

## CHEMICAL THERMODYNAMICS

### INTRODUCTION

- Identify the intensive quantity from the following -  
 (1) Enthalpy and temperature  
 (2) Volume and temperature  
 (3) Enthalpy and volume  
 (4) Temperature and refractive index
- Which of the following is an extensive property  
 (1) Mass (2) Enthalpy  
 (3) Energy (4) All of these
- For an adiabatic process which of the following relations is correct  
 (1)  $\Delta E = 0$  (2)  $P\Delta V = 0$   
 (3)  $q = 0$  (4)  $q = +W$
- In which of the following process work is independent of path :  
 (1) Isothermal (2) Isochoric  
 (3) Adiabatic (4) Isobaric
- Out of boiling point (I), entropy (II), pH (III) and emf of a cell (IV), intensive properties are :  
 (1) I, III, IV (2) I, II  
 (3) I, II, III (4) All of these
- Enthalpy of 1 mole monoatomic ideal gas is equals to :-  
 (1)  $\frac{3}{2}RT$  (2)  $\frac{5}{2}RT$  (3)  $RT$  (4)  $2RT$
- Which statement is true for reversible process :-  
 (1) It takes place in single step  
 (2) Driving force is much greater than opposing force  
 (3) Work obtain is minimum  
 (4) None

### FIRST LAW OF THERMODYNAMICS ( $\Delta E = q + W$ )

- If work done by the system is 300 joule when 100 cal. heat is supplied to it. The change in internal energy during the process is :-  
 (1) - 200 Joul (2) 400 Joul  
 (3) 720 Joul (4) 120 Joul
- A system has internal energy equal to  $E_1$ , 450 J of heat is taken out of it and 600 J of work is done on it. The final energy of the system will be -  
 (1) ( $E_1 + 150$ ) (2) ( $E_1 + 1050$ )  
 (3) ( $E_1 - 150$ ) (4) None of these

- The work done by a system is 8J when 40J heat is supplied to it. The change in internal energy of the system during the process :  
 (1) 32 J (2) 40 J (3) 48 J (4) -32 J

### ENTHALPY [ $\Delta H = \Delta E + P\Delta V$ / $\Delta H = \Delta E + \Delta n_g RT$ ]

- For a gaseous reaction,  
 $A(g) + 3B(g) \longrightarrow 3C(g) + 3D(g)$   
 $\Delta E$  is 17 kCal at 27°C assuming  $R = 2 \text{ Cal K}^{-1} \text{ mol}^{-1}$ , the value of  $\Delta H$  for the above reaction is:  
 (1) 15.8 Kcal (2) 18.2 Kcal  
 (3) 20.0 Kcal (4) 16.4 Kcal
- Which of the following statements is correct for the reaction;  $CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$  at constant temperature and pressure  
 (1)  $\Delta H = \Delta E$  (2)  $\Delta H < \Delta E$   
 (3)  $\Delta H > \Delta E$  (4) None of the above
- For the reaction  $Ag_2O(s) \longrightarrow 2Ag(s) + \frac{1}{2}O_2(g)$ , which one of the following is true :  
 (1)  $\Delta H = \Delta E$  (2)  $\Delta H = \frac{1}{2}\Delta E$   
 (3)  $\Delta H < \Delta E$  (4)  $\Delta H > \Delta E$
- For the reversible isothermal expansion of one mole of an ideal gas at 300 K, from a volume of 10 dm<sup>3</sup> to 20 dm<sup>3</sup>,  $\Delta H$  is -  
 (1) 1.73 kJ (2) -1.73 kJ  
 (3) 3.46 kJ (4) Zero
- The reaction :-  
 $NH_2CN_{(s)} + \frac{3}{2}O_{2(g)} \rightarrow N_{2(g)} + CO_{2(g)} + H_2O_{(l)}$   
 was carried out in a bomb calorimeter. The heat released was 743 kJ mol<sup>-1</sup>. The value of  $\Delta H_{300K}$  for this reaction would be :-  
 (1) - 740.5 kJ mol<sup>-1</sup> (2) - 741.75 kJ mol<sup>-1</sup>  
 (3) - 743.0 kJ mol<sup>-1</sup> (4) - 744.25 kJ mol<sup>-1</sup>
- The heat of combustion of ethanol determined in a bomb calorimeter is - 670.48 kCal mole<sup>-1</sup> at 27°C. What is  $\Delta H$  at 27°C for the reaction :-  
 (1) - 335.24 kCal (2) - 671.08 kCal  
 (3) - 670.48 kCal (4) + 670.48 kCal
- For which of the following reactions  $\Delta H$  is less than  $\Delta E$  :-  
 (1)  $C_{12}H_{22}O_{11}(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$   
 (2)  $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$   
 (3)  $N_2O_4(g) \rightarrow 2NO_2(g)$   
 (4)  $N_2(g) + O_2(g) \rightarrow 2NO(g)$

