2017

CHEMISTRY

[Honours]

PAPER – II

Full Marks : 90

Time : 4 hours

The figures in the right hand margin indicate marks

Use separate answer scripts for Group–A and Group–B

GROUP – A

(*Physical*)

Group – A(a)

Answer any **one** of the following from **Q. Nos. 1 & 2** 15×1

1. (*a*) Starting from the Maxwell's distribution of molecular speeds in three-dimensions, derive a distribution for the kinetic energies for a system of gas at temperature T. Plot the

kinetic energy distribution function versus the energy at a definite temperature T. 3 + 1

(*b*) Evaluate the Boyle temperature in terms of the known constants A, b and R for a gas having the equation of state

$$pV_m = RT + \left(b - \frac{A}{RT^{2/3}}\right)p \qquad 3$$

(*c*) A reversible Carnot cycle for an ideal gas with a net work done of 60·0 J operates between the temperatures of 500 K and 200 K. What is the thermodynamic efficiency of the engine ? How much heat is absorbed at 500 K ? How much heat is rejected at 200 K ? In order for the engine to perform 1·00 kJ of work, how much of heat must be absorbed ? 4

(*d*) Show that the half-life $t_{1/2}$ of a reaction of order n, with all the reactants having an inital concentration of a_0 is given by

$$t_{1/2}\frac{2^{n-1}-1}{ka_0^{n-1}(n-1)} \cdot \qquad 4$$

2. (*a*) At N.T.P., the viscosity of hydrogen is $8{\cdot}4 \times 10^{-5}$ poise and the average velocity of the molecules is $1{\cdot}7 \times 10^{5}$ cm/sec. Calculate the mean free path and molecular diameter. 4

(*b*) Consider the following rate equation.

$$\frac{-dc}{dt} = KC^{1/2}$$

(*i*) Integrate the rate equation.

(*ii*) Derive an expression for $t_{1/2}$ in terms of K and C_0.

(*iii*) Justify whether the reaction would be completed within a finite time. 2+1+1

(*c*) Explain why the contribution of each translational and rotational mode to the average molecular energy is half that of a vibrational mode. 2

(*d*) Find the change in surface energy when two identical Hg droplets of diameter 2 mm

merged isothermally to form one drop. [Surface tension of Hg is 490 dyne/cm at that temperature]. 4

(*e*) What is CMC ? 1

Group – A(b)

Answer any **two** of the following questions : 10 × 2

3. (*a*) State the second law of thermodynamics in terms of entropy. 2

(*b*) For the fusion of ice ΔH is given by $\Delta H = 1100 - 9T$. Calculate ΔG for the change $H_2O(l, 1\ atom) \rightarrow H_2O(S, 1\ atom)$ at $-10^{\circ}C$. 4

(*c*) Write down BET equation and explain the terms involved. Under what conditions is it converted into Langmuir equation ? 4

4. (*a*) For the reversible reaction $A \rightleftharpoons B$ in which both the opposing reactions are of first order, deduce an expression for the rate constant in terms of the equillibrium constant of the reversible reaction. 4

(*b*) Some $PH_3(g)$ is introduced into a flask at 600° C, where it decomposes into $P_4(g)$ and

$H_2(g)$ and the reaction goes to completion. The total pressure is given below as a function of time.

Time (min)	0	40	80
P (mm)	100	150	166·7

Show that the decomposition is first order and find out the rate constant. 4

(*c*) What is induced catalyst ? Give an example. 2

5. (*a*) The following mechanism has been proposed for the thermal decomposition of pure ozone in the gas phase.

$$2O_3^* \xrightarrow{k} O_3 + O_2 + O$$

$$O + O_3 \xrightarrow{k} 2O_2$$

Derive the rate equation for the above mechanism. 3

(*b*) An ideal gas undergoes a thermodynamic cycle consisting of the following steps :
Process 1-2 : Constant pressure, $p = 1{\cdot}4$ bar, $V_1 = 0{\cdot}028$ m^3, $W_{12} = 10{\cdot}5$ kJ

Process 2-3 : Compression, with pV = Constant $U_3 = U_2$.

Process 3-1 : Constant volume, $U_1 - U_3 =$ – 26·4 kJ.

