# CHEMICAL THERMO DYNAMICS

# ADDITIONAL POINTS FOR SYNOPSIS: System:

A specific portion of matter under study which is isolated from the rest of the universe with a bounding surface is called a system's surroundings. The rest of the universes which might be in a position to exchange energy and matter with the system is called the surroundings.

### **Types of Systems**

- a) A system which can exchange mass as well as energy with the surroundings is called "open system". e.g. lime kiln, ice in an open beaker.
- **b**) A system that can exchange energy with the surrounding and not mass is called a 'closed system i.e., ice in a closed beaker.
- c) A system which can exchange neither mass nor energy with the surroundings is called isolated system e.g., ice in a thermous flask.

#### **Extensive Property**

A property which depends upon the amount of the substance(s) present in the system, e.g., mass, volume, energy, work, internal energy, enthalpy, entropy, etc.

#### **Intesnsive Property**

A property which is independent upon the amount of the substance(s) present in the system is called 'intensive property' e.g., temperature, pressure, density, concentration, viscosity, refractive index, surface tension, specific heat, etc.,

#### **State Function**

The thermodynamic parameters which depend only upon initial and final states of the system and are independent of how the change is accomplished are called state functions.

#### Example:

Internal energy, enthalpy, entropy, free energy, pressure, temperature, volume, etc. Work and heat energy are not state functions.

### Internal Energy (E):

The total energy stored in a substance by virtue of its chemical nature is called its internal energy, i.e., it is the sum of its translational, vibrational, rotational, chemical bond energy, electronic energy, nuclear energy of constituent atoms as potential energy due to interaction with neighbouring molecules is called Internal or Intrinsic Energy:

 $E = E_t + E_r + E_v + E_e + E_n + E_{PE}$ 

It is a state function and its absolute value can't be determined.

Change in intenal energy can be determined with help of Bomb Calorimeter.

It depends upon quantity of a substance, its chemical nature, temperature, pressure and volume of the substance.

For a given system, E is directly proportional to its absolute temperature.

At constant volume, the quantity of heat supplied to a system (isochoric process) is equal to the increase in this internal energy, i.e.,

In the adiabatic expansion of a gas, it gets cooled because of decrease in internal energy In a reversible process, the change in internal energy is zero, since E is a state function.

For exothermic reactions, the sign is positive i.e.

In endothermic process while for exothermic processes.

### The modynamic Process:

The operation by which a thermodynamic system change from one state to another is called a thermodynamic process which is always accompained by change in energy although in case of open system, change of matter may also occur.

### (i) Isothermal process:

A process in which although heat enters or leaves the system yet temperature of system remains constant throughout the process. In this change of state (e.g. freezing, melting,

evaporation, condensation) is an isothermal process, Isothermal processes are often carried out by placing the system in a thermo state (a constant temperature bath)

### (ii) Adiabatic process:

A process during which no heat enters or leaves the system during any step of the process, so that temperature will decrease or increase when the reaction is endothermic and exothermic respectively.

Such process are often carried out in closed insulated containers such as thermous bottle. for this change in heat

