

2 0 1 4

CHEMISTRY

(Major)

Paper : 1.1

Full Marks : 60

Time : 2½ hours

*The figures in the margin indicate full marks
for the questions*

1. (a) When a spring was wound, 100 J of work was done on it, but 15 J escaped to the surroundings as heat. What was the change in internal energy of the spring? 1
- (b) Define standard state of a substance. 1
- (c) Give molecular interpretation of work and heat. 2

2. (a) Entropy is not a convenient criterion for predicting the spontaneity of a process. Why? 1
- (b) State the third law of thermodynamics. 1

(2)

- (c) Calculate the entropy change of a system containing a perfect gas when 1.00 mol of the gas doubles its volume at any temperature. 2

3. (a) For the reaction, $N_2 + 3H_2 \rightarrow 2NH_3$ the rate is expressed as

$$r = -\frac{d[N_2]}{dt} = -\frac{1}{3} \frac{d[H_2]}{dt} = \frac{1}{2} \frac{d[NH_3]}{dt}$$

Under what conditions these expressions are valid? 1

- (b) The rate law of a homogeneous reaction $A \rightarrow P$ was found to be $r = k[A]^{1.38}$. What does the rate law indicate? 1
- (c) What are zeolites? Give one example of a reaction catalyzed by zeolite catalyst. 2

4. Answer any two of the following : 3×2=6

- (a) Calculate the work done when 50 g of iron (molar mass = 55.85 g mol⁻¹) reacts with hydrochloric acid to produce hydrogen gas in an open beaker at 25 °C.

(3)

- (b) Check whether dP is an exact differential or not.
- (c) Deduce Kirchhoff's equation to show the variation of enthalpy of a reaction with temperature.

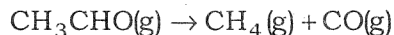
5. Answer any two of the following : 3×2=6

- (a) Show that for a reversible cyclic process $\oint dS = 0$.
- (b) Show that the maximum non-expansion work we can obtain from a system at constant pressure and temperature is given by the value of ΔG for the process.
- (c) Define chemical potential. What is its physical significance? For the following pair of substances, state which substance has the higher chemical potential :

$H_2O(l)$ at 25 °C and 1 atm vs.
 $H_2O(g)$ at 25 °C and 1 atm

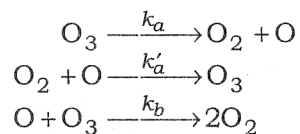
6. Answer any *two* of the following : $3 \times 2 = 6$

- (a) Express the rate of the following reaction in terms of rate of change of pressure :



- (b) The rate of the reaction $2A + B \rightarrow 2C$ is doubled when the concentration of B is doubled but increases by a factor of eight when the concentrations of both the reactants are doubled. Find out the rate law of the reaction. What is the overall order of the reaction?

- (c) Applying steady-state approximation, derive the rate law for the reaction $2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g})$ on the basis of following mechanism :



7. Answer any *two* of the following : $5 \times 2 = 10$

- (a) Why is C_P always greater than C_V ? Show that

$$C_P - C_V = \left(\frac{\delta V}{\delta T} \right)_P \left[\left(\frac{\delta U}{\delta V} \right)_T + P \right] \quad 5$$

- (b) What is Joule-Thomson effect? Show that Joule-Thomson expansion of a gas is an isoenthalpic process. 5

- (c) (i) State the Hess's law. Explain the law taking a suitable example. 3

- (ii) A sample of Ar ($\gamma = 5/3$) at 1.00 atm expands reversibly and adiabatically to twice its initial volume. Calculate its final pressure. 2

8. Answer any *two* of the following : $5 \times 2 = 10$

- (a) (i) Obtain the expressions to show the variation of entropy with temperature under various conditions of pressure and volume. 3

- (ii) Calculate the molar entropy of a constant-volume sample of neon at 500 K given that it is $146.22 \text{ JK}^{-1} \text{ mol}^{-1}$ at 298 K. [Consider $C_{V,m}$ for Ne = $12.5 \text{ JK}^{-1} \text{ mol}^{-1}$] 2

- (b) Starting from the definition of Gibbs' free energy (G), deduce the expressions to show the variation of G with T and P . Based on these expressions, draw necessary graphs to show the variation of G with T and P for solid, liquid and gaseous phases of a substance. 5

(6)

- (c) Deduce van't Hoff equations to show the effect of temperature on equilibrium constant of a reaction. Use a van't Hoff equation to predict the effect of temperature on the equilibrium of an exothermic reaction and an endothermic reaction.

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9. Answer any *two* of the following : $5 \times 2 = 10$

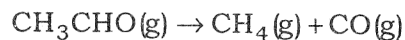
- (a) For the second-order reaction



- (i) integrate the rate law;
(ii) on the basis of this integrated rate law, draw a plot of $\frac{[A]}{[A]_0}$ against t ;
(iii) derive an expression for the half-life of the reaction in terms of k and $[A]_0$.

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- (b) Give the Rice-Herzfeld mechanism for the following thermal decomposition of ethanal in absence of air :



Based on this mechanism, derive a rate law for the reaction.

5

(7)

- (c) For the consecutive reactions



obtain the expressions for the concentrations of the species A , B and C . Draw the plots of $[A]$, $[B]$ and $[C]$ against time.

5
