2012

CHEMISTRY

(Major)

Paper : 1.1

Full Marks : 60

Time : 2½ hours

The figures in the margin indicate full marks for the questions

1. *(a)* What is the relationship between C_p and C_v for real gases? 1

(b) State the definition of work in thermodynamics. 1

(c) Give molecular interpretation of work and heat. 2

2. *(a)* Define the entropy change of a system to which heat has been transferred reversibly and isothermally. 1

(b) Slope of the line obtained by plotting ΔG against T is

(i) ΔH

(ii) ΔS

(iii) $-\Delta S$

(iv) 0

State the correct choice. 1

(c) What is meant by a state function? Give example of one state function and one that is not. 2

3. (a) What is 'turnover number' of an enzyme catalyst? 1

(b) The reaction $2A + B + C \rightarrow D + E$ is first order with respect to A, second order with respect to B and zeroth order with respect to C. Write the differential rate equation for the reaction. 1

(c) For the general reaction $0 \rightarrow \Sigma \nu_i A_i$, show that the rate of reaction is given by

$$r = \frac{1}{V}\frac{d\xi}{dt}$$

where ξ is the extent of reaction. 2

4. Answer any *two* : 3×2

(a) Explain the principle of liquefaction of gases by Joule-Thomson effect.

(b) For a system which can do only expansion work, show that $\Delta H = q_p$.

(c) What is the ΔH when 1 mole of H_2O at 101 kPa is heated from 353 K to 393 K? The following data are available :

C_p (l, H_2O) = 75·0 JK^{-1} mol^{-1}

ΔH (vaporization) = 47·3 kJ mol^{-1} at 373 K

C_p (g, H_2O) = 35·4 JK^{-1} mol^{-1}

5. Answer any *two* : 3×2

(a) Show how entropy will change for the following processes :

(i) Freezing of ethanol

(ii) Dissolving glucose in water

(iii) Cooling nitrogen gas from 373 K to 273 K

(b) For an ideal gas, show that $\mu = \mu_0 + RT \ln\left(\frac{p}{p^0}\right)$, where p^0 is the standard pressure.

(c) For the reaction equilibrium $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, calculate the equilibrium constant at 500 K from its value at 298 K. ($K = 6 \times 10^5$ at 298 K, standard enthalpy of reaction is $-92 \cdot 2$ kJ mol^{-1})

6. Answer any *two* : 3×2

(a) For the set of reactions

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \text{ and } C + B \xrightarrow{k_2} D$$

find $-dC_A / dt$, $-dC_B / dt$, dC_A / dt and dC_D / dt.

(b) The reaction $2HI = H_2 + I_2$ is second order with a rate constant $k_2 = 1 \cdot 2 \times 10^{-3}$ mol^{-1} s^{-1} at 700 K. A sample of HI at a pressure of 100 kPa is maintained at 700 K. How long will it take to decompose 40% of the original HI?

(c) What is meant by Arrhenius plot? Write briefly, how this plot can be obtained for a particular reaction.

7. Answer any *two* : 5×2

(a) Derive an expression for the work done in a reversible isothermal expansion of n mol of an ideal gas from volume V_1 to volume V_2. Show that work obtained in isothermal reversible expansion of an ideal gas is more than that in an irreversible expansion.

(b) Draw the skeletal diagram for the experimental setup of Joule-Thomson effect, and show that Joule-Thomson expansion is an isoenthalpic process.

(c) Define internal energy and enthalpy of a system. The ΔH for the formation of NOCl (g) from the gaseous elements is $51 \cdot 71\ kJ\ mol^{-1}$ at 25 °C. If the gases are ideal, calculate ΔU.

8. Answer any *two* : 5×2

(a) Deduce all the forms of Gibbs-Helmholtz equation.

(b) Find an expression for the entropy change in an isothermal reversible expansion of n mol of an ideal gas from a volume V_1 to volume V_2. Volume of 1·00 mol of an ideal gas is doubled by a reversible isothermal expansion at 298 K. Calculate ΔS for the gas. What will be the entropy change of the gas when the same expansion is carried out irreversibly?

(c) Discuss the variation of the enthalpy function with temperature under various conditions of pressure and volume deriving the appropriate relations.

9. Answer any *two* : 5×2

(a) For the first-order reaction

$$A \rightarrow \text{products}$$

obtain the integrated rate law

$$[A] = [A]_0 e^{-kt}$$

Draw a graph to show the variation of concentration of the reactant with time. Show that first-order reaction can never be completed.

(b) What is rate determining step of a reaction? For the following pre-equilibrium mechanism

$$A + B \underset{k'_a}{\overset{k_a}{\rightleftharpoons}} C \xrightarrow{k_b} P$$

under what conditions the pre-equilibrium exists? Show that the overall order of the reaction is two.

(c) Derive the rate law for the formation of HBr in hydrogen-bromine reaction.

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