matter and energy both. A thermo flask or a steel flask if not closed is an example. A system is said to be homogeneous when it is completely uniform throughout, made up of one phase only, pure liquid. solid, gas.

A system is said to be heterogeneous if it consists of two or more phases, liquid in contact with vapour.

STATE OF A SYSTEM :

The state of a system is defined by a particular set of its measurable properties. For example, we can describe the state of a gas by quoting its pressure (P), volume (V) and temperature (T) etc.

Variables like P, V, T are *State Functions* OR *State Variables* because their values depend only on the state of a system and not on how the state was reached.

State variables can be intensive or extensive. An intensive variable (eg. temperature, pressure, concentration) is one whose value is independent of the size of the system. An extensive variable (eg. volume, mass, surface area is one whose value is proportional to the size of the system.

Extensive Properties (Depend upon quantity of Matter present and are additive)	**Intensive Properties (Do not depend upon quantity of Matter present and are non additive)**
Volume	Molar volume
Number of moles	Density
Mass	Refractive index
Free Energy G	Surface tension
Entropy S	Viscosity
Enthalpy H	Free energy per mole
Internal energy E	Specific heat
Heat capacity	Pressure
	Temperature
	Boiling point, freezing point etc

THERMODYNAMIC PROCESS :

A thermodynamic process involves change of a system from one state to another state.

TYPES:

A process is called ***Isothermal***, if the temperature of the system remains constant during the change. It is carried out in a thermostat and in such a process the exchange of energy between the system and surroundings takes place. In such a process $dT = 0$ & $dE = 0$.

A process is called ***Adiabatic***, if the system does not exchange energy with surroundings. Such a process is carried out in perfectly insulated containers. During it the temperature of the system may change. In such a process $dQ = 0$.

A process carried out at a constant pressure is called an **isobaric** process. In such a process $dP = 0$.

A process in which the volume of the system remains constant is called an **isochoric** process, whereby $dV = 0$.

CYCLIC PROCESS :

When a system undergoes a number of different processes and finally returns to its initial state.

$\Delta E = 0$ & $\Delta H = 0$.

REVERSIBLE PROCESS : (QUASI-STATIC)

A process which is carried out so slowly that the system and the surroundings are always in equilibrium is known as a ***Reversible Process***. If this condition does not hold good, the process is said to be, ***Irreversible***.

In a reversible process the driving force is infinitesimally larger than the opposing force. If the driving force is made infinitely smaller than opposing force, the system can be brought back without producing any permanent change.

A process which proceeds of its own i.e. without any external help, is called as ***Spontaneous Process*** (or a natural process).

Internal Energy (Intrinsic Energy) E – Every system having some quantity of matter is associated with a definite amount of energy, called internal energy.

$E = E_{\text{Translational}} + E_{\text{Rotational}} + E_{\text{vibrational}} + E_{\text{Bonding}} + E_{\text{Electronic}} + \ldots$

It is a state function & is an extensive property.

$\Delta E = E_{\text{final}} - E_{\text{initial}}$; $\Delta E = q_v$

ZEROTH LAW OF THERMODYNAMICS

It states that, two systems in thermal equilibrium with a third system, are also in thermal equilibrium with each other.

FIRST LAW OF THERMODYNAMICS

It is law of conservation of energy. Mathematically, this law is written as :

$\Delta E = q + w$, where ΔE is change in internal energy of the system and is a state function, q is the transfer of heat from / to the system and w is the work involved (either done on the system or by the system).

According to IUPAC, heat, added to the system and work done on the system are assigned positive values as both these *Modes* increase the internal energy of the system.

TYPES OF WORK :

Two TYPES of work normally come across in chemistry. These are *Electrical Work* in system involving ions, while the *Mechanical Work* is involved when a system changes its volume in the, presence of an externally applied pressure (i.e. pressure volume work). It is especially important in system containing gases.

If a system expands from a volume V_1 to V_2 at constant pressure P, then the first law equation becomes,
$\Delta E = q - P\,\Delta V \qquad (\Delta V = V_2 - V_1) \qquad ....(1)$

For a process carried at constant volume A B = q (heat absorbed at constant volume)

Work = Intensity factor X capacity factor
W – by the system (Expansion) negative
W – on the system (compression) positive
q → absorbed by the system positive
q → given out by the system negative
Work done in irreversible process (Expansion) $W = -P_{Ext}\,\Delta V$

Work done in isothermal reversible process $W = -2.303\ nRT \log \frac{V_2}{V_1}$

(maximum work) (Expansion) $= -2.303\ nRT \log \frac{P_1}{P_2}$

work done is adiabatic reversible process $W = \frac{nR}{\gamma - 1}[T_2 - T_1]$

$\gamma = \frac{C_P}{C_V}$ = Poisson's ratio

ENTHALPY :

Chemical reactions are generally carried out at constant pressure (atmospheric pressure) so it has been found useful to define a new state function ***Enthalpy*** (H) as :

$H = E + PV$ (By definition) or $\Delta H = \Delta E + P\,\Delta V + V\Delta P$

or $\Delta H = \Delta E + P\,\Delta V$ (at constant pressure) combining with first law. Equation (1) becomes

$\Delta H = q_p$

Hence transfer of heat at constant volume brings about a change in the internal energy of the system whereas that at constant pressure brings about a change in the enthalpy of the system.
The difference between ΔH & ΔE becomes significant only when gases are involved (insignificant in solids and liquids) and is given by: $\Delta H = \Delta E + (\Delta n)\,RT$, where Δn is the INCREASE in the number of moles of the gases involved (i.e. Total number of moles of product gases less the total number of moles of reactant gases).

FACTORS AFFECTING ΔH OF THE REACTIONS ARE :

(i) Temperature (ii) Physical states of reactants & products
(iii) Allotropic forms of elements & (iv) Pressure & volume (in case of gases)

Two Types of Reactions may be distinguished :

(i) **Exothermic Reactions :** For these ΔH is negative, which implies that

$\sum H$ (products) $< \sum H$ (reactants)

(ii) **Endothermic Reactions :** For these ΔH is positive, which implies that

$\sum H$ (products) $> \sum H$ (reactants)

HESS'S LAW OF CONSTANT HEAT SUMMATION :

According to Hess's law (a consequence of first law), if a set of reactants is converted into a set of product by more than one sequence of reactions, the total enthalpy change will be the same for every sequence.

As such, the chemical equations can be treated ordinary algebraic expressions and can be added or subtracted to yield the required equation. The corresponding enthalpy changes are also manipulated in the same way to obtain the enthalpy change for the desired equation.

APPLICATIONS OF HESS'S LAW :

It helps us in Calculation of :

(i) Heat of formation (ΔH_f) of many substances which cannot be synthesised directly from their elements.

(ii) Bond energies.

(iii) Enthalpy changes of slow reactions and

(iv) Enthalpy of transformation, say from one allotropic form to the other.

CONVENTIONAL VALUES OF MOLAR ENTHALPIES :

It is not possible to determine the absolute value of enthalpy of a substance and further it also depends on the conditions under which its determination is carried out. It is therefore necessary to choose some standard conditions for reporting the enthalpy data.

Conventionally, the enthalpy of every element in its most stable state of aggregation at 1 atm. (101.325 k Pa) and 298 K is assigned a zero value.

Based on the above convention, the relative values of "Standard molar enthalpies" ($\Delta H°$) of other substances are obtained and it is obvious that in terms of ΔH_f^o values, the enthalpy change of any reaction is given as :

$$\Delta H° = \sum \Delta H_f^o \text{ (products)} - \sum \Delta H_f^o \text{ (reactants)}$$

i.e. $$\Delta H° = \begin{pmatrix} \textit{sum of standard enthalpies} \\ \textit{of formation of product} \end{pmatrix} - \begin{pmatrix} \textit{sum of standard enthalpies} \\ \textit{of formation of reactants} \end{pmatrix}$$

Reactions are frequently classified according to type of thermochemical purpose and the enthalpies of reactions are given different names.

A balanced chemical equation which expresses the heat changes taking place in a reaction as well as the physical states of various reactants and products is known as a thermochemical equation.

Heat capacity $C = \dfrac{dq}{dT}$; $\quad C_V = \left(\dfrac{\partial E}{\partial T}\right)_V$; $\quad Cp = \left(\dfrac{\partial H}{\partial T}\right)_P$

$q = C\,(T_2 - T_1)$ for 1 mole; $\quad q = nC\,(T_2 - T_1)$ for n moles

Kirchoffs Equation: $\dfrac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_P$; $\quad \dfrac{\Delta E_2 - \Delta E_1}{T_2 - T_1} = \Delta C_V$

Trouton's Rule : Entropy of vaporization of non-associated or non-dissociated liquid is constant & may be taken as about 87.3 J $k^{-1}mol^{-1}$.

Thermochemical Equations : An equation which indicates the amount of heat change in the reaction. These can be added, subtracted or multiplied whenever required.

The various named Enthalpies are defined as the Enthalpy change when ....

Enthalpy of reaction : "quantities of substances indicated in the balanced equation react completely to form the product."

Enthalpy of formation : "one mole of the substance is formed directly from its constituent elements."

Enthalpy of combustion : "one mole of the substance undergoes complete combustion" (it is always negative)

Calorific Value : "it is the amount of heat given out by complete combustion of unit weight of a solid or liquid or unit volume of a gas".

Enthalpy of solution : "one mole of the substance is completely dissolved in a large excess of the given solvent under given conditions of temperature and pressure".

Enthalpy of neutralisation : "one gram equivalent of an acid is neutralised by one gram equivalent of a base in fairly dilute solution".

Enthalpy of hydration : "one mole of an anhydrous (or a partly hydrated salt) combines with the required number of mole of water to form a specific hydrate".

Enthalpy of sublimation : "one mole of a solid is directly converted into its vapour at a given temperature below its melting point".

Enthalpy of fusion : "one mole of the solid substance is completely converted into the liquid state at its melting point".

Enthalpy of vaporisation : "one mole of a substance is converted from the liquid state to its vapour state at its boiling point".

Resonance Energy = Observed heat of formation - Calculated heat of formation

BOND ENTHALPIES' (BOND ENERGIES) :

The bond enthalpy of a diatomic molecule (H_2, Cl_2, O_2) is equal to its dissociation energy and is defined as "the enthalpy change involved in breaking the bond between atoms of a gaseous molecule" (Bond breaking is an endothermic process). Average bond enthalpy (energy) is the average value of bond energy obtained from molecules that contain more than one bond of that type.

$$\text{Av. BE} = \frac{\Delta H_f \text{ of molecules}}{\text{no. of bonds}}$$

BE is an additive property.

SECOND LAW OF THERMODYNAMICS

The essence of first law is that all physical and chemical processes take place in such a manner that the total energy of the universe remain constant.

However, it is observed that all processes have a natural direction ,i.e. a direction in which they take place spontaneously. First law fails to answer this. Another feature of the spontaneous processes is that they proceed only until an equilibrium is achieved.

The direction of a spontaneous process and that it eventually reaches equilibrium, can be understood on the basis of entropy concept introduced through the second law of thermodynamics.

ENTROPY AND SPONTANEITY:

Entropy (denoted by S) in s state function. When the state of a system changes, entropy also changes.

The change of entrops ΔS is defined by, $\Delta S = \frac{q_{rev}}{T}$, where q_{rev} means that the heat is being supplied "Isothermally" and "Reversibly" (JK^{-1}).

One can think entropy as a measure of the degree of randomness or disorder in a system. The greater the disorder, in a system, the higher is the entropy.
A useful form of 2nd law of thermodynamics is :
"The entropy of the universe increases in the course of every spontaneous (natural) change".

OR

"For a spontaneous process in an isolated system, the change in entropy is positive".

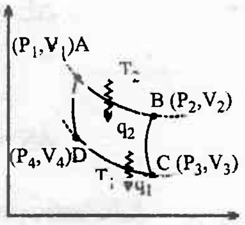
When a system is in equilibrium the entropy is maximum. So mathematically
$\Delta S = 0$ (at equilibrium)

SECOND LAW :

Statements :

(i) No cyclic engine is possible which take heat from one single source and in a cycle completely convert it into work without producing any change in surrounding.