18. For a reaction  $2X(s) + 2Y(s) \rightarrow 2C(l) + D(g)$   
The  $q_p$  at  $27^\circ\text{C}$  is  $-28 \text{ kCal mol}^{-1}$ .  
The  $q_v$  is -----  $\text{kCal mol}^{-1}$  :-  
(1)  $-27.4$  (2)  $+27.4$   
(3)  $-28.6$  (4)  $28.6$

#### WORK DONE IN DIFFERENT PROCESS

19. The work done in ergs for a reversible expansion of one mole of an ideal gas from a volume of 10 litres to 20 litres at  $25^\circ\text{C}$  is :  
(1)  $-2.303 \times 8.31 \times 10^7 \times 298 \log 2$   
(2)  $-2.303 \times 0.0821 \times 298 \log 2$   
(3)  $-2.303 \times 0.0821 \times 298 \log 0.5$   
(4)  $-2.303 \times 2 \times 298 \log 2$
20. Two moles of an ideal gas expand spontaneously into vacuum. The work done is :-  
(1) Zero (2) 2 J (3) 4 J (4) 8 J
21. One mole of a gas occupying  $3 \text{ dm}^3$  expands against a constant external pressure of 1 atm to a volume of 13 lit. The workdone is :-  
(1)  $-10 \text{ atm dm}^3$  (2)  $-20 \text{ atm dm}^3$   
(3)  $-39 \text{ atm dm}^3$  (4)  $-48 \text{ atm dm}^3$

#### ENTROPY/SECOND LAW OF THERMODYNAMICS

22. An adiabatic reversible process is one in which :-  
(1) Temperature of the system does not change  
(2) The system is not closed to heat transfer  
(3) There is no entropy change  
(4) None of these
23. Entropy means  
(1) Disorderness (2) Randomness  
(3) Orderness (4) both 1 & 2
24. Change in entropy is negative for  
(1) Bromine (l)  $\rightarrow$  Bromine (g)  
(2)  $\text{C}(s) + \text{H}_2\text{O}(g) \rightarrow \text{CO}(g) + \text{H}_2(g)$   
(3)  $\text{N}_2(g, 10 \text{ atm}) \rightarrow \text{N}_2(g, 1 \text{ atm})$   
(4)  $\text{Fe}(at 400 \text{ K}) \rightarrow \text{Fe}(at 300 \text{ K})$
25. In which reaction  $\Delta S$  is positive :-  
(1)  $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(s)$   
(2)  $3\text{O}_2(g) \rightarrow 2\text{O}_3(g)$   
(3)  $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$   
(4)  $\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)$

