

This question paper contains 4 printed pages]

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S. No. of Question Paper : 7791

Unique Paper Code : 2171202 F-2

Name of the Paper : Chemical Thermodynamics and System of Variable Compositions
(DC-1.3)

Name of the Course : Bachelor with Honours in Chemistry

Semester : II

Duration : 3 Hours

Maximum Marks : 75

(Write your Roll No. on the top immediately on receipt of this question paper.)

Answer six questions in all, first question is compulsory.

Use of scientific calculators is permitted.

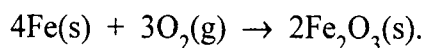
$$R = 8.314 \text{ J K}^{-1}\text{mol}^{-1}.$$

1. Attempt any five of the following : 5×3=15

- (a) A process can be spontaneous even if the corresponding change in entropy of the system is negative. Explain with example.
- (b) What is the difference between bond energy and bond dissociation energy ?
- (c) What is the significance of Debye's T^3 law ?
- (d) Why the chemical potential is called 'escaping tendency' ?

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- (e) 'Internal energy is state function'. This is statement of first law of thermodynamics.
- (f) Why rusting of iron represented by the following equation is a spontaneous process ?

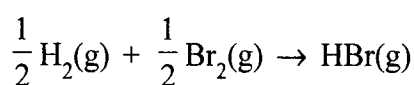


- (g) Residual entropy of O_2 is zero, but that of CO is not zero at absolute zero. Why ?
2. (a) What is Joule-Thomson coefficient ? Prove that its value is zero for an ideal gas. 4

- (b) Starting from I and II laws of Thermodynamics derive the relation :

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P. \quad 4$$

- (c) One mole of an ideal gas at 300 K is compressed reversibly and isothermally from volume 25 dm^3 to 5 dm^3 . Calculate ΔS_{System} and ΔS_{Total} . 4
3. (a) Derive Kirchhoff's law and explain its physical significance. 5
- (b) Calculate $\Delta H_{370\text{K}}$ for the reaction : 4



Given : $\Delta H_{298\text{K}} = -51.535 \text{ kJ mol}^{-1}$

$$C_p(\text{H}_2, \text{g}) = 29.06 - 0.830 \times 10^{-3} T$$

$$C_p(\text{HBr}, \text{g}) = 27.52 + 3.995 \times 10^{-3} T$$

$$C_p(\text{Br}_2, \text{g}) = 35.24 + 4.075 \times 10^{-3} T.$$

- (c) Distinguish between integral heat of solution and integral heat of dilution. 3

4. (a) Using Euler's reciprocity relation prove that pressure of an ideal gas is a state function. 2

- (b) Derive the relation for entropy as a function of T, P :

$$dS = \frac{C_p}{T} dT - \left(\frac{\partial V}{\partial T} \right)_p dP. \quad 4$$

- (c) (i) Derive the following expression for the free energy of mixing involving ideal gases :

$$\Delta G_{\text{mix}} = nRT \sum_i x_i \ln x_i.$$

How does the above equation indicate that mixing of gases is a spontaneous process ?

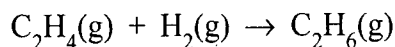
- (ii) Prove that $\Delta V_{\text{mix}} = 0$ for an ideal mixture. Give its significance. 6

5. (a) Show that work done in reversible isothermal expansion of an ideal gas is greater than that of real gas. 4

- (b) Show that for isothermal expansion of an ideal gas $\Delta G = \Delta A$. 2

- (c) For defining the spontaneity of a process ΔS_{System} and $\Delta S_{\text{Surroundings}}$ is required but ΔG alone is sufficient for the same. Explain. 2

- (d) Using the bond enthalpy data given below calculate the enthalpy change for the reaction : 4



Bond	Bond enthalpy (kJ mol ⁻¹)
C—C	336.8
C = C	606.7
C—H	410.9
H—H	431.8

6. (a) Derive the expressions for ΔU , ΔH , w and q for adiabatic expansion of an ideal gas for reversible and irreversible change. 6
- (b) 1.6 moles of an ideal gas ($C_{v,m} = 2.5 R$) at 300 K was allowed to expand adiabatically from 5 atm to final pressure of 2 atm against a constant external pressure of 1 atm. Calculate ΔU , ΔH , w and q . 4
- (c) At low temperature enthalpy change dominates the change in free energy and at high temperature entropy change dominates. 2
7. (a) Derive Gibbs-Duhem equation and explain its significance. 3
- (b) Calculate the free energy of mixing ΔG_{mix} , Enthalpy of mixing ΔH_{mix} and Entropy of mixing ΔS_{mix} at 25°C, when :
- (i) 10 moles of A are mixed with 10 moles of B
- (ii) 10 moles of A are mixed with 20 moles of B. 6
- (c) Show that chemical potential of a component in a mixture is less than its chemical potential in pure state at same temperature and pressure. 3
8. Write short notes on any *three* of the following : 3×4=12
- (a) Adiabatic flame temperature
- (b) Hess's law of constant heat summation
- (c) Trouton's rule
- (d) Coupled reaction
- (e) Second Law of Thermodynamics.