Free	energy	and	Work	function
------	--------	-----	------	----------

1	d	2	b	3	а	4	b	5	acd
6	C	7	С	8	C	9	а	10	a
11	d	12	а	13	d	14	d	15	b
16	d	17	b	18	C	19	d	20	b
21	b	22	d	23	b	24	а	25	d
26	d	27	а	28	d				

Critical Thinking Questions

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

Assertion & Reason

1	b	2	b	3	b	4	c	5	а
6	b	7	b	8	а	9	b	10	а
11	а	12	d	13	а	14	е	15	c
16	а	17	С	18	b	19	а	20	е
21	с	22	с						





Basic concepts

- (b) Internal energy of an ideal gas is a function of temperature 1. only.
- In cyclic process, a system in a given state goes through a 2. (d) series of different processes, but in the end returns to its initial state.
- (c) $\Delta E = 0$ for isothermal reversible cycle. 4.
 - $(c) \ \ \, \mbox{In isolated system neither exchange of matter nor exchange of}$ energy is possible with surroundings.
 - (c) It is the definition of calorific value.

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(d) When a real gas is forced through a porous plug into a region of low pressure, it is found that due to expansion, the gas on the side of low pressure gets cooled.

			He	at of	reac	tion			
1	b	2	b	3	d	4	d	5	d
6	b	7	с	8	a	9	b	10	а
11	bcd	12	a	13	d	14	b	15	с
16	a	17	b	18	a	19	b	20	с
21	c	22	a	23	d	24	c	25	с
26	b	27	b	28	b	29	a	30	с
31	а	32	а	33	d	34	b	35	b
36	а	37	a	38	d	39	b	40	b
41	с	42	с	43	b	44	b	45	b
46	b	47	а	48	с	49	е	50	b
51	а	52	b	53	с	54	с	55	b
56	с	57	с	58	d	59	с	60	b
61	d	62	с	63	b	64	a	65	b
66	b	67	а	68	с	69	a	70	d
71	а	72	b	73	d	74	c	75	b
76	b	77	а	78	d	79	d	80	а
81	b	82	b	83	а	84	b	85	b
86	с	87	а	88	b	89	d	90	d
91	а	92	с	93	b	94	а	95	d
96	d	97	с	98	а	99	с	100	с
101	b	102	с	103	d	104	d	105	с
106	а	107	с	108	d	109	d	110	с
111	a	112	b	113	a	114	a	115	a
116	а	117	b	118	C	119	b	120	а
121	а	122	а	123	d	124	b	125	b
126	b	127	C	128	d	129	d	130	b
131	d	132	b	133	d	134	а	135	а
136	а	137	d	138	C	139	d	140	b
141	C	142	d	143	C	144	b	145	C
146	d	147	b	148	C	149	b	150	b
151	d	152	а	153	b	154	b	155	b
156	b	157	а	158	d	159	C	160	d
161	a	162	с	163	c	164	c	165	c
166	b	167	d	168	d	169	C	170	b
171	а	172	C						

Bond energy

1	b	2	а	3	а	4	d	5	c
6	С	7	b	8	d	9	b	10	b

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The phenomenon of producing lowering of temperature when a gas is made to expand adiabatically from a region of high pressure into a region of low pressure is known as Joule-Thomson effect.

- 12. (d) In isothermal reversible process ideal gas has constant volume and so $\Delta E = 0$ and $\Delta H = \Delta E = 0$.
- 13. (a) The compressor has to run for longer time releasing more heat to the surroundings.
- 14. (c) This is based on Joule-Thomson effect.
- **15.** (b) Enthalpy is an extensive property.
- **16.** (b) dV = 0 for an isochoric process.
- 17. (d) Total energy of an isolated system is constant.
- **18.** (a) For isochoric process $\Delta V = 0$ so $q_V = \Delta E$ i.e. heat given to a system under constant volume is used up in increasing ΔE .
 - (b) The less energy of a system and more is its stability.
- **20.** (b) The functions whose value depends only on the state of a system are known as state functions.
- **21.** (d) For adiabatic process q = 0.

19.

- 22. (b) The intensive property is mass/volume.
- **23.** (c) Volume is not an intensive property.
- 24. (c) An isolated system neither shows exchange of heat nor matter with surroundings.
- **25.** (d) ΔQ is not a state function.
- **26.** (c) For adiabatic process $\Delta Q = 0$.
- 27. (c) Work is not a state function as during a process its value depends on the path followed. The value of enthalpy, internal energy and entropy depends on the state and not on the path followed to get that state, hence these are state functions.
- 28. (c) Surface tension is an intensive property which do not depend upon the quantity of matter present in the system.

First law of thermodynamics and Hess law

- (d) First low of thermodynamics is also known as Law of conservation of mass and energy.
- 2. (b) Formation of CO_2 from CO is an exothermic reaction; heat is evolved from the system, *i.e.*, energy is lowered. Thus, exothermic reactions occur spontaneously on account of decrease in enthapy of system. Thus, $\Delta E > \Delta H$.

4. (b)
$$\Delta H = \Delta E + P \Delta V$$
.

5. (c)
$$\Delta n_g = 1 - \frac{3}{2} = \frac{-1}{2}$$
, As Δn_g is negative, thus $\Delta H < \Delta E$.

6. (a) Bomb calorimeter is commonly used to find the heat of combustion of organic substances which consists of a sealed combustion chamber, called a bomb. If a process is run in a sealed container then no expansion or compression is allowed, so w = 0 and $\Delta U = q$. $\Delta U < 0, w = 0$

9. (b)
$$\Delta H = \Delta E + \Delta n R T$$

Since $\Delta n = -2$
Than $\Delta H = \Delta E - 2RT$.

- 10. (d) If $\Delta n = -ve$ than $\Delta H < \Delta E$.
- $\label{eq:constraint} \textbf{12.} \qquad (c) \quad \text{Hess's law is an application of first law of thermodynamics} \ .$
- **13.** (c) At constant P or T

$$\Delta H = \Delta U + \Delta n RT \implies \Delta n = n_p - n_R = 2 - 4 = -2$$

 $\therefore \quad \Delta H < \Delta U \; .$

- **16.** (b) It is a combustion reaction, $\Delta H = -ve$.
- 17. (c) During isothermal expansion of ideal gas, $\Delta T = 0$

$$\Delta H = \Delta E + P \Delta V = \Delta E + nR \Delta T = 0 + 0 = 0$$

18. (b) $W = 2.303 \ nRT \log \frac{V_2}{V}$

$$2.303\times1\times8.314\times10^{7}\times298\log\frac{20}{10}$$

 $= 298 \times 10^7 \times 8.314 \times 2.303 \log 2$.

20. (a) The enthalpies of all elements in their standard state at $25^{\circ} C$ or 298*K* are zero.

21. (c)
$$\Delta E_v = E_P - E_R$$
.

22. (c)
$$\Delta E = q + w$$

=

- **23.** (a) $\Delta E = 0$ for reversible isothermal process.
- **25.** (b) Hess law includes initial reactants and final products.
- **26.** (a) At constant *T* and *P* internal energy of ideal gas remains unaffected.
- **27.** (a) ΔE increases with temperature.
- **28.** (a) $\Delta H = \Delta E + W$ or $\Delta H = \Delta E + P\Delta V$.
- **29.** (bc) Heat of neutralisation of a strong acid and strong base is equal to $-13.7 \, kcal$.

30. (c)
$$-W = +2.303 \, nRT \log \frac{p_1}{p_2}$$

 $-W = 2.303 \times 1 \times 2 \times 300 \log \frac{10}{1} = 1381.8 \, cal.$

- **31.** (b) Joule-Thomson expansion is isoenthalpic.
- **32.** (c) Here $\Delta n = 0$ so, $\Delta E = \Delta H$.
- **33.** (b) $q = \Delta E W$ if q = 0 for adiabatic process, than $\Delta E = W$.
- **34.** (a) For this reaction $\Delta n = 0$ than $\Delta E = \Delta H$.
- **35.** (c) As the system is closed and insulated no heat enter or leave the system, *i.e.* q = 0; $\therefore \Delta E = Q + W = W$.

37. (c)
$$\Delta H - \Delta E = \Delta nRT$$
; $\Delta n = -3$
so, $\Delta H - \Delta E = -3RT$.

38. (b) According to Hess's law. The heat of reaction depends upon initial and final conditions of reactants.

39. (d)
$$\Delta H - \Delta E = \Delta n R T$$

also, $2NH_{3(g)} \rightarrow N_{2(g)} + 3H_{2(g)}$
 $\Delta n = 2$.
40. (c) $\Delta n = 0$ for this reaction so, $\Delta E = \Delta H$

41. (d)
$$W = 0$$
 is not true

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(a)
$$W = 2.303 nRT \log \frac{P_2}{P_1}$$

$$= 2.303 \times 1 \times 2 \times 300 \log \frac{10}{2} = 965.84$$

at constant temperature, $\Delta E = 0$.

$$\Delta E = q + w$$
; $q = -w = -965.84 \, cal$.

