

## Topic : Thermodynamics (II<sup>nd</sup> Law)

Type of Questions	M.M., Min.
Single choice Objective ('-1' negative marking) Q.1 to Q.8	(3 marks, 3 min.) [24, 24]
Multiple choice objective ('-1' negative marking) Q.9 to Q.11	(4 marks, 4 min.) [12, 12]
Subjective Questions ('-1' negative marking) Q.12 to Q.13	(4 marks, 5 min.) [8, 10]

1. (a) The  $\Delta G$  in the process of melting of ice at  $-15^\circ\text{C}$  is :  
(A) -ve (B) +ve (C) 0 (D) All of these

(b) The Gibbs energy change and standard Gibbs energy change for a reaction are same if the reaction quotient  $Q$  has value equal to :  
(A)  $> 1$  (B)  $< 1$  (C) 0 (D) 1

2. A reaction has  $\Delta H = -33 \text{ kJ}$  and  $\Delta S = -58 \frac{\text{J}}{\text{K}}$ . This reaction would be :  
(A) spontaneous at all temperatures (B) non-spontaneous at all temperatures  
(C) spontaneous above a certain temperature (D) spontaneous below a certain temperature

3. The enthalpy change for a given reaction at  $298 \text{ K}$  is  $-x \text{ J mol}^{-1}$  ( $x$  being positive). If the reaction occurs spontaneously at  $298 \text{ K}$ , the entropy change at that temperature :  
(A) can be negative but numerically larger than  $x/298$   
(B) can be negative but numerically smaller than  $x/298$   
(C) cannot be negative  
(D) cannot be positive

4. For perfectly crystalline solid  $C_{p,m} = aT^3$ , where  $a$  is constant. If  $C_{p,m}$  is  $0.42 \text{ J/K mol}$  at  $10 \text{ K}$ , molar entropy at  $20 \text{ K}$  is :  
(A)  $0.42 \text{ J/K mol}$  (B)  $0.14 \text{ J/K mol}$  (C)  $1.12 \text{ J/K mol}$  (D) zero

5. Given that :  
$$\Delta G_f^\circ (\text{CuO}) = -30.4 \text{ kcal/mole}$$
$$\Delta G_f^\circ (\text{Cu}_2\text{O}) = -34.98 \text{ kcal/mole}$$
$$T = 298 \text{ K}$$

Now on the basis of above data which of the following predictions will be most appropriate under the standard conditions and reversible reaction.

(A) Finely divided form of  $\text{CuO}$  kept in excess  $\text{O}_2$  would be completely converted to  $\text{Cu}_2\text{O}$   
(B) Finely divided form of  $\text{Cu}_2\text{O}$  kept in excess  $\text{O}_2$  would be completely converted to  $\text{CuO}$   
(C) Finely divided form of  $\text{CuO}$  kept in excess  $\text{O}_2$  would be converted to a mixture of  $\text{CuO}$  and  $\text{Cu}_2\text{O}$  (having more of  $\text{CuO}$ )  
(D) Finely divided form of  $\text{CuO}$  kept in excess  $\text{O}_2$  would be converted to a mixture of  $\text{CuO}$  and  $\text{Cu}_2\text{O}$  (having more of  $\text{Cu}_2\text{O}$ )

6. The molar entropy content of 1 mole of oxygen ( $O_2$ ) gas at 300 K and 1 atm is  $250 \text{ J mole}^{-1} \text{ K}^{-1}$ . Calculate  $\Delta G$  when 1 mole of oxygen is expanded reversibly and isothermally from 300 K, 1 atm to double its volume (Take  $R = 8.314 \text{ J mole}^{-1} \text{ K}^{-1}$ ,  $\log e = 2.303$ )

(A)  $1.728 \text{ KJ mole}^{-1} \text{ K}^{-1}$  (B) 0  
(C)  $-1.728 \text{ KJ mole}^{-1} \text{ K}^{-1}$  (D)  $0.75 \text{ KJ mole}^{-1} \text{ K}^{-1}$

7. When a bottle of perfume is opened, odorous molecules mix with air and slowly diffuse throughout the entire room. The **incorrect** fact about the process is :