26. The enthalpy of vaporization for water is  $186.5 \text{ kJ mol}^{-1}$ , the entropy of its vaporization will be -  
(1)  $0.5 \text{ kJ K}^{-1} \text{ mol}^{-1}$  (2)  $1.0 \text{ kJ K}^{-1} \text{ mole}^{-1}$   
(3)  $1.5 \text{ kJ K}^{-1} \text{ mole}^{-1}$  (4)  $2.0 \text{ kJ K}^{-1} \text{ mole}^{-1}$
27. If  $900 \text{ J/g}$  of heat is exchanged at boiling point of water, then what is increase in entropy?  
(1)  $43.4 \text{ JK}^{-1} \text{ mole}^{-1}$  (2)  $87.2 \text{ JK}^{-1} \text{ mole}^{-1}$   
(3)  $900 \text{ JK}^{-1} \text{ mole}^{-1}$  (4) Zero
28. In a spontaneous irreversible process the total entropy of the system and surroundings  
(1) Remains constant (2) Increases  
(3) Decreases (4) Zero
29. Calculate the entropy of  $\text{Br}_2(g)$  in the reaction  $\text{H}_2(g) + \text{Br}_2(g) \rightarrow 2\text{HBr}(g)$ ,  $\Delta S^\circ = 20.1 \text{ JK}^{-1}$  given, entropy of  $\text{H}_2$  and  $\text{HBr}$  is  $130.6$  and  $198.5 \text{ J mol}^{-1} \text{ K}^{-1}$  :-  
(1)  $246.3 \text{ JK}^{-1}$  (2)  $123.15 \text{ JK}^{-1}$   
(3)  $24.63 \text{ JK}^{-1}$  (4)  $20 \text{ KJK}^{-1}$
30. In which of the following case entropy decreases-  
(1) Solid changing to liquid  
(2) Expansion of a gas  
(3) Crystals dissolve  
(4) Polymerisation
31. Entropy of an adiabatic reversible process is:-  
(1) Positive (2) Zero  
(3) Negative (4) Constant

#### GIBBS FREE ENERGY

32. For a reaction at  $25^\circ\text{C}$  enthalpy change ( $\Delta H$ ) and entropy change ( $\Delta S$ ) are  $-11.7 \times 10^3 \text{ J mol}^{-1}$  and  $-105 \text{ J mol}^{-1} \text{ K}^{-1}$  respectively. The reaction is :  
(1) Spontaneous (2) Non spontaneous  
(3) At equilibrium (4) Can't say anything
33. If  $\Delta H > 0$  and  $\Delta S > 0$ , the reaction proceeds spontaneously when :-  
(1)  $\Delta H > 0$  (2)  $\Delta H < T \Delta S$   
(3)  $\Delta H = T \Delta S$  (4) None
34. The enthalpy change for a given reaction at  $298 \text{ K}$  is  $-x \text{ cal mol}^{-1}$ . If the reaction occurs spontaneously at  $298 \text{ K}$ , the entropy change at that temperature  
(1) Can be negative but numerically larger than  $x/298 \text{ Cal K}^{-1} \text{ mol}^{-1}$   
(2) Can be negative but numerically smaller than  $x/298 \text{ Cal K}^{-1} \text{ mol}^{-1}$   
(3) Cannot be negative  
(4) Cannot be positive

- 35.** For the reaction  $\text{Ag}_2\text{O(s)} \longrightarrow 2\text{Ag(s)} + \frac{1}{2} \text{O}_2\text{(g)}$  the value of  $\Delta H = 30.56 \text{ kJ mol}^{-1}$  and  $\Delta S = 66 \text{ JK}^{-1} \text{ mol}^{-1}$ . The temperature at which the free energy change for the reaction will be zero is :-  
 (1) 373 K (2) 413 K  
 (3) 463 K (4) 493 K
- 36.** What is the free energy change  $\Delta G$ , when 1.0 mole of water at  $100^\circ\text{C}$  and 1 atm pressure is converted into steam at  $100^\circ\text{C}$  and 1 atm pressure :-  
 (1) 540 Cal (2) -9800 Cal  
 (3) 9800 Cal (4) 0 Cal
- 37.** The Vant Hoff equation is :  
 (1)  $\Delta G^\circ = RT \log_e K_p$  (2)  $-\Delta G^\circ = RT \log_e K_p$   
 (3)  $\Delta G^\circ = RT^2 \ln K_p$  (4) None
- 38.** The Gibbs free energy change of a reaction at  $27^\circ\text{C}$  is  $-26 \text{ kCal}$ . and its entropy change is  $-60 \text{ Cals K}$ .  $\Delta H$  for the reaction is :-  
 (1)  $-44 \text{ kCals}$ . (2)  $-18 \text{ kCals}$ .  
 (3)  $34 \text{ kals}$ . (4)  $-24 \text{ kCals}$ .

