

## THERMODYNAMICS-2

### 1) Hess's law states that

- 1) The standard enthalpy of an overall reaction is the sum of the enthalpy changes in individual reaction
- 2) enthalpy of formation of compound is same as the enthalpy of decomposition of the compound into constituent elements, but with opposite sign
- 3) at constant temperature the pressure of a gas is inversely proportional to its volume.
- 4) the mass of a gas dissolved per lit of a solvent is proportional to the pressure of the gas in equilibrium with the solution

### 2.) For change in entropy units are

- 1) mol/lit
- 2) Mol. lit<sup>-1</sup> sec<sup>-1</sup>
- 3) J. mol<sup>-1</sup> K<sup>-1</sup>
- 4) s<sup>-1</sup>

### 3). In standard state the non spontaneous reaction is

- 1) Melting of ice
- 2) Natural radioactivity
- 3) Freezing of water
- 4) Rusting of iron

### 4) The incorrect statement according to second law of thermodynamics is

- 1) Heat can't flow from colder body to a hotter body on its own
- 2) All spontaneous processes are thermodynamically irreversible
- 3) Heat can be converted into work completely without causing some permanent change in the system (or) surroundings
- 4) Perpetual motion machine of second kind is not possible

### 5). Incorrect statement related to an irreversible process is

- 1) Entropy of the universe goes on increasing
- 2) Gibbs energy of the system goes on decreasing
- 3) Total energy of the universe goes on decreasing
- 4) Total energy of the universe remain constant

### 6). Entropy of a system depends upon

- 1) Volume only
- 2) Temperature only
- 3) Pressure only
- 4) Pressure, Volume and temperature

### 7). One of the following reaction involves in decrease of entropy

- 1) Sublimation of dry ice
- 2) Crystallisation of salt from brine (aq)
- 3) Burning of rocket fuel
- 4) Decomposition of gaseous N<sub>2</sub>O<sub>4</sub>.

### 8. The least random state of H<sub>2</sub>O system is

- 1) Ice
- 2) Liquid water
- 3) Steam
- 4) Randomness is same all.

### 9. Which of the following process has negative value of $\Delta S$ ?

- 1) Dissolution of sugar in water
- 2) Stretching of rubber band
- 3) Decomposition of lime stone
- 4) Evaporation of water

### 10 For the reaction $\cdot \text{Iodine(g)} \rightarrow \text{Iodine(s)}$ , $\Delta H = -Ve$ Then choose the correct statement/s from the following

- a) The process is spontaneous at all temperatures
- b) The process is accompanied by an increase in entropy
- c) The process is accompanied by a decrease in entropy
- d) The process is accompanied by a decrease in enthalpy

The correct statements are

- 1) Only a, b and c
- 2) Only b and d
- 3) Only c and d
- 4) Only a, c and d

### 11. For a spontaneous process in a reaction

- 1)  $\Delta S_{\text{total}} = (\Delta S_{\text{system}} + \Delta S_{\text{surroundings}}) < 0$
- 2)  $\Delta S_{\text{total}} = (\Delta S_{\text{system}} + \Delta S_{\text{surroundings}}) = 0$
- 3)  $\Delta S_{\text{total}} = (\Delta S_{\text{system}} + \Delta S_{\text{surroundings}}) > 0$
- 4)  $\Delta S_{\text{sys}} > 0$  only

12. Some statements are given with regard to entropy. The incorrect statements are  
 A) The absolute entropy of substances cannot be determined  
 B) In standard state entropy of elements is always positive  
 C) The entropy of universe always decreases  
 D) In a spontaneous process, for Isolated system the entropy of a system generally increases  
 1) A, B2) B, C3) A, C4) Only C

13. For an irreversible process, the value of  $[\Delta S_{\text{sys}} + \Delta S_{\text{surrounding}}]$  is  
 1)  $>0$  2)  $<0$  3) 0 4)  $2\Delta S_{\text{sys}}$

14.  $2\text{H}_{2(g)} + \text{O}_{2(g)} \rightarrow 2\text{H}_2\text{O}_{(l)}$   $\Delta H = -ve$  and  $\Delta G = -ve$  Then the reaction is  
 1) Spontaneous and instantaneous 2) Spontaneous and endothermic  
 3) Spontaneous and slow 4) Non spontaneous and slow

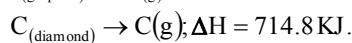
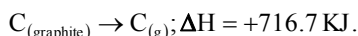
15. What is necessary condition for spontaneity of a process?  
 1)  $\Delta S > 0$  2)  $\Delta E < 0$  3)  $\Delta H < 0$  4)  $\Delta G < 0$