(A)  $\Delta G = -ve$  (B)  $\Delta H \approx 0$  (C)  $\Delta S = -ve$  (D)  $\Delta S = +ve$

8. For a perfectly crystalline solid  $C_{p.m.} = aT^3$ , where  $a$  is constant. If  $C_{p.m.}$  is  $0.42 \text{ J/K-mol}$  at 10 K, molar entropy at 10 K is

(A)  $0.42 \text{ J/K-mol}$  (B)  $0.14 \text{ J/K-mol}$  (C)  $4.2 \text{ J/K-mol}$  (D) zero

9.\* For free expansion of an ideal gas (expansion against vacuum) adiabatically, which of the following will have zero value :

(A)  $W$  (B)  $q$  (C)  $\Delta U$  (D)  $\Delta H$

10.\* The normal boiling point of a liquid 'X' is 400 K. Which of the following statement is true about the process  $X(l) \longrightarrow X(g)$ ?

(A) at 400 K and 1 atm pressure  $\Delta G = 0$  (B) at 400 K and 2 atm pressure  $\Delta G = + ve$   
(C) at 400 K and 0.1 atm pressure  $\Delta G = - ve$  (D) at 410 K and 1 atm pressure  $\Delta G = + ve$

11.\* One mole of an ideal diatomic gas ( $C_v = 5 \text{ cal}$ ) was transformed from initial  $25^\circ\text{C}$  and 1 L to the state when temperature is  $100^\circ\text{C}$  and volume 10 L. Then for this process ( $R = 2 \text{ calories/mol/K}$ ) (take calories as unit of energy and kelvin for temp)

(A)  $\Delta H = 525$   
(B)  $\Delta S = 5 \ln \frac{373}{298} + 2 \ln 10$   
(C)  $\Delta E = 525$   
(D)  $\Delta G$  of the process can not be calculated using given information.

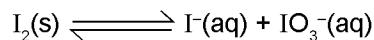
12. Calculate the pH {  $\text{pH} = -\log[\text{H}^+]$  } at which the following reaction will be at equilibrium in basic medium

$$I_2(s) \rightleftharpoons I^-(aq) + IO_3^-(aq)$$

when the concentrations at 300 K are  $[I^-] = 0.10 \text{ M}$  and  $[IO_3^-] = 0.10 \text{ M}$

Given that  $\Delta G_f^0(I^-, \text{aq}) = -50 \text{ kJ/mole}$ ,  $\Delta G_f^0(IO_3^-, \text{aq}) = -123.5 \text{ kJ/mole}$ ,  $\Delta G_f^0(H_2O, \ell) = -233 \text{ kJ/mole}$ ,  
 $\Delta G_f^0(OH^-, \text{aq}) = -150 \text{ kJ/mole}$ , Ideal gas constant  $R = \frac{25}{3} \text{ Jmole}^{-1} \text{ K}^{-1}$ ,  $\log e = 2.3$

13. The equilibrium constant for the reaction given below is  $2.0 \times 10^{-7}$  at 300 K. Calculate the standard free energy change for the reaction;

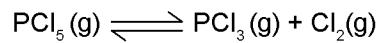


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$$\Delta G_f^{\circ}(\text{OH}^-, \text{aq}) = -150 \text{ kJ/mole, Ideal gas constant } R = \frac{25}{3} \text{ Jmole}^{-1}\text{K}^{-1}, \log e = 2.3$$

13. The equilibrium constant for the reaction given below is  $2.0 \times 10^{-7}$  at 300 K. Calculate the standard free energy change for the reaction;



Also calculate the standard entropy change if  $\Delta H^\circ = 28.40 \text{ kJ/mol}$ .

# Answer Key

## DPP No. # 25

1. (a) (B) (b) (D)	2. (D)	3. (B)	4. (C)	5. (B)
6. (A)	7. (C)	8. (B)	9.* (A,B,C,D)	10.* (A,B,C)
11.* (A,B,D)	12. 8	13. $\Delta G^\circ = 38.48 \text{ KJ/mol}$ ; $\Delta S^\circ = -33.6 \text{ JK}^{-1} \text{ mol}^{-1}$ .		