- 43. (c) q = 40 J w = -8 J (work done by the system) $\Delta E = q + w = 40 - 8 = 32 J$.
- 44. (a) We know that $\Delta E = Q + W = 600 + (-300) = 300 J$ W = 300, because the work done by the system.
 - (c) Given that $P_1 = 10 \ atm, \ P_2 = 1 \ atm, \ T = 300 K \ , \ n = 1$

R = 8.314 J/K/molNow, by using

$$W = 2.303 \, nRT \, \log_{10} \frac{P_2}{P_1}$$

$$= 2.303 \times 1 \times 8.314 \times 300 \log_{10} \frac{1}{10}$$

W = 5744.1 Joule

(c) We know that internal energy of a gas depends upon its 46. pressure and temperature. Thus if a gas expands at constant temperature and pressure, then its internal energy remains same. DOL (

47. (b)
$$PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$$

For this reaction $\Delta ng = 2 - 1 = 1$
 Δng is positive, *i.e.*, there is an increase in the number of gaseous moles then $\Delta H > \Delta E$

(c) Enthalpy (H) is defined as the sum of internal energy 48. E + PV, H = E + PV.

49. (d)
$$(CH_3)_2 C = CH_2(g) + 6O_2(g) \rightarrow 4CO_2(g) + 4H_2O(l)$$

 $\Delta ng = 4 - 6 = -2$ (i.e., negative)
we know that $\Delta H = \Delta E + \Delta ngRT$
 $= \Delta E - (\Delta ng)RT$ ($\because \Delta ng = -ve$)
 $\therefore \Delta H < \Delta E$
50. (b) Given number of moles =1

Initial temperature $= 27^{\circ} C = 300 K$ Work done by the system = 3 KJ = 3000K

It will be (-) because work is done by the system.

Heat capacity at constant volume (Cv) = 20 J/k

We know that work done

 $W = -nC_V(T_2 - T_1); \ \ 3000 = -1 \times 20 \ (T_2 - 300)$ $2000 - -20T_{2} + 6000$

$$3000 = -20T_2 + 600$$

$$20T_2 = 3000; \quad T_2 = \frac{3000}{20} = 150K$$

Internal energy of a system is a state function and extensive 51. (a) property and is independent of the path by which it is obtained.

52. (d)
$$N_2O_4(g) \to 2NO_2(g)$$

For this reaction $\Delta ng = 2 - 1 = 1$

 Δng is positive *i.e.*, there is an increase in the number of gaseous moles then $\Delta H > \Delta E$

53. (b)
$$2C + O_2 \rightarrow 2CO$$
; $\Delta H = -220 \text{ KJ}$

This reaction does not represent complete combustion of carbon, hence heat of combustion of carbon will not be equal to $110 \, kJ$. The negative sign of ΔH indicates that this reaction is exothermic. Also, despite being spontaneous reaction, it requires initiation.

54. (c)
$$W = -P\Delta V = -1 \times 10^5 (1 \times 10^{-2} - 1 \times 10^{-3})$$

= $-1 \times 10^5 \times 9 \times 10^{-3} = -900 J$

The exact value of internal energy is not known as it includes (a) 55 all type of energies of molecules constituting the given mass of matter such as translational, vibrational, rotational. The kinetic & potential energy of the nuclei & electron with in the individual molecules and the manner in which the molecule are linked together etc.

$$E = E_{translational} + E_{rotational} + E_{vibrational}$$

Thus, we can say that internal energy is partly potential and partly kinetic.

56. (b)
$$N_2(g) + O_2(g) \rightarrow 2NO(g); \Delta n_g = 2 - 2 = 0$$

$$\Delta H = \Delta E + \Delta n_a RT; \quad \Delta H = \Delta E + 0; \quad \Delta H = \Delta E$$

(d)
$$W = -p\Delta V; W = -3 \times (6-4)$$

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$$W = -6 \times 101.32 \quad (:.1 \, Latm = 101.32 \, J)$$
$$W = -608 \, J$$

58. (d)
$$A(s) + 3B(g) \rightarrow 4C(s) + D(l)$$

 $\Delta ng = 0 - 3 = -3; \quad \Delta H = \Delta E + \Delta ngRT [:: \Delta E = \Delta U]$
 $\therefore \Delta H = \Delta U + (-3)(RT)$
 $\Delta H = \Delta U - 3(RT); \quad \Delta H = \Delta U - 3RT$

IInd & IIIrd Law of thermodynamics and Entropy

- 2. (d) When $\Delta S = +ve$ the change is spontaneous.
 - (d) Heat is always flow from the higher to lower temperature.
- Mixing of non-reacting gases increases randomness and so 4. (b) increase entropy.
- Entropy of the system increases as the process occur (b) 5. irreversibly and isothermally in an isolated system.

6. (d)
$$\Delta S^o = 2S^o_{HCl} - (S^o_{H_2} + S^o_{Cl_2})$$

$$= 2 \times 186.7 - (130.6 + 223.0) = 19.8 \, JK^{-1}mol^{-1}$$

9. (b) For adiabatic expansion q = 0 than according to following

relation
$$\Delta S = \frac{q}{T}, \Delta S = 0$$
.

- (c) It is the third law of thermodynamics. 10.
- Entropy of gases is highest. 11. (c)
 - $\Delta G = \Delta H T \Delta S$ (c) for spontaneous process ΔG should be negative in option (3) $\Delta H = -ve$ and $\Delta S = +ve$ than

 $\Delta G = (-ve) - T(+ve) = -ve$

- (c) For reverse reaction sign will be change. 15.
- (b) Solid \longrightarrow Gas, ΔS is maximum. 16.
- + $ve \Delta H$ and $ve \Delta S$ both oppose the reaction. 17. (d)

18. (a)
$$\Delta S_{vap} = 186.5 / 373 = 0.5 \ JK^{-1} \ mol^{-1}$$
.

- (a) When $\Delta H = -ve$, $\Delta S = +ve$ and $\Delta G = -ve$ than reaction is 20. spontaneous.
- For endothermic process ΔS increases. 21. (d)
- Calculation of change in entropy is done at constant 22. (c) temperature and pressure both.
- When the value of entropy is greater, then ability of work is 23. (a) maximum.

(d) At equilibrium,
$$\Delta G = 0$$

Hence $0 = \Delta H - T\Delta S$ or $\Delta H = T\Delta S$.

25. (c)
$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T} = \frac{37.3 \ KJ \ mol^{-1}}{373 \ K}$$

= 0.1 kJ mol^{-1} K^{-1} = 100 \ J mol^{-1} K^{-1}

- (d) Solid \rightarrow Liquid, ΔS increases . 26.
- 27. (c) $\Delta S = +ve$ than process is spontaneous.
- $\Delta S = +ve$ than the system is more disordered. 28. (b)
- Because solid \rightarrow solid, ΔS is same and ΔH is *-ve*. 29. (c)

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30. (b)
$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T} = \frac{386}{298} = 1.2 kJ$$

- **31.** (b) Processes (a) and (c) take place with the increase of no. of moles of gaseous species and hence the disorder or entropy increases. (b) on increasing pressure, disorder or randomness decreases and so also the entropy (d) is endothermic process and ΔS is positive.
- **32.** (d) This is the statement of third law of thermodynamics.
- **33.** (d) For isothermal expansion of ideal gas, $\Delta E = 0$.

34. (a)
$$\Delta S_{vap} = \frac{(900 \times 18)}{373} = 43.4 \ JK^{-1} \ mol^{-1}$$
.

35. (c) Entropy of the mixture increases due to increase in impurity.

37. (c) If $\Delta H = +ve$ and $\Delta S = -ve$ than the reaction is non-spontaneous *i.e.* can not occur.

38. (a)
$$T_2 = 150 + 273 = 423 K$$

$$T_1 = 25 + 273 = 298 K$$
$$Q = 500 K$$
$$\frac{W}{M} = \frac{T_2 - T_1}{T_1}, W = 500 \left(\frac{423 - 298}{T_2}\right) = 1$$

$$\frac{1}{Q} = \frac{1}{T_2}; W = 500 \left(\frac{1}{423} \right) = 147.7 J.$$

- **39.** (c) According to III law of thermodynamics.
- **40.** (c) When $\Delta H = +\upsilon e$ and $\Delta S = -\upsilon e$ reaction is non-spontaneous.

41. (c)
$$T_m = \frac{\Delta H_{\text{fusion}}}{\Delta S_{\text{fusion}}} = \frac{9.2}{0.008} = 1150 \, K$$
.

42. (c) Here: Change in

Volume (V) = 500 - 300 = 200cc = 0.2 litre

Pressure (P) = 0.6 atm and heat liberated (q) = 10J

Work done (*W*) = $P\Delta V = (0.2 \times 0.6) = 0.12 litre - atm$

But
$$1 litre - atm = 101.3 J$$
.

hence $W = 0.12 \times 101.3 = 12.156 J$. We also know that heat is liberated, therefore it would be negative. Thus change in $\Delta E = q + W = -10 + 12.16 = 2.16 J$.