(ii) Efficiency of Carnot engine working reversibly is maximum.
Carnot cycle



AB – Iso. Rev.Exp. $W_{AB} = -nRT_2 \ln \frac{V_2}{V_1}$

BC – Ada. Rev. Exp. $W_{BC} = C_V(T_1 - T_2)$

CD – Iso. Rev. Comp. $W_{CD} = -nRT_1 \ln\left(\frac{V_4}{V_3}\right)$

DA – Iso. Rev. Comp. $W_{DA} = C_V(T_2 - T_1)$

Carnot efficiency $\eta = \frac{-W_{Total}}{q_2} = \frac{T_1 - T_2}{T_2} = \frac{q_1 + q_2}{q_2}$

CARNOT CYCLE :

$\frac{q_1}{T_1} + \frac{q_2}{T_2} = 0$ for rev. cycle

Irreversible engine $\frac{q_1}{T_1} + \frac{q_2}{T_2} < 0$

$\oint \frac{q_{rev}}{T} = 0 \Rightarrow \frac{q_{rev}}{T}$ is a state function.

$\Delta S = \int \frac{dq_{rev}}{T}$

Also $\Delta S_{syt} + \Delta S_{surr} = 0$ for rev. process
$\Delta S_{syt} + \Delta S_{surr} > 0$ for irrev. process
$\Rightarrow \Delta S_{syt} + \Delta S_{surr} \geq 0$ (In general)

ENTROPY CHANGE (General Expression):

$$\Delta S = nC_V\, ln\, \frac{T_2}{T_1} + nR\, ln\, \frac{V_2}{V_1}$$

Change in state function for various processes.

Reversible irreversible isothermal expansion and contraction : (ideal gas)

$$\Delta E = 0;\ \Delta H = 0;\ \Delta S = nR\, ln\, \frac{V_2}{V_1}$$

Isobaric heating or cooling :

$$\Delta E = C_V\, \Delta T$$
$$\Delta H = C_P\, \Delta T = q_P$$
$$\Delta S = nC_P\, ln\left(\frac{T_2}{T_1}\right)$$

Isochoric heating or cooling :

$$\Delta E = C_V\, \Delta T = q_V$$
$$\Delta H = C_P\, \Delta T$$
$$\Delta S = nC_V\ ln\left(\frac{T_2}{T_1}\right)$$

Adiabatic process :

$$\Delta E = C_V\, \Delta T$$
$$\Delta H = C_P\, \Delta T$$
$$\Delta S = nC_V\, ln\frac{T_2}{T_1} + nR\, ln\, \frac{V_2}{V_1} \text{ for irreversible process}$$

$\Delta S = 0$ for reversible adiabatic compression and expansion.

Gibb's function :

$$G = H - TS$$

at constant T and pressure

$$\Delta G = \Delta H - T\Delta S$$

$\Delta G = (\Delta H - T\Delta S) \le 0$ for rev. process.

$(-\Delta G)_{T.P}$ = work done by system max. non P – V

$$\frac{\Delta G}{T} = -(\Delta S_{syst} + \Delta S_{surr})$$

$\Delta G < 0$ for spontaneous process

$\Delta G = 0$ for equilibrium.

GIBBS FREE ENERGY (G) AND SPONTANEITY:

A new thermodynamic (state) function G, the Gibbs free energy is defined as :

$G = H - TS$ or $\Delta G = \Delta H - T\,\Delta S$ (at constant temperature and pressure)

For a spontaneous reaction ΔG must be negative. The use of Gibbs free energy has the advantage that it refers to the system only (and not surroundings also as in entropy).

To summaries, the spontaneity of a chemical reaction is decided by two factors taken together:

(i) the enthalpy factor and (ii) the entropy factor.

The equation $\Delta G = \Delta H - T\,\Delta S$ takes both the factors into consideration.

The most favorable situation for a negative value of ΔG is a negative value of ΔH and a positive value of ΔS. However a large negative value of ΔH may outweigh an unfavorable ΔS value and a large value of ΔS may outweigh an unfavorable value of ΔH.

STANDARD FREE ENERGY CHANGE (ΔG°) :

The standard free energy change ΔG° is defined as the free energy change for a process at a specified temperature in which the reactants in their standard state are converted to the products in their standard state. It is denoted by ΔG°.

Like the standard enthalpy of formation of an element "the standard free energy of formation of an element in its standard state is zero". And so :

$$\Delta G_r^\circ = \sum \Delta G_f^\circ \text{ (products)} - \sum \Delta G_f^\circ \text{ (reactants)}$$

The standard free energy change. ΔG° is related to the equilibrium constant k_{eq} by the relation;

$$\Delta G^\circ = -2.303\,RT \log k_{eq}.$$

It can be shown that free energy change for a process is equal to the maximum possible work that can be derived from the process i.e.

$\Delta G^\circ = W_{max}$ (for a reversible change at constant pressure and temperature)

In case of a galvanic cell, free energy change, ΔG is related to the electrical work done in the cell.

$\Delta G = -nFE_{cell}$, where E_{cell} = e.m.f. of the cell ; F = Faraday constant and

n = number of electrons being transferred in the chemical process

So $\Delta G = -nF\,E^\circ_{cell}$, where E°_{cell} is the standard cell potential.

Clausius Claperyon's Equation : $\log \dfrac{p_2}{p_1} = \dfrac{\Delta H}{2.303R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]$ (For liquid ⇔ gas equilibrium)

p_1 & p_2 are vapour pressure at T_1 & T_2

THIRD LAW OF THERMODYNAMICS

"At absolute zero, the entropy of a perfectly crystalline substance is taken as zero", which means that at absolute zero every crystalline solid is in a state of perfect order and its entropy should be zero.

By virtue of the third law, the absolute value of entropy (unlike absolute value of enthalpy) for any pure substance can be calculated at room temperature.

The standard absolute entropy of, a substance" So, is the entropy of the substance in its standard at 298K and 1 atm.

Absolute entropies of various substances have been tabulated and these value are used to calculate entropy changes for the reactions by the formula;

$$\Delta S^\circ = \sum S^\circ \text{ (products)} - \sum S^\circ \text{ (reactants)}$$

EXERCISE-I

Heat, work and change in ΔU, ΔH (First Law)

Q.1 In which of the following changes at constant pressure is work done by system on surrounding? By the surrounding on system?

	Initial state		Final state
(i)	H_2O (g)	$\longrightarrow$	H_2O (l)
(ii)	H_2O (s)	$\longrightarrow$	H_2O (g)
(iii)	H_2O (l)	$\longrightarrow$	H_2O (s)
(iv)	$2H_2(g) + N_2(g)$	$\longrightarrow$	$2NH_3$ (g)
(v)	$CaCO_3$ (s)	$\longrightarrow$	CaO (s) + CO_2 (g)

Q.2 The gas is cooled and loses 65 J of heat. The gas contracts as it cools and work done on the system equal to 20 J is exchanged with the surroundings. What are q, w and ΔE ?

Q.3 The enthalpy change for the reaction of 50 ml of ethylene with 50.0 ml of H_2 at 1.5 atm pressure is $\Delta H = -0.31$ KJ. What is the ΔE.

Q.4 The enthalpy of combustion of glucose is -2808 KJmol^{-1} at 25°C. How many grams of glucose do you need to consume [Assume wt = 62.5 Kg].

(a) to climb a flight of stairs rising through 3M.

(b) to climb a mountain of altitude 3000 M?

Assume that 25% of enthalpy can be converted to useful work.

Q.5 What is ΔE when 2.0 mole of liquid water vaporises at 100°C ? The heat of vaporisation, ΔH vap. of water at 100°C is 40.66 KJmol^{-1}.

Q.6 If 1.0 k cal of heat is added to 1.2 L of O_2 in a cylinder of constant pressure of 1 atm, the volume increases to 1.5 L. Calculate ΔE and ΔH of the process.

Q.7 When the following reaction was carried out in a bomb calorimeter, ΔE is found to be -742.7 kJ/mol of NH_2CN (s) at 298 K.

$$NH_2CN\,(s) + \frac{3}{2}O_2\,(g) \rightarrow N_2\,(g) + CO_2\,(g) + H_2O\,(l)$$

Calculate ΔH_{298} for the reaction.

Q.8 When 1 mole of ice melt at 0°C and at constant pressure of 1 atm. 1440 calories of heat are absorbed by the system. The molar volumes of ice and water are 0.0196 and 0.0180 litre respectively. Calculate ΔH and ΔE for the reaction.

Q.9 Water expands when it freezes. Determine amount of work in joules, done when a system consisting of 1.0 L of liquid water freezes under a constant pressure of 1.0 atm and forms 1.1 L of ice.

Q.10 Lime is made commercially by decomposition of limestone $CaCO_3$. What is the change in internal energy when 1.00 mole of solid $CaCO_3$ (V = 34.2 ml) absorbs 177.9 kJ of heat and decomposes at 25°C against a pressure of 1.0 atm to give solid CaO. (Volume = 16.9 ml) and CO_2 (g) (V = 24.4 L).

Q.11 Calculate the work done by system in an irreversible (single step) adiabatic expansion of 1 mole of a polyatomic gas from 300K and pressure 10 atm to 1 atm.($\gamma = 1.33$).

Q.12 One mole of solid Zn is placed in excess of dilute H_2SO_4 at 27 °C in a cylinder fitted with a piston. Find the value of ΔE, q and w for the process if the area of piston is 500 cm^2 and it moves out by 50 cm against a pressure of 1 atm during the reaction. The heat given to surrounding is 36.5 KJ.

$$Zn(s) + 2H^+(aq) \rightleftharpoons Zn^{2+}(aq) + H_2(g)$$

Internal energy and enthalpy changes in thermodynamics processes (First Law)

Q.13 1 mole of CO_2 gas at 300 K is expanded under reversible adiabatic condition such that its volume becomes 27 times.

(a) What is the final temperature. (b) What is work done.

Given $\gamma = 1.33$ and $C_V = 25.08$ J $mol^{-1}K^{-1}$ for CO_2.

Q.14 Three moles of a ideal gas at 200 K and 2.0 atm pressure undergo reversible adiabatic compression until the temperature becomes 250 K for the gas C_V is 27.5 JK^{-1} mol^{-1} in this temperature range. Calculate q, w, ΔU, ΔH and final V and final P.

Q.15 A sample of a fluorocarbon was allowed to expand reversibly and adiabatically to twice its volume. In the expansion the temperature dropped from 298.15 K to 248.44 K. Assume the gas behaves perfectly. Estimate the value of $C_{V,m}$.

Q.16 Find the work done when one mole of the gas is expanded reversibly and isothermally from 5 atm to 1 atm at 25°C.

Q.17 One mole of a perfect monoatomic gas is put through a cycle consisting of the following three reversible steps :

(CA) Isothermal compression from 2 atm and 10 litres to 20 atm and 1 litre.

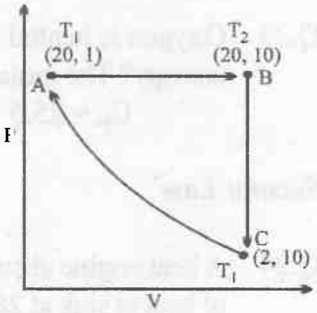
(AB) Isobaric expansion to return the gas to the original volume of 10 litres with T going from T_1 to T_2.

(BC) Cooling at constant volume to bring the gas to the original pressure and temperature.

The steps are shown schematically in the figure shown.

(a) Calculate T_1 and T_2.

(b) Calculate ΔE, q and W in calories, for each step and for the cycle.

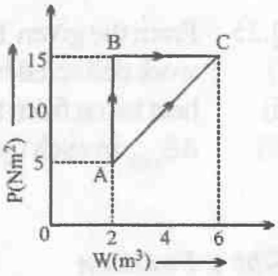


Q.18 The given figure shows a change of state A to state C by two paths ABC and AC for an ideal gas. Calculate the:

(a) Path along which work done is least.

(b) Internal energy at C if the internal energy of gas at A is 10 J and amount of heat supplied to change its state to C through the path AC is 200 J.

(c) Amount of heat supplied to the gas to go from A to B, if internal energy change of gas is 10 J.

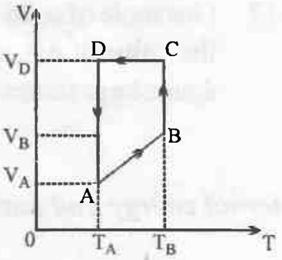


Q.19 A monoatomic ideal gas of two moles is taken through a reversible cyclic process starting from A as shown in figure. The volume ratios are $\frac{V_B}{V_A} = 2$ and $\frac{V_D}{V_A} = 4$. If the temperature T_A at A is 27°C, calculate:

(a) The temperature of the gas at point B.