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(iii)	Isobaric process:	Lav	vs of Thermodynamics:
	A process during which pressure of the system		First law of Thermodunamics: It is simply the
	remains constant throughout the reaction e.g.,		law of conservation of energy which states that
	heating of water to its boiling point and its		"Energy can neither be created nor destroyed
	vaporisation take place at the same atmospheric		although it can be converted from one form to
	pressure. Expansion of gas in a system is an		another".
	example of it.		When work is done by the system
vi)	Isochoric process:		
)	Volume of the system remains constant through-		When work is done on the system
	out the reaction in such process. The heating of		when work is done on the system
	a substance in non-expanded chamber or		
	change taking place in a closed system are ex-		In case of small changes
	amples of these process. In such cases		(In case work is done by the
	Cyclic process.		system i.e., expansion) or
vj	A magazing during such is how to mag to its init		(in case work is done on the
	A process during which system comes to its imi-		in ease work is done off the
	that state unough a number of different pro-		system compression) =
	cesses, is called a cyclic process, , In	(i)	When , i.e., cyclic process,
	such cases,	(ii)	When volume remains constant where
	Nature of Work and Heat: Work $(W) =$	( <sup>u</sup> )	vindicates constant volume
	, where		
	intensity factor is a measure of force respon-	(111)	For adiabatic process, ,
	sible for work and capacity factor is a measure		where q indicates constant heat.
	of extent for which work is done	(iv)	When a gas expands against an external pres-
	Thus,		sure P, the work done by it will be:
	a) Mechanical Work =		i.e., $W = -P\Lambda V$
	=	$(\mathbf{v})$	<u>When a gas is compressed</u> work is done on
	b)Electrical Work = Prrential difference		the system and is given by
	Charge flown =	(vi)	When a gas expands into vaccum, work done
	c)Expansion work = Pressure Change in		by it is zero, since $P = 0$ , there fore $W = 0$ .
	volume=	(vii)	In case of expansion of a gas, maximum work is
	d) Gravitational work = Gravitational force		done, if the process is isothermal and reversible.
	Height - Units of work - dyna	Limit	tations of First Law of the Thermodynamics:
	$\operatorname{Height} = \operatorname{OHits} OHits$	(i)	It does not predict whether the process can
	or Joula (MKS system)		occur spontaneously or not i.e., whether it is
	i)Work Heat and Energy have some units		feassiable or not and if so, in which direction. The
	i) Work is not a state function because emount		first law does not indicate whether heat can flow
	of work performed depends upon the neth		from a colder end to a hotter end or not. All that
	followed		the first law tells that, if the process occurs, the
	iii)Positive value of work signifies that the work		heat energy gained by one end would be exactly
	has been done on the system by the surround-		equal to that lost by the other end. Similarly, the
	ings and it leads to an increase in the internal		first law does not tell whether a gas can diffuse
	energy of the system Negative value of work		from low pressure to high pressure or not, whether
	indicates that work has been done by the		water can run up hill or not, etc.,
	system and it leads to decrease in the inter	(ii)	The first law states that energy of one form can
	nal energy of the system		be converted into an equivalent amount of en-
	iv The general expression for all type of DV		ergy of another form. However, by experience,
	work can be written as		it has been observed that although various forms
N	work can be written as . Thus		of enrgy can be completely transformed into
7	for expansion, i.e., when , is		another, heat energy cannot be completely con-
	positive. Hence . For		verted into equivalent amount of work without
	compression is negative honor		producing some change elsewhere.
	compression, , is negative nence		
5	nal energy of the system. iv) The general expression for all type of PV- work can be written as . Thus for expansion, i.e., when , is positive. Hence . For compression, , is negative hence =		ergy of another form. However, by experied it has been observed that although various for of enrgy can be completely transformed another, heat energy cannot be completely verted into equivalent amount of work with producing some change elsewhere.

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#### Second Law of Thermodynamics:

This states that "heat cannot itself pass from a colder to a warmer body. "Thus, if heat is to be transferred from the cold to the hot body, work must be provided by an external agency.. An alternative and useful expression of the second law is " any system of its own accord will always undergo change in such a way as to increase the entropy". "Every perfect machine working reversibly between the same temperature of source and sink have the same efficiency whatever be nature of substance used" (Carnot-theorm)

#### Lord Kelvin Statement:

" It is impossible to take heat from a hotter revervoir and convert it completely into work by a cyclic process without transferring a part of it to a cooler reservoir". This statement recognizes the fact that the heat engine can never be 100% efficient

#### **Clausius Statement:**

"It is impossible for a cyclic proces to transfer heat from a system at a lower temperature to one at higher temperature without applying some work". i.e., without converting some work to heat.

#### Third Law of Thermodynamics"

This states that for a perfect crystal at about zero on the Kelvin scale, the entropy is zero. " This follows, the predictions of Einstein that the specific heats of all substances would approach zero at **0** Kelvin and the conclusion of Planck that the entropy of all pure solids and liquids approach zero at this tempeature.

#### Spontaneous, Natural (OR) Irreversible Process: "A process which proceeds of its own accord without the help of any external agency, is called a spontaneous process.

"All natural processes are spontaneous, hence the term, natural is also used for the spontaneous process, also spontaneous processes cannot be reversed without the help of an external energy, these are also said to be irreversible.

The term 'non-spontaneous' is applied to processes which has not natural tendency or urge to occur, e.g. electrolysis of water. The term spontaneous does not give any idea of the rate of the process.

#### **Examples:**

- (i) Water flows down-hills spontaneously and the direction cannot be reversed unless some external work is done on it.
- (ii) Heat flows spontaneously from the hot end of a metallic bar to its cold end but never from cold end to hot end.

- (iii) Heat flows spontaneously from a hot reservior to a cold reservoir. However, transference of heat from a cold reservoir to hot reservoir as in a refrigerator need energy from outside the system
- (iv) Diffusion of a solute from a concentrated solution to a less concentrated solution, when these are in contact with each other, occur spontaneously till the equilibrium is achieved.
- (v) electricity flows spontaneously from a point. The direction of flow can be reversed only when an external field is applied in the opposite direction.
- (vi) A gas expands spontaneosly from a region of high pressure to a region of low pressure. The reverse process cannot occur unless work is done on it.
- (vii) A piece of zinc dissolution occurs spontaneously in copper sulphate solution, precipitating copper and evolving some heat.