#### HESS LAW

- 39.** Given  $\text{C(s)} + \text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)} + 94.2 \text{ kCal}$   
 $\text{H}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \longrightarrow \text{H}_2\text{O(l)} + 68.3 \text{ kCal}$   
 $\text{CH}_4\text{(g)} + 2\text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)} + 2\text{H}_2\text{O(l)} + 210.8 \text{ kCal}$   
 The heat of formation of methane in Kcal will be  
 (1)  $-45.9$  (2)  $-47.8$   
 (3)  $-20.0$  (4)  $-47.3$
- 40.** If,  $\text{H}_2\text{(g)} + \text{Cl}_2\text{(g)} \longrightarrow 2\text{HCl(g)} ; \Delta H^\circ = -44 \text{ kCal}$   
 $2\text{Na(s)} + 2\text{HCl(g)} \longrightarrow 2\text{NaCl(s)} + \text{H}_2\text{(g)} ;$   
 $\Delta H = -152 \text{ kCal}$   
 Then,  $\text{Na(s)} + 0.5 \text{ Cl}_2\text{(g)} \longrightarrow \text{NaCl(s)} ; \Delta H^\circ = ?$   
 (1)  $108 \text{ kCal}$  (2)  $196 \text{ kCal}$   
 (3)  $-98 \text{ kCal}$  (4)  $54 \text{ kCal}$
- 41.** If  $\text{S} + \text{O}_2 \longrightarrow \text{SO}_2 ; \Delta H = -298.2$   
 $\text{SO}_2 + \frac{1}{2} \text{O}_2 \longrightarrow \text{SO}_3 ; \Delta H = -98.7$   
 $\text{SO}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4 ; \Delta H = -130.2$   
 $\text{H}_2 + \frac{1}{2} \text{O}_2 \longrightarrow \text{H}_2\text{O} ; \Delta H = -287.3$   
 Then the enthalpy of formation of  $\text{H}_2\text{SO}_4$  at  $298 \text{ K}$  is -  
 (1)  $-814.4 \text{ kJ}$  (2)  $-650.3 \text{ kJ}$   
 (3)  $-320.5 \text{ kJ}$  (4)  $-433.5 \text{ kJ}$
- 42.** Given that :  
 $\text{Zn} + \frac{1}{2} \text{O}_2 \rightarrow \text{ZnO} + 84000 \text{ Cal} \dots\dots\dots 1$   
 $\text{Hg} + \frac{1}{2} \text{O}_2 \rightarrow \text{HgO} + 21700 \text{ Cal} \dots\dots\dots 2$   
 The heat of reaction ( $\Delta H$ ) for,  
 $\text{Zn} + \text{HgO} \rightarrow \text{ZnO} + \text{Hg}$  is :-  
 (1)  $105700 \text{ Cal}$  (2)  $62300 \text{ Cal}$   
 (3)  $-105700 \text{ Cal}$  (4)  $-62300 \text{ Cal}$
- 43.** The heat of reaction for  
 $\text{A} + \frac{1}{2} \text{O}_2 \rightarrow \text{AO}$  is  $-50 \text{ kCal}$  and  
 $\text{AO} + \frac{1}{2} \text{O}_2 \rightarrow \text{AO}_2$  is  $100 \text{ kCal}$ .  
 The heat of reaction for  $\text{A} + \text{O}_2 \rightarrow \text{AO}_2$  is:-  
 (1)  $-50 \text{ kCal}$  (2)  $+50 \text{ kCal}$   
 (3)  $100 \text{ kCal}$  (4)  $150 \text{ kCal}$
- 44.** Using the following thermochemical data:  
 $\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}, \Delta H = -94.0 \text{ kCal}$   
 $\text{H}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{H}_2\text{O(l)}, \Delta H = -68.0 \text{ kCal}$   
 $\text{CH}_3\text{COOH(l)} + 2\text{O}_2\text{(g)} \rightarrow 2\text{CO}_2\text{(g)} + 2\text{H}_2\text{O(l)},$   
 $\Delta H = -210.0 \text{ kCal}$   
 The heat of formation of acetic acid is:-  
 (1)  $116.0 \text{ kCal}$  (2)  $-116.0 \text{ kCal}$   
 (3)  $-114.0 \text{ kCal}$  (4)  $+114.0 \text{ kCal}$
- 45.**  $\text{H}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} = \text{H}_2\text{O(l)} ; \Delta H_{298\text{K}} = -68.32 \text{ kCal}$ .  
 Heat of vapourisation of water at 1 atm and  $25^\circ\text{C}$  is  $10.52 \text{ kCal}$ . The standard heat of formation (in kCal) of 1 mole of water vapour at  $25^\circ\text{C}$  is  
 (1)  $10.52$  (2)  $-78.84$   
 (3)  $+57.80$  (4)  $-57.80$
- 46.** The heat of solution of anhydrous  $\text{CuSO}_4$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  are  $-15.89$  and  $2.80 \text{ kCal mol}^{-1}$  respectively. What will be the heat of hydration of anhydrous  $\text{CuSO}_4$  ?  
 (1)  $-18.69 \text{ kCal}$  (2)  $18.69 \text{ kCal}$   
 (3)  $-28.96 \text{ kCal}$  (4)  $28.96 \text{ kCal}$
- 47.** Which of the following expressions is true:-  
 (1)  $H_f^\circ(\text{CO,g}) = \frac{1}{2} \Delta H_f^\circ(\text{CO}_2\text{g})$   
 (2)  $\Delta H_f^\circ(\text{CO,g}) = \Delta H_f^\circ(\text{C,graphite}) + \frac{1}{2} \Delta H_f^\circ(\text{O}_2\text{g})$   
 (3)  $\Delta H_f^\circ(\text{CO,g}) = \Delta H_f^\circ(\text{CO}_2\text{g}) - \frac{1}{2} \Delta H_f^\circ(\text{O}_2\text{g})$   
 (4)  $\Delta H_f^\circ(\text{CO,g}) = \Delta H_{\text{comb}}^\circ(\text{C,graphite}) - \Delta H_{\text{comb}}^\circ(\text{CO,g})$