(b) Heat absorbed or released by the gas in each process.

(c) The total work done by the gas during complete cycle.



Kirchoff's Rule : Variation of Enthalpy with Temperature

Q.20 The standard enthalpy of formation of water liquid is – 285.76 kJ at 298 K. Calculate the value of 373K. The molar heat capacities at constant pressure (C_P) in the given temperature range of H_2 (g), O_2(g) and H_2O (*l*) are respectively 38.83, 29.16 and 75.312 $JK^{-1}mol^{-1}$.

Q.21 Methan (Considered to be an ideal gas) initially at 25°C and 1 bar pressure is heated at constant pressure until the volume has doubled. The variation of the molart heat capacity with ansolute temperature is given by

$$C_P = 22.34 + 48.1 \times 10^{-3}\, T$$

where C_P is in $JK^{-1}\ mol^{-1}$. Calculate molar (a) ΔH (b) ΔU.

Entropy change in thermodynamic processes

Q.22 One mole of NaCl (s) on melting absorbed 30.5 KJ of heat and its entropy is increased by 28.8 JK^{-1}. What is the melting point of sodium chloride?

Q.23 Oxygen is heated from 300 to 600 at a constant pressure of 1 bar. What is the increases in molar entropy? The molar heat capacity in $JK^{-1}\ mol^{-1}$ for the O_2 is

$$C_P = 25.5 + 13.6 \times 10^{-3}\, T - 42.5 \times 10^{-7}\, T^2 ,$$

Second Law

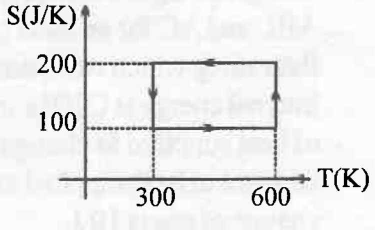
Q.24 A heat engine absorbs 760 kJ heat from a source at 380K. It rejects (1) 650 kJ, (ii) 560 kJ, (iii) 504 kJ of heat to sink at 280 K. State which of these represent a reversible, an irreversible and an impossible cycle.

Q.25 From the given T-S diagram of a reversible carnot engine, find

(i) work delivered by engine in each cycle

(ii) heat taken from the source in each cycle.

(iii) ΔS_{sink} in each cycle.



Gibb's Function

Q.26 Calculate the free energy change at 298 K for the reaction ;
$Br_2\,(l) + Cl_2\,(g) \longrightarrow 2\,BrCl\,(g)$. For the reaction $\Delta H^\circ = 29.3$ kJ & the entropies of $Br_2\,(l)$, Cl_2 (g) & BrCl (g) at the 298 K are 152.3, 223.0, 239.7 $J\ mol^{-1}\ K^{-1}$ respectively.

Q.27 Using the date given below, establish that the vaporization of $CCl_4(l)$ at 298 K to produce $CCl_4(g)$ at 1 atm pressure does not occur spontaneously.

Given : $CCl_4(l, 1\text{ atm}) \longrightarrow CCl_4(g, 1\text{ atm})$; $\Delta S° = 94.98\ JK^{-1}\ mol^{-1}$;

$\Delta H°_f(CCl_4, g) = -106.7\ kJ\ mol^{-1}$ & $\Delta H°_f(CCl_4, l) = -139.3\ kJ\ mol^{-1}$

Q.28 Animals operate under conditions of constant pressure and most of the processes that maintain life are electrical (in a broad sense). How much energy is available for sustaining this type of muscular and nervous activity from the combustion of 1 mol of glucose molecules under standard conditions at 37°C (blood temperature)? The entropy change is $+182.4\ JK^{-1}$ for the reaction as stated.

$\Delta H_{\text{combustion [glucose]}} = -2808$ KJ

Q.29 Assume that only change in volume is due to the production of hydrogen and calculate W, the work done, when 2 mole of Zn dissolves in HCl, giving $H_2(g)$ as 35°C and 1 atm.

$Zn(s) + 2HCl(aq.) \rightarrow ZnCl_2(aq.) + H_2(g)$

Q.30 From the given table answer the following questions:

	CO(g)	CO_2(g)	H_2O(g)	H_2(g)
$\Delta H°_{298}$ (-KCal/mole)	–26.42	–94.05	–57.8	0
$\Delta G°_{298}$ (-KCal/mole)	–32.79	–94.24	–54.64	0
$S°_{298}$ (-Cal/Kmole)	47.3	51.1	?	31.2

Reaction: $H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$

(i) Calculate $\Delta_r H^\circ_{298}$ (ii) Calculate $\Delta_r G^\circ_{298}$ (iii) Calculate $\Delta_r S^\circ_{298}$

(iv) Calculate $\Delta_r E^\circ_{298}$ (v) Calculate $S^\circ_{298}\ [H_2O(g)]$

PROFICIENCY TEST

Q.1 *Mark the following statement as True or False.*

1. Pressure is an intensive property.
2. Like U and H, S is also a state function.
3. When a system undergoes a change at constant pressure, it is referred to an isothermal process.
4. A reversible process is always quasi-static.
5. The workdone by a gas during free expansion is equal to zero.
6. First law of T.D. is applicable to all processes irrespective to whether they are reversible or irreversible.
7. All spontaneous processes proceed in one direction only.
8. Whenever a system undergoes a cyclic change

$$\oint \frac{dQ}{T} \le 0$$

9. Positive value of ΔS_{system} during the process can be taken as sole criterion of spontaneity.
10. A real crystal has higher entropy than the ideal crystal.

Q.2 *Fill in the blank with appropriate items:*

1. According to IUPAC conventions work done on the surroundings is________.
2. A system is said to be _______ if it can neither exchange matter nor energy with surrounding.
3. A carnot cycle uses only _______ thermal reservoir.
4. A carnot cycle consists of only _______ processes.
5. The efficiency of a carnot engine can be increased by _________ sink temperature when the source temperature is held constant.
6. For a reversible adiabatic process, S = constnat and hence it is called as an ______ process.
7. Entropy change of a system is determined by the ________ and ______ states only, irrespective of how the system has changed its states.
8. Solidification of liquid shows ________ in entropy.
9. When Fe(s) is dissolved in a aqueous HCl in a closed vessel the work done is ______.
10. For Non-spontaneous process ΔG is _________.

EXERCISE-II

Q.1 Calculate ΔS_f° at 298 K of ; (i) $NaCl(s)$, (ii) $NH_4Cl(s)$ & (iii) diamond.
The values of S° of Na, Cl_2, NaCl, NH_4Cl, N_2, H_2, diamond & graphite are 51, 223, 72, 95, 192, 131, 2.43 & 5.69 $JK^{-1}\ mol^{-1}$ respectively.

Q.2 1 mole of ice at 0°C and 4.6 mm Hg pressure is converted to water vapour at a constant temperature and pressure. Find ΔH and ΔE if the latent heat of fusion of ice is 80 cal/gm and latent heat of vaporisation of liquid water at 0°C is 596 cal per gram and the volume of ice in comparison of that water (vapour) is neglected.

Q.3 Two moles of helium gas ($\gamma = 5/3$) are initially at a temperature of 27°C and occupy a volume of 20 litre. The gas is first expanded at constant pressure until the volume is doubled. It then undergoes adiabatic change until the temperature returns to its initial value.
(a) Sketch the process on P – V diagram.
(b) What are final pressure and final volume of gas.
(c) What is the work done by the gas.

Q.4 One mole of an ideal gas is expanded isothermally at 298 K until its volume is tripled. Find the values of ΔS_{gas} and ΔS_{total} under the following conditions.
(i) Expansion is carried out reversibly.
(ii) Expansion is carried out irreversibly where 836.8J of heat is less absorbed than in (i)
(iii) Expansion is free.

Q.5 10 g of neon initially at a pressure of 506.625 kPa and temperature of 473 K expand adiabatically to a pressure of 202.65 kPa. Calculate entropy change of the system and total entropy change for the following ways of carrying out this expansion.
(i) Expansion is carried out reversibly.
(ii) Expansion occurs against a constant external pressure of 202.65 kPa.
(iii) Expansion is a free expansion.

Q.6 20.0 dm^3 of an ideal gas (diatomic $C_{v,m} = 5R/2$) at 673 K and 0.7 MPa expands until pressure of the gas is 0.2 MPa. Calculate q, w, ΔU and ΔH for the process if the expansion is :
(i) Isothermal and reversible (ii) Adiabatic and reversible
(iii) Isothermal and adiabatic (iv) Against 0.2 MPa and adiabatic
(v) Against 0.2 MPa and isothermal.

Q.7 One mole of an ideal monoatomic gas ($C_{V,m} = 1.5\,R$) is subjected to the following sequence of steps:
(a) The gas is heated reversibly at constant pressure of 101.325 kPa from 298 K to 373 K.
(b) Next, the gas is expanded reversibly and isothermally to double its volume.
(c) Finally, the gas is cooled reversibly and adiabatically to 308K.
Calculate q , w , ΔU and ΔH for the overall process.

Q.8 One mole of an ideal gas (not necessarily monoatomic) is subjected to the following sequence of steps.
(a) It is heated at constant volume from 298 K to 373 K
(b) It is expanded freely into a vacuum to double volume.
(c) It is cooled reversibly at constant pressure to 298 K.
Calculate q, w , ΔU and ΔH for the overall process.

Q.9 Calculate the heat of vaporisation of water per gm at 25°C and 1 atm.
Given $\Delta H_f^\circ[H_2O(l)] = -285.57$ kJ/mol, $\Delta H_f^\circ[H_2O(g)] = -241.6$ kJ/mol.
Comment why ΔH_{vap} (25°C) > ΔH_{vap} (100°C).
Use data of **Q.17**

Q.10 1 mole of H_2O (l) is at 373 K allowed to expand
(I) against zero external pressure to a volume of 30.6 litres.
(II) against constant external pressure of 1 atm. In this process 40.7 kJ of heat was absorbed.
Calculate ΔH and ΔE in process I and II.

Q.11 Calculate the entropy of a substance at 600 K using the following data.
(i) Heat capacity of solid from 0 K to normal melting point 200 K
$C_{P,m}(s) = 0.035\ T \quad JK^{-1}mol^{-1}$.
(ii) Enthalpy of fusion = 7.5 KJ mol^{-1}, (iii) Enthalpy of vaporisation = 30 KJ mol^{-1}.
(iv) Heat capacity of liquid from 200 K to normal boiling point 300 K
$C_{P,m}(l) = 60 + 0.016\ T \quad JK^{-1}mol^{-1}$.
(v) Heat capacity of gas from 300 K to 600 K at 1 atm
$C_{P,m}(g) = 50.0 \quad JK^{-1}mol^{-1}$.

Q.12(a) An ideal gas undergoes a single stage expansion against a constant opposing pressure from (P_1, V_1, T) to (P_2, V_2, T). What is the largest mass m which can be lifted through a height h in this expansion?
(b) The system in (a) restored to its initial state by a single stage compression. What is the smallest mass m' which must fall through the height h to restore the system?
(c) What is the net mass lowered through height h in the cyclic transformation in (a) and (b)?

Q.13 Calculate the free energy change in the freezing of 18 gm of water at 263.15 K, given that the vapour pressure of water and ice at 263.15 K are 0.287 Pa and 0.260 Pa, respectively. at 1 atm

Q.14 A 32 g sample of CH_4 gas initially at 101.325 kPa and 300K is heated to 550 K. $C_{P,m}/JK^{-1}mol^{-1} = 12.552 + 8.368 \times 10^{-2}\ T/K$. Assuming CH_4 behaves ideally, compute w, q . ΔU and ΔH for (a) an isobaric reversible process, and (b) an isochoric reversible process.

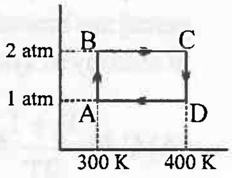
Q.15 Derive a mathematical expression for the work done on the surrounding when a gas that has the equation of state $PV = nRT - \frac{n^2a}{V}$ expands reversibly from V_i to V_f at constant temperature.