#### Entropy (S)

It is a thermodynamic quantity which is a measure of the degree of disorder within any system. The greater the degree disorder, the higher the entropy.

Thus, for a given substance,

Any change taking place which results in an increase in entropy has a positive entropy change  $(\Delta S)$ . Most spontaneous thermodynamic pro- *Lasser as accompained by an increase in entropy.* Entropy has units of joules per degree per mole. The entropy of the universe always increase in the course of every natural change i.e.,

> and energy of universe is conserved while entropy of universe always increases in any natural or spontaneous process

#### Gibb's Free Energy (

It is a thermodynamic state function represented by G (after Willard Gibbs). the free energy change in any system is related to the enthalpy and entropy changes by the equation: is a measure of the maxi-

mum amount of useful work which may be obtained from the change under consideration.

In any system, the value of the free energy change determines the position of equilibrium in that equilibirum the free energy . For substances in their standard state, i.e., 1 mole at 1 atmospheric pressure and a specified temperature, the change in free energy is called the

#### standard free energy change

This latter quantity is of considerable importance, in that, it determines the thermodynamic feasibility of a reaction.

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For a reaction to be thermodynamically feasible and this for more products than reactants to be	The specific heat capacity is denoted by c and can be calculated with the help of formula
formed at equalibrium, the value of must be negative, i.e., there must be a decrease on standard free energy from reactants to prod- ucts. and are usually expressed in kilojoule per mole for chemical reactions. (i) For spontaneous process, is negative (ii) For process in equilibirum, is zero (iii) For process occuring in backward direction and not in forward direction is positive Stan- dard free energy change () and equilibirum constant are related as below: Where $\Delta G^0 =$	where, q = heat requred to raise the tempera- ture by one degree c = specific heat capacity m = mass = temperature chagne For gases two molar heats viz, molar heat at constant pressure and molar heat at con- stant volume are defined. is always greater than and both of them are related as where R = 2 cal Note:
(Free energy of formation of products - Free energy of formation of reactants) Standard	From the ratio of and we get the idea of atomicity of a gas.
enthalpies of formation , standard free	(a) For monoatomic gas ; $C_v = 3  cal$
<ul> <li>energies of formation (ΔG<sup>0</sup><sub>f</sub>) and absolute entropies of selected substances at 298 K are given below:</li> <li>The quantity of heat required to raise the temperature of a system of one degree is called heat capacity of that system. This is denoted by (Heat capacity when volume is constant) and</li> </ul>	hence, $\gamma = \frac{C_p}{C_v} = \frac{5}{3} = 1.67$ (b) For diatomic gas $C_p = 7 \ cal$ ; $C_v = 5 \ cal$ hence, $\gamma = \frac{C_p}{C_v} = \frac{7}{5} = 1.40$
(Heat capacity when volume is constant) and (Heat capacity when pressure is constant) Thus, in general we can say	$C_{p} = 8 \ cal; C_{v} = 6 \ cal$
Heat capacity = For solids and lquids there is not much differ- ence between the values of and . How- ever for gases these quntities differ which can be calculated as as at constant volume Similarly as at constant pressure	<ul> <li>If an ideal gas expands in vacuum adiabatically, no cooling is produced in the process i.e., . However if a real gas is allowed to expand through a porous plug into the region of lower pressure, the gas is cooled and the extent of cooling is proportional to the difference in pressures of two sides. This phenomenon of cooling of gas is called Joule-Thomson effect. This effect is observed when i.e., at constant enthalpy. The effect is also called Joule-Kelvin effect.</li> </ul>
The heat capacity of a substance is directly pro- portional to the amount of substance i.e., de- pends upon amount of substance In chemical calculations we often use specific heat capacity and molar heat capacities of which specific heat is defined as "The heat required	Where, $T_m$ = melting point of substance
to raise the temperature of one unit mass by one degree (either celcius or kelvin)". When the above definition is given in terms of mole it is considered as molar heat capacities i.e., the heat	Where, $T_b$ = boiling point of substance similarly