43. (c) Formation of CO_2 is,

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$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$$

 $\Delta S^{o} = 213.5 - 5.690 - 205 = 2.81 JK^{-1}.$

(b)
$$H_2 O_{(g)} \rightleftharpoons H_2 O_{(l)}$$

we know $\Delta G = \Delta H - T\Delta S$ at equilibrium $\Delta G = 0$ Therefore $\Delta H = T\Delta S$.

46. (a) We know that work done, $W = C_{\nu}(T_1 - T_2)$ $3 \times 1000 = 20(300 - T_2); \therefore 3000 = 6000 - 20 T_2$ $\therefore T_2 = \frac{3000}{100} = 150 K.$

$$T_2 = \frac{3000}{20} = 150$$

48. (d) It does not violates the first law of thermodynamics but violates the II law of thermodynamics.

49. (d)
$$C_v = \frac{3}{2}RT; C_p = \frac{5}{2}RT$$
 for monoatomic gas
 $C_v = \frac{5}{2}RT; C_p = \frac{7}{2}RT$ for diatomic gas

Thus for mixture of 1 *mole* each, $C_v = \frac{\frac{3}{2}RT + \frac{5}{2}RT}{2}$ and

$$C_p = \frac{\frac{5}{2}RT + \frac{7}{2}RT}{2}$$

Therefore, $C_p / C_v = \frac{3RT}{2RT} = 1.5$.

(c)
$$\Delta S = \frac{q_{rev}}{T}$$
 : unit of S is $JK^{-1}mol^{-1}$

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(b)
$$H_2 O_{(l)} \rightleftharpoons H_2 O_{(g)}, \ \Delta S = \frac{\Delta H_{vap}}{T},$$

 $\Delta H_{vap.} = 2.257 \ KJ \ / g$
or $\Delta H_{vap} = 2.257 \times 18 \ kJ \ / mol. = 40.7 \ KJ \ / mol$
hence, $\Delta S = \frac{40.7}{373} = 0.109 \ kJ \ / mol/K.$

- (a) Liquid → Vapour, entropy increases.
- (c) NaNO₃ is a solid, which is converted to liquid ions.

55. (c) Heat capacity of water per gram
$$=\frac{75}{18} = 4.17J$$

 $Q = mst$; 1000 $= 100 \times 4.17 \times t$
 $t = \frac{1000}{100 \times 4.17} = 2.4K$.

56. (c) As the work is done on system, it will be positive *i.e.*
$$W = +462 \text{ joule, } E = -128 \text{ joule}$$
 (heat is evolving).
From the 1⁻ law of thermodynamics
 $\Delta E = q + w = (-128) + (+462) = +334 \text{ Joules.}$

57. (a) Gases show highest entropy.

58. (b)
$$\begin{array}{c} H^{+}{}_{(aq)} + OH^{-}{}_{(aq)} \rightarrow H_{2}O_{(l)} \\ S^{o}{}_{(298 \ K)K^{-}mol^{-1}} & {}^{-10.7} & {}^{+70} \end{array}$$
$$\Delta S^{o}{}^{(298 \ K)} = \Delta S_{P} - \Delta S_{R} = 70 - (-10.7 + 0) \\ 80.7 \ JK^{-1} \ mol^{-1} \end{array}$$

- **59.** (d) The entropy change $=\frac{\text{heat of vaporisation}}{\text{temperatur e}}$
 - Here, heat of vaporisation = 540 cal/gm= $540 \times 18 calmol^{-1}$ Temperature of water = 100 + 273 = 373K

: entropy change
$$=\frac{540 \times 18}{373} = 26.06 \, calmol^{-1}K^{-1}$$

60. (b) Given that, $T_1 = 500K$, $T_2 = 300K$

By using,
$$\eta = \frac{T_1 - T_2}{T_1} = \frac{500 - 300}{500} = \frac{200}{500} = 0.4$$

(b) It is molar heat capacity.

61.

- 62. (d) Entropy is the measure of randomness in the molecules. Randomness is maximum in case of gases. Hence, entropy is maximum for water vapours.
- **63.** (a) Standard entropy of formation of $CO_2(g)$ = standard entropy of $CO_2(g)$ – [Standard entropy of C(s) – standard entropy of $O_2(g)$]

= 213.5 - [5.740 + 205] = 2.76 J/K.

- **64.** (c) Third law of thermodynamics help in calculating entropy of different temperatures.
- **65.** (a) In case of gas randomness is maximum therefore entropy is maximum in case of steam.
- **66.** (c) $\Delta S_{system} + \Delta S_{surroundin gs} > O$ (for spontaneity)

Because of
$$\Delta S = R \ln \frac{V_2}{V_1}$$

Here the volume of gas increase from V_1 to V_2 at constant temperature T.

The total increase in entropy of the system and its surrounding during the spontaneous process of expansion considered above

is, thus
$$R \ln \left(\frac{V_2}{V_1} \right)$$
 since $V_2 > V_1$ it is obvious that the

spontaneous (irreversible) isothermal expansion of a gas is accompanied by an increase in the entropy of the system and its surrounding considered together.

$$\Delta S_{system} + \Delta S_{surroundin\,gs} > 0$$

67. (b)
$$\Delta G = \Delta H - T \Delta S$$

1.

at constant temperature and pressure $\Delta G = 0$ $0 = \Delta T - T\Delta S$ so $\Delta H = T\Delta S$

68. (b)
$$dS = \frac{dQ_{rev.}}{T}$$
; $T = \frac{30 \times 10^3}{75}$; $T = 400K$

Heat of reaction

)
$$C + O_2 \rightarrow CO_2 + 94.2$$
 Kcal.(i)
 $H_2 + \frac{1}{2}O_2 \rightarrow H_2O + 68.3$ Kcal.(ii)

On multiplication of
$$eq.$$
 (ii) by 2 and than adding in $eq.$ (i)

$$C + 2H_2 + 2O_2 \rightarrow CO_2 + 2H_2O + 230.8 \ \ {\it Kcal} \qquad ... (iii)$$
 On subtracting eq. (iii) by following eq.

 $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + 210.8$ Kcal. we get,

$$C + 2H_2 \rightarrow CH_4 \quad \Delta H = 20 \quad Kcal.$$

2. (b) $\Delta S = 16J mole^{-1} K^{-1}$

$$T_{b.p.} = \frac{\Delta H_{\text{vapour}}}{\Delta S_{\text{vapour}}} = \frac{6 \times 1000}{16} = 375K$$

- **4.** (d) Heat of neutralisation between strong acid and a strong base is about -13.7 *Kcal*.
- **6.** (b) Effect of temperature in heat of reaction is given by Kirchoff's equation.
- (c) Heat of neutralisation between strong acid and a strong base is about -13.7 Kcal.
- 8. (a) For exothermic reactions $H_p < H_R$. For endothermic reactions $H_p > H_R$.
- 9. (b) 78g of benzene on combustion produces heat = $-3264.6 \ kJ$

$$\therefore 39g$$
 will produce $=\frac{-3264.6}{2} = -1632.3 \, kJ$.

- 10. (a) eq. (i) + eq. (ii) gives the required result.
- (bcd) (b,c,d) are endothermic reactions because they proceeds by the absorption of heat.
- (a) Change of liquid to vapour takes energy in the form of heat so it is endothermic reaction.
- 13. (d) In exothermic reactions heat is evolute.

(c) $\Delta H = -ve$ for exothermic reaction. $\Delta H = +ve$ for endothermic reaction Enthalpy of fusion is + *ve*.

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16. (a) Heat of neutralisation will be less than $-57.33 \ kJ \ / mole$ because some amount of this energy will be required for the dissociation of weak base (*MgO*)

(a)
$$H_2 + O_2 \rightarrow H_2O_2 \quad \Delta H_f^o = -188 \, kJ \,/\,mole \qquad \dots$$
(i)

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad \Delta H_f^o = -286 kJ / mole \qquad \dots (ii)$$

eq. (i) – eq. (ii)
$$\times$$
 2 gives the required result.

(b) Graphite
$$\longrightarrow$$
 diamond $\Delta H_t = (x - y)kJ mol^{-1}$

21. (c) Heats of combustions are always exothermic except oxidation of *N* as,

$$N_2 + \frac{1}{2}O_2 \rightarrow N_2O \quad \Delta H = +ve$$

 $N_2 + O_2 \rightarrow 2NO \quad \Delta H = +ve$

22. (a) For exothermic reactions $H_p < H_R$. For endothermic reactions $H_p > H_R$.

(d) Aim:
$$2C + H_{2(g)} \to C_2 H_{2(g)}$$
.

eq. (ii) + eq. (iii)
$$\rightarrow$$
 eq. (iv) – eq. (i) find the required result.

- (c) Enthalpy of formation of HCl.
- **25.** (c) Heat of neutralisation between strong acid and a strong base is about -13.7 *Kcal*.
- **26.** (b) For endothermic reaction, $\Delta H = +ve$.
- **27.** (b) Heat of neutralisation is less than 56.1 *Kcal* when a strong base and a weak acid reacts.