Q.16 For the reaction
$FeCO_3(s) = FeO(g) + CO_2(g)$
$\Delta_rG^\circ/J\ mol^{-1} = 78073.4 - 60.33\ (T/K) \log (T/K) - 25.397\ (T/K) + 34.476 \times 10^{-3}\ (T/K)^2$
find Δ_rH° and Δ_rS° for the reaction at 25°C.

Q.17 Compute Δ_rG for the reaction $H_2O\ (l, 1\ atm, 323\ K) \rightarrow H_2O\ (g, 1\ atm, 323\ K)$
Given that : $\Delta_{vap}H$ at 373 K = 40.639 $kJmol^{-1}$, $C_p(H_2O, l) = 75.312\ J\ K^{-1}mol^{-1}$,
$C_p\ (H_2O, g) = 33.305\ J\ K^{-1}mol^{-1}$.

Q.18 If p is the vapour pressure of water at 323 K, then the following reaction will be at equilibrium :
$H_2O\ (l, p, 323\ K) \rightarrow H_2O\ (g, p, 323\ K)$
and Δ_rG for this reaction will be zero. Compute the value of p at 323 K.
Use the data of the previous problem.

EXERCISE-III



Q.1 Two moles of Helium gas undergo a cyclic process as shown in figure. Assuming gas to be ideal, what is the net work involved in the cyclic process?
(A) $-100R\ln 4$ (B) $+100R\ln 4$
(C) $+200R\ln 4$ (D) $-200R\ln 4$

Q.2 Benzene burns according to the following equation

$$2C_6H_6(l) + 15\,O_2\,(g) \longrightarrow 12\,CO_2\,(g) + 6H_2O(l) \quad \Delta H° = -6542\text{ kJ}$$

What is the ΔE° for the combustion of 1.5 mol of benzene
(A) –3271 kJ (B) –9813 kJ (C) – 4906.5 kJ (D) None of these

Q.3 One mole of ideal gas is allowed to expand reversibly and adiabatically from a temperature of 27°C. If the work done by the gas in the process is 3 kJ, the final temperature will be equal to (C_V=20 J/K mol)
(A) 100 K (B) 450 K (C) 150 K (D) 400 K

Q.4 Two moles of an ideal gas ($C_V = \frac{5}{2}R$) was compressed adiabatically against constant pressure of 2 atm. Which was initially at 350 K and 1 atm pressure. The work involve in the process is equal to
(A) 250 R (B) 300 R (C) 400 R (D) 500 R

Q.5 The maximum efficiency of a heat engine operating between 100°C and 25°C is
(A) 20% (B) 22.2% (C) 25% (D) none

Q.6 A heat engine operating between 227°C and 27°C absorbs 2 Kcal of heat from the 227°C reservoir reversibly per cycle. The amount of work done in one cycle is
(A) 0.4 Kcal (B) 0.8 Kcal (C) 4 Kcal (D) 8 Kcal

Q.7 For the reaction at 300 K

$$A(g) + B(g) \longrightarrow C\,(g)$$

ΔE = –3.0 kcal ; ΔS = – 10.0 cal/K
value of ΔG is
(A) –600 cal (B) –6600 cal (C) –6000 cal (D) None

Q.8 The entropy change when two moles of ideal monoatomic gas is heat from 200 to 300°C reversibly and isochorically
(A) $\frac{3}{2}R\ln\left(\frac{300}{200}\right)$ (B) $\frac{5}{2}R\ln\left(\frac{573}{273}\right)$ (C) $3R\ln\left(\frac{573}{473}\right)$ (D) $\frac{3}{2}R\ln\left(\frac{573}{473}\right)$

Q.9 What is the free energy change (ΔG) when 1.0 mole of water at 100°C and 1 atm pressure is converted into steam at 100°C and 1 atm pressure?
(A) 80 cal (B) 540 cal (C) 620 cal (D) zero

Q.10 What is the free energy change (ΔG) when 1.0 mole of water at 100°C and 1 atm pressure is converted into steam at 100°C and 2 atm pressure?
(A) zero cal (B) 540 cal (C) 515.4 cal (D) none

Q.11 When two equal sized pieces of the same metal at different temperatures T_h (hot piece) and T_c(cold piece) are brought into contact into thermal contact and isolated from it's surrounding. The total change in entropy of system is given by

(A) $C_v \ln \frac{T_c + T_h}{2T_c}$ (B) $C_v \ln \frac{T_2}{T_1}$ (C) $C_v \ln \frac{(T_c + T_h)^2}{2T_h.T_c}$ (D) $C_v \ln \frac{(T_c + T_h)^2}{4T_h.T_c}$

Q.12 Pick out the incorrect statement among the following

I Change in Gibb's function at constant temperature and pressure in a process envolving no non PV work is equal to $q_{rev} - q_{irr}$

II For a reaction with ΔS^0 is positive, as temperature is increased, K_{eq} for the reaction increases necessarily

III Exothermic reactions have lesser tendency to go in forward direction at higher temperature

IV Decrease in Gibb's function at constant temperature and pressure is equal to non PV work done by system in spontaneous process

(A) I, IV (B) I, II, IV (C) II, IV (D) I, II

Q.13 Which of the following statement(s) is/are incorrect:

Statement (a) : Reversible isothermal compression of an ideal gas represents the limiting minimum value of the workdone (|w|) by the surrounding on the system.

Statement (b) : In an irreversible process, the cyclic integral of work is not zero.

Statement (c) : For thermodynamic changes in adiabatic process $T^{\left(\frac{C_{p,m}}{R}\right)}.P = \text{constant}$

Statement (d) : ΔS_{system} is zero for reversible adiabatic expansion of an ideal gas.

(A) Statement c (B) Statement a, b, c (C) Statement a, b, d (D) All

Q.14 9.0 gm ice at 0°C is mixed with 36 gm of water at 50°C in a thermally insulated container. Using the following data, answer the question that follow

$C_P (H_2O) = 4.18 \text{ Jg}^{-1}\text{K}^{-1}$; $\Delta H_{fusion} (\text{ice}) = 335 \text{ J g}^{-1}$

(i) final temperature of water is

(A) 304.43 K (B) 296.97 K (C) 303.93 K (D) 287 K

(ii) ΔS_{ice} is

(A) 11.04 JK^{-1} (B) 3.16 JK^{-1} (C) 14.2 JK^{-1} (D) 7.84 JK^{-1}

(iii) ΔS_{water} is

(A) –12.64 JK^{-1} (B) –0.34 JK^{-1} (C) –5.42 JK^{-1} (D) 12.64 JK^{-1}

(iv) What is the total entropy change in the process?

(A) –1.56 JK^{-1} (B) –1.60 JK^{-1} (C) 1.56 JK^{-1} (D) 1.60 JK^{-1}

Q.15 Liquid water freezes at 273 K under external pressure of 1 atm. The process is at equilibrium $H_2O\,(l) \rightleftharpoons H_2O\,(s)$ at 273 K & 1 atm.
However it was required to calculate the thermodynamic parameters of the fusion process occuring at same pressure & different temperature. Using the following data, answer the question that follow.
$d_{ice} = 0.9$ gm/cc ; $d_{H_2O(l)} = 1$ gm/cc ; $C_P\,[H_2O\,(s)] = 36.4\ JK^{-1}mol^{-1}$;
$C_P\,[H_2O\,(l)] = 75.3\ JK^{-1}mol^{-1}$; $\Delta H_{fusion} = 6008.2\ Jmol^{-1}$.

(i) The value of "ΔH_{fusion}" at 263 K & 1 atm will be
(A) +6008.2 J $mole^{-1}$ (B) 5619.2 J $mole^{-1}$ (C) –5619.2 J $mole^{-1}$ (D) 6619.2 J $mole^{-1}$

(ii) "ΔS_{fusion}" at 263 K & 1 atm will be
(A) 22.01 $JK^{-1}\,mol^{-1}$ (B) 22.84 $JK^{-1}\,mol^{-1}$ (C) 21.36 $JK^{-1}\,mol^{-1}$ (D) 20.557 $KJ^{-1}\,mol^{-1}$

(iii) At 1 atm & at diffrent temperature given below. Match the conditions & the temperature for the "fusion" process

	Condition		**Temperature**
(1)	Spontaneous	(a)	273 K
(2)	At equilibrium	(b)	260 K
(3)	Not feasible	(c)	280 K

(A) (1–c), (2–a), (3–b) (B) (1–b), (2–a), (3–c)
(C) (1–c), (2–b), (3–a) (D) (1–a), (2–b), (3–c)

(iv) For the fusion process at 263 K, match the conditions with the pressure

	Conditions		**Pressure**
(1)	Spontaneous	(a)	1 atm
(2)	At equilibrium	(b)	1054 atm
(3)	Not feasible	(c)	2000 atm

(A) (1–b), (2–c), (3–a) (B) (1–a), (2–b), (3–c)
(C) (1–c), (2–b), (3–a) (D) (1–a), (2–c), (3–b)

EXERCISE-IV

OBJECTIVE

Q.1 One mole of monoatomic ideal gas expands adiabatically at initial temp. T against a constant external pressure of 1 atm from one litre to two litre. Find out the final temp. ($R = 0.0821$ litre. atm K^{-1} mol^{-1})

(A) T

(B) $\dfrac{T}{(2)^{\frac{5}{3}-1}}$

(C) $T - \dfrac{2}{3 \times 0.0821}$

(D) $T + \dfrac{2}{3 \times 0.0821}$

[JEE 2005]

Q.2 Two mole of an ideal gas is expanded isothermally and reversibly from 1 litre to 10 litre at 300 K. The enthalpy change (in kJ) for the process is

(A) 11.4 kJ
(B) –11.4 kJ
(C) 0 kJ
(D) 4.8 kJ **[JEE 2004]**

Q.3 The enthalpy of vapourization of a liquid is 30 kJ mol^{-1} and entropy of vapourization is 75 J mol^{-1} K. The boiling point of the liquid at 1 atm is

(A) 250 K
(B) 400 K
(C) 450 K
(D) 600 K **[JEE 2004]**

Q.4 One mol of non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95 K) to (4.0 atm, 5.0 L, 245 K) with a change in internal energy (ΔU) = 30.0 L-atm. The change in enthalpy (ΔH) of the process in L-atm.

(A) 40.0
(B) 42.3
(C) 44.0
(D) not defined, because pressure is not constant **[JEE 2002]**

Q.5 Which of the following statement is false?

(A) Work is a state function
(B) Temperature is a state function
(C) Change of state is completely defined when initial and final states are specified.
(D) Work appears at the boundary of the solution. **[JEE 2001]**

Q.6 Molar heat capacity of water in equlibrium with ice at constant pressure is

(A) zero
(B) ∞
(C) 40.45 kJ K^{-1} mol^{-1}
(D) 75.48 JK^{-1} mol^{-1} **[JEE 1997]**

SUBJECTIVE

Q.7 One mole of a liquid (1 bar, 100 ml) is taken in an adiabatic container and the pressure increases steeply to 100 bar. Then at a constant pressure of 100 bar, volume decreases by 1 ml. Find ΔU and ΔH

[JEE 2004]

Q.8 Two moles of a perfect gas undergoes the following processes : **[JEE 2002]**
(a) a reversible isobaric expansion from (1.0 atm, 20.0 L) to (1.0 atm, 40.0 L);
(b) a reversible isochoric change of state from (1.0 atm, 40.0 L) to (0.5 atm, 40.0 L);
(c) a reversible isothermal compression from (0.5 atm, 40.0 L) to (1.0 atm, 20.0 L);
(i) Sketch with labels each of the processes on the same P-V diagram.
(ii) Calculate the total work (w) and the total heat change (q) involved in the above processes.
(iii) What will be the values of ΔU, ΔH and ΔS for the overall process ?