capacity of 1 mole of a substance. **CHEMICAL THERMODYNAMICS & ENERGETICS** 

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13. The change in internal energy of a system	23.	Work done by the system in a cyclic process is equal to
a Intial and final states of a system		a. Zero b. c. d.
a. Initial and final states of a system	24.	Internal energy of an ideal gas depends on /
b. Whether the path is reversible		a. Pressure b. Temparature
d. None of the above		c. Volume d. None
1. The amount of heat measured for a reaction in	25.	Vibrational energy is
14. The amount of heat measured for a reaction in		a. Partially potential and partially kinetic
		b. Only potential c. Only kinetic
a. b. c. d.		d. None of the above
15. The enthalpies of elements in their standard	26.	All the naturally occuring processes i.e. spon-
states are taken as zero. Hence the enthalpy of		taneous processes proceed spontaneously in a
formation of a compound		direction which leads to
a. Should always be negative		a. Decrease of free energy
b. Should always be positive		b. Increase of free energy
c. Will be equal to twice the energy of combustion		c. Decrease of entropy d. 2 & 3
d. May be positive or negative	27.	Select the correct limitations of IIIrd law of ther-
16. Evaporation of water is		modynamics
a. An exothermic change		a. Glassy solids at zero Kelvin has entropy
b. An endothermic change		greater than zero
c. A process where no heat change occurs		b. Solids having mixtures of isotopes do not have
d. A process accompanied by chemical reaction		entropy zero at zero Kelvin
17. Which of the following fuels will have highest		o Crystals of do not
calorific value (kJ/kg)?		
a. Charcoal b. Kerosene		have zero entropy at zero Kelvin
c. Wood d. Dung		d. All the above
18. A spontaneous reaction is impossible if	RT RT	La hannage in free an ange
a. Both and are negative	272	a. Increase in interences
b. Both and are positive		o. Decrease in entropy
c. is negative and is positive		d No change in entropy
d is positive and is negative	20	When hydrogen and evygen hurn to form water
19 In which of the following case, entropy decrease.	29.	in an oxybydrogen torch, the entropy change is
a Solid changing to liquid		h an oxynydrogen toren, the entropy enange is
b. Expansion of a gas c Crystals dissolve	30	a. $\neg v = 0$ .
d. Polymerisation	50.	a Room cooled h Room heated
20 In which case a spontaneous reaction is im-		a. Noon coolea U. Noon neater
possible at any temparature		d No effect on room
a h	31	In a reversible isothermal process, the change
a. U.	51.	in internal energy is
c. d. In all the cases		a Zero h Positive
21. Warming ammonium chloride with sodium hy-		c Negative d None
droxide in a test tube is an example of	32	When the value of entrony is greater then the
a. Closed system b. Isolated system	52.	ability for work is
c. Open system d. None of the above		a Maximum h Minimum
22. When an ideal gas is compressed adiabatically		c Medium d None of these
and reversibly, the final temparature is	33	The internal energy of one mole of gas is
a. Higher than the intial temprature	55.	The memorie chergy of one more of gas is
b. Lower than the intial temparature		a b c d
c. The same as the initial temparature		u. c. c. u.
1		
d. Dependent on the system of compression		

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34.	Which of the following statements is incorrect? a. The entropy of an isolated system increase in	42.	Mechanical work is specially important in sys- tems that contain
	an irreversible process b. The entropy of an isolated system remains		a. solid - liquid b. liquid - liquid c. solid - solid d. gases
	unchanged in a reversible process	43.	For the reaction
	c. as well as $\Delta S_{surrounding}$ are nega-	15.	a. $\Delta H > \Delta E$ b.
	tive quantities		c. d. None of these
	d. Entropy can never decrease	44.	The value of free energy change at equilibrium is
35.	Choose the correct relation :		a. Positive b. Negative c. Zero d. Not definite
	a. $\Delta G = \Delta H + \Delta n R T$	45.	According to third law of thermodynamics,
	b.		which one of the following quantities for a per-
			Entropy b Frog energy
	G		a. Entropy 0. Fice energy
	0.	46	Which one of the following is an extensive quantity?
	d. None of these	10.	a) surface tension b) Density
36.	Which of the following are thermodynamically		c) Heat capacity d) Specific heat
	stable?	47.	Which one of the following is an intensive quantity?
	a. C (diamond) b. C (graphite)		a) Temperature b) Volume
	c. (red) d. All are equally stable		c) Number of moles d) Work
37.	In which one of the following sets, all the prop-	48.	Which change would have a negative value?
	erties belong to same category?	C	a)
	a. mass, volume, Pressure		b)
	b. Temparature, Pressure, Volume		
	d Enthalpy internal energy volume	A 160.98	$\mathbf{\mathcal{L}}_{\mathbf{\mathcal{L}}} = \mathbf{\mathcal{L}}_{\mathbf{\mathcal{L}}} + \mathcal{$
38.	The difference between and at con-	20 -	$\stackrel{\text{dif}}{\text{d}} \stackrel{\tau}{Cl}(g) \stackrel{\text{dif}}{\rightarrow} Cl^{-}(g)$
	stant volume is equal to :	49.	Unit of entropy is
			a) $JK^{-1}mole^{-1}$ b)
	a. b. c. d.		c) $JK mole^{-1}$ d) None of these
39.	If the internal energy an ideal gas decreases by	50.	For a spontaneous reaction which one is true?
	the same amount as work done by the system,		a) b)
	the process is :		c) d) None of these
	a. cyclic D. Isolnermal	51	represents calculation of at
40	Select the exothermic compund among the fol-	011	a) b)
	lowing with respect to enthalpy of formation :		
	a. b.		c) d) None of these
	c d	52.	of a system is not equal to
41	When a gas is allowed to expand from a region		a) b) c) $n \times Q$ d)
	of extremely high pressure to a region of ex-	53.	sublimation of graphite and diamond
	tremely low pressure, there occurs a change of		respectively are x and y What is
	temparature. This phenomenon is connected with:		for the change; Graphite diamond
	a. first law of thermodynamics		a) b)
	b. Joule Thomson effect		() $(n + 1) h I m a l^{-1} = A$ $(n + 1) h I m a^{-1}$
	c. Gibbs Helmholt'z equation		$(x - y) K_J mol$ (y - x) KJ mol
	d. None of the above		
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d) work