28. (b) Aim:
$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$

$$\Delta H = \Delta H_f^0 (CO_2) - \left[\Delta H_f^0 (CO) + \frac{1}{2}\Delta H_f^0 (O_2)\right]$$

$$=-94.0-(-26.4)=-67.6$$
 kcal.

29. (a)

(i)
$$H_2 + \frac{1}{2}O_2 \to H_2O, \ \Delta H = -241kJ$$

(ii)
$$C_6 H_{10} + \frac{17}{2}O_2 \rightarrow 6CO_2 + 5H_2O, \Delta H = -3800 \, kJ$$

(iii)
$$C_6H_{12} + 9O_2 \rightarrow 6CO_2 + 6H_2O, \Delta H = -3920 kJ$$

$$C_{6}H_{10} + H_{2} \rightarrow C_{6}H_{12}$$

Eq. (i) + Eq. (ii) – Eq. (iii)
$$\Delta H = -241 - 3800 - (-3920)$$
$$= -4041 + 3920 = -121 kJ$$

- **30.** (c) NH_4OH is a weak base. Heat of neutralisation < 13.7 kcal.
- **31.** (a) CH_4 is the best fuel because its calorific value = $\frac{-212.8}{16} = -13.3 \, kcal/g$ is higher among the other gases.
- **32.** (a) Find ΔH for $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O_{(q)}$
- **34.** (b) In neutralisation of a strong acid and base only H^+ and OH^- ions react.

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35.	(b)	When both acid and base are strong than heat of neutralisation is $57.1 kJ mol^{-1}$.
36.	(a)	$C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O$ substitute the values.
37.	(a)	Decomposition is an endothermic process.
38.	(d)	ΔH for this reaction is Heat of reaction.
40.	(b)	One mole of H_2O is formed from its initial components.
41.	(c)	One mole of a substance is completely oxidized in air.
42.	(c)	$S(\text{rhombic}) + O_2 \rightarrow SO_2, \Delta H = 70900 \text{ cal.} \qquad \dots(1)$
		$S \text{ (monoclinic)} + O_2 \rightarrow SO_2 \ \Delta H = /1030 \ cal \qquad \dots \text{(ii)}$
		e_{a} (i) $-e_{a}$ (ii) gives the required result.
43.	(b)	When $H_2O_{(l)}$ is convert to form $H_2O_{(g)}$, heat is absorbed
		hence $\Delta H_1 > \Delta H_2$.
44.	(b)	Out of given substances, kerosene oil has maximum calorific value.
45.	(b)	$C_{(S)} + O_{2(g)} \rightarrow CO_{2(g)}, \ \Delta n_g = 1 - 1 = 0$
		$\therefore \Delta E = \Delta H = -94 \ kcal$
		$\Delta E = E_{CO_2} - (E_C + E_{O_2}) = E_{CO_2} - (0 + 0)$
		or $E_{CO_2} = \Delta E = -94$ kcal.
46.	(b)	0.2 mole will neutralize 0.2 mole of HNO_3 , heat evolved $= 57 \times 0.2 = 11.4 \ kJ$.
47.	(a)	Suppose heat evolved in 1 case is Q_1 and that in the 11 case it
		is Q_2 . Then $Q_2 = \frac{1}{2}Q_{1.}$
		But $Q_1 = 1000 T_1$ and $Q_2 = 500 T_2$
		$\therefore 500 \ T_2 = \frac{1}{2} \times 1000 \ T_1 \ i.e. \ T_2 = T_1.$
48 .	(c)	Enthalpy of a compound = Heat of reaction of that compound.
49. 50.	(e) (b)	$\Delta H = -ve$ for exothermic compound.
51.	(a)	If acid or base or both are strong, heat of neutralization $= 13.7 \ kcal$.
52.	(b)	Both NH_4OH and CH_3COOH are weak.
53.	(c)	$57.1 \times 0.25 = 14.3 \ kJ \ mol^{-1}$.
54.	(c)	Heat of formation is for 1 <i>mole.</i>
	(L)	Hence $\Delta H_f^{\prime}(H) = -12.40/2 = -6.20 kcal.$
55. 57.	(\mathbf{c})	Given,
		(i) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$, $\Delta H = +20$ kcal
		(ii) $C + O_2 \rightarrow CO_2$, $\Delta H = -40$ kcal.
		(iii) $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$, $\Delta H = -10$ kcal.
		Aim: $C + 2H_2 \rightarrow CH_4$
		(ii) + 2 × (iii) – (i) gives. $\Delta H = -40 + 2(-10) - (+20) = -80 \ kec^{1}$
58.	(d)	For exothermic reaction heat is evolved.
59.	(c)	$H_2O_{40} \xrightarrow{\text{electrolysis}} H_{40} + \frac{1}{2}O_{40}$
61.	(d)	All other are combustion phenomena.
62.	(c)	$\Delta H_{\text{combusion}} = -ve$, so exothermic process.

_	_	
63.	(b)	Aim: $K_{(S)} + \frac{1}{2}O_{2(g)} + \frac{1}{2}H_{2(g)} \to KOH_{(S)}$
		eq. (ii) + $eq.$ (i) - $eq.$ (iii) gives
c .		$\Delta H = -48 + (-68.39) - (-14) = -68.39 - 48 + 14.$
64. 69	(a)	By definition of heat of formation. $C \rightarrow C \rightarrow H = 453.5$ cal
08.	(C)	$C_D \rightarrow C_G, \Delta I = -435.5$ cut.
60	(a)	<i>i.e.</i> energy of C_G is less and thus more stable.
09.	(u)	combustion is always negative :
70.	(d)	$\Delta H_{\text{reaction}} = \Delta H_f^* (N_2 O_4) - 2\Delta H_f^* (N O_2)$ $= 2 - 2(8) = -14 \text{ kead}$
_	()	= 2 - 2(0) = -14 Kcul.
71.	(a)	$\Delta H = \Delta E = \Delta I K I = 5 \times 6.514 \times 296$
70	(b)	= -/432 J = -/.43 kJ.
72.	(D)	Aim: $C_{(graphite)} \rightarrow C_{(diamond)}$; eq. (1) – (1) gives the result.
73.	(d)	In the formation of a compound, more the heat absorbed, less stable is the compound.
74.	(c)	$C_{(\text{graphite})} + 2H_{2(g)} = CH_{4(g)}.$
75.	(b)	Heat of formation is the formation of one mole of the substance from its elements.
76.	(b)	$\Delta H_{(\text{reaction})} = 2\Delta H_f^0 (MgO) = -\Delta H_f^0 (SiO_2)$
-		= 2(-34.7) - (-48.4) = -21kJ.
77.	(a)	eq. (i) + $eq.$ (ii) + $eq.$ (iii) gives
		$X = 131 - 282 - 242 = -393 kJ \; .$
78.	(d)	It is the definition of heat of transition.
79.	(d)	$C_{(\text{graphite})} \rightarrow C_{(\text{diamond})}, \Delta H = 1.9 kJ$
		$C_{(\text{graphite})} + O_2 \rightarrow CO_2, \Delta H = -\Delta H_1$
		$C_{(\text{diamond})} + O_2 \rightarrow CO_2, \Delta H = -\Delta H_2$
		$(-\Delta H_1)-(-\Delta H_2)=1.9kJ$ or $\Delta H_2=\Delta H_1+1.9$
		For combustion of $6g$, $\Delta H_2 > \Delta H_1$ by $1.9/2 = 0.95 kJ$.
80.	(a)	$H_{\mathrm{product}} imes H_{\mathrm{reactant}}$ for exothermic reaction.
81.	(b)	Due to high electron affinity of <i>Cl</i> the highest energy is evolved.
82.	(b)	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
		Molecular weight of $CH_4 = 12 + 4 = 16$
		\therefore On the combustion of 2.0 <i>gm</i> of methane = 25.0 <i>kcal</i>
		\therefore On the combustion of $16.0 gm = \frac{25 \times 16}{2} = 200 kcal$.
83.	(a)	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O.$
84.	(b)	$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$
		$\Delta H_{\text{reaction}} = [2 \times \Delta H_f^o(CO_2) + 2 \times \Delta H_f^o(H_2O)]$
		$-\left[\Delta H_{f}^{o}\left(C_{2}H_{4}\right)+3\times\Delta H_{f}^{o}\left(O_{2}\right)\right]$
		= [2(-394) + 2(-286)] - [52 + 0] = -1412kJ.
85.	(b)	$C+O_2 \rightarrow CO_2 + 394 kJ \; .$
		$2C + 2O_2 \rightarrow 2CO_2 + 788 kJ \qquad \dots (i)$

- $\begin{array}{ll} 2C+2O_2 \to 2CO_2 + 788 \, kJ & \dots(i) \\ 2CO+O_2 \to 2CO_2 + 569 \, kJ & \dots(ii) \\ 2CO_2 \to 2CO+O_2 569 \, kJ & \dots(iii) \\ eq. \, (i) + eq. \, (iii) = -109.5 \, kJ \, mol. \end{array}$
- **86.** (c) $\Delta H_f = \frac{44}{2} kcal = 22 kcal$.