Q.9 Show that the reaction $CO\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow CO_2\,(g)$ at 300 K is spontaneous and exothermic, when the standard entropy is – 0.094 kJ mol^{-1} K^{-1}. The standard Gibbs free energies of formation for CO_2 and CO are – 394.4 and – 137.2 kJ mol^{-1}, respectively. **[JEE 2001]**

Q.10 A sample of argon gas at 1 atm pressure and 27°C expands reversibly and adiabatically from 1.25 dm^3 to 2.50 dm^3. Calculate the enthalpy change in this process. C_{vm} for argon is 12.48 JK^{-1} mol^{-1}. **[JEE 2000]**

ANSWER KEY

EXERCISE I

Heat, work and change in ΔU, ΔH (First Law)

Q.1 (i) W, (ii) – W, (iii) – W, (iv) W, (v) – W Q.2 $q = -65$ J ; $w = 20$ J; $\Delta E = -45$ J

Q.3 – 0.3024 kJ Q.4 (a) 0.47 gm, (b) 0.47 kg Q.5 $\Delta E = 75.11$ kJ

Q.6 $\Delta E = 0.993$ k cal, $\Delta H = 1$ k cal Q.7 – 741.5 kJ Q.8 $\Delta H \simeq \Delta E = 1440$ calories

Q.9 – 10 J Q.10 $q = 177.9$ kJ, $w = -2.5$ kJ ; $\Delta E = 175.4$ kJ

Q.11 – 1.683 kJ Q.12 $\Delta E = -39.03$ KJ/mole; $q = -36.5$ KJ; $w = -2.53$ KJ]

Internal energy and enthalpy changes in thermodynamics processes (First Law)

Q.13 $T_2 = 100$ K ; $W = 5.016$ KJ

Q.14 $q = 0$; $W = \Delta U = 4.12$ KJ; $\Delta H = 5.37$ KJ; $V_f = 11.8$ dm^3; $P = 5.21$ atm

Q.15 $C_{V,m} = 31.6\ JK^{-1}mol^{-1}$ Q.16 $w = -3.988$ kJ

Q.17 (a) $T_1 = 243.60$ K; $T_2 = 2436.0$ K, (b) $\Delta E = 0$; $q = -w = +3262.88$ cal

Q.18 (a) AC, (b) 170 J, (c) 10 J

Q.19 (a) 600 K, (b) $q_{AB} = 3000$ cal; $q_{BC} = 1663$ cal; $q_{CD} = -1800$ cal; $q_{DA} = -1663$ cal; Total Q = 1200 cal, (c) $W = -1200$ cal

Kirchoff's Rule : Variation of Enthalpy with Temperature

Q.20 ΔH°_{373} (H_2O (l)) = – 284.11 kJ Q.21 (a) 13.064 kJ mol^{-1}, (b) 10.587 kJ mol^{-1}

Entropy change in thermodynamic processes

Q.22 $T = 1059$ K Q.23 21.18 JK^{-1} mol^{-1}

Second law

Q.24 (i) irreversible, (ii) reversible, (iii) impossible Q.25 (i) 30 kJ, (ii) + 60 kJ, (iii) 100 J/K

Gibb's Function

Q.26 – 1721.8 J Q.27 $\Delta G^{\circ} = 4.3$ kJ mol^{-1} > 0

Q.28 – 2864.5 KJ Q.29 -5.12×10^3 J

Q.30 (i) – 9.83 Kcal/mole; (ii) – 6.81 Kcal/mole, (iii) – 10.13 Cal / Kmole, (iv) –9.83 Kcal/mole, (v) + 45.13 Cal/ K mole

PROFICIENCY TEST

Q.1

1.	T	2.	T	3.	F	4.	T	5.	T
6.	T	7.	T	8.	T	9.	F	10.	T

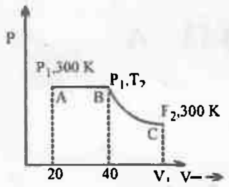
Q.2

1.	negative	2.	isolated	3.	two	4.	reversible
5.	decresing	6.	isentropic	7.	Initial, final	8.	decrease
9.	zero	10.	positive				

EXERCISE II

Q.1 (i) –90.5 (ii) –374.5 (iii) –3.26 (all in J mol^{-1} K^{-1})

Q.2 ΔH = 12168 calories; ΔE = 11623 calories

Q.3 (a) 

, (b) $P_2 = 0.435$ atm $V_1 = 113.13$ litre, (c) $W_T = -3000$ cal

Q.4 (i) $\Delta S_{gas} = -\Delta S_{surr}$ and $\Delta S_{total} = 0$, (ii) $\Delta S_{total} = 2.808$ J K^{-1} (iii) $\Delta S_{total} = \Delta S_{sys} = 9.134$ J K^{-1}

Q.5 (i) $\Delta S_{sys} = 0$; $\Delta S_{surr} = 0$ and $\Delta S_{total} = 0$, (ii) $\Delta S_{surr} = 0$; $\Delta S_{total} = \Delta S_{sys} = 0.957$ JK^{-1}
(iii) $\Delta S_{sys} = \Delta S_{total} = 3.81$ JK^{-1}

Q.6 (i) q = – w = 17.54 kJ , ΔU = 0 and ΔH =0 ; (ii) q = 0 , w = ΔU = –10.536 kJ and ΔH = –14.75kJ
(iii) q = 0 , w = 0 , ΔU = 0 and ΔH =0 (iv) q = 0; ΔU = w = – 7.14 KJ; ΔH = – 9.996 KJ,
(v) q = –w = 10. 0 KJ, ΔU = ΔH = 0

Q.7 (a) q = ΔH = 1558.88, ΔU = 935.33 ; w = – P(ΔU) = – 623.55 J mol^{-1}
(b) w = – 2149.7 ; ΔU & ΔH = 0, q = – w
(c) q = 0, w = – 810.62 , ΔH = – 1351.03 Jmol^{-1}
for overall process q = 3708.59 ; w = – 3583.88, ΔU = 124.71 ; ΔH = 207.85]

Q.8 ΔU & ΔH = 0 ; w = 623.55 ; q = – 623.55 J mol^{-1}

Q.9 ΔH_{vap}(25°C) = 4397 kJ/mol = 2.433 kJ/gm, ΔH_{vap} (100°C) = 40.62 kJ/mol (given)

Q.10 $\Delta E_I = \Delta E_{II} = +37.6$ kJ ; $\Delta H_I = \Delta H_{II} = 40.7$ kJ

Q.11 205.08 JK^{-1} mol^{-1}

Q.12 (a) $m = \frac{nRT}{gh}\left(1-\frac{P_2}{P_1}\right)$, (b) $m' = \frac{nRT}{gh}\left(\frac{P_1}{P_2}-1\right)$, (c) $m'-m = \frac{nRT}{gh}\left(\frac{(P_1-P_2)^2}{P_1P_2}\right)$

Q.13 $-216.198\ J\ mol^{-1}$

Q.14 (a) $q_P = \Delta H = 24.058$ kJ , $w = -4.157$ kJ , $\Delta U = 19.90$ kJ ; (b) $\Delta U = 19.90$ kJ ; $\Delta H = 24.058$; $w = 0$

Q.15 $w = -nRT\,ln\frac{V_f}{V_i} - n^2a\left(\frac{1}{V_f}-\frac{1}{V_i}\right)$

Q.16 $\Delta_rH° = 82.801\ kJ\ mol^{-1}$, $\Delta_rS° = 180.33\ J\ K^{-1}\ mol^{-1}$

Q.17 $\Delta_rG = 5.59\ kJ\ mol^{-1}$ Q.18 12.63 kPa

EXERCISE III

Q.1 A Q.2 D Q.3 C Q.4 D Q.5 A Q.6 B Q.7 A

Q.8 C Q.9 D Q.10 C Q.11 D Q.12 B Q.13 A

Q.14 (i) B (ii) C (iii) A (iv) C Q.15 (i) B (ii) D (iii) A (iv) C

EXERCISE IV

Q.1 C Q.2 C Q.3 B Q.4 C Q.5 A

Q.6 B Q.7 $\Delta U = 0.1$ litre atm, $\Delta H = 9.9$ litre atm

Q.8 (ii) $-W = q = 620.77$ J, (iii) $\Delta H = 0$; $\Delta U = 0$, $\Delta S = 0$

Q.9 $\Delta H° = -285.4$ kJ/mol, $\Delta G° = -257.2$ kJ/mol Q.10 $\Delta H = -114.52$ J

BANSAL CLASSES

TARGET IIT JEE 2007

PHYSICAL CHEMISTRY

XII (ALL)

THERMOCHEMISTRY

" A SPECIALLY DESIGNED KIT FOR LEARNING."

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EXERCISE I

Heat of reaction & it's type

Q.1 When 2 moles of C_2H_6 are completely burnt 3120 kJ of heat is liberated . Calculate the heat of formation, ΔH_f° for C_2H_6 . Given ΔH_f° for $CO_2(g)$ & $H_2O\,(l)$ are – 395 & – 286 kJ respectively.

Q.2 The standard heats of formation of CH_4 (g) , CO_2 (g) and H_2O (*l*) are – 76.2 , – 398.8 , – 241.6 kJ mol^{-1} . Calculate amount of heat evolved by burning 1 m^3 of methane measured under normal (STP) conditions.

Q.3 Calculate the enthalpy change when infinitely dilute solution of $CaCl_2$ and Na_2CO_3 mixed ΔH_f° for Ca^{2+}(aq), CO_3^{2-} (aq) and $CaCO_3$ (s) are – 129.80, – 161.65, – 288.5 kcal mol^{-1} repectively.

Q.4 The enthalpies of neutralization of NaOH & NH_4OH by HCl are – 13680 calories and – 12270 cal respectively . What would be the enthalpy change if one gram equivalent of NaOH is added to one gram equivalent of NH_4Cl in solution ? Assume that NH_4OH and NaCl are quantitatively obtained.

Q.5 The heat of solution of anhydrous $CuSO_4$ is – 15.9 kcal and that of $CuSO_4.5H_2O$ is 2.8 kcal. Calculate the heat of hydration of $CuSO_4$.

Q.6 The heat of reaction $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g)$ at 27°C is – 22.1 k cal . Calculate the heat of reaction at 77° C . The molar heat capacities at constant pressure at 27°C for hydrogen , chlorine & HCl are 6.82, 7.70 & 6.80 cal mol^{-1} respectively.

Q.7 Calculate standard heats of formation of carbon–di–sulphide (*l*) . Given the standard heat of combustion of carbon (s) , sulphur (s) & carbon–di–sulphide (*l*) are : – 393.3, – 293.72 and – 1108.76 kJ mol^{-1} respectively.

Q.8 A cylinder of gas supplied by a company contains 14 kg of butane . The heat of combustion of butane is 2658 kJ/mol . A normal family requires 20 MJ of energy per day of cooking. If the cylinder lasts for 26 days, what percentage of gas is wasted due to inefficient combustion.

Q.9 The enthalpy change for the reaction $C_3H_8 + H_2(g) \longrightarrow C_2H_6(g) + CH_4(g)$ at 25° C is – 55.7 kJ/mol. Calculate the heat of combustion of $C_2H_6(g)$. The heats of combustion of H_2, CH_4 & $C_{graphite}$ are – 285.8, – 890.0 & – 393.5 kJ/mole respectively. Heat of combustion of propane is –2220 kJ mol^{-1}.

Q.10 The standard enthalpy of neutralization of KOH with (a) HCN (b) HCl in dilute solution is – 2480 cal . g eq^{-1} and – 13.68 kcal . g eq^{-1} respectively . Find the enthalpy of dissociation of HCN at the same temperature.

Q.11 At 300 K, the standard enthalpies of formation of $C_6H_5COOH(s)$, CO_2 (g) & H_2O (*l*) are ; – 408, – 393 & – 286 KJ mol^{-1} respectively . Calculate the heat of combustion of benzoic acid at: (i) constant pressure & (ii) constant volume.

Q.12 The heat liberated on complete combustion of 7.8 g of benzene is 327 kJ . This heat has been measured at constant volume & at 27° C . Calculate the heat of combustion of benzene at constant pressure.

Q.13 A cylinder of gas is assumed to contains 11.2 kg of butane. If a normal family needs 20,000 kJ of energy per day for cooking, how long will the cylinder last if the enthalpy of combustion, $\Delta H = -2658$ kJ/mole for butane.

Q.14 The molar enthalpy of vaporization of benzene at its boiling point (353 K) is 30.84 kJmol^{-1} What is the molar internal energy change? For how long would a 12 volt source need to supply a 0.5 A current in order to vaporise 7.8 g of the sample at its boiling point ?

Q.15 When 12.0 g of carbon reacted with oxygen to form CO & CO_2 at 25° C & constant pressure, 75.0 kcal of heat was liberated and no carbon remained. Calculate the mass of oxygen which reacted. $\Delta H_f^\circ(CO_2) = -95$ kcal mol^{-1}, $\Delta H_f^\circ(CO) = -24$kcal mol^{-1}.