- Which one of the following quantity is indepen-54. dent of path? b) volume
  - a) molar internal energy c) q + W
- 55. Evaporation of water is
  - a) an exothermic process
  - b) an endothermic process
  - c) an exothermic process at  $100^{\circ}C$

#### d) an endothermic process at

		KEY	7	
1.a	2.d	3.c	4.d	5.d
6.c	7.c	8.c	9.d	10.d
11.d	12.d	13.a	14.c	15.d
16.b	17.b	18.d	19.d	20.b
21.c	22.c	23.d	24.b	25.a
26.a	27.d	28.b	29.a	30.b
31.a	32.a	33.a	34.c	35.c
36.b	37.d	38.c	39.c	40.c
41.b	42.d	43.c	44.c	45.a
46.c	47.a	48.d	49.a	50.b
51.b	52.d	53.c	54.c	55.b

### **LEVEL-II**

- The heat of combustion of solid benzoicacid and 1. at constant volume is at . The heat of combustion at constant pressure is a) b) d)
  - c)
- The heats of combustion of yellow P and red P 2. and respectively. The are heat of transition of yellow to red phosporus is
  - a)
  - c)

3.

- of a reaction
  - a) Depends only on the nature of the reactants

**b**)

d)

- b) Depends only on the nature of the products
- c) Depends on the nature of reactants, products and path used to bring about the change
- d) Depends on the nature of reactants and the products but not on path used to bring about the change.
- Which of the following statements is true about the entropy of the universe?
  - a) Increases and tends towards maximum value
  - b) Decreases and tends to be zero
  - c) Different intermediate reaction
  - d) Decreases and Increases with a periodic rate.

5. Given

6.

7.

8.

9.

 $X^+(g) \rightarrow X^{+2}(g) + e^-; \Delta H = 420 \ kJ \ mol^{-1}$  $X^{+2}(g) \rightarrow X^{+3}(g) + e^{-}; \Delta H = 3547 \, kJ \, mol^{-1}$ Which ion is most likely to be present in the crystalline compound formed between X and fluorine? a)  $\chi^{+3}$ b) c) d) For precipitation reaction of with which of the following statements is correct? for the reaction is zero a) b) for the reaction is negative c) for the reaction is part-time d) Entropy decreases during a) crystallization of sucrose from solution b) vaporisation of water c) Melting of ice d) Vaporization of Camphor The enthalpy for the following reactions at  $25^{\circ}C$  are given below : ii)  $\hat{H}_{2}(g) \rightarrow 2H(g); 104.18 kcal$ iii)  $O_2(g) \rightarrow 2O(g)$ ; 118.32 kcal Calculate the Q - H bond energy in the hydroxyl radical. a. - 101.19 kcal b. + 206.13 kcal c. - 206.13 kcal d. + 101.19 kcal If 50 calorie are added to a system does work of 30 calorie on surroundings, the change in internal energy of system is a. 20 cal b. 50 cal c. 40 cal d. 30 cal 10. Latent heat of vaporisation of a liquid at 500 K and 1 atm. pressure is 10.0 kcal/mol. What will be the change in internal energy of 3 mole of liquid at same temparature a. 13.0 kcal b. -13.0 kcal c. 27.0 kcal d. -27.0 kcal 11. Boiling point of a liquid is 50 K at 1 atm. and . What will be its b.p. at 10 atm. a. 150 K b. 75 K c. 100 K d. 200 K

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12. The expression representing Gibbs-Helmholtz equation is :

a. 
$$\Delta G^0 = \Delta H^0 + T \left[ \frac{\partial \left( \Delta G^0 \right)}{\partial T^2} \right]$$

b.

c. 
$$\left[\frac{\partial \left(\Delta G^{0} / T\right)}{\partial \left(1 / T\right)}\right]_{p} = \Delta H^{0}$$
  
d. 
$$\left[\frac{\partial \left(\Delta G^{0} / T\right)}{\partial T}\right]_{p} = -\Delta H^{0}$$