87. (a)
$$CaO_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_2$$
 is exothermic.
88. (b) $\Delta H = -\upsilon e$ in exothermic reaction.
89. (d) According to the definition of heat of formation. III.
90. (d) Multiplying eq. (ii) by (iii) and eq. (iii) by (vi), and then add
 $6C + 3H_2 + \frac{15}{2}O_2 \rightarrow 6CO_2 + 6H_2O; \Delta H = 3218.7$ II3.
Subtract eq. (i) from the above equation and find the required
result.
91. (a) HF is more stable than HCl .
92. (c) $\Delta H (H_P - H_R) = q_P$.
93. (b) $\Delta H = +\upsilon e$ for endothermic reaction. II5.
94. (a) $\Delta H = \frac{13.95 \times 44}{2.2016} = 278.7 \ kcal$.
95. (d) eq. (i) + eq. (ii) gives the required result.
96. (d) Standard heat of formation from most stable states of initial
components.
97. (c) In the complete combustion of butanol $\Delta H > \Delta E$.
98. (a) $X - Y$ and find the required result.
99. (c) $S + O_2 \rightarrow SO_2$ $\Delta H = -298.2 \ kJ$ (i)
 $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$ $\Delta H = -98.2 \ kJ$ (ii)
 $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$ $\Delta H = -98.2 \ kJ$ (ii)
 $CS_2 + 3O_2 \rightarrow CO_2 \ \Delta H = -393.3 \ kJ$ (ii)
 $CS_2 + 3O_2 \rightarrow CO_2 + 2SO_2 \ \Delta H = -1108.76 \ kJ$ (iii)
 $eq. (i) - (ii)$ and find the required result.
100. (b) Fermentation is exothermic reaction.
101. (b) Fermentation is exothermic reaction.
102. (c) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$.
103. (d) Use $\Delta H = \Delta E + \Delta n RT$
 $\Delta H = 19 + 2 \times 2 \times 10^{-3} \times 300 = 20.2 \ kcal ; \ \Delta n = 2$.
104. (d) $-20.6 - 8.8 \ KJ \ mol^{-1} = -29.4 \ kJ$.
105. (a) Subtract equation (ii) from (i).
107. (c) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O, \ \Delta H = -890.4 \ kJ$ (ii)
 $C + O_2 \rightarrow CO_2, \ \Delta H = -395.5 \ kJ$ (ii) 122.
 $C + O_2 \rightarrow CO_2, \ \Delta H = -395.5 \ kJ$ (ii) 123.
(b) $C + O_2 \rightarrow CO_2, \ \Delta H = -395.5 \ kJ$ (ii) 124.
(c) $C + O_2 \rightarrow CO_2, \ \Delta H = -395.5 \ kJ$ (ii) 123.

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O, \ \Delta H = -285.8 \ kJ$$
(iii)
from (i), (ii), (iii).

$$\begin{split} & \Delta H_{comb.}(CH_4) \\ & = \Delta H_f(CO_2) + 2\Delta H_f(H_2O) - \Delta H_f(CH_4) - 2\Delta H_f(O_2) \\ & = -890.4 = -395.5 + 2(-285.5) - \Delta H_f(CH_4) - 2 \times 0 \end{split}$$

$$\Delta H_f(CH_4) = -76.7 \, kJ \, mol^{-1}$$

- **108.** (d) As methanoic acid is weak acid, heat of neutralization < x.
- $\label{eq:constraint} \textbf{109.} \qquad (d) \quad \text{Neutralization of a strong acid by a strong base is always same.}$

110. (c)
$$S + O_2 \rightarrow SO_2$$
, $\Delta H_f = -4.6 \, kJ$

 \because 0.5 gm. of sulphur on burning produce 1gm of $~SO_2$

$$\therefore\,$$
 32 gm of sulphur on burning produce 64 $\mathit{gm.}$ of $\,$ SO $_2$

$$\therefore \Delta H = (-4.6 \, kJ) \times 64 = -294.4 \, kJ.$$

(a)
$$3O_2 \rightleftharpoons 2O_3$$
 – energy is given out

2. (b)
$$\Delta H \ per 1.6g = \frac{72 \times 1.6}{180} = 0.64 \ kcal$$
.

(a)
$$C + O_2 \rightarrow CO_2$$
, $\Delta H = -394 \, kJ$

$$2H_2 + O_2 \rightarrow 2H_2O, \ \Delta H = -568 \, kJ$$
(ii)
 $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O, \ \Delta H = -892 \, kJ$ (iii)

- (i) + (ii) (iii) and find the required result.
- 5. (a) No doubt heat evolved during neutralisation of $250 \, cm^3$ of each acid and base is five time the heat evolved during neutralisation of $50 \, cm^3$ of each acid and base but the quantity if solution taking heat is also five time thus same temperature rise is noticed.

116. (a)
$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O_{(l)}; \ \Delta H = -285.8 \ KJ$$

 $H_2O_{(l)} \rightarrow H_2O_{(g)}; \ \Delta H = 44 \ KJ$
 $\therefore H_2 + \frac{1}{2}O_2 \rightarrow H_2O_{(g)}; \ \Delta H^o = -241.8 \ KJ$

(b) Given: Weight of iron burnt = 4g; Heat liberated = 29.28 KJ and atomic weight of iron (Fe) = 56. We know that in ferric oxide (Fe_2O_3) , 2 moles of iron or $2 \times 56 = 112 gram$ firon are burnt. We also know that when 4grams of iron are burnt, then heat liberated = 29.28 k/, therefore when 112 grams of the iron are burnt, then heat liberated = $\frac{29.28 \times 112}{4} = -819.8 kJ$ (Minus sign due to liberation of heat).

18. (c)
$$H^+ + OH^- \rightarrow H_2O$$
, $\Delta H_{\text{neutralization}} = 13.7 \, kcal$.

19. (b)
$$\Delta H / mole$$
 of $FeS = \frac{3.77 \times 56}{2.1} = 100.5$

20. (a) Heat of formation $=\frac{194}{2}=97 \, kJ$.

121. (a)
$$\Delta H = \Delta H_{\text{ioniz}} + \Delta H_{\text{neu}} = -50.6 = \Delta H_{\text{ioniz}} + (-55.9)$$

 $\Delta H_{\text{ioniz}} = +5.3 \, kJ \,/ \,mol$.

122. (a) Strong acid (HNO_3) and strong base (LiOH).

23. (d)
$$\Delta H = \Delta E + \Delta nRT$$
 or $\Delta E = \Delta H - \Delta nRT$

$$\therefore \Delta E = +7.3 - \frac{1}{2} \times 0.002 \times 298 = 7.3 - 0.298 = 7 \ kcal.$$

124. (b) Heat evolved during burning of
$$39g$$

$$C_6 H_6 = \frac{781.0 \times 39}{78} = 390.5 \ kcal \ mol^{-1}$$

(b)By (i) + (ii) : $Na + \frac{1}{2} Cl_2 \rightarrow NaCl, \ \Delta H = -196 \ kcal$

125. (b)By (i) + (ii);
$$Na + \frac{1}{2}Cl_2 \rightarrow NaCl, \Delta H = -196 \, kcal.$$

126. (b) $C + O_2 \to CO_{2(g)}, \ \Delta H_f^o = -393.5 \, kJ \, mol^{-1}$ (i)

$$C + \frac{1}{2}O_2 \to CO_{(g)}, \ \Delta H_f^o = -110.5 \, kJ \, mol^{-1}$$
(ii)

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.....(i)

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$$\begin{split} H_2 + \frac{1}{2}O_2 &\to H_2O_{(g)}, \ \Delta H_f^o = -241.8 \ kJmol^{-1} \qquad ...(iii) \\ \text{By (ii) + (iii) - (i)} \\ CO_{2(g)} + H_{2(g)} &\to CO_{(g)} + H_2O_{(g)}, \ \Delta H = +41.2 \ . \end{split}$$

- **127.** (c) More +ve is ΔH_s more is heat of solution.
- **128.** (d) CS_2 is formed from its initial components carbon and sulphur so, ΔH is heat of formation of CS_2 .
- 129. (d) $\Delta H = 18500 = \Delta E + \Delta nRT$ or $18500 = \Delta E + (-1) \times 2 \times 298 = 19096 \, cal$.
- **130.** (b) Heat evolved during combustion of 0.39*g* $C_6H_6 = \frac{3250 \times 0.39}{78} = 16.25 \, kJ.$

131. (d) By (i) – (ii):
$$C + \frac{1}{2}O_2 \to CO; \Delta H = -229.2.$$

- 132. (b) Strong acid (*HCl*) and strong base (*NaOH*) shows $\Delta H_{\rm neutralization} = -57.3 \ \text{kJ}.$
- **133.** (d) By (i) (ii) and find required result.

