2018

CHEMISTRY

(Major)

Paper : 1.1

(Physical Chemistry)

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Answer the following as directed : 1×7=7

(a) In a certain process, 600 J of work is done on a system which gives off 250 J of heat. Calculate the internal energy change for the process.

(b) State zeroth law of thermodynamics.

(c) Why is in some reactions heat evolved while some reactions take place only on absorption of heat?

(d) The dissolution of ammonium chloride in water is endothermic still it dissolves in water. Give reasons.

(e) Which one of the following demonstrates a decrease in entropy?

(i) Dissolving a solid into solution

(ii) In expanding universe

(iii) Burning a log in a fireplace

(iv) Raking up leaves into a trash bag

(Choose the correct option)

(f) Oxygen is available in plenty in air yet fuels do not burn by themselves at room temperature. Explain.

(g) For a reaction $A + H_2O \rightarrow B$, rate $\propto [A]$, what are its molecularity and order of reaction?

2. Answer the following : 2×4=8

(a) Write two limitations of the first law of thermodynamics.

(b) Under what conditions enthalpy change (ΔH) becomes equal to internal energy change (ΔU) in a process?

(c) For the reaction $2Cl(g) \rightarrow Cl_2(g)$, what are the signs of ΔH and ΔS?

(d) What are zeolites? Why are zeolites suitable for cracking of hydrocarbons?

3. Answer any *three* of the following : 5×3=15

(a) Distinguish between isothermal and adiabatic processes. One mole of nitrogen gas contained in a cylinder at 300 K is allowed to expand isothermally against an external pressure of 5 atm from a volume of 1·0 dm^3 to a volume of 3·0 dm^3. Assuming ideality, calculate q, W, ΔU and ΔH. 2+3=5

(b) Derive Kirchhoff's equation relating the variation of enthalpy of a reaction with temperature. The heat evolved in the combustion of glucose is shown in the equation

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(g)$$

$$\Delta_C H = -2840 \text{ kJ mol}^{-1}$$

What is the energy requirement for production of 0·36 g of glucose by the reverse reaction? 3+2=5

(c) State and explain Nernst heat theorem. How does it lead to the enunciation of the third law of thermodynamics? What do you mean by residual entropy of a substance? 2+2+1=5

(d) Discuss van't Hoff's differential method for determination of order of a reaction. The half-life for radioactive decay of ^{14}C is 5730 years. An archaeological artifact contained wood that had only 80% of the ^{14}C found in living tree. Estimate the age of the sample. 3+2=5

(e) Explain the terms 'frequency factor' and 'activation energy' of the Arrhenius equation. The rate of a particular reaction doubles when temperature changes from 27 °C to 37 °C. Calculate the activation energy of the reaction. 3+2=5

4. Answer *either (a), (b), (c) or (d), (e), (f)* :

(a) What are state functions? Writing V as a function of T and P, show that for an ideal gas, dV is an exact differential.

(b) Define heat capacity of a system. Explain the molecular basis of the differences between heat capacity of a gas at constant pressure (C_p) and at constant volume (C_v).

(c) What is Joule-Thomson effect? Explain the principle of liquefaction of gases by Joule-Thomson effect. 3+4+3=10

(d) What do you mean by internal energy? What are the possible contributions to the internal energy of a system? Which of these contributions will be present if the temperature of a system is reduced to $T = 0$ K?

(e) In what way is average bond energy different from bond energy of a diatomic molecule? Calculate the bond enthalpy of HCl. Given that the bond enthalpies of H_2 and Cl_2 are 430 kJ mol^{-1} and 242 kJ mol^{-1} respectively and $\Delta_f H^\circ$ for HCl is –91 kJ mol^{-1}.

(f) Prove that change in enthalpy of a system is equal to the heat supplied to the system at constant pressure.

5+2+3=10

5. Answer *either (a), (b), (c) or (d), (e), (f)* :

(a) Define entropy. Why is it a state function? Discuss entropy changes in reversible and irreversible processes.

(b) Derive an expression for the entropy of a mixture of ideal gases.

(c) For the reaction $2A(g) + B(g) \rightarrow 2D(g)$, $\Delta U^{\circ} = 10 \cdot 5$ kJ and $\Delta S^{\circ} = -44 \cdot 10$ J K^{-1}. Calculate ΔG° for the reaction and predict whether the reaction may occur spontaneously. 5+2+3=10

(d) Show that

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

(e) Define chemical potential. Show how it varies with temperature.

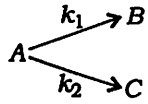
(f) What do you mean by standard Gibbs' energy of formation? Obtain the relation between the equilibrium constant and the standard Gibbs' energy change. Calculate Gibbs' energy change and standard Gibbs' energy change for the reaction $A + B \rightleftharpoons C + D$ at 27 °C. Equilibrium constant (K) for the reaction= 10^2. 2+3+5=10

6. Answer *either (a), (b), (c) or (d), (e)* :

(a) Define rate of reaction with respect to the reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$.

(b) For a second-order reaction of the type $2A \rightarrow$ products, find an expression for the rate constant. Show that for the second-order reaction, half-life is inversely proportional to the initial concentration of the reactant.

(c) For the concurrent elementary reaction



show that $\frac{[B]}{[C]} = \frac{k_1}{k_2}$. 2+4+4=10

Or

(d) What is steady state approximation? Applying steady state approximation, derive the rate expression for the H_2—Br_2 thermal reaction. Show that in the initial stage, the order of the reaction is 1·5.

(e) Discuss Michaelis-Menten mechanism of enzyme catalyzed reaction. What type of potential energy diagram is expected for enzyme catalyzed reaction? How does the rate of enzyme catalyzed reaction depend on temperature? 6+4=10

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