ANSWER KEY

## CHEMICAL THERMODYNAMICS

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Ans.	4	4	3	3	1	2	4	4	1	1	2	2	4	4	2	2	2	3	1	1
Que.	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
Ans.	1	3	4	4	3	1	1	2	1	4	4	2	2	2	3	4	2	1	3	3
Que.	41	42	43	44	45	46	47													
Ans.	1	4	2	3	4	1	4													

# SOLUTION

- Intensive quantity : Properties that does not depends upon amount ie Temperature, Refractive index
- Extensive properties depends upon amount of matter. ie mass, enthalpy, energy etc.
- For adiabatic process  $q = 0$
- For adiabatic process  $q = 0$   

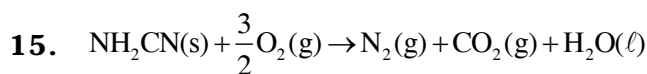
$$\omega = \Delta U = nC_v\Delta T$$
- Intensive properties : Boiling point, pH, emf of cell.
- 1 mole mono atomic ideal gas

$$\Delta H = nC_p\Delta T = 1 \times \frac{5}{2} R \Delta T$$

$$= \frac{5}{2} RT$$

- Reversible process take place in  $\infty$  step. Driving force is almost equal to opposing force and work obtained maximum.
- $\Delta U = q + w$   
 $= (100\text{Cal}) + (-300 \text{ Joule})$   
 $= (100 \times 4.2 \text{ joule}) - 300 \text{ joule}$   
 $= 120 \text{ Joule}$
- $\Delta U = q + \omega$   
 $E_2 - E_1 = (-450\text{J}) + (+600\text{J})$   
 $E_2 = E_1 + 150$
- $\Delta U = q + \omega$   
 $= (+40\text{J}) + (-8\text{J})$   
 $= 32 \text{ J}$
- $A(g) + 3B(g) \rightarrow 3C(g) + 3D(g)$   
 $\Delta n_g = 3 + 3 - 1 - 3 = 2$   
 $\Delta H = \Delta U + \Delta n_g RT$   
 $= 17\text{Kcal} + (2) \times 2 \times 10^{-3} \text{ Kcal} \times 300$   
 $= 18.2 \text{ Kcal}$
- $CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g)$   
 $\Delta H = \Delta E + \Delta n_g RT$   
 $\Delta H = \Delta E - \frac{1}{2} RT$   
 $\Delta H < \Delta E$
- $Ag_2O(s) \longrightarrow 2Ag(s) + \frac{1}{2} O_2(g); \Delta n_g = \frac{1}{2}$   
 $\Delta H = \Delta E + \Delta n_g RT$   
 $\Delta H = \Delta E + \frac{1}{2} \times RT, \Delta H > \Delta E$