134. (a)
$$CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}, \Delta n = 1 - 1 + \frac{1}{2} = -\frac{1}{2}$$

 $\Delta H = \Delta E + \Delta nRT$
 $\Delta H = -283.3 - \frac{1}{2} \times \frac{8.314}{1000} \times 290 = -284.5 kJ$.

135. (a)
$$H_2 + \frac{1}{2}O_2 \to H_2O \quad \Delta H = -188 \, kJ/mole$$
(i)

$$H_2 + O_2 \rightarrow H_2O_2; \ \Delta H = -286 \, kJ/mole$$
(ii)
By 2 × (i) and (ii)

$$2H_2 + O_2 \rightarrow 2H_2O$$
; $\Delta H = -376 \, kJ/mole$ (iii)

$$2H_2 + 2O_2 \rightarrow 2H_2O_2 \quad \Delta H = -572 \, kJ/mole$$
(iv)
By (iii) – (iv)

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad \Delta H = +196 \, kJ$$
.

136. (a)
$$\Delta H$$
 for $C_2 H_6 = -341.1 K cal$

its calorific value
$$= \frac{-341.1}{30} = -11.37 \, kcal / g$$
.
 ΔH for $C_2 H_2 = -310.0 \, kcal$

its Calorific value
$$=\frac{51000}{26} = -11.92$$
,
hence C_2H_2 is a better fuel.

138. (c) For the decomposition of 9gm of water heat required = 142.5 kJ

we know
$$H_2O = 2 + 16 = 18$$

Therefore heat required for decomposition of 18gm water = $\frac{18}{9} \times 142.5 = 285 \text{ KJ}$

Than, enthalpy of formation of water is reverse of heat required = $-285 \ kJ$.

139. (d)
$$C_6H_{6(g)} + \frac{15}{2}O_{2(g)} \to 6CO_{2(g)} + 3H_2O_{(g)}$$

$$\Delta n = 6 + 3 - 1 - \frac{15}{2} = +\frac{1}{2}.$$

- 140. (b) By $2 \times (i) + (ii) (iii)$ ΔH of methane = 20.0 kcal.
- 141. (c) Heat of neutralization of strong acid and weak base is less than $13.7 \, kcalmol^{-1}$.
- **142.** (d) $\Delta E = 0$ for a cyclic process.
- **143.** (c) $22.0 \times 2 = 44 \, kcal$.

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144. (b) 0.3 mole OH^- , neutralize 0.3 mole of HNO_3

Evolved heat, $= 57.1 \times 0.3 = 17.13 kJ$

146. (d) Compounds with high heat of formation are less stable because energy rich state leads to instability.

47. (b)
$$CH_4$$
 required $=\frac{445.15 \times 16}{890.3} = 8 gm$

48. (c)
$$C_{(s)} + 2H_{2(g)} \to CH_{4(g)}$$
(i)

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \quad \Delta H = -94 \ kcal \ mol^{-1} \qquad \dots(ii)$$

$$\begin{split} H_{2(g)} &+ \frac{1}{2} O_{2(g)} \to H_2 O_{(l)} \quad \Delta H = -68 \ kcal \ mol^{-1} \dots \qquad \text{(iii)} \\ CH_4 &+ 3/_2 O_2 \to CO_2 + 2H_2 O \\ \Delta H &= -213 \ kcal \ mol^{-1} \qquad \qquad \dots \qquad \text{(iv)} \end{split}$$

to obtain equation (i) operate-(ii) +
$$2 \times$$
 (iii) – (iv).

- **149.** (b) $\Delta H = +ve$ for endothermic reactions.
- **150.** (b) It pertains to neutralization of strong acid weak base.
- **151.** (d) Strong base (*KOH*) and strong acid (*HCl*)
- $\label{eq:bound} \textbf{153.} \qquad (b) \quad \text{This reaction absorbed heat, so it is endothermic reaction.}$

154. (b)
$$C + O_2 \to CO_2, \ \Delta H = -94.3$$

This is also heat of formation of CO_2

$$C + \frac{1}{2}O_2 \rightarrow CO, \ \Delta H = -26.0$$

- 155. (b) $X = \frac{1}{2}Y$.
- **157.** (a) Molecular weight of $NH_4NO_3 = 80$

Heat evolved $= 1.23 \times 6.12$ \therefore Molar heat capacity $= 1.23 \times 6.12 \times C$.

- **158.** (d) Both X_e and F_2 are gaseous elements at $25^{\circ}C$ and in their standard states and form $XeF_{4(e)}$ hence $\Delta H_{(f)}^{\circ} = \Delta H_{react}^{\circ}$.
- 159. (c) According to Hess low, enthalpy change for a reaction does not depend on the nature of inter mediate reaction steps.

160. (d) By (ii) – (i),
$$C_{gr} \rightarrow C_{dia}$$
, $\Delta H = +1.9$.

- **162.** (c) Heat of neutralization of strong acid and strong base is equal to the $-57.32 \text{ KJ mol}^{-1}$
- 163. (c) $C + O_2 \rightarrow CO_2 \Delta H = -393.5 \text{ KJ} / mol$

 $:: 44 \ gm$ of CO_2 form by which heat released

 $= -393.5 \, kJ$

- $\therefore 1gm$ of CO_2 form by which heat released $= -\frac{393.5}{44}$
- $\therefore~35.2\,gm~({\rm given})$ of $CO_2~{\rm form}$ by which heat released

$$= -\frac{393.5}{44} \times 35.2 = -315 kJ$$

- 164. (c) $C_{(graphite)} + 2H_2(g) \rightarrow CH_4(g)$
- 165. (c) Heat of formation of a substance is the heat exchanged when one mole of that substance is formed by its constituent elements.

: Heat evolved when 1 mole $(44g)CO_2$ is formed = 393 kJ

- $\therefore \qquad \text{Heat evolved when } 0.156 \, Kg \, (156g) \text{ is formed} \\ = \frac{393 \times 156}{44}$
- $\therefore \Delta H$ for the process = 1572kJ = -1572.0kJ
- 166. (b) It is heat of neutralisation (13.7 Kcal) for strong acid and strong base.

167. (d)
$$C(s) + O_2(g) \to CO_2(g)$$

$$\Delta H = -393.5 \, KJ \, mol^{-1} \qquad \dots (i)$$

$$CO(g) + 1/2O_2(g) \rightarrow CO_2(g)$$

$$\Delta H = -283 \, KJ \, mol^{-1} \qquad \dots \dots (ii)$$

On substracting equation (ii) from equation (i) We get

$$C(s) + O_2(g) \rightarrow CO(g); \Delta H = -110.5 \text{ KJ mol}^{-1}$$

The enthalpy of formation of carbon monooxide per mole $= -110.5 \text{ KJ mol}^{-1}$

168. (d) 1 mole (i.e.,) 16gm of methane on combustion liberate 890 kJ

$$\therefore 3.2 \, gm \text{ will liberate } = \frac{890 \times 3.2}{16} = 178 \, KJ$$

169. (c)
$$C + O_2 \rightarrow CO_2$$
; $\Delta H = q$
 $C + 1/2O_2 \rightarrow CO$; $\Delta H = -12$ (i)
 $CO + 1/2O_2 \rightarrow CO_2$; $\Delta H = -10$ (ii)
adding equation (i) and (ii) we can get
 $\Delta H = -12 + (-10) = -22$

170. (b)
$$C + O_2 \rightarrow CO_2$$
; $\Delta H_F = -490 \text{ KJ/mol} - (1)$
 $H_2 + 1/2O_2 \rightarrow H_2O$; $\Delta H_F = -240 \text{ KJ/mol} - (11)$
 $8C + 18H \rightarrow C_8H_{18}$; $\Delta H_F = +160 \text{ KJ/mol} - (111)$
applying
 $(1) \times 8 + (11) \times 9 + (111)$

$$C_8H_{18} + \frac{25}{2}O_2 \rightarrow 8CO_2 + 9H_2O$$

$$\Delta H^{\circ} = -3920 - 2160 - 160 = 6240 \, \text{KJ} \,/ \,\text{mol}$$

$$\Delta H^{o} =$$
 for 6 moles of octane $= 6240 \times 6$

$$= 37440 \, \text{KJ} \, / \, \text{mol} = -37.4 \, \text{KJ}$$

171. (d)
$$2Fe + \frac{3}{2}O_2 \rightarrow Fe_2O_3; \Delta H = -193.4 \, kJ$$
(i)

$$Mg + \frac{1}{2}O_2 \rightarrow MgO; \Delta H = -140.2 \, kJ$$
(ii)

On multiplying eq. (ii) by 3

$$3Mg + \frac{3}{2}O_2 \rightarrow 3MgO; \Delta H = -420.6 \, kJ$$
(iiii)

Resulting equation can be obtained by subtracting eq. (i) from (iii)

$$3Mg + \frac{3}{2}O_2 \rightarrow 3MgO; \Delta H = -420.6 \, kJ$$
$$2Fe + \frac{3}{2}O_2 \rightarrow Fe_2O_3; \Delta H = -193.4 \, kJ$$
Subtraction :

$$3Mg + Fe_2O_3 \rightarrow 2Fe + 3MgO; \Delta H = -227.2 kJ$$

172. (c) HCl and KOH both are strong

1.