16. Based on the third law of thermodynamics, the entropy can be obtained using the equation.

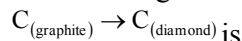
1)  $\Delta S = \frac{\Delta H}{T}$  2)  $\int_0^T C_p^{-1} dT = S$   
 3)  $\Delta G = T\Delta S$  4)  $\int_0^T C_p T^{-1} dT = S$

17. The process of evaporation of a liquid is accompanied by  
 a) Increase in enthalpy  
 b) Increase in entropy  
 c) Decrease in Gibbs energy  
 The correct statement (s) is or are  
 1) Only a and c 2) Only b and c 3) Only a and b 4) All

18. Given that



The  $\Delta H$  for the following reaction



- 1) 1.9 KJ 2) -1.9 KJ 3) Zero 4) 714.8 KJ

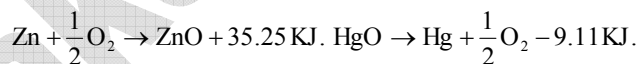
Solution:  $\Delta H = \text{Equation 1} - \text{equation 2} = 716.7 - 714.8 = 1.9 \text{ KJ}$

19. At  $25^\circ\text{C}$  the heat of formation of  $\text{H}_2\text{O} (l)$  is  $-285.9 \text{ KJ mole}^{-1}$  and that for  $\text{H}_2\text{O} (g)$  is  $-242.8 \text{ KJ mole}^{-1}$ . The heat of vaporization of water at the same temperature is

- 1)  $43.1 \text{ KJ mole}^{-1}$  2)  $242.8 \text{ KJ mole}^{-1}$  3)  $-43.1 \text{ KJ mole}^{-1}$  4)  $-242.8 \text{ KJ mole}^{-1}$

Solution:  $\text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{O}_{(g)}$ ,  $\Delta H = H_p - H_R = -242.8 - (-285.9) = +43.1 \text{ KJ}$

20. Given that

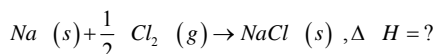
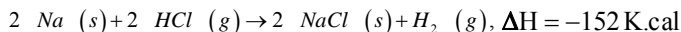


The heat of the reaction  $\text{Zn} + \text{HgO} \rightarrow \text{ZnO} + \text{Hg}$  is

- 1) -26.14 KJ 2) 44.39 KJ 3) -44.39 KJ 4) 26.14 KJ

Solution: The  $\Delta H$  for the reaction  $= E_{q1} + E_{q2} = \text{Zn} + \text{HgO} \rightarrow \text{ZnO} + \text{Hg} + 26.14 \text{ KJ}$   
 Therefore  $\Delta H = -26.14 \text{ KJ}$

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- 1) +108 K.cal      2) -196 K.cal      3) -98 K.cal      4) 50 K.cal

Solution:  $\Delta H = 1/2[\text{Eq1} + \text{Eq2}] = 1/2[-44 - 152] = -98 \text{ K.cal}$

22. If the heats of formation of  $CO_2(g)$ ,  $H_2O(l)$  and  $CH_4(g)$  are  $-394 \text{ kJ mol}^{-1}$ ,  $-286 \text{ kJ mol}^{-1}$  and  $-76 \text{ kJ mol}^{-1}$  respectively then the heat of combustion of methane is

- 1) +1042KJ/mole      2) +890KJ/mole      3) -890KJ/mole      4) -1042KJ/mole

Solution : ; The required equation is ,  $CH_4(g) + 2O_2(l) \rightarrow CO_2(g) + 2H_2O(l)$  ;  $\Delta H = ?$

$$\Delta H = \text{Heat of formation of Products} - \text{Heat of formation of Reactants}$$

$$= [-394 + 2(-286)] - (-76) = -890 \text{ kJ.}$$

The heat of combustion of methane =  $-890 \text{ kJ mol}^{-1}$ .