Q.16 If the enthalpy of formation of HCl (g) and Cl^- (aq) are –92.3 kJ/mole and – 167.44 kJ/mol, find the enthalpy of solution of hydrogen chloride gas.

Calorimeter

Q.17 0.16 g of methane was subjected to combustion at 27°C in a bomb calorimeter. The temperature of calorimeter system (including water) was found to rise by 0.5°C. Calculate the heat of combustion of methane at (i) constant volume (ii) constant pressure.
The thermal capacity of calorimeter system is 17.7 kJ K^{-1}. (R = 8.313 mol^{-1} K^{-1})

Q.18 1.00 *l* sample of a mixture of CH_4(g) & O_2(g) measured at 25° C & 740 torr was allowed to react at constant pressure in a calorimeter which together with its contents had a heat capacity of 1260 cal/K. The complete combustion of the methane to CO_2 & H_2O caused a temperature rise in the calorimeter of 0.667 K. What was the mole percent of CH_4 in the original mixture?
$\Delta H^\circ_{comb}(CH_4) = -215$ k cal mol^{-1}.

Bond energy

Q.19 The enthalpy of dissociation of PH_3 is 954 kJ/mol and that of P_2H_4 is 1.485 M J mol^{-1}. What is the bond enthalpy of the P–P bond?

Q.20 Using the bond enthalpy data given below, calculate the enthalpy change for the reaction.
$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$
Data:

Bond	C–C	C = C	C–H	H–H
Bond Enthalpy	336.81 KJ/mol	606.68 KJ/mol	410.87 KJ/mol	431.79 KJ/mol

Q.21 From the following data :
Enthalpy of formation of CH_3CN = 87.86 KJ/mol, Enthalpy of formation of C_2H_6 = – 83.68 KJ/mol
Enthalpy of sublimation of graphite = 719.65 KJ/mol
Enthalpy of dissociation of nitrogen = 945.58 KJ/mol ; Enthalpy of dissociation of H_2 = 435.14 KJ/mol
C–H bond enthalpy = 414.22 KJ/mol
Calculate the (i) ϵ_{C-C} ; (ii) $\epsilon_{C=N}$

Q.22 The heat of combustion of acetylene is 312 kcal. If heat of formation of CO_2 & H_2O are –94.38 & –68.38 kcal respectively, calculate C ≡ C bond energy. Given that heat of atomisation of C & H are 150.0 & 51.5 k cal respectively and C — H bond energy is 93.64 k cal.

Q.23 Using the given data calculate enthalpy of formation of acetone (g). [All values in kJ mol^{-1}] binding energy of : C — H = 413.4 ; C — C = 347.0 ; C = O = 728.0 ;
O = O = 495.0 ; H — H = 435.8 ; ΔH_{sub} of C = 718.4.

Q.24 Find the enthalpy of S–S bond from the following data.

(i) $C_2H_5-S-C_2H_5$ (g) $\Delta H_f^\circ = -147.2$ kJ/mol

(ii) $C_2H_5-S-S-C_2H_5$ (g) $\Delta H_f^\circ = -201.9$ kJ/mol

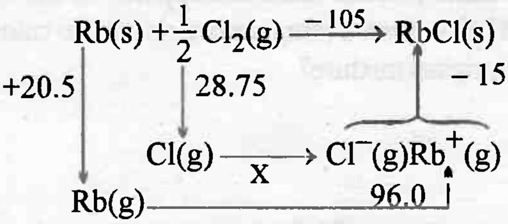
(iii) S (g) $\Delta H_f^\circ = 222.8$ kJ/mol

Born Haber cycle

Q.25 Calculate the electron affinity of fluorine atom using the following data. Make Born–Haber's cycle. All the values are in kJ mol^{-1} at 25° C. ΔH_{diss} (F_2) = 160, ΔH_f° (NaF(s)) = – 571, I.E. [Na(g)] = 494, ΔH_{vap} [Na(s)] = 101. Lattice energy of NaF(s) = – 894.

Q.26 Cesium chloride is formed according to the following equation
$Cs(s) + 0.5Cl_2(g) \longrightarrow CsCl(s)$.
The enthalpy of sublimation of Cs, enthalpy of dissociation of chlorine, ionization energy of Cs & electron affinity of chlorine are 81.2, 243.0, 375.7 and – 348.3 kJ mol^{-1}. The energy change involved in the formation of CsCl is – 388.6 kJ mol^{-1}. Calculate the lattice energy of CsCl.

Q.27 The Born–Haber cycle for rubidium chloride (RbCl) is given below (the energies are in k cal mol^{-1})



Find out the electron affinity of chlorine in kJ mol^{-1}.

Resonance Energy

Q.28 The enthalpy of formation of ethane, ethylene and benzene from the gaseous atoms are –2839.2, –2275.2 and –5506 KJmol^{-1} respectively. Calculate the resonance energy of benzene. The bond enthalpy of C–H bond is given as equal to + 410.87 KJ/mol.

Q.29 Calculate the heat of combustion of methyl alcohol at 298 K from the following data

Bond	C – H	C – O	O – H	O = O	C = O
Energy kJ mol^{-1}	414	351.5	464.5	494	711

Resonance energy of CO_2 = – 143 kJ mol^{-1}
Latent heat of vaporisation of methyl alcohol = 35.5 kJ mol^{-1}.
Latent heat of vaporisation of water = 40.6 kJ mol^{-1}.

Q.30 Calculate the enthalpy of combustion of benzene (*l*) on the basis of the following data :

(i) Resonance energy of benzene(*l*) = – 152 kJ/mol
(ii) Enthalpy of hydrogenation of cyclohexene(*l*) = – 119 kJ/mol
(iii) ΔH°_f of $C_6H_{12}(l)$ = – 156 kJ/mol
(iv) ΔH°_f of $H_2O(l)$ = – 285.8 kJ/mol
(v) ΔH°_f of $CO_2(g)$ = – 393.5 kJ/mol

PROFICIENCY TEST

Q.1 Fill in the blanks with appropriate items:

1. The combustion of a substance is always__________.
2. If heat content of X is smaller than that of Y then the process $X \longrightarrow Y$ is __________.
3. C (Diamond) $\longrightarrow$ C (Graphite) + x kJ. The heat change in this process is called__________.
4. For any reaction, ΔH° =__________.
5. As per reaction, $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g) - 66$ kJ the value of ΔH_f of NO_2 is __________.
6. Heats of combustion of methane, carbon and hydrogen are –212, –94, –68 kcal mol^{-1}. The heat of formation of CH_4 is __________.
7. The heat of neutralisation of 1 mole of $HClO_4$ with 1 gm-equivalent of NaOH in aqueous solutions is ______kJ mol^{-1}.
8. The heat of combustion of graphite and carbon monoxide respectively are – 393.5 kJ mol^{-1} and – 283 kJ mol^{-1}. Thus, heat of formation of carbon monoxide in kJ mol^{-1} is __________.
9. At 298 K, the bond energies of C–H, C–C, C = C and H–H bonds are respectively 414, 347, 615 and 435 kJ mol^{-1}. The value of enthalpy change for the reactions
   $H_2C = CH_2(g) + H_2(g) \longrightarrow H_3C - CH_3(g)$ at 298 K will be__________.
10. For the reaction,
    $C_3H_8\,(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O\,(l)$
    at constant temperature, $\Delta H - \Delta U$ is__________.

Q.2 Mark the following statements as True or False:

1. The ΔH of a reaction is independent of temperature.
2. The enthalpies of elements are always taken to be zero.
3. Integral heat of solution is same as heat of hydration of substance.
4. Heat of neutralisation of weak acid-strong base is not constant.
5. Combustion reactions are always exothermic.
6. Resonance energy is always negative.
7. $\Delta E = 0$ Combustion of benzene in a sealed container that is immersed in a water bath at 25°C and has rigid, thermally conducting walls.
8. For reaction $2A(g) + B(g) \longrightarrow 3\,C(g)\ \Delta H = -x$ kJ
   then for reactiion $\frac{3}{2}C\,(g) \longrightarrow A(g) + \frac{B}{2}\,(g)\ \Delta H = \frac{x}{2}$ kJ.
9. ΔH°_f (C, diamond) $\neq 0$.
10. For a particular reaction $\Delta E = \Delta H + P.\,\Delta V$

EXERCISE II

Q.1 Calculate the mass of mercury which can be liberated from HgO at 25° C by the treatment of excess HgO with 41.84 kJ of heat at

(a) constant pressure (b) constant volume conditions.

Given : ΔH_f° (HgO, s) = – 90.8 kJ mol^{-1} & M(Hg) = 200.6 g mol^{-1}.

Q.2 For reduction of ferric oxide by hydrogen, $Fe_2O_3(s) + 3H_2(g) \longrightarrow 2Fe(s) + 3H_2O(l)$; $\Delta H^\circ_{298} = -35.1$ kJ. The reaction was found to be too exothermic to be convenient. It is desirable that ΔH° should be at the most – 26 kJ. At what temperature is it possible?

$C_P[Fe_2O_3] = 104.5$, $C_P[Fe(s)] = 25.5$, $C_P[H_2O(l)] = 75.3$, $C_P[H_2(g)] = 28.9$ (all in J/mol)

Q.3 From the following data of ΔH of the following reactions

$C(s) + 1/2O_2(g) \longrightarrow CO(g)$; $\Delta H = -110$ KJ

and $C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$; $\Delta H = 132$ KJ

Calculate the mole composition of the mixture of steam and oxygen on being passed over coke at 1273 K, keeping the reaction temperature constant.

Q.4 Although C_P is usually assumed to be constant, for more accurate calculations we must consider its variation with temperature as well. This relation is given by;

$C_P = a + bT + cT^2 + dT^3$ cal mol^{-1} K^{-1}.

(a) Find the expression for the amount of heat required to raise the temperature of 1 mole of gas from T_1K to T_2K, while

(i) keeping the first term [i.e. $C_P = a$] (ii) keeping the first two terms.

(iii) keeping all the terms. of the above expression. Note that each successive term introduces higher accuracy.

(b) For CO_2, a = 5.0, b = 15 x 10^{-5}. Find the heat required to raise its temperature from 300 K to 500 K in case (i) and case (ii). (number of moles = 1). Case (ii) gives a more accurate value. Find the percent error in case (i).

Q.5 An intimate mix of ferric oxide & Al is used as solid rocket fuel. Calculate the fuel value per gm & fuel value per CC of the mix. Heats of formation & densities are :

$\Delta H_f^\circ (Al_2O_3) = -399$ k cal/mole ; $\Delta H_f^\circ (Fe_2O_3) = -199$ kcal / mole,

density of Fe_2O_3 = 5.2 g/cc ; density of Al = 2.7 g/cc.

Q.6 A person takes 15 breaths per minute. The volume of air inhaled in each breath is 448 ml and contains 21% of oxygen by volume. The exhaled air contains 16% of oxygen by volume. If all the oxygen is used in the combustion of sucrose, how much of the latter is burnt in the body per day & how much heat is evolved. ΔH_{com} of sucrose is = – 6000 kJ mol^{-1}. Take temperature to be 300 K throughout.

Q.7 The enthalpies of neutralization of a strong acid HA & a weaker acid HB by NaOH are – 13680 cal/equivalent & – 2900 cal/equivalent respectively. When one equivalent of NaOH is added to a solution containing one equivalent of HA & one equivalent of HB, the enthalpy change was – 6900 calories. In what ratio is the base distributed between HA & HB?

Q.8 Calculate the heat produced when 3.785 litre of octane (C_8H_{18}) reacts with oxygen to form CO & water vapour at 25° C. The density of octane is 0.7025 gm/ml. Heat of combustion of C_8H_{18} is – 1302.7 k cal/mol.