Bond energy

(b)
$$XY \longrightarrow X_{(g)} + Y_{(g)}; \Delta H = +a kJ / mole$$
(i)

$$X_{2} \longrightarrow 2X ; \Delta H = +a \ kJ \ / mole \qquad \dots \dots \dots (ii)$$

$$Y_{2} \longrightarrow 2Y ; \Delta H = +0.5 \ a \ kJ \ / mole \qquad \dots \dots \dots (iii)$$

$$\frac{1}{2} \times (ii) + \frac{1}{2} \times (iii) \cdot (i), \text{ gives}$$

$$\frac{1}{2} X_{2} + \frac{1}{2} Y_{2} \longrightarrow XY ;$$

$$\Delta H = \left(+ \frac{a}{2} + \frac{0.5}{2} a - a \right) kJ \ / mole$$

$$+ \frac{a}{2} + \frac{0.5a}{2} - a = -200$$

$$a = 800$$

2. (a) $4gH_2 = 2$ moles. Bond energy for 1 mole of $H_2 = 208/2 = 104$ kcal.

4. (d) By definition of Hess's law.

5. (c) Aim:
$$\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \rightarrow HCl$$

 $\Delta H = \sum B.E._{(\text{Products})} - \sum B.E._{(\text{Reactants})}$
 $= B.E.(HCl) - \left[\frac{1}{2}B.E.(H_2) + \frac{1}{2}B.E.(Cl_2)\right]$
 $= -103 - \left[\frac{1}{2}(-104) + \frac{1}{2}(-58)\right]$
 $= -103 - (-52 - 29) = -22 \ kcal$.

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6. (c) First ionization potential of
$$Li = 5.4eV$$

Electron affinity of $Cl = 3.61eV$
We have $\Delta H = I.P. - E.A.$
 $= 5.4 - 3.61 = 1.80eV = 1.80 \times 1.6 \times 10^{-22} kJ$
 $\Delta H = 2.86 \times 10^{-22} kJ$,
for 1mol Avogadro's number $= 6.02 \times 10^{23}$.
 $\Delta H = 2.86 \times 10^{-22} \times 6.02 \times 10^{23} = 170 kJ / mole$.
7. (b) $\frac{-166}{4} = -41.5 kJ / mole$.
8. (d) $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \rightarrow HCl$, $\Delta H = -90 KJ$
 $\therefore \Delta H = \frac{1}{2}E_{H-H} + \frac{1}{2}E_{Cl-Cl}$
or $-90 = \frac{1}{2} \times 430 + \frac{1}{2} \times 240 - E_{HCl}$
 $\therefore E_{H-Cl} = 425 kJ mol^{-1}$.
9. (b) $CH_4 \rightarrow C + 4H$, $\Delta H = 320$
 $E_{C-H} = 90 cal$
 $C_2H_6 \rightarrow 2C + 6H$, $\Delta H = 360$
 $\therefore 360 = E_{C-C} + 6E_{C-H}$
 $\therefore E_{C-C} = 360 - 320 = 40 cal$.
10. (b) $H - H + Br - Br \rightarrow 2H - Br$
 $433 + 192$ 2×364
 625 728
Energy absorbed = Energy released
Net energy released = $728 - 625 = 103kJ$

i.e.,
$$= \Delta H = -103 \, KJ$$

Free energy and Work function

1. (d) ΔG at equilibrium = 0.

- **2.** (b) For spontaneous change $\Delta G = -ve$.
- **3.** (a) When $\Delta G = -ve$ than the reaction is spontaneous in nature.
- **5.** (acd)When $\Delta H = +ve$ and $\Delta S = -ve$ than the reaction is non-spontaneous.
- 7. (c) Because the reaction is spontaneous .
- 8. (c) $\Delta G = -ve$.

9. (a)
$$\Delta G_T = nRT \ln \frac{P_2}{P_1}$$

10. (a) $\Delta G = 0$ for equilibrium.

11. (d) At equilibrium $\Delta G = 0$.

12. (a) $\Delta G^o = -2.303 RT \log K$

 $-4.606 = -2.303 \times 0.002 \times 500 \log K$

$$\log K = 2, \ K = 100$$

14.	(d)	Spontaneous change shows $\Delta G = -ve$.
15.	(b)	$\Delta G = \Delta H - T \Delta S, \ T = 25 + 273 = 298K$
		$= -11.7 \times 10^{3} - 298 \times (-105) = 19590J = 19.59kJ$
18.	(c)	If $\Delta G = -ve$ reaction is spontaneous.
20.	(b)	$(dS)_{V,E} > 0, (dG)_{T,P} < 0$.
21.	(b)	Only high pressure favours the conversion.
22.	(d)	By $2 \times (ii) - (i) - (iii)$
		$H_{2(g)} + 2C_{(s)} \rightarrow C_2 H_{2(g)}, \ \Delta G^{\circ} = 209 kJ .$
23.	(b)	$\Delta G = -2.303 RT \log K'$, Here $R = 2 cal$, $T = 300K$
		$K' = \frac{10 \times 15}{3 \times 5} = 10$; $\Delta G = -2.303 \times 2 \times 300 \times \log_{10} 10$
		$= -2.303 \times 2 \times 300 \times 1 = -1381.8 cal$
24.	(a)	$\Delta G = \Delta H - T \Delta S$ (Gibb's free energy equation)
25.	(d)	$\Delta G = \Delta H - T \Delta S$
		$\Delta G = -382.64 - (-145.6) \times 10^{-3} \times 298$
		$= -339.3 KJ mol^{-1}$
26.	(d)	$\Delta G = \Delta H - T \Delta S \; ; \; \Delta G = \Delta E + P \Delta V - T \Delta S$
		For spontaneity $(\Delta G = -ve)$
		$\therefore \Delta G = -ve \ , \ \Delta E = +ve$
27.	(a)	$\Delta G = \Delta H - T \Delta S = 31400 - 1273 \times 32$
		= 31400 - 40736 = -9336 cal
28.	(d)	$\Delta G = \Delta H - T \Delta S$
		$0 = +30.558 - T \times 0.066$
		or $T = \frac{30.558}{0.066} = 463K$
		If $(dG)_{T,P} = 0$ sign '=' mean. If is reversible process

Critical Thinking Questions

- 1. (b) Due to randomness of particles is reduced since entropy decreases.
- 2. (c) $\Delta H = n C p \Delta T$ The process is isothermal therefore $\Delta G = 0$; $\therefore \Delta H = 0$
 - (d) 13.7 $kcal = 57 kJ = 5.7 \times 10^4 J$.
- **4.** (b) When strong acid and strong base neutralize each other than the value of heat generated is about 13.7 *kcal*.
- 5. (b) Due to fall in temperature.

6. (d)
$$q_p = \Delta H$$
.

3.

7. (d)
$$w = 2.303 RT \log \frac{V_2}{V_1}$$
. As it involves the ratio $\frac{V_2}{V_1}$, volume can be used in any units. (R should be in joules).

8. (b)
$$-\frac{dQ}{dW} = \frac{dQ}{dQ - dE}$$
; $dE = dW + dQ$; $-dW = dQ - dE$
 $= \frac{nc_p dT}{nc dT - nc dT} = \frac{c_p}{(c_p - c_p)}$

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$$=\frac{7R}{2R}$$
 [for diatomic of gas $c_p = \frac{7R}{2}$]

(a)
$$C_2H_2(g) + H_2(g) \to C_2H_4(g)$$

9

 $\Delta ng = 1 - 2 = -1; \quad \Delta H = -0.31 \, KJ \, mol^{-1}$

 $P=1.5\,atm$, $\Delta V=-50\,mL=-0.050L$

 $\Delta H = \Delta E + P \Delta V$

 $-0.31 = \Delta E - 0.0076$; $\Delta E = -0.3024 \text{ KJ}$

 (a) Since process is exothermic then heat is evolved due to this temperature of water increases.

11. (a) Because randomness is decreases.

- 12. (c) Conversion of graphite into diamond is an endothermic reaction. So, heat of diamond is higher than that of graphite. But ΔS would be negative for the conversion of graphite into diamond.
- **13.** (c) ΔH and ΔS both are $+\upsilon e$ for spontaneous change, and $\Delta H = +\upsilon e$ for endothermic reaction.
- 14. (a) $\Delta G = \Delta H T \Delta S$ is negative for spontaneity.
- 15. (a) Entropy (a measure of disorder) of universe is increasing toward maximum. This is II law of thermodynamics.
- **16.** (a) For a pure substance T_A and T_B represent the same temperature. Hence A is a correct choice.
- **17.** (a) For endothermic reaction enthalpy of products (H_P) > enthalpy of reactant (H_P)

Hence, change in enthalpy,

 $\Delta H = H_P - H_R = \text{Positive}$

18. (d) Suppose the no. of gm, 1gm for each case so the max. no of mole expected for $SO_2(g)$ which has to expected maximum entropy.