# Hints & Solutions

## PHYSICAL / INORGANIC CHEMISTRY

### DPP No. # 25

2.  $\Delta G = (\Delta H) - T(\Delta S)$   
↓      ↓  
-ve      -ve

since both are -ve, the reaction would have a -ve  $\Delta G$  below a temperature of  $\frac{33000}{58} \text{ K} (= 569 \text{ K})$

3. It is because of the fact that for spontaneity, the value of  $\Delta G = (\Delta H - T\Delta S)$  should be  $< 0$ . If  $\Delta S$  is - ve, the value of  $T\Delta S$  shall have to be less than  $\Delta H$  or the value of  $\Delta S$  has to be less than  $\frac{\Delta H}{T}$  i.e.,  $\frac{x}{298}$ .

4. (C)  $0.42 = a(10)^3 \Rightarrow a = 0.42 \times 10^{-3}$

$$S_m = \int_0^{20} \frac{C_{p,m}}{T} dT$$
$$= \int_0^{20} aT^2 dT = \frac{a}{3} [20^3 - 0] = 1.12 \text{ J/K-mol.}$$

5. (B)  $\text{Cu}_2\text{O}(s) + \frac{1}{2}\text{O}_2(g) \rightleftharpoons 2\text{CuO}(s)$

Activ  
Go to

$$\Delta G_{\text{reaction}}^\circ = [2 \times (-30.4)] - [-34.98] = -25.82 \text{ kcal}$$

$$\text{and } -25.82 \times 10^3 = 2.303 \times 2 \times 298 \log K$$

$\therefore K \approx 10^{19}$ , a very high value, hence reaction will be almost complete with a trace of  $\text{Cu}_2\text{O}$ .

6.  $\Delta G = \Delta H - \Delta(TS)$   
 $= \Delta H - T\Delta S \quad (\text{isothermal})$

$$= 0 - T\Delta S = -T \left( \int \frac{dq_{\text{rev}}}{T} \right)$$

$$= - \int dq_{\text{rev}} = -q_{\text{rev}} = W_{\text{rev}}$$

as process is isothermal so  $\Delta E = 0 = q_{\text{rev}} + W_{\text{rev}}$

so  $\Delta G = -nRT \ln \left( \frac{V_f}{V_i} \right)$

$$= -RT \ln 2 = -8.314 \times 300 \times 0.693 \times 10^{-3} \text{ KJ mol}^{-1} \text{ K}^{-1}$$

$$= 1.728 \text{ KJ mol}^{-1} \text{ K}^{-1}$$

8.  $0.42 = a(10)^3 \Rightarrow a = 0.42 \times 10^{-3}$

$$S_m = \int_0^{10} \frac{C_{p,m.}}{T} dT = \int_0^{10} aT^2 = \frac{a}{3} [10^3 - 0] = \frac{0.42}{3} = 0.14 \text{ J/K-mol}$$

9.\* Adiabatic process. So,  $q = 0$ .

Expansion against vacuum. So,  $P_{ext} = 0$ . Therefore,  $W = 0$ .

So, from 1<sup>st</sup> law,  $\Delta U = 0$ . So,  $\Delta T = 0$ . So,  $\Delta H = 0$ .

$\Delta S_{sys} > 0$ , since expansion of gas occurs.

10.\* Boiling of a liquid at normal boiling point is an equilibrium process and on decreasing the pressure equilibrium will go forward and  $\Delta G$  will be negative and vice versa.

11.\*  $\Delta S = nC_v \ln \left( \frac{T_f}{T_i} \right) + nR \ln \left( \frac{V_f}{V_i} \right)$

$$\Delta H = nC_p \Delta T$$

$$\Delta E = nC_v \Delta T$$

$$\Delta G = \Delta H - \Delta(TS)$$

13.  $\Delta G^\circ = -2.303 \times 8.314 \times 300 \log [2 \times 10^{-7}]$   
 $= 38.48 \text{ kJ/mol}$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = -33.6 \text{ J mol}^{-1} \text{ K}^{-1}$$