23. The enthalpy of combustion of  $H_{2(g)}$  to give  $H_2O_{(g)}$  is  $-249 \text{ KJ mol}^{-1}$  and bond enthalpies of H-H and O=O are  $433 \text{ KJ mol}^{-1}$  and  $492 \text{ KJ mol}^{-1}$  respectively, The bond enthalpy of O-H is

- 1)  $464 \text{ KJ mol}^{-1}$       2)  $-464 \text{ KJ mol}^{-1}$       3)  $232 \text{ KJ mol}^{-1}$       4)  $-232 \text{ KJ mol}^{-1}$

Solution: required equation is  $H_2 + 1/2 O_2 \rightarrow H_2O$ ,  $\Delta H = -249 \text{ KJ mol}^{-1}$

$$\Delta H = 1(\text{H-H}) + 1/2(\text{O=O}) - 2(\text{O-H}) = -249 \text{ KJ/mol}$$

$$= 433 + 1/2(492) - 2(\text{O-H}) = -249$$

$$\text{O-H bond enthalpy} = 464 \text{ KJ/mole}$$

24 If at 298K the bond energies of  $C-H$ ,  $C-C$ ,  $C=C$  and H-H bonds are respectively 414, 347, 615 and  $435 \text{ kJ mol}^{-1}$ , the value of enthalpy change for the reaction  $H_2C=CH_2(g) + H_2(g) \rightarrow H_3C-CH_3(g)$  at 298 K will be

- (1) - 250 kJ      (2) + 125 kJ      (3) - 125 kJ      (4) + 250 kJ

Solution:  $CH_2=CH_2(g) + H_2(g) \rightarrow CH_3-CH_3$

$$\Delta H = 1(\text{C=C}) + 4(\text{C-H}) + 1(\text{H-H}) - 1(\text{C-C}) - 6(\text{C-H})$$

$$= 1(\text{C=C}) + 1(\text{H-H}) - 1(\text{C-C}) - 2(\text{C-H})$$

$$= 615 + 435 - 347 - 2 \times 414 = 1050 - 1175 = -125 \text{ kJ.}$$

25. The enthalpies of combustion of carbon and carbon monoxide are  $-393.5$  and  $-283 \text{ kJ mol}^{-1}$  respectively. The enthalpy of formation of carbon monoxide per mole is

- (1)  $-676.5 \text{ kJ}$       (2)  $676.5 \text{ kJ}$       (3)  $110.5 \text{ kJ}$       (4)  $-110.5 \text{ kJ}$

Solution: i)  $C + O_2 \rightarrow CO_2$ ,  $\Delta H = -393 \text{ KJ/mole}$

ii)  $CO + 1/2 O_2 \rightarrow CO_2$ ,  $\Delta H = -283 \text{ KJ/mole}$

After, (i) - (ii),

$$\text{We have } C + \frac{1}{2} O_2 \rightarrow CO \quad \Delta H = -110.5 \text{ kJ mol}^{-1}$$

26. The entropy change for the conversion of 1 mole of  $\alpha$ -tin (at  $35^\circ\text{C}$ , 2 atm) to 1 mole of  $\beta$ -tin ( $35^\circ\text{C}$ , 2 atm) if the enthalpy of transition is  $2.095 \text{ KJ mol}^{-1}$

- 1)  $7.32 \text{ J mol}^{-1} \text{ K}^{-1}$       2)  $14.62 \text{ J K mol}^{-1}$       3)  $56. \text{ J mol}^{-1} \text{ K}^{-1}$       4)  $28.64 \text{ J mol}^{-1} \text{ K}^{-1}$

Solution:  $\Delta S = \frac{\Delta H}{T}$ ,  $T = 273 + 13 = 286 \text{ K}$

$$\Delta S = 2.095 \times 1000 \text{ J mol}^{-1} / 286 \text{ K} = 7.32 \text{ J mol}^{-1} \text{ K}^{-1}$$

27.  $\Delta H$  (vap) for water is  $40.7 \text{ KJ mol}^{-1}$ . The entropy of vapourisation of water is  
 1)  $-40.7 \text{ KJ mol}^{-1}$     2)  $407 \text{ J mol}^{-1} \text{K}^{-1}$     3)  $109 \text{ J mol}^{-1} \text{K}^{-1}$     4)  $722 \text{ J mol}^{-1}$

solution:  $\Delta S = \Delta H/T = 40.7 \times 1000 \text{ J mole}^{-1} / 373 \text{ K} = 109 \text{ J mol}^{-1} \text{K}^{-1}$

28. The following data is known about the melting of a compound AB.  $\Delta H = 9.2 \text{ KJ mol}^{-1}$   $\Delta S = 0.008 \text{ KJK}^{-1} \text{ mol}^{-1}$ . Its melting point is  
 1)  $736 \text{ K}$     2)  $1050 \text{ K}$     3)  $1150 \text{ K}$     4)  $1150^\circ \text{C}$