19. (b)
$$2Al + \frac{3}{2}O_2 \to Al_2O_3$$
, $\Delta H = -1596 \, kJ$ (i)

$$2Cr + \frac{3}{2}O_2 \to Cr_2O_3, \ \Delta H = -1134 \, kJ$$
(ii)

A 1

20.

(a) Bomb calorimeter is used to measure heat of reaction.

 $2Al + Cr_2O_3 \rightarrow 2Cr + Al_2O_3, \Delta H = -462kJ.$

- **21.** (b) Larger the number of *C* and *H* atoms, greater is the heat of combustion.
- **22.** (c) The bomb calorimeter is used to measure ΔE .

23. (c)
$$\stackrel{\widehat{C}}{\underset{H}{\operatorname{ref}}}_{\operatorname{ref}}$$
 $\stackrel{\widehat{C}}{\underset{H}{\operatorname{ref}}}_{\operatorname{Energy}} \xrightarrow{E > \Delta H}$

24. (b)
$$\Delta H_{\text{Neutralization}} = -57.1 \, kJ = -13.7 \, kcal$$
.

25. (b) Backmann thermometer is used to measure low temperature.

- 26. (b) Heat required to rise the temperature of a body by 1K called thermal capacity of the body.
- **27.** (e) Mechanical work is important only in gases as they undergo appreciable change in volume.
- 28. (d) It is Lavoisier and Laplace law. This is another law of thermochemistry which was put forward before Hess's law.
- 29. (a) It is also known as "constant heat summation" law. It state that the total amount of heat evolved or absorbed in a reaction is same whether the reaction takes place in one step or in a number of steps.
- **30.** (c) In this reaction $\Delta n = 2 4 = -2$ so $\Delta H \neq \Delta E$.

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(a)
$$Q = \frac{18.94 \times 0.632 \times 0.998 \times 122}{1.89} = 771.1 \ Kcal$$

- **32.** (c) $\Delta H = E_a$ for forward reaction $-E_a$ for backward reaction = $19 - 9 = 10 \, kJ$.
- **33.** (d) $Q = 18.94 \times 0.632 \times 0.998 \times 1000$

$$-57.4 + x = -12.13$$

 $x = 45.2$

31.

34. (c) Thermodynamics is a reversible process in which surroundings are always equilibrium with system.

35. (a)
$$1 cal = 4.18 J = 4.18 \times 10^7 erg = \frac{4.18}{1.602} \times 10^{19} eV$$
.

- $\textbf{36.} \qquad (b) \quad \text{Order of bond energy}: \ Cl_2 > Br_2 > F_2 > I_2.$
- **37.** (c) Heat energy is also involved when one allotropic form of an element is converted in to another. graphite is the stabler allotrope because the heat of transformation of $C_{(diamond)} \rightarrow C_{(graphite)}$.
 - (i) $C_{(dia)} + O_{2(g)} = CO_{2(g)}\Delta H = -94.5kcal$
 - (ii) $C_{(graphite)} + O_{2(g)} = CO_{2(g)}\Delta H = -94.0 \, k \, cal$

 $\Delta H_{transformation} = -94.5 - (-94.0)$

 $= -0.5k \, cal$.

- **38.** (b) The compound Y possess less energy than the X and thus Y is more stable than X.
- **39.** (c) Both ΔH and Δp are positive.
- **40.** (a) For equilibrium $\Delta G^o = 0$.
- **41.** (b) Equilibrium constant is decreases with temperature and ΔH is also decreases so it is *-ve*.
- 42. (a) The fusion temperature of napthalene is minimum, because it is non-polar covalent compound and has less fusion temperature.
- **43.** (a) The bond energy of C H bond is y kcal mol^{-1} .

44. (a)
$$N \equiv N + 3H - H \longrightarrow 2N - H$$

Energy absorbed $\downarrow 2 \times (3 \times 391) = 2346$
Energy released

Net. energy released = 2346 - 2253 = 93 kJ

i.e.
$$\Delta H = -93 \ kJ$$

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- **45.** (d) If E = +ve than the cell reaction will be spontaneous.
- **46.** (d) All are the correct statements.
- **47.** (d) $CH_2 = CH_{2(g)} + H_{2(g)} \rightarrow H_3C CH_{3(g)}$ $414 \times 4 = 1656$ $414 \times 6 = 2484$
 - $615 \times 1 = 615$ $347 \times 1 = 347$

$$435 \times 1 = \frac{435}{2706}$$

- $\Delta H = 2706 2831 = -125 \, kJ$
- **48.** (b) It means that the heat absorbed when one gram molecule of HCl is formed from its elements at 298K is

= 22.060 k cal.

- **49.** (d) eq. (i) + eq. (ii) find the required result and divide by 2.
- 50. (d) For complete neutralization of strong acid and strong base energy released is 57.32 KJ / mol

No. of mole of
$$H_2SO_4 = \frac{0.2 \times 50}{1000} = 10^{-2}$$

No. of mole of
$$KOH = \frac{1}{1000} \times 50 = 5 \times 10^{-2}$$

So $= 57.32 \times 10^{-2} = 0.5732 \, KJ = 573.2 \, Joule$.

- **51.** (b) For Combustion reaction, ΔH is negative, $\Delta n = (16+18) - (25+2) = +7$, so ΔS is +ve, reaction is spontaneous, hence ΔG is -ve.
- **52.** (a) $\Delta G = \Delta H T \Delta S$, T = 27 + 273 = 300 K

 $\Delta G = (-285.8) - (300)(-0.163) = -236.9 \, kJ \, mol^{-1}$

Assertion & Reason

- **1.** (b) Assertion and reason show, reaction at equilibrium state in which $\Delta G = 0$, $\Delta S = 0$, $\Delta H = 0$.
- (b) It is correct that on touching the ice we feel cold because ice absorb heat from our hand.
- 3. (b) Entropy of ice is less than water because water molecules in solid state lose kinetic energy and hence their tendency of movement minimise. Hence entropy decrease in solid state. The reason that ice have cage like structure is also correct but reason is not or correct explanation for assertion.
- 4. (c) During isothermal expansion of an ideal gas against vacuum is zero because expansion is isothermal. The reason, that volume occupied by the molecules of an ideal gas is zero, is false.
- 5. (a) it is fact that absolute values of internal energy of substances can not be determined. It is also true that to determine exact values of constituent energies of the substance is impossible.
- **6.** (b) Mass and volume are extensive properties. mass/volume is also an extensive parameter. Here, both assertion and reason are true.
- 7. (b) The molar entropy of vaporization of water it differ from ethanol due to hydrogen bonding according to VSEPR theory water molecule having two lone pair of electron by which it

angular and show some polarity which is higher than that of ethanol so both assertion and reason are correct but reason is not explaination assertion.

- (a) The assertion that the increase in internal energy for the vaporisation of one mole of water at 1 *atm* and 373 *K* is zero is true and this is because that for all isothermal process internal energy is zero.
- (b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

8

9.

We know that $\Delta H = \Delta E + \Delta n R T$

 $\Delta n = 2 - 2 = 0$ hence, $\Delta nRT = 0$

Therefore, $\Delta H = \Delta E$

- 10. (a) The enthalpies of neutralisation of strong acids and strong bases are same they are 13.7 Kcal. The reason is that it is heat of formation of water from H^+ and OH^- ions. $H^+ + OH^- \rightarrow H_2O, \Delta H = 13.7 \ Kcal$. Thus, both assertion and reason are true.
- (a) Zeroth (law of temperature) can also be summarized as two objects at different temperature in thermal contact with each other tend to move towards the same temperature.
- 12. (d) Photo chemical reactions have $+ve \ \Delta G$.

- 14. (e) Heat absorbed in a reaction at constant temperature and constant volume (Qv) = E.
- 15. (c) Values of state functions depend only on the state of the system and not on how it is reached.
- 16. (a) The properties whose magnitude depends upon the quantity of matter present in the system are called extensive properties.
- 17. (c) Combustion reactions are always accompanied by the evolution of heat therefore, for such reactions the value of ΔH is always negative.

18. (b) In an isothermal process change in internal energy (ΔE) is zero (as it is a fucntion of temperature). \therefore According to first law of thermodynamics

 $\therefore q + w = \Delta E$, hence Q = -W (if $\Delta E = 0$)

If a system undergoes a change in which internal energy of the system remains constant (*i.e.*, $\Delta E=0$), then -W=Q.

This means that work done by the system equals the heat absorbed by the system.

- 20. (e) If a refrigerator's door is kept open room gets heated as heat energy is released to the surroundings.
- (c) Enthalpy is zero but entropy is not zero. Vibrational motion exists even at absolute zero.
- 22. (c) It may involve increase or decrease in temperature of the system. Systems in which such process occur, are thermally insulated from the surroundings.