

Topic : Thermodynamics (IInd 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]

- (a) The ΔG in the process of melting of ice at -15°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
- 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
- The enthalpy change for a given reaction at 298 K is $-x \text{ J mol}^{-1}$ (x being positive). If the reaction occurs spontaneously at 298 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
- For perfectly crystalline solid $C_{p,m} = aT^3$, where a is constant. If $C_{p,m}$ is 0.42 J/K mol at 10 K, molar entropy at 20 K is :
 (A) 0.42 J/K mol (B) 0.14 J/K mol (C) 1.12 J/K mol (D) zero
- Given that :
 $\Delta G_f^\circ (\text{CuO}) = -30.4 \text{ kcal/mole}$
 $\Delta G_f^\circ (\text{Cu}_2\text{O}) = -34.98 \text{ kca/mole}$ $T = 298 \text{ K}$
 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 CuO kept in excess O_2 would be completely converted to Cu_2O
 (B) Finely divided form of Cu_2O kept in excess O_2 would be completely converted to CuO
 (C) Finely divided form of CuO kept in excess O_2 would be converted to a mixture of CuO and Cu_2O (having more of CuO)
 (D) Finely divided form of CuO kept in excess O_2 would be converted to a mixture of CuO and Cu_2O (having more of Cu_2O)



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 ΔG 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 J/K-mol at 10 K, molar entropy at 10 K is
 (A) 0.42 J/K-mol (B) 0.14 J/K-mol (C) 4.2 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) ΔU (D) ΔH
- 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°C and 1 L to the state when temperature is 100°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) ΔG of the process can not be calculated using given information.
12. Calculate the pH { $\text{pH} = -\log[H^+]$ } 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 $\Delta G_f^\circ(I^-, aq) = -50 \text{ kJ/mole}$, $\Delta G_f^\circ(IO_3^-, aq) = -123.5 \text{ kJ/mole}$, $\Delta G_f^\circ(H_2O, l) = -233 \text{ kJ/mole}$,
 $\Delta G_f^\circ(OH^-, aq) = -150 \text{ kJ/mole}$, 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 2.0×10^{-7} at 300 K. Calculate the standard free energy change for the reaction;

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$
 Also calculate the standard entropy change if $\Delta H^\circ = 28.40 \text{ KJ/mol}$.



Answer Key

DPP No. # 25

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|--------------------|--------|---|---------------|--------------|
| 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. $\Delta G = (\Delta H) - T(\Delta S)$
 $\downarrow \quad \downarrow$
 $-ve \quad -ve$

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 ΔS is $-ve$, the value of $T\Delta S$ shall have to be less than ΔH or the value of ΔS 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) $\text{Cu}_2\text{O(s)} + \frac{1}{2} \text{O}_2\text{(g)} \rightleftharpoons 2\text{CuO(s)}$

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

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

$\therefore K \approx 10^{19}$, a very high value, hence reaction will be almost complete with a trace of Cu_2O .

6. $\Delta G = \Delta H - T\Delta S$
 $= \Delta H - T\Delta S$ (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 $\Delta E = 0 = q_{\text{rev}} + W_{\text{rev}}$

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

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

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

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Go to

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

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

- 9.* Adiabatic process. So, $q = 0$.
Expansion against vacuum. So, $P_{\text{ext}} = 0$. Therefore, $W = 0$.
So, from 1st law, $\Delta U = 0$. So, $\Delta T = 0$. So, $\Delta H = 0$.
 $\Delta S_{\text{sys}} > 0$, since expansion of gas occurs.

- 10.* Boiling of a liquid at normal boiling point is a equilibrium process and on decreasing the pressure equilibrium will go forward and ΔG 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. $\Delta G^\circ = -2.303 \times 8.314 \times 300 \log [2 \times 10^{-7}]$
 $= 38.48 \text{ KJ/mol}$

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

