2014

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

(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 $r = k[A]^{1\cdot38}$. 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.

(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 : 3×2=6

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

$$CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$$

(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 $2O_3(g) \rightarrow 3O_2(g)$ on the basis of following mechanism :

$$O_3 \xrightarrow{k_a} O_2 + O$$
$$O_2 + O \xrightarrow{k'_a} O_3$$
$$O + O_3 \xrightarrow{k_b} 2O_2$$

7. Answer any *two* of the following : 5×2=10

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

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

(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 : 5×2=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 $JK^{-1} mol^{-1}$ at 298 K. [Consider $C_{V,m}$ for Ne = 12·5 $JK^{-1} mol^{-1}$] 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

(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. 5

9. Answer any *two* of the following : 5×2=10

(a) For the second-order reaction

$$aA \rightarrow \text{products}$$

(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 $[A]_0$. 2+1+2

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

$$CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$$

Based on this mechanism, derive a rate law for the reaction. 5

(c) For the consecutive reactions

$$A \rightarrow B \rightarrow C$$

obtain the expressions for the concentrations of the species A, B and C. Draw the plots of $[A]$, $[B]$ and $[C]$ against time. 5

★ ★ ★