13. The enthalpy of dissolution of  $BaCl_2(s)$  and are and per mole respectively. The enthalpy of hydration for, is

14. The enthalpy of vapourisation of a substance is 840 J per mol and its boiling point is  $-173^{\circ}C$ . Calculate its entropy of vaporisation : a) 8.4 Joule/K/mole b) 21 Joule/K/mole

- 15. Which has the highest entropy per mol of the substance?
  - a)  $H_2$  at at 1 atm
  - b) at STP

for

- c) at 100K at 1 atm
- d) at 0 K at 1 atm
- 16. The heat of atomisation of is 228 kcal per mol and that of is 355 kcal per mol. The energy of bond is :

  a. 102 kcal per mol
  b. 51 kcal per mol
  c. 26 kcal per mol
  d. 204 kcal per mol

  17. Calculate the free energy change

Give  $\Delta H = 145.6 \, kJ$  per mol

a. 110.8 kJ per molb. 221.5 kJ per molc. 55.4 kJ per mold. 145.6 kJ per mol

18. A hypothetical reaction proceeds through following sequence of steps :

(ii)

b.

d.

 $\rightarrow E$ 

a.

(i)

Then the heat of reaction is :

- c.
- 19. If E,R and D represent the tendency of minimum energy(E), tendency for maximum randomness (R) and overall driving force (D) respectively and arrows represent the direction and magnitude of these tendencies, choose the correct option applies to following reaction :

 $\begin{array}{cccc} & & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ \hline \\ \\ \hline \\ \\ \hline \\ \hline \\ \\ \hline \\ \\ \hline \\ \\ \hline \\ \hline \\ \hline \\ \\ \hline \\ \hline \\ \hline \\ \hline \\ \\ \hline \\ \\ \hline \\ \\ \hline \\$ 

(i) 
$$H_2(g) + \frac{1}{2}O_2(g) \to H_2O(l) + a_1 kJ$$
  
(ii)  $H_2(g) + \frac{1}{2}O_2(g) \to H_2O(g) + a_2 kJ$ 

The correct relation between  $a_1$  and is:

b.

d.

C.

21. The mathematical expression for the standard enthalpy of sublimation is given by :

DISHA

b. 
$$\Delta H_{sub}^{0} = \Delta H_{fus}^{0} - \Delta H_{vap}^{0}$$
  
c.  $\Delta H_{sub}^{0} = \Delta H_{fus}^{0} + \Delta H_{vap}^{0}$   
d.  $\Delta H_{sub}^{0} = \Delta H_{comb}^{0} - \Delta 2 H_{diss}^{0}$   
Here,  $\Delta H_{sub}^{0} = \Delta H_{sub \text{ limation}}^{0}$ ;  
 $\Delta H_{fus}^{0} = \Delta H_{fusion}^{0}$ ;  $\Delta H_{vap}^{0} = \Delta H_{vaporization}^{0}$ ;  
 $\Delta H_{diss}^{0} = \Delta H_{dissociation}^{0}$ 