ΔH_f° $CO_2(g)$ = – 94.05 k cal mol^{-1} ; ΔH_f° CO(g) = – 26.41 k cal mol^{-1} ;

ΔH_f° $H_2O(l)$ = – 68.32 k cal mol^{-1} ; ΔH_f° $H_2O(g)$ = – 57.79 k cal mol^{-1}

Q.9 Using the data (all values are in kJ/mol at 25°C) given below :

$\Delta H^\circ_{combustion}$ (ethane) = – 1559.8 ; $\Delta H^\circ_{combustion}$ (ethene) = – 1410.9

$\Delta H^\circ_{combustion}$ (acetylene) = – 1299.7 ; $\Delta H^\circ_{combustion}$ (acetaldehyde) = – 1192.3

ΔH°_f $CO_2(g)$ = – 393.5 ; ΔH°_f of $H_2O(l)$ = – 285.8

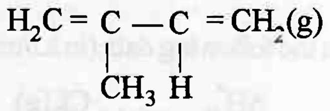
ΔH° for $C_{(s)}$ (graphite) $\to C_{(g)}$ = + 716.68 ; Bond energy of H – H = 435.94

Bond energy of O = O = 498.94

Calculate the following bond energies :

(i) C – C (ii) C – H (iii) C = O (iv) C = C (v) C ≡ C

Q.10 Using bond energy data, calculate heat of formation of isoprene .



$$5\,C(s) + 4\,H_2(g) \longrightarrow H_2C = \underset{\displaystyle CH_3}{\underset{|}{C}} - \underset{\displaystyle H}{\underset{|}{C}} = CH_2(g)$$

Given : C — H = 98.8 k cal ; H — H = 104 k cal ;

C — C = 83 k cal ; C = C = 147 k cal &

C(s) → C(g) = 171 k cal .

Q.11 Use the following data to calculate the enthalpy of formation of As_2O_3 .

(i) $As_2O_3(s) + [(3\,H_2O + aq)] \to 2\,H_3AsO_3\,(aq)$; $\Delta H = +\,7550$ cal

(ii) $As(s) + \frac{3}{2}Cl_2(g) \to AsCl_3\,(l)$; $\Delta H = -\,71390$ cal

(iii) $AsCl_3(l) + (3\,H_2O + aq) \to H_3AsO_3\,(aq) + 3\,HCl(aq)$; $\Delta H = -\,17580$ cal

(iv) $HCl(g) + aq \to HCl\,(aq)$; $\Delta H = -\,17315$ cal

(v) $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \to HCl(g)$; $\Delta H = -\,22000$ cal

(vi) $H_2(g) + \frac{1}{2}O_2(g) \to H_2O\,(l)$; $\Delta H = -\,68360$ cal

Q.12 Calculate the enthalpy change for the reaction $XeF_4 \longrightarrow Xe^+ + F^- + F_2 + F$.
The average Xe–F bond energy is 34 kcal/mol, first I.E. of Xe is 279 kcal/mol, electron affinity of F is 85 kcal/mol & bond dissociation energy of F_2 is 38 kcal/mol.

Q.13 By using the following data draw an appropriate energy cycle & calculate the enthalpy change of hydration of (i) the chloride ion ; (ii) the iodide ion.
Comment on the difference in their values.

* enthalpy change of solution of NaCl(s) = – 2 kJ/mol.

* enthalpy change of solution of NaI(s) = + 2 kJ/mol.

* enthalpy change of hydration of $Na^+(g)$ = – 390 kJ/mol.

* lattice energy of NaCl = – 772 kJ/mol.

* lattice energy of NaI = – 699 kJ/mol.

Q.14 The standard enthalpy of combustion of sucrose is – 5645 kJ mol^{-1} . What is the advantage (in kJ mol^{-1} of energy released as heat) of complete aerobic oxidation compared to anaerobic hydrolysis of sucrose to lactic acid ? ΔH_f° for lactic acid, CO_2 and H_2O is –694, –395.0 and –286.0 respectively.

Q.15 In the combustion of solid naphthalene ($C_{10}H_8$) at 298 K and atmospheric pressure 5157 kJ/mol of heat are evolved. Calculate resonance energy of naphthalene. Given

Latent heat of sublimation of naphthalene = 72.0 kJ/mol
Enthalpy of formation of $H_2O = -286.0$ kJ mol^{-1}
Enthalpy of formation of $CO_2 = -393.5$ kJ mol^{-1}
Enthalpy of atomization of C = 715.5 kJ mol^{-1}
B.E. for C– C bond = 345.5 kJ mol^{-1}
C = C bond = 617.0 kJ mol^{-1}
C – H bond = 413.0 kJ mol^{-1}
H–H bond = 436 kJ/mol

Q.16 Calculate the proton affinity of $NH_3(g)$ from the following data (in kJ/mole)

$\Delta H^\circ_{dissociation}$: $H_2(g)$ = 218 ; $\Delta H^\circ_{dissociation}$: $Cl_2(g)$ = 124

$\Delta H^\circ_{formation}$. $NH_3(g)$ = – 46 ; ΔH°_f : $NH_4Cl(s) = -314$

Lattice energy of NH_4Cl (s) = – 683
Ionization energy of H = 1310
Electron affinity of Cl = 348

Q.17 The standard enthalpy of formation of FeO & Fe_2O_3 is – 65 kcal mol^{-1} and –197kcalmol^{-1} respectively. A mixture of two oxides contains FeO & Fe_2O_3 in the mole ratio 2 : 1 . If by oxidation, it is changed into a 1 : 2 mole ratio mixture, how much of thermal energy will be released per mole of the initial mixture ?

Q.18 The enthalpy of formation of $C_2H_5OH(l)$ is – 66 k cal/mol . The enthalpy of combustion of $CH_3–O–CH_3$ is – 348 k cal/mol . Given that the enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ are – 94 k cal/mol & – 68 k cal/mol respectively, calculate ΔH for the isomerisation of ethanol to methoxymethane. All data are at 25° C.

Q.19 During one of his adventures, Chacha Chaudhary got trapped in an underground cave which was sealed two hundred years back. The air inside was poisonous, having some amount of carbon monoxide in addition to O_2 and N_2. Sabu, being huge, could not enter the cave. So, in order to save Chacha Chaudhary, he started sucking the poisonous air out of the cave by mouth. Each time he used to fill his lungs with cave air and exhale it out in the surroundings. In the meantime, fresh air from the surroundings effused into the cave till the pressure was again one atmosphere. Each time Sabu sucked out some air, the pressure in the cave dropped to half its initial value of one atmosphere.

An initial sample of air taken from the cave measured 11.2 mL at STP and gave 7J on complete combustion at constant pressure.

(i) If the safe level of CO in the atmosphere is less than 0.001% by volume, how many times does Sabu need to suck out air in order to save Chacha Chaudhary?

(ii) Sabu should rescue Chacha Chaudhary within 6 minutes else he will die. Precious 80 seconds are wasted in thinking of a way to rescue him. At maximum, how much time should each cycle of inhaling–exhaling take?

$\Delta H_{comb}(CO) = -280$kJ.mol^{-1}. Neglect any use of Graham's Law.

Q.20 Fe_xO_4 a mixed oxide of iron consists of only Fe^{+2} & Fe^{+3} ions, with the ratio of $Fe^{+2} : Fe^{+3} = 1:2$ in the mixed oxide. From the data given below,

Enthalpy of formation, $\Delta H_f(Fe_xO_4) = -1092$ kJ/mol.

Enthalpy of sublimation, $\Delta H_{sub}(Fe) = 390$ kJ/mol.

B.D.E of O_2 = 490 kJ/mol.

$I.E_1$ of Fe = 760 kJ/ mol.

$I.E_2$ of Fe = 1560 kJ/mol.

$I.E_3$ of Fe = 2960 kJ/mol.

$I.E_1$ of $O^{2-} = -844$ kJ/mol.

LE_2 of $O^{2-} = 142$ kJ/mol.

Lattice Energy of Fe_xO_4 = 18930 kJ/mol.

Prove that value of x is 3 with the help of given data.

EXERCISE III

Q.1 For which of the following change $\Delta H \neq \Delta E$?

(A) $H_2(g) + I_2(g) \longrightarrow 2HI(g)$ (B) $HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$
(C) $C(s) + O_2(g) \longrightarrow CO_2(g)$ (D) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

Q.2 $\Delta_r H$ of which of the following reactions is zero?

(A) $H_2(g) \longrightarrow 2H^+(g) + 2e^-$ (B) $2H(g) + aq \longrightarrow 2H^+(aq) + 2e^-$
(C) $2H(g) \longrightarrow 2H^+(g) + 2e^-$ (D) $H_2(g) + aq \longrightarrow 2H^+(aq) + 2e^-$

Q.3 ΔH_f^0 of water is -285.8 kJ mol^{-1}. If enthalpy of neutralisation of monoacid strong base is -57.3 kJ mol^{-1}, ΔH_f^0 of OH^- ion will be

(A) -228.5 kJ mol^{-1} (B) 228.5 kJ mol^{-1} (C) 114.25 kJ mol^{-1} (D) -114.25 kJ mol^{-1}

Q.4 50.0 mL of 0.10 M HCl is mixed with 50.0 mL of 0.10 M NaOH. The solution temperature rises by 3.0°C. Calculate the enthalpy of neutralization per mole of HCl.

(A) -2.5×10^2 kJ (B) -1.3×10^2 kJ (C) -8.4×10^1 kJ (D) -6.3×10^1 kJ

Q.5 The enthalpy of neutralisation of a weak acid in 1 M solution with a strong base is -56.1 kJ mol^{-1}. If the enthalpy of ionization of the acid is 1.5 kJ mol^{-1} and enthalpy of neutralization of the strong acid with a strong base is -57.3 kJ equiv^{-1}, what is the % ionization of the weak acid in molar solution (assume the acid to be monobasic)?

(A) 10 (B) 15 (C) 20 (D) 25

Q.6 For the allotropic change represented by the equation C (graphite) $\longrightarrow$ C (diamond), $\Delta H = 1.9$ kJ. If 6 g of diamond and 6 g of graphite are separately burnt to yield CO_2, the heat liberated in first case is

(A) less than in the second case by 1.9 kJ (B) more than in the second case by 11.4 kJ
(C) more than in the second case by 0.95 kJ (D) less than in the second case by 11.4 kJ

Q.7 If x_1, x_2 and x_3 are enthalpies of H–H, O=C and O–H bonds respectively, and x_4 is the enthalpy of vaporisation of water, estimate the standard enthalpy of combustion of hydrogen

(A) $x_1 + \frac{x_2}{2} - 2x_3 + x_4$ (B) $x_1 + \frac{x_2}{2} - 2x_3 - x_4$ (C) $x_1 + \frac{x_2}{2} - x_3 + x_4$ (D) $2x_3 - x_1 - \frac{x_2}{2} - x_4$

Q.8 $NH_3(g) + 3Cl_2(g) \rightleftharpoons NCl_3(g) + 3HCl(g); -\Delta H_1$
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \Delta H_2$
$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g); \Delta H_3$
The heat of formation of NCl_3 (g) in the terms of ΔH_1, ΔH_2 and ΔH_3 is

(A) $\Delta H_f = -\Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$ (B) $\Delta H_f = \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$

(C) $\Delta H_f = \Delta H_1 - \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$ (D) None

Q.9 Ethanol can undergoes decomposition to form two sets of products

$$C_2H_5OH\,(g) \longrightarrow \begin{cases} \xrightarrow{1} C_2H_4(g) + H_2O\,(g) & \Delta H^\circ = 45.54 \text{ kJ} \\ \xrightarrow{2} CH_3CHO(g) + H_2\,(g) & \Delta H^\circ = 68.91 \text{ kJ} \end{cases}$$

if the molar ratio of C_2H_4 to CH_3CHO is 8 : 1 in a set of product gases, then the energy involved in the decomposition of 1 mole of ethano*l* is

(A) 65.98 kJ (B) 48.137 kJ (C) 48.46 kJ (D) 57.22 kJ

Q.10 Reactions involving gold have been of particular interest to alchemists . Consider the following reactions,

$Au(OH)_3 + 4\,HCl \longrightarrow HAuCl_4 + 3\,H_2O$, $\Delta H = -28$ kcal

$Au(OH)_3 + 4\,HBr \longrightarrow HAuBr_4 + 3\,H_2O$, $\Delta H = -36.8$ kcal

In an experiment there was an absorption of 0.44 kcal when one mole of $HAuBr_4$ was mixed with 4 moles of HCl . What is the percentage conversion of $HAuBr_4$ into $HAuCl_4$?

(A) 0.5 % (B) 0.6 % (C) 5 % (D) 50 %

Q.11 (i) Cis–2 – butene → trans – 2 – butene, ΔH_1

(ii) Cis – 2– butene → 1 – butene, ΔH_2

(iii) Trans – 2 – butene is more stable than cis – 2 – butene.