Solution:  $T = (\Delta H/\Delta S) = 9.2/0.008 = 9200/8 = 1150 \text{ K}$

29. For the process  $\text{CO}_2(\text{s}) \rightarrow \text{CO}_2(\text{g})$

- 1) Both  $\Delta H$  and  $\Delta S$  are +ve    2)  $\Delta H$  is -ve,  $\Delta S$  is +ve  
 3)  $\Delta H$  is +ve,  $\Delta S$  is -ve    4) Both  $\Delta H$  and  $\Delta S$  are -ve

30. Which of the following reaction is associated with an increase in entropy?

- 1)  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$     2)  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$   
 3)  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$     4)  $\text{C}(\text{graphite}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$

31. For the reaction,  $2\text{HgO}(\text{s}) \rightarrow 2\text{Hg}(\text{l}) + \text{O}_2(\text{g})$

- 1)  $\Delta H > 0$  &  $\Delta S < 0$     2)  $\Delta H > 0$  &  $\Delta S > 0$     3)  $\Delta H < 0$  &  $\Delta S < 0$     4)  $\Delta H < 0$  &  $\Delta S > 0$

32. randomness is minimum in case of

- 1)  $\text{H}_2$  gas at 1 atm    2)  $\text{H}_2$  gas at 5 atm  
 3)  $\text{H}_2$  gas at 10 atm    4) All have same randomness

33. The value of  $S$  is negative for the process

- 1) Burning of rocket Fuel    2) Dissolution of sugar  
 3) Sublimation of Iodine    4) condensation of a vapour.

34. The quantity which is not zero for an element in its standard state at  $298 \text{ K}$  is

- 1)  $S^0$     2)  $H^0$     3)  $G^0$     4) Both  $H^0$  and  $S^0$

35. Which of the following process involves decrease in the entropy of system?

- 1)  $\text{Br}_2(\text{l}) \rightarrow \text{Br}_2(\text{g})$     2) Diamond  $\rightarrow$  graphite  
 3)  $\text{N}_2(\text{g})$  10 atm  $\rightarrow$   $\text{N}_2(\text{g})$  1 atm    4) Boiling of egg so that it become hard

36. In which of the following process entropy increases?

- 1) Rusting of iron    2) Vapourisation of Camphor  
 3) Crystallisation of sugar from syrup    4) Atomisation of di Nitrogen  
 1) a and b    2) b and c    3) b and d    4) Only d

37. For the spontaneous process  $2\text{F}(\text{g}) \rightarrow \text{F}_2(\text{g})$ , the sign of  $\Delta H$  and  $\Delta S$  respectively are

- 1) +ve, -ve    2) +ve, +ve    3) -ve, -ve    4) -ve, +ve

38. Entropy of a perfect crystalline solid at absolute zero is

- 1) zero    2) less than zero    3) Greater than zero    4) unity

39. Which of the following has highest Entropy

- 1) Mercury    2) Hydrogen    3) Water    4) Graphite

40. Identify the correct statement regarding a spontaneous process:

- 1) Lowering of energy in the process is the only criterion for spontaneity.  
 2) For a spontaneous process in an isolated system, the change in entropy is positive.  
 3) Endothermic process are never spontaneous.  
 4) Exothermic process are always spontaneous.

41. **Assertion:** At absolute zero the entropy of a perfectly crystalline substance is taken as zero  
**Reason:** At absolute zero the constituent particles become completely motionless  
 1) both A and R are true and R is the correct explanation of A.  
 2) both A and R are true but R is not the correct explanation of A.  
 3) A is true but R is false.  
 4) both A and R are false.
42. **Assertion:** Decrease in free energy causes spontaneous reaction  
**Reason:** Spontaneous reactions are invariably exothermic reactions  
 1) both A and R are true and R is the correct explanation of A.  
 2) both A and R are true but R is not the correct explanation of A.  
 3) A is true but R is false. 4) both A and R are false.
43. For a spontaneous reaction the  $\Delta G$ , equilibrium constant ( $K_C$ ) and  $E_{cell}^0$  will be respectively  
 (1) -ve, >1, -ve (2) -ve, <1, -ve (3) +ve, >1, -ve (4) -ve, >1, +ve
44. Which of the following relationship is correct ?  
 1)  $\Delta G^0 = -RT \ln K$  2)  $K = e^{-\Delta G^0/RT}$  3)  $K = 10^{-\Delta G^0/2.303RT}$  4) All are correct
45. Which of the following is the condition for a non spontaneous reaction at high temperature but spontaneous at low temperature

- |            |            |
|------------|------------|
| $\Delta H$ | $\Delta S$ |
| 1) -ve     | -ve        |
| 2) +ve     | +ve        |
| 3) -ve     | +ve        |
| 4) +ve     | -ve        |

46. If  $S_{surroundings} = +959.1 \text{ JK}^{-1}\text{mol}^{-1}$   
 $S_{system} = -163.1 \text{ Jk}^{-1} \text{ mol}^{-1}$  Then the process is  
 1) Spontaneous 2) Non spontaneous  
 3) At equilibrium 4) Cannot be predicted

Solution:  $S_{total} = S_{sys} + S_{surr} = +ve$ . Thus the process is spontaneous.

