2018

CHEMISTRY - HONOURS

Paper: CC-2
Full Marks: 50

The figures in the margin indicate full marks.

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

Write the answers to *Physical Chemistry* (Group-A) and *Organic Chemistry* (Group-B) questions in *separate* answer scripts.

Group - A

[Physical Chemistry - 1]

Answer question no. 1 (compulsory) and any five questions from the rest (question nos. 2 to 9)

1. Answer the following questions:

 1×8

- (a) Find out the SI unit of the van der Waals constant 'a'.
- (b) Is it possible to liquefy a gas obeying the equation of state $P(V_m b) = RT$? Justify.
- (c) At what temperature will the average speed of hydrogen molecules be the same as that of oxygen molecules at 27°C?
- (d) The potential energy of attraction between two molecules is given by $u(r) = A/r^n$. State the sign of A and the value of n.
- (e) For a given reaction whose rate is independent of concentration of reactants, justify whether it goes to completion in finite time.
- (f) The rate constant of decomposition of a substance is represented by $ln \ k = 5.5 11000/T$. Calculate the activation energy for the reaction at 300 K, in joules.
- (g) Find the dimension of the viscosity coefficient.
- (h) Write down Fick's first law of diffusion, mentioning the terms involved.
- 2. (a) Write down the Maxwell function for distribution of molecular speed in three dimensions in case of an ideal gas, explaining the terms involved. Draw the distribution curves on the same graph, for two gases of molar mass M_1 and M_2 ($M_2 = 2M_1$) at the same temperature.
 - (b) In the absolute method of determination of viscosity coefficient (η) by Poiseuille's formula, what would be the error in radius of the capillary if error in η is +4%? 3+2

Please Turn Over

3. (a) Gases X and Y obeying van der Waals equation have T_c and P_c values as given below:

	T_c/K	P_c / atm
X	177	64
Y	500	45

Find which gas has (i) smaller value of 'a'

- (ii) smaller value of 'b'.
- (b) 'A zero order reaction cannot be a single step reaction'. Explain.

3+2

4. (a) Show that if A reacts to form B and C according to $A \xrightarrow{K_1} B$, $A \xrightarrow{K_2} C$ then prove that the overall activation energy E_a is given by $E_a = \frac{K_1 E_1 + K_2 E_2}{K_1 + K_2}$,

where E_1 and E_2 are the activation energies for the first and second reaction respectively.

(b) Find the dimension of A that appears in Maxwell's speed distribution equation

$$\frac{1}{N}\frac{dNc}{dc} = Ac^2 \exp\left[-mc^2/2kT\right].$$

where the terms have their usual significance.

What is its SI unit?

5. (a) The molecules of a gas are confined to move in a plane. Derive the expression for rms speed.

Given
$$\int_0^\infty c^3 \exp\left(-ac^2\right) dc = \frac{1}{2a^2}$$

(b) The rate constant of a chemical reaction increases by 2 times when the temperature changes from T K to (T+10) K, whereas that of another reaction increases by 3 times for the same change of temperature. Find the ratio of their activation energies, if they have the same pre-exponential factors.

3+2

- 6. (a) Gases A and B (separate gases in separate flasks) are at the same pressure and have the same molecular weight. Gas A is at twice the absolute temperature of gas B. Calculate the ratio of the self diffusion coefficient of gas A to that of gas B. (Given $\sigma_A = 1.2 \sigma_B$).
 - (b) When 10 ml of water at 20°C is placed in an Ostwald Viscometer, it takes 136.5 sec for the liquid level to drop from the first mark to the second. For the same volume of hexane at 20°C in the same viscometer the corresponding time is 67.3 sec. Find the viscosity coefficient of hexane at 20°C. [Given, at 20°C, $\eta_{\rm H_2O} = 1.002$ cp, $\rho_{\rm H_2O} = 0.998$ g.cm⁻³, $\rho_{\rm hexane} = 0.659$ g.cm⁻³] 3+2
- 7. (a) Derive Michaelis Menten equation for the enzyme catalyzed reaction and show that the reaction is zero order with respect to the substrate at large substrate concentration.
 - (b) Explain why the initial slope $(P \to 0)$ of the compressibility factor (z) versus Pressure (P) plot is negative at temperatures below Boyle temperature for a van der Waals gas. 3+2

- **8.** (a) Write down the mathematical form of the Maxwell's Kinetic energy distribution in three dimension at a particular temperature and represent it graphically.
 - (b) Viscosity coefficient of a liquid decreases by 2% per 1° increase in temperature. Show that $\eta(350K)/\eta(300K) = 1/e$, where terms have their usual meaning.
- 9. (a) Calculate the pressure at which the mean free path of nitrogen molecules will be 1 mm at 246K, given that $\sigma_{N_2} = 3.70 \text{ Å}$.
 - (b) For a reaction $A \to \text{product}$, the plot of $[A]^{-1}$ versus time is a straight line with a positive intercept. What is the order of the reaction?

Group - B

[Organic Chemistry (1B)]

Answer question no. 10 (compulsory) and any three from the rest (question nos. 11 to 15)

10. (a) Specify E/Z configuration of the following molecule:

(b) Arrange the following species in order of increasing stability:

1+1

$$Me_3\dot{C}$$
, CH_2 = CH - $\dot{C}H_2$, $Ph\dot{C}H_2$

11. (a) Designate the marked (*) centres of the following compounds as stereogenic/non-stereogenic, chirotopic/achirotopic. Give reason.

- (b) Draw Fischer projection formula of (1R, 2S)-1-chloro-1, 2-diphenylpropane and label it as *erythro* or *threo* form.
- 12. (a) Discuss the procedure adopted to resolve a racemic carboxylic acid. Give the name of resolving agent used and principle of the method.
 - (b) Assign R/S descriptor of the following molecules showing the priority sequence of the ligands. 3+2

(i)
$$H_{I_{IIII}}$$
 CMe_3 (ii) $HO \longrightarrow CHMe_2$ $CH = CH_2$

Please Turn Over

M(1st Sm.)-Chemistry-H/CC-2/(CBCS)

(4)

- 13. (a) Calculate the enantiomeric excess (*ee*) and specific rotation of a mixture containing 10g of (+)-2-butanol and 6g of (-)-2-butanol. The specific rotation of enantiomerically pure (+)-2-butanol is (+)13·5°.
 - (b) Rank the following carbocations in order of increasing stability and explain the order.

3+2

(iii)
$$Me_2^{\oplus}C - CH = CH - CH_3$$

14. (a) Identify whether the following pairs of molecules represents enantiomer, diastereoisomer or homomer.

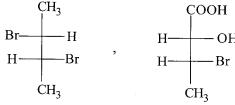
(i)
$$HO_2C$$
 H $COOH$ $COOH$

(b) State whether the following molecules are resolvable or not with explanation.

3+2

(i)
$$H_3C^{mm}N$$
 , (ii) $H_3C^{mm}P$ CH_2CH_3 CH_2CH_3

15. (a) Give saw horse, flying wedge and Newman projection formulae of the following:



(b) Define non classical carbocation with an example.

3+2