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22. 23. 24.	The enthalpy change when 1 g of water is frozen at $0^{\circ}C$ . is: a1.435 cal/g b80.0 calg c. 80 cal/g d55.6 cal/g Mark the incorrect relationship: a. $\frac{\Delta H_{vapour}}{Tb} \approx 88 J / K / mole$ b. $\Delta H = \Delta E = \Delta \eta_{(g)} RT$ c. specific heat X atomic mass = 6 cal/mol ${}^{\circ}C$ d. One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0L 95K) (4.0 atm, 5.0L, 245K) with a change in internal energy, The change in enthalpy	<ul> <li>30. In thermodynamics, a process is called reversible when <ul> <li>a. surroundings and system change into each other</li> <li>b. there is no boundary between system and surroundings</li> <li>c. The surroundings are always in equilibrium with the system</li> <li>d. the system changes into the surroundings spontaneously</li> </ul> </li> <li>31. Bond enthalpies of and HX are in the ratio 2:1:2. If enthalpy of formation of HX is -50 , the bond enthalpy of is <ul> <li>a.</li> <li>b.</li> <li>c.</li> </ul> </li> </ul>
<ul> <li>25.</li> <li>a.</li> <li>26.</li> <li>27.</li> <li>28.</li> <li>29.</li> <li>29.</li> </ul>	of the process in L atm is. a. 40.0 b. 42.3 c. 44.0 d. Not defined because pressure is not constant One mole of an ideal gas at 300 K is expanded Isothermally from an intial volume of 1 litre to 10 litres. The $\Delta E$ for this process is 163.7 cal b. zero c. 1381.1 cal d. 9 lit atm If 900J/g of heat is exchanged at boiling point of water, then what is increase in entropy? a. 43.4 J/mole b. 87.2 J/mole c. 900 J/mole d. Zero Entropy change involved in the conversion of 1 mole of liquid water at 373 K to vapour at the same temparature will be $(\Delta H_{vap} = 2.257kJ/g)$ a. 0.119kJ b. 0.109kJ c. 0.129kJ d.0.12kJ The bond energy of an O-H bond is 109 K.cal.mole <sup>1</sup> . When a mole of water is formed a. 218 K.cal. is released b. 109 K.cal. is released c. 218 K.cal. is released For the process and $\Delta S = 1.20 X 10^2 Jk mol^{-1}$ . At what temparature the above process is at equilibrium? a. 273K b. c. d.	<b>KEY</b> <b>1.c</b> 2.d 3.d 4.a 5.b <b>6.b</b> 7.a 8.d 9.a 10.c <b>11.c</b> 12.c 13.b 14.a 15.a <b>16.b</b> 17.a 18.c 19.c 20.d <b>21.c</b> 22.b 23.d 24.c 25.b <b>26.a</b> 27.b 28.a 29.d 30.c <b>31.a</b> <b>1.</b> The specific heat of a gas is found to be 0.075 calories at constant volume and its formula wt is 40. The atomicity of the gas would be: a) One b) Two c) Three d) four <b>2.</b> When 12.0 g of carbon reacted with a limited quantity of oxygen, 57.5 kcal of heat was pro- duced. Calculated the no. of moles of CO and the no. of moles produced. [ $\Delta H(CO) =$ a) 0.54 mol of CO b) 0.46 mol of CO c) 0.64 mol of CO d) 0.74 mol of CO <b>3.</b> For the reaction at 298 K , and .As- suming and to be constant, at what minimum temperature will the reaction become spontanous? a) 2,000 K b) 200 K c) 4,000 K d) 400 K
29.	c. 218 K. cal. is absorbed d. 109 K. cal. is released For the process and $\Delta S = 1.20 \times 10^2 Jk  mol^{-1}$ . At what temparature the above process is at equilibrium? a. 273 K b. c. d.	3. For the reaction at 298 K and . As suming and to be constant, at wha minimum temperature will the reaction become spontanous? a) 2, 000 K b) 200 K c) 4,000 K d) 400 K

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(CHEMICAL THERMODYNAMICS & ENERGETICS)

11. Select the correct alternate about entropy A reaction happens to be in state of equilibrium 4. at 400 K and occurs spontanously below 400 b) a) K in forward direction. The for the prod) c) cess is . The at 400 K for 12. Which of the following process is spontaneous? this process would be: a) diffusion of perfume molecules from one side b) a) of the room to the other d) c) b) decomposition of solid  $CaCO_3$ c) heat flow from a cold object to a hot object 5. The volume of a gas expands by at a d) climbing up a mountain constant pressure of . The work done 13. is equal to a) b) 250 J  $\Delta S^0 = 22.0 \ J \ K^{-1} \ mol^{-1}$ c) 250 watt d) 250 newton A gas expands against a constant external pres-6. Formation of ice is favoured at a temperature? sure of 2.00 atm from an initial volume of 1.50 L b) below a) above  $0^{\circ}$ to a final volume of 3.50 L. The container is well d) above c) at insulated so that no heat enters or leaves the sys-Following reaction occcurs at 14. tem. Calculate the change in internal energy ( ) of the gas in joules. [1 L atm = 101 J]a) b) c) 4.00 d) 25.3  $\Rightarrow 2NOCl(g, 1 \times 10^{-2} \text{ atm})$ is: 7. At a certain temperature and pressure, the reb) action is endothermic but d) spontaneous. Which of the following is true? The change of entropy, at 298K for the a)  $\Delta G > 0$ **E E E E (2)** (42 0) (2 g a tm) 2 (S reaction a) which urea is formed from and b) and c) and  $\rightarrow NH_2CONH_2(aq) + H_2O(l)$ . The standard d) and 8. A gas obsorbs 100 J of heat and is NH<sub>2</sub>CONH<sub>2</sub> of entropy is simulataneously compressed by a constant external pressure of 1.5 atm from 8 to 2L in vola) + 354.4b) ume. What is in joules for the gas? c) + 177.2d) a) b) c) d) 16 for conversion of oxygen to ozone 9. The lattice energy of solid NaCl is 180 and enthalpy of solution is 1 . If the at 298 K, if  $K_p$  for this hydration energies of and ions are in the ratio 3:2, what is enthalpy of hydration of conversion is sodium ion? a) 163 kJ  $mol^{-1}$ b) b. 107.4 K Calmol<sup>-1</sup> a. c) d) d. 17. Fo the reaction at 10. **8g** of *O*<sub>2</sub> gas at is compressed to half of the volume under isothermal and reversible con- $\Delta G^0 = -27 \, kJ$ ,  $P_{CO_2} 0.0033$  atm, hence  $\Delta G$ dition. Work done on the system is: the temperature is a) b) b) a) c) c) d) d) **CHEMICAL THERMODYNAMICS & ENERGETICS** DISHA SCIENCE ACADEM