(iv) Enthalpy of combustion of 1–butene, $\Delta H = -649.8$ kcal/mol

(v) $9\Delta H_1 + 5\,\Delta H_2 = 0$

(vi) Enthalpy of combustion of trans 2 – butene, $\Delta H = -647.0$ kcal/mol.

The value of ΔH_1 & ΔH_2 in Kcal/mole are

(A) –1.0 , 1.8 (B) 1.8, -1.0 (C) –5, 9 (D) –2, 3.6

Q.12 The reaction $CH_4(g) + Cl_2(g) \longrightarrow CH_3Cl(g) + HCl(g)$ has $\Delta H = -25$ kCal.

Bond	**Bond Energy kCal**
ε_{C-Cl}	84
ε_{H-Cl}	103
ε_{C-H}	x
ε_{Cl-Cl}	y
x : y = 9 : 5	

From the given data, what is the bond energy of Cl—Cl bond

(A) 70 kCal (B) 80 kCal (C) 67.75 kCal (D) 57.75 kCal

Q.13 From the following data at 25°C

Reaction	**$\Delta_r H°$ kJ/mol**
$\frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) \longrightarrow OH(g)$	42
$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$	–242
$H_2(g) \longrightarrow 2H(g)$	436
$O_2(g) \longrightarrow 2O(g)$	495

Which of the following statement(s) is/are correct:

Statement (a) : $\Delta_r H°$ for the reaction $H_2O(g) \longrightarrow 2H(g) + O(g)$ is 925.5 kJ/mol

Statement (b) : $\Delta_r H°$ for the reaction $OH(g) \longrightarrow H(g) + O(g)$ is 502 kJ/mol

Statement (c) : Enthalpy of formation of H(g) is –218 kJ/mol

Statement (d) : Enthalpy of formation of OH(g) is 42 kJ/mol

(A) Statement c (B) Statement a, b, d (C) Statement b, c (D) Statement a, d

Q.14 A mixture of hydrogen gas and the theoretical amount of air at 25°C and a total pressure of 1 atm, is exploded in a **closed rigid vessel**. If the process occurs under **adiabatic condition** then using the given datas answer the questions that follow :

Given $C_P(N_2) = 8.3$ cal deg^{-1} mol^{-1}; $C_P[H_2O(g)] = 11.3$ cal deg^{-1} mol^{-1} ; $\Delta H_f [H_2O(g)] = –57.8$ Kcal

[Take air as 80% N_2, 20% O_2 by volume]

(i) The value of C_P of N_2 & H_2O in the order N_2, H_2O will be (in cal. deg.$^{-1}$ mol^{-1})

(A) 8.3, 8.3 (B) 8.3, 11.3 (C) 11.3, 11.3 (D) 11.3, 8.3

(ii) What will be the maximum temperature attained if the process occurs in adiabatic container.

(A) ≅ 2940 K (B) ≅ 2665 K (C) ≅ 1900 K (D) ≅ 298 K

(iii) What will be the final pressure in atm.

(A) ≅ 8.5 (B) ≅ 7.6 (C) ≅ 5.46 (D) ≅ 0.85

(iv) If at initial temperature $T_1 E_1$ is initial internal energy & at higher final temperature. $T_2 E_2$ is the final internal energy, then which option is true

(A) $E_1 > E_2$ (B) $E_2 > E_1$

(C) $E_1 = E_2$ (D) can't be compared from the given data

Q.15 The commerical production of "Water gas" utilises the endothermic reaction $C(s) + H_2O(g) \longrightarrow H_2(g) + CO(g)$. The heat required for this reaction is generated by combustion of coal to CO_2 using stoichiometric amount of air.(79% N_2 by volume and 21% O_2 by volume). The superheated steam undergoes 75% conversion. Using the following data, answer the question that follows :

$\Delta H_f [CO(g)] = –110.53$ kJ/mol ; $\Delta H_f [H_2O(g)] = –241.81$ kJ/mol ; $\Delta H_f [CO_2(g)] = –314.0$ kJ/mol

(i) The amount of heat liberated when one litre of product gases are burnt at 373 K and one atm is

(A) ≅ 3.6 kJ (B) ≅ 3.9 kJ (C) ≅ 4.43 kJ (D) ≅ 5.34 kJ

(ii) Match the gas and percentage of each gas in one litre product gases.

	Gas		**Percentage**
(I)	N_2	(a)	≈ 23.1
(II)	CO_2	(b)	≈ 36.4
(III)	H_2	(c)	≈ 7.7
(IV)	H_2O	(d)	≈ 9.7

(A) (I-a), (II-b), (III-c), (IV-d) (B) (I-b), (II-a), (III-d), (IV-c)

(C) (I-c), (II-d), (III-a), (IV-c) (D) (I-b), (II-d), (III-a), (IV-c)

EXERCISE IV

OBJECTIVE

Q.1 Which of the following reactions defines ΔH°_f ?

(A) $C_{(diamond)} + C_2(g) \longrightarrow CO_2(g)$ (B) $1/2\,H_2(g) + 1/2\,F_2(g) \longrightarrow HF(g)$

(C) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3$ (D) $CO(g) + 1/2O_2(g) \longrightarrow CO_2(g)$ **[JEE 2003]**

Q.2 ΔH°_f for $CO_2(g)$, $CO(g)$ and $H_2O(g)$ are – 393.5, –110.5 and –241.8 kJ mol^{-1} respectively. The standard enthalpy change (in kJ) for the reaction

$$CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O\,(g) \text{ is}$$

(A) 524.1 (B) 41.2 (C) –262.5 (D) – 41.2 **[JEE 2000]**

Q.3 Which of the following is not an endothermic reaction?

(A) Combustion of methane

(B) Decomposition of water

(C) Dehydrogenation of ethene to ethylene

(D) Conversion of graphite to diamond **[JEE 1999]**

Q.4 Standard molar enthalpy of formation of CO_2 is equal to

(A) zero

(B) standard molar enthalpy of combustion of carbon (graphite)

(C) standard molar enthalpy of combustion of gaseous carbon

(D) sum of molar enthalpies of formation of CO and O_2 **[JEE 1997]**

SUBJECTIVE

Q.5 Diborane is a potential rocket fuel which undergoes combustion according to the reaction,

$$B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(s) + 3H_2O(g)$$

From the following data, calculate the enthalpy change for the combustion of diborane :

$$2B(s) + \frac{3}{2}O_2(g) \longrightarrow B_2O_3(s); \qquad \Delta H = -1273 \text{ kJ}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l); \qquad \Delta H = -286 \text{ kJ}$$

$$H_2O(l) \longrightarrow H_2O(g); \qquad \Delta H = 44 \text{ kJ}$$

$$2B(s) + 3H_2(g) \longrightarrow B_2H_6(g); \qquad \Delta H = 36 \text{ kJ}$$

[JEE 2000]

Q.6 Estimate the average S–F bond energy in SF_6. The ΔH_f° values of SF_6 (g), S(g), and F (g) are – 1100 , 275 and 80 kJ/mol respectively. **[JEE 99, 5]**

Q.7 From the following data, calculate the enthalpy change for the combustion of cyclopropane at 298 k. The enthalpy of formation of CO_2 (g), H_2O (*l*) and propene (g) are – 393.5, – 285.8 & 20.42 kJ/mol respectively. The enthalpy of isomerisation of cyclopropane to propene is – 33.0 kJ/mol. **[JEE '98, 5]**

Q.8 Compute the heat of formation of liquid methyl alcohol in kJ mol^{-1}, using the following data. Heat of vaporisation of liquid CH_3OH = 38 kJ/ mol . Heat of formation of gaseous atoms from the elements in their standard states ; H, 218 KJ / mol ; C, 715 KJ / mol ; O, 249 KJ / mol.

Average Bond energies C – H, 415 KJ / mol ;

C – O , 356 KJ / mol ; O – H , 463 KJ / mol **[JEE '97, 5]**

Q.9 The Enthalpy change involved in the oxidation of glucose is –2880 KJ mol^{-1} . 25% of this energy is availbale for muscular work . If 100 kJ of muscular work is needed to walk one km. What is the maximum distance a person will be able to walk after eating 120 g of glucose. **[JEE '97, 2]**

ANSWER KEY

EXERCISE I

Q.1 −88kJ/mol Q.2 35.973 MJ Q.3 2.95 kcal Q.4 − 1410 cal

Q.5 − 18.7 kcal Q.6 −22.123 k cal Q.7 128.02 kJ Q.8 18.95 %

Q.9 $-1560.1\ kJmol^{-1}$ Q.10 11.2Kcal.

Q.11 **(i)** − 3201 kJ/mol ; **(ii)** − 3199.75 kJ/mol Q.12 − 3273.77 kJ/mol Q.13 25.66 days

Q.14 $\Delta E = 27.91\ KJ\ mol^{-1}$, t = 514 sec.

Q.15 27.43 g O_2 Q.16 − 75.14 kJ/mole Q.17 **(i)** − 885 kJ/mol **(ii)** − 889.980 kJ/mol

Q.18 10.0 mol % CH_4 Q.19 213 kJ / mol

Q.20 − 120.08 J/ml Q.21 (i) 343.08 ; (ii) 891.2 Q.22 $E_{C\equiv C} = 160.86$ k cal

Q.23 $-192.3\ kJ\ mol^{-1}$ Q.24 277.5 kJ/mol Q.25 E.A. = $-352\ kJ\ mol^{-1}$

Q.26 $-618.7\ kJ\ mol^{-1}$ Q.27 $-90.75\ kcal\ mol^{-1}$

Q.28 − 23.68 KJ/mol Q.29 $-669.7\ kJ\ mol^{-1}$

Q.30 $H_f°$(benzene) = 49 $kJ\ mol^{-1}$, $H_C°$(benzene) = $-3267.4\ kJ\ mol^{-1}$]

PROFICIENCY TEST

Q.1 1. exothermic 2. endothermic 3. Heat of transition 4. $\sum \nu_p \Delta H°_{(P)} - \sum \nu_r \Delta H°_{(R)}$

5. $+33\ kJ\ mol^{-1}$ 6. $-18\ kcal\ mol^{-1}$ 7. −57.2 kJ 8. −110.5

9. −125.0 kJ 10. − 3RT

Q.2 1. False 2. False 3. False 4. True 5. True

6. True 7. False 8. True 9. True 10. False

EXERCISE II

Q.1 (a) 92.435 g (b) 93.72 g Q.2 404 K Q.3 mole % $O_2(g) = 37.5$, $H_2O(g) = 62.5$

Q.4 **(a) (i)** $a\Delta T$ **(ii)** $a\Delta T + \frac{b}{2}(T_2^2 - T_1^2)$ **(b)** 1000 cal, 1012 cal, 1.1858 % error

Q.5 $0.9346\ k\ cal\ g^{-1}$, $3.94\ kcal\ cm^{-3}$ Q.6 9.822 MJ/day evolved

Q.7 0.371 : 0.629 Q.8 – 666.81 k cal mol^{-1}, 15.55 Mcal

Q.9 C – C = 97.81 kJ, C – H = 454.64 kJ, C= O = 804.26 kJ, C = C = 434.3 kJ, C ≡ C = 733.48 kJ

Q.10 + 20.6 k cal Q.11 – 154.68 k cal

Q.12 292 kcal/mol Q.13 for Cl^- – 384 kJ mol^{-1}, for I^- – 307 kJ mol^{-1}

Q.14 advantage = 53.96 kJ.mol^{-1} Q.15 –287.0 kJ mol^{-1} Q.16 – 718 kJ/mol

Q.17 Heat released= 13.4 kcal. per mol of initial mixture Q.18 22 kcal mol^{-1}

Q.19 (i) 13 times, (ii) 21.53 sec

EXERCISE III

Q.1 D Q.2 D Q.3 A Q.4 A Q.5 C Q.6 C Q.7 B

Q.8 A Q.9 B Q.10 C Q.11 A Q.12 D Q.13 D

Q.14 (i) B (ii) A (iii) A (iv) C Q.15 (i) A (ii) D

EXERCISE IV

Q.1 B Q.2 B Q.3 A Q.4 B Q.5 –2035kJ mol^{-1}

Q.6 309.6 kJ/mol Q.7 – 2091.32 kJ mol^{-1} Q.8 – 266 kJ mol^{-1}

Q.9 4.82 km