- For isothermal ideal gas  
 $\Delta H = nC_p\Delta T = 0 \quad (\Delta T = 0)$



$$\Delta n_g = 1 + 1 - \frac{3}{2} = \frac{1}{2}$$

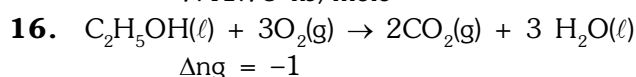
Bomb calorimeter means

$$\Delta E = -743 \text{ kJ/mole}$$

$$\Delta H = \Delta E + \Delta n_g RT$$

$$= -743\text{kJ} + \frac{1}{2} \times 8.314 \times 10^{-3} \text{ kJ} \times 300$$

$$= -741.75 \text{ kJ/mole}$$



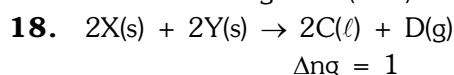
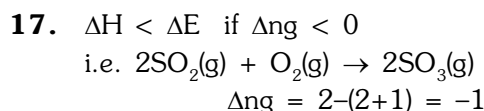
Bomb calorimeter means

$$\Delta E = -670.48 \text{ kcal/mole}$$

$$\Delta H = \Delta E + \Delta n_g RT$$

$$= -670.48 \text{ kcal} - 1 \times 2 \times 10^{-3} \text{ kcal} \times 300$$

$$= -671.08 \text{ kcal/mole}$$



$$\Delta H = \Delta E + \Delta n_g RT$$

$$q_p = q_v + (1) \times 2 \times 10^{-3} \text{ kcal} \times 300$$

$$q_v = q_p - 0.6 \text{ KCal}$$

$$= -28 \text{ kcal} - 0.6 \text{ Kcal}$$

$$= -28.6 \text{ Kcal}$$

$$19. \quad W_{\text{rev}}(\text{isothermal}) = -nRT \ln \left( \frac{v_2}{v_1} \right)$$

$$= -1 \times 8.31 \times 10^7 \text{ ergs} \times 298. \ln \left( \frac{20}{10} \right)$$

$$= -2.303 \times 8.31 \times 10^7 \times 298. \ln(2) \text{ ergs}$$

$$20. \quad w(\text{vacuum}) = 0$$

$$21. \quad w_{\text{isobaric}} = -p_{\text{ext}}(v_2 - v_1)$$

$$= -1\text{atm} (13 \text{ lit} - 3\text{lit})$$

$$= -10 \text{ lit atm}$$

$$= -10 \text{ atm dm}^3 (1\text{dm}^3 = 1 \text{ lit})$$

$$22. \quad \text{Adiabatic reversible process} \quad q = 0$$

$$\Delta S = 0$$

23. Entropy means dis orderness or randomness

$$24. \quad \Delta S < 0 \quad \text{if } \Delta n_g < 0 \text{ for reaction}$$

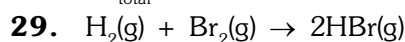
$$P \uparrow \text{ or } T \downarrow \text{ for state change}$$

- 25.**  $\Delta S > 0$  if  $\Delta_{\text{ng}} > 0$  for reaction or melting occurs.

**26.** 
$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_{\text{BP}}} = \frac{186.5 \text{ kJ}}{373} = 0.5 \text{ kJ / mole-K}$$

$$\begin{aligned}\Delta S_{\text{H}_2\text{O}}(\text{at B.P.}) &= \frac{\Delta H_{\text{vap}}}{T_{\text{BP}}} = \frac{9000 \text{ J / gm}}{373 \text{ K}} \\ &= \frac{9000 \times 18}{373 \text{ K}} \text{ J / mole} \\ &= 43.4 \text{ J/mole-K}\end{aligned}$$