### ADEM

		D	<b>SHA</b>	30	IENCE	. A	
ſ						6.	If
	<b>1.</b> a	2.a	3.a	4.c	5.b		
	6.a	7.c	<b>8.d</b>	9.a	10.c		a)
	11.c	<b>12.</b> a	13.b	<b>14.</b> a	15.b		b)
	16.a	17.b					c)
Р	revio	is Ones	stions				d)
1	Ifa	n endothe	ermic react	ion is non-	spontaneous	7.	In
	at f	reezing po	oint of wate	er and becc	mes feasible		sta
	at i	ts boiling	point, then	AIEEE	2002]		ur f
	a)	is -ve	e, is+	ve			sa sa
	b)	and	both a	re+ve			5 <b>u</b>
	c)	and	both a	re -ve			a)
	d)	is+v	re, is -	ve			b)
2.	. Al	eat engine	e abosrbs h	eat at te	mperature		c)
	and	l heat	at tempera	ture . W	Vork done by		d)
	the	engine is		. This dat	a [AIEEE 2002]	8.	Tł
	a) v	violates 1s	t law of the	ermodynar	nics		ch
	b) v	violates 1st	law of them	nodynamic	sisif $Q_1$ is-ve		lit
	c) v	violates 1st	law of them	modynamie	cs of is-ve		a)
	d) (	does not v	iolate 1st l	aw of theri	nodynamics		
3.	Fo	r the reac	tions,		-		С) Тl
			;	$\Delta H = -3$	93J	9.	
			;Δ	H = -412.	J	(8) ***	a)
					[AIEEE 2002]		b)
	a) c	carbon cai	n oxidise Z	Zn			of
	b) (	oxidation	of carbon $1$	s not feasi	ble		d)
	d) 2	Zn can ox	idise carbo	on		10.	Tł
4.	. The	e internal e	energy cha	nge when a	system goes		fir
	fro	m state A	to B is 40	kJ/mole. l	If the system		as
	goo	es from A	to B by a p	reversible	path and re-		
	wo	uld be the	net change	in interna	le path what		0
		und of the	indicitient		[AIEEE 2003]		Tł
	a)	6		b )			a)
	c) 2	Zero	U	d) 40 k J			1)
5.	. Ifa	t 298K the	e bond ener	rgies of	, ,		b) c)
		and	b	onds are	respectively		d)
	414	<b>4, 3</b> 47, 61	5 and 435	kJ ,	the value of		)
	en	halpy	change	for the	reaction	11.	A
							to
	at 2	298 K wil	l be [AIEE]	E 2003]			su
	a)	–250 kJ		b)			
	c)			d)		a)	270

liquids A and B form an ideal solution [AIEEE 2003] the entropy of mixing is zero the free energy of mixing is zero the free energy as well as the entropy of mixing are each zero the enthalpy of mixing is zero an irreversible process taking place at conant T and P and in which only pressure-volne work is being done, the change in Gibbs ee energy (dG) and change in entropy (dS), tisfy the criteria [AIEEE 2003] he correct relationship between free energy hange in a reaction and the corresponding equiorium constant is [AIEEE 2003] b)  $\Delta G^0 = RT \ln K_c$  $-\Delta G^0 = RT \ln K_c$  d)  $\Delta G = RT \ln K_c$ he entropy change for a reaction does not de- $H_2(g) = H_2(g)$ use of different reactants for the same product the nature of intermediate reaction steps the differences in initial or final temperatures involved substances the phiscal states of reactants and products he formation of the oxide ion  $O_{(g)}^{2-}$  requires rst an exothermic and then an endothermic step shown below [AIEEE 2004]  $O_{(g)} + e^- = O_{(g)}^{2-} \Delta H^0 = 844 \ KJ \ mol^{-1}$ his is because  $O^-$  ion will tend to resist the addition of another electron Oxygen has high electron affinity Oxygen is more electronegative ion has comparatively larger size than oxygen atom

n ideal gas expands in volume from  $1 \times 10^{-2} m^3$  at 300 K against a constant prestre of  $1 \times 10^5 Nm^{-2}$ . The work done is [AIEEE 2004] a) 270 kJ b) -900 kJ c) d)

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6.d

12.b