For this, sketch the cycle on a $p = V$ diagram. Calculate the net work for the cycle in kJ. Show that

$$\sum_{\text{cycle}} Q = \sum_{\text{cycle}} W. \qquad 1+2+2$$

(*c*) Write down the expression for the Freundlich adsorption isotherm and show how one can determine the unknown quantities graphically. 2

6. (*a*) Deduce the reduced van der Waals' equation of state and hence state the law of corresponding states. Comment on the extent of validity of this law. 3+1+1

(*b*) The partial pressure of argon in the atmosphere is 0·0093 atm. What is the argon pressure at 50 km if the temperature is 20° C ? Given, atomic mass of argon = 39·9; $g = 9{\cdot}807$ m/s^2. 3

(*c*) Distinguish between physical adsorption and chemisorption by mentioning at least two important points. 2

Group – A(c)

7. Answer any *five* questions : 2×5

(*a*) What are the thermodynamic criteria for a gas to be ideal ?

(*b*) When water is evaporated at 100° C and 1 atm, the free energy change is zero. Justify properly.

(*c*) "Volatile liquids must have lower surface tension and viscosity"– Explain.

(*d*) Show that for a van der Waals' gas

$$\left(\frac{\partial C_v}{\partial V}\right)_T = 0 .$$

(*e*) Show that for *n* th order reaction $\frac{t_{1/2}}{t_{3/4}}$ is a function of *n* alone.

(*f*) State the zeroth law of thermodynamics.

(*g*) The average speed for a gas at 27° C is 400 ms^{-1}. At what temperature the speed will be 800 ms^{-1} ?

(*h*) Show that the slops of the the $P - V$ curve for an isothermal expansion is less than that of an adiabatic expansion process.

GROUP – B

(*Industrial*)

Group – B(a)

Answer any **one** question : 15×1

8. (*a*) Discuss the principle involved in the separation of components by paper chromatography. Give two advantages of HPLC technique. $3 + 2$

(*b*) Describe low temperature carbonisation of coal. What are the products of low temperature carbonisation ? Give their uses. $3 + 2 + 2$

(*c*) Distinguish between high temperature carbonisation tars and low temperature carbonisation tars. 3

9. (*a*) What are liquid fuels ? Give approximate composition of crude petroleum. 1 + 3

(*b*) Describe briefly the distillation process of crude petroleum into principal products with flow sheet diagram. 4

(*c*) Discuss the basic principle of HPLC. State advantages of ion-exchange chromatography. 3 + 2

(*d*) What do you mean by TOC ? 2

Group – B(b)

Answer any two questions : 10 × 2

10. (*a*) Distinguish between drying and non-drying oils. Give uses of drying oils. 2 + 2

(*b*) Define saponification value of an oil. 2

(*c*) Discuss the method of manufacturing of BHC with a flow diagram. 4

11. (*a*) What are ceramics ? Give examples. Write down the raw materials for the manufacturing port land cement. (1 + 1) + 2

(*b*) What is deionised water ? What are the uses of deionised water ? 1 + 2

(*c*) What are the advantages of gaseous fuels ? 2

(*d*) Give uses of carbon black. 1

12. (*a*) Write down the raw materials for the manufacturing of terylene. State physical properties and uses of terylene. 2 + (1 + 1)

(*b*) Name two commonly used binders in paint industry. 2

(*c*) Briefly describe the manufacturing of bakelite. Give uses of bakelite polymer. 3 + 1

13. (*a*) Briefly discuss about "shaping of glass". 3

(*b*) Describe the process of manufacturing of triple superphosphate with flow sheet diagram. 3

(*c*) Give differences between natural rubber and artificial rubber. 2

(*d*) What is vitrification of glass ? 2

Group – B(c)

Answer any **five** questions : 2×5

14. (*a*) Define power alcohol.

(*b*) What are detergent builders ? Give one example.

(*c*) What are the qualities of a good fertilizer ?

(*d*) Explain the term "retarder" with respect to cement.

(*e*) Write down briefly about "cleaning action of detergent".

(*f*) What are determinate and indeterminate errors ?

(*g*) Give chemical structure of repeating unit of natural rubber. Give one example of thermo-setting plastic.

(*h*) Define the term calorific value.

(*i*) What is "setting of cement" ?