- 28.**  $\Delta S_{\text{total}}$  (irreversible)  $> 0$



$$\Delta S_{\text{Re}^n}^{\circ} = \sum S_{\text{p}}^{\circ} - \sum S_{\text{R}}^{\circ}$$

$$20.1 \text{ J/k} = S_{\text{H}_2}^{\circ} + S_{\text{Br}_2}^{\circ} - 2 \times S_{\text{HBr}}^{\circ}$$

$$20.1 = 130.6 + S_{\text{Br}_2}^{\circ} - 2 \times 198.5$$

$$S_{\text{Br}_2}^{\circ} = 246.3 \text{ JK}^{-1}$$

- 30.** In polymerisation entropy decreases

- 31.** Adiabatic reversible process

$$\Delta S_{\text{total}} = 0$$

means entropy remains constant.

**32.** 
$$\begin{aligned}\Delta G &= \Delta H - T \cdot \Delta S \\ &= -11.7 \times 10^3 \text{ J} - 298 \times -105 \text{ J} \\ &= -11700 + 298 \times 105 \\ &> 0\end{aligned}$$

So non spontaneous.

**33.** 
$$\begin{aligned}\Delta G &= \Delta H - T \cdot \Delta S \\ \text{given } \Delta H &> 0 \\ \Delta S &> 0\end{aligned}$$

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

$\Delta G$  will be -ve if  $\Delta H < T \cdot \Delta S$

- 34.** For spontaneous process

$$\Delta G < 0$$

$$\Delta H - T \cdot \Delta S < 0$$

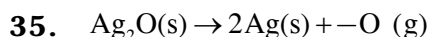
$$(-x) - 298 \cdot \Delta S < 0$$

$$-298 \cdot \Delta S < +x$$

$$\Delta S > \left( \frac{-x}{298} \right)$$

$\Delta S$  can be -ve but numerically

smaller than  $\frac{x}{298} \text{ cal/k}$



$$\Delta G = 0$$

$$\Delta H - T \cdot \Delta S = 0$$

$$T = \frac{\Delta H}{\Delta S} = \frac{30.56 \times 10^3 \text{ J}}{66 \text{ J / k}}$$

$$T = 463 \text{ K}$$



1mole                      1mole

(1atm, 100°C)    (1atm, 100°C)

Reversible phase transfer take place at equilibrium so  $\Delta G = 0$

- 37.** Vant Haff equation is

$$\Delta G^{\circ} = -RT \ln K_p$$

**38.**  $\Delta G = \Delta H - T \cdot \Delta S$

$$-26 \times 10^3 \text{ cal} = \Delta H - 300 \times 60 \text{ cal/k}$$

$$\Delta H = -26000 \text{ cal} - 18000 \text{ cal}$$

$$= -44 \text{ Kcal}$$

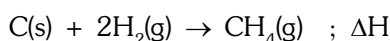
- 39.** From given reaction it can be easily predicted that

$$\Delta H_f(\text{CO}_2) = \Delta H_c(\text{C}) = -94.2 \text{ Kcal}$$

$$\Delta H_f(\text{H}_2\text{O}) = \Delta H_c(\text{H}_2) = -68.3 \text{ Kcal}$$

$$\Delta H_c(\text{CH}_4) = -210.8 \text{ Kcal}$$

Now heat of formation of  $\text{CH}_4$



$$\Delta H_f(\text{CH}_4) = \Delta H$$

$$= \sum H_c(\text{R}) - \sum H_c(\text{P})$$

$$= \Delta H_c(\text{C}) + 2 \times \Delta H_c(\text{H}_2) - \Delta H_c(\text{CH}_4)$$

$$= -94.2 + 2 \times -68.3 - (-210.8)$$

$$= -20 \text{ kcal}$$

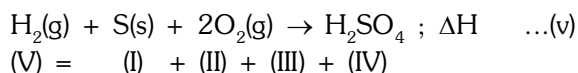
- 40.** From given equation

$$\text{(III)} = \frac{\text{(II)}}{2} + \frac{\text{(I)}}{2}$$

$$\Delta H^{\circ} = \left( \frac{-44}{2} \right) + \left( \frac{-152}{2} \right)$$

$$= -22 - 76$$

$$= -98 \text{ Kcal}$$

**41.** Enthalpy of formation of  $\text{H}_2\text{SO}_4$ 

$$\Delta H = -298.2 - 98.7 - 130.2 - 287.3$$

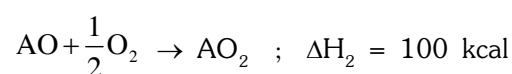
$$\Delta H = -814.4 \text{ kJ} = \Delta H_f(\text{H}_2\text{SO}_4).$$