47.  $\Delta G^0$  for conversion of oxygen to ozone,  $\frac{3}{2} \text{O}_{2(g)} \rightarrow \text{O}_{3(g)}$  at 298K is [  $K_p$  for this conversion is  $2.47 \times 10^{-29}$  ]  
 1) 163 j /mole 2) 163 KJ/mole 3) 16.3J/mole 4) 16.3 KJ/mole

**Solution** : We know  $\Delta G^0 = -2.303 RT \log K_p$  and  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ .

Therefore  $\Delta G^0 = -2.303(8.314 \text{ JK}^{-1} \text{ mol}^{-1})(298 \text{ K})(\log 2.47 \times 10^{-29}) = 163000 \text{ J mol}^{-1}$  or  $163 \text{ kJ mol}^{-1}$

48. The standard free energy of  $\text{Cu}_{aq}^+$  is  $50 \text{ kJ mol}^{-1}$  and that of  $\text{Cu}_{aq}^{+2}$  is  $66 \text{ kJ. mol}^{-1}$ . The change in free energy for the reaction,  $\text{Cu}_{aq}^+ \rightarrow \text{Cu}_{aq}^{+2} + e^-$  is  
 1) 116KJ/mole 2) -16KJ/mole 3) 16KJ/mole 4) -34KJ/mole

**Solution** : Standard free energy change,

$$\Delta G^0 = \Delta G^0_{\text{Cu}^{+2}} - \Delta G^0_{\text{Cu}^+} = 66 \text{ kJ mol}^{-1} - 50 \text{ kJ mol}^{-1} = 16 \text{ kJ mol}^{-1}.$$

49) The entropy change for vapourisation of a liquid is  $109.3 \text{ JK}^{-1}\text{mol}^{-1}$ . The molar heat of vapourisation of that liquid is  $40.77 \text{ kJ mol}^{-1}$ . The boiling point of the liquid is

- 1)  $373^{\circ}\text{C}$     2)  $100^{\circ}\text{C}$     3)  $100\text{K}$     4)  $646\text{K}$

**Solution :** Entropy change for vapourisation,  $= 109.3 \text{ JK}^{-1} \text{ mol}^{-1}$ . Molal heat of vapourisation of water is  $40.77 \text{ kJ mol}^{-1}$ .

From the entropy change,  $\Delta S = q_{\text{rev}}/T$ .

Boiling point,  $T = \frac{q_{\text{rev}}}{\Delta S}$  (or)  $T = \frac{40.77 \times 1000}{109.3} = 373\text{K} = 373 - 273 = 100^{\circ}\text{C}$

50)  $\Delta S$  for vapourization of 900 g water (in KJ/K) is [ $\Delta H_{\text{vap}} = 40 \text{ KJ/mol}$ ]

- 1)  $(900 \times 40)$     2)  $(50 \times 40)/373$     3)  $(90 \times 40)/373$     4)  $(18 \times 40)/373$

KEY

- |       |       |       |       |      |       |       |      |      |       |
|-------|-------|-------|-------|------|-------|-------|------|------|-------|
| 1)1   | 2) 3  | 3) 3  | 4) 3  | 5) 3 | 6)4   | 7)2   | 8) 1 | 9)2  | 10) 3 |
| 11) 3 | 12) 3 | 13) 1 | 14) 3 | 15)4 | 16) 4 | 17) 4 | 18)1 | 19)1 | 20)1  |
| 21)3  | 22)3  | 23)1  | 24)3  | 25)4 | 26)1  | 27)3  | 28)3 | 29)1 | 30)4  |
| 31)2  | 32)3  | 33)4  | 34)1  | 35)3 | 36)3  | 37)3  | 38)1 | 39)2 | 40)2  |
| 41)1  | 42)3  | 43)4  | 44)4  | 45)1 | 46)1  | 47)2  | 48)3 | 49)2 | 50)2  |