

2017

3rd Semester

CHEMISTRY

PAPER—C7

(Honours)

Full Marks : 40

Time : 2 Hours

The figures in the right-hand margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

Physical Chemistry-II

1. Answer any *five* questions :

5×1

- (a) Find the unit of $\ln k/dT$ for a n -th order reaction.
- (b) According to the second law $\Delta G \leq 0$. State the conditions under which the equality sign hold good.
- (c) What is the time for completion for a first order reaction?

(Turn Over)

- (d) Give examples of a process in each of which for the system (i) $\Delta G < 0$, $\Delta S > 0$ and (ii) $\Delta G < 0$, $\Delta S < 0$.
- (e) NaCl has an fcc lattice. How many Na^+ and Cl^- ions are there in the unit cell?
- (f) What do you mean by buffer capacity?
- (g) Calculate the number of ways of arranging 5 different particles among 3 energy levels such that one energy level has 1 particle, two have 2 each.
- (h) Write down the key steps of chain reaction.

2. Answer any *five* questions :

5×2

- (a) Rate and rate constant of some reactions are identical. Explain what type of reactions they are?
- (b) What is Hammett acidity function?
- (c) Which stoichiometric defect does affect density and why?
- (d) Show that the Joule-Thomson expansion is isoenthalpic in nature.
- (e) Below 0°C , super-cooled water changes spontaneously into ice—Justify or Criticise.

- (f) Calculate the pH of 10^{-8}N H_2SO_4 solution.
- (g) Which state function of the system is related to the maximum value of thermodynamic probability and how?
- (h) Write down the physical significance of work function (A).

3. Answer any *three* questions from the following : 3×5

- (a) (i) Show that for a cubic lattice the spacing between adjacent (hkl) planes is $d = a/(h^2+k^2+l^2)^{1/2}$.
- (ii) Calculate the spacing between two successive (110) planes in a simple cubic lattice. 3+2
- (b) Deduce the expression of pH of a solution of salt of strong acid and weak base. 5
- (c) (i) Show that a zero order reaction can lead to completion.
- (ii) A reaction $\text{A} \rightarrow \text{products}$ is of zero order with respect to A. Two experiments are performed with initial concentrations $[\text{A}]_0 = 0.1(\text{M})$ and $0.05(\text{M})$ respectively. Sketch the plots to show variation of the concentration of A with time. 3+2

(d) Establish that number of molecules in three successive levels with equal spacings are in geometric progression for a system obeying Boltzmann distribution. 5

(e) Find the value of μ_{JT} for a gas obeying (i) $P(V - b) = RT$, (ii) $(P + a/V^2)V = RT$. Comment on the results. 5

4. Answer any one question : 1×10

(a) (i) State the results of Joule-Thomson experiment and explain them.

(ii) 2 moles of He is heated from 473 K to 673 K at a constant pressure of 1 atm. Assuming He is a perfect gas, calculate ΔG , ΔH and ΔS for the process. Given that $S_{473}^0 = 135 \text{ J.K}^{-1}.\text{mole}^{-1}$. Is this process spontaneous?

(iii) From the definition of Chemical potential (m) arrive at the Gibbs-Duhem equations of the form $dG = Smdn$ and $Sndm = 0$. 3+4+3

(b) (i) Arrive at an expression for C_V of a monatomic solid according to the Einstein model.

(ii) Find a relation between the thermodynamic function A and the molecular partition function (Q).

(iii) Suppose there are two energy levels and the difference between them is $2kT$. Calculate the ratio of number of molecules in the two levels. 4+4+2

(c) (i) Explain Carnot's cycle with the help of T-P diagram.

(ii) A gas decomposes according to second order kinetics. When the initial pressure of the gas is 500 torr, 40% decomposition occurs in 30 min. Find out the time required for 75% decomposition of the gas and the value of the rate constant.

(iii) Ionic product and dissociation constant of water are not identical—Explain. 4+4+2