**42.** From given equation

$$(\text{III}) = (\text{I}) - (\text{II})$$

$$\Delta G = -84000 - (-21700)$$

$$= -62300 \text{ cal.}$$

**43.**  $\text{A} + \frac{1}{2}\text{O}_2 \rightarrow \text{AO} ; \Delta H_1 = -50 \text{ kcal}$ 

$$(\text{III}) = (\text{I}) + (\text{II})$$

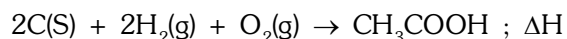
$$\Delta H = -50 + 100 = +50 \text{ kcal}$$

**44.** from given reaction

$$\Delta H_f(\text{CO}_2) = \Delta H_c(\text{C}) = -94 \text{ kcal}$$

$$\Delta H_f(\text{H}_2\text{O}) = \Delta H_c(\text{H}_2) = -68 \text{ kcal}$$

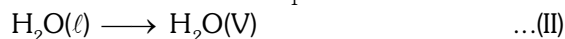
$$\Delta H_c(\text{CH}_3\text{COOH}) = -210 \text{ kcal}$$

Heat of formation of  $\text{CH}_3\text{COOH}$ 

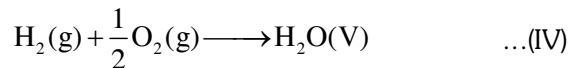
$$\begin{aligned} \Delta H_f(\text{CH}_3\text{COOH}) &= \Delta H = \Sigma \Delta H_c(\text{R}) - \Sigma \Delta H_c(\text{P}) \\ &= 2 \times -94 + 2 \times -68 + 0 - (-210) \\ &= -114 \text{ Kcal} \end{aligned}$$

**45.**  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\ell) \quad \dots(\text{I})$ 

$$\Delta H_1 = -68.32 \text{ kcal}$$



$$\Delta H_2 = 10.52 \text{ kcal}$$



$$\Delta H = \Delta H_f(\text{H}_2\text{O}(\text{v}))$$

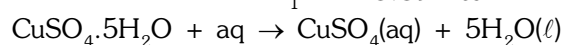
$$(\text{III}) = (\text{I}) + (\text{II})$$

$$\Delta H_f(\text{H}_2\text{O}(\text{v})) = -68.32 + 10.52$$

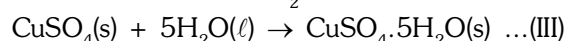
$$= -57.80 \text{ Kcal}$$

**46.**  $\text{CuSO}_4 + \text{aq} \rightarrow \text{CuSO}_4(\text{aq}) \quad \dots(\text{I})$ 

$$\Delta H_1 = -15.89 \text{ kcal}$$



$$\Delta H_2 = +2.80 \text{ kcal}$$

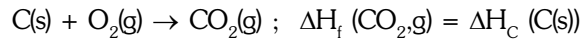


$$\Delta H.$$

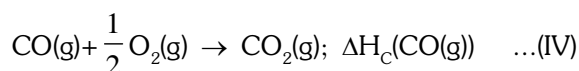
$$(\text{III}) = (\text{I}) - (\text{II})$$

$$\Delta H = -15.89 - 2.80$$

$$= -18.69 \text{ kcal}$$

**47.**  $\text{C}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g}); \Delta H_f = (\text{CO}, \text{g}) \quad \dots(\text{I})$ 

$$\Delta H_f(\text{O}_2(\text{g})) = 0 \quad \dots(\text{III})$$



$$(\text{I}) + (\text{IV}) = (\text{II})$$

$$\Delta H_f(\text{CO}(\text{g})) + \Delta H_c(\text{CO}(\text{g})) = \Delta H_c(\text{C}(\text{s}))$$