2020

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 book.

Group - A

[Physical Chemistry – I]

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) The van der Waals constants for the gas A and gas B are given below :

Gas	a/Pa m^6mol^{-2}	b/$10^{-6}m^3mol^{-1}$
A	0·0247	26·6
B	0·366	42·9

Which of the above two gases can be liquefied easily and why?

(b) Consider the following reaction :

$A \rightarrow$ product; Rate of the reaction $-\frac{dA}{dt}=K[A]^{\alpha}$; which of the following statements is correct?

In the above rate law [A] is the concentration of A

(i) at time t = 0 (ii) at time t = t

(c) Represent graphically (P vs. V) the behaviour of a typical van der Waals gas at three different temperatures ($T > T_C$, $T = T_C$, $T < T_C$) where T_C is the critical temperature of the gas.

(d) A reaction goes to completion at a finite time. Choose the correct answer from the following :

The reaction is (i) first-order (ii) zero-order (iii) second-order.

(e) Calculate the rms speed of O_2 gas at 20ºC taking $R = 8{\cdot}314\ JK^{-1}mol^{-1}$.

(f) At 25ºC the half life for the decomposition of N_2O_5 is $2{\cdot}05\times10^4$s and is independent of the initial concentration of N_2O_5. What is the order and rate constant of the reaction?

(g)

Substance	A	B	C	D	E
$\eta(cp)$	0·60	0·89	19	80	0·021

Arrange the above substances in increasing order of their boiling points.

Where $\eta(cp)$ is the viscosity coefficient in centipoise.

(h) Maxwell distribution of velocity is given by $\frac{1}{N}\frac{dN_C}{dC} = 4\pi\left(\frac{m}{2\pi KT}\right)^{3/2} \cdot e^{\frac{-mC^2}{2KT}} \cdot C^2$

(i) What is $\frac{1}{N}\frac{dN_C}{dC}$?

(ii) Plot $\frac{1}{N}\frac{dN_C}{dC}$ vs. C and indicate the most probable velocity in the plot.

2. (a) Write Maxwell speed distribution in two dimension mentioning all the terms in the expression. Draw Maxwell speed distribution curve (in 2D) for a particular gas at two different temperatures T_2 and T_1 ($T_2 > T_1$) and also for two different gases with molecular weight M_2 and M_1 ($M_2 > M_1$).

(b) Poiseuillie's equation for coefficient of viscosity of a liquid is $\eta = \frac{\pi h \rho g r^4 t}{8Vl}$

(i) Explain all the terms of the equation.

(ii) How will you determine the relative viscosity coefficient of two liquids in an Ostwald viscometer using the above equation? (Write only the principle.) 3+2

3. (a) For a reaction the plot of $\log t_{1/2}$ vs. $\log a$ (where a is the initial concentration of the reactant) turns out to be a straight line with positive slope and intercept, which makes an angle of 45° with the $\log a$ axis, what is the order of the reaction?

(b) The average speed for a gas at 27°C is 400 ms^{-1}. At what temperature the speed will be 800 ms^{-1}? 3+2

4. (a) The absolute viscosity of water at 293 K is 0·01002 poise. Time taken by equal volumes of water and chloroform to flow through a capillary tube are 39·7 seconds and 15 seconds respectively. Density of water is 1·0 g/cm^3 and density of chloroform is 1·49 g/cm^3. Calculate the relative and absolute viscosities of chloroform at 293 K.

(b) Gases A, B, C and D obey the van der Waals equation with 'a' and 'b' values as given below (in SI unit) :

	A	***B***	***C***	***D***
a :	0·6	0·6	0·2	0·005
$10^3 b$:	0·025	0·15	0·1	0·02

Identify the gas / gases which have the largest molecule and most nearly ideal behaviour at S.T.P. 3+2

5. (a) Draw the graph of concentration versus time of the three species A, B, C undergoing the first-order consecutive reactions

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

under the conditions (i) $k_1 = k_2$ (ii) $k_1 \ll k_2$ (iii) $k_1 \gg k_2$.

(b) Give the general expression for Lennard Jones 6 – 12 potential explaining the terms involved. 3+2

6. (a) Express the Fick's Law of Diffusion in the general equation of transport. What is the phenomenological coefficient involved? What are the physical parameters on which the coefficient is dependent?

(b) If the molecular diameter of H_2 is 0·292 nm, calculate the number of collisons made by a hydrogen molecule in 1 sec at 1 atm and 27ºC. 3+2

7. (a) When thermal decomposition of acetaldehyde was studied at 518ºC according to the equation :

$$2\,CH_3CHO(g) \xrightarrow{518^oC} 2\,CH_4(g) + 2\,CO(g)$$

Following results were obtained :

Time in second :	0	393	695	1080
Pressure in mm :	119	130·7	138·2	146·4

Show that the above data establishes that the reaction follows second-order kinetics.

(b) The critical constants for water are $T_C = 374^oC$, $P_C = 22{\cdot}1$ MPa. Calculate the van der Waals' constants a and b using the value $R = 8{\cdot}3144\ JK^{-1}mol^{-1}$. 3+2

8. (a) The virial equation of state in terms of P is given by (neglecting higher order term)

$$Z = 1 + \frac{1}{RT}\left(b - \frac{a}{RT}\right)P + \frac{a}{(RT)^3}\left(2b - \frac{a}{RT}\right)P^2$$

Set up an expression for the initial slope of Z versus P curve of a real gas and obtain expression for the Boyle temperature of the gas.

(b) From the one-dimensional velocity distribution, find out the average kinetic energy of a molecule. 3+2

9. (a) State the Michaelis-Menten Equation for an enzyme catalyzed reaction, explaining the terms involved. Starting from this expression, derive the Lineweaver Burk Equation. What information is obtained from the slope and intercept of Lineweaver Burk plot?

(b) Using the law of equipartition of energy, arrive at the C_V value for the molecule acetylene (C_2H_2). 3+2

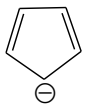
Group - B

[Organic Chemistry (1B)]

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

10. (a) Draw an optically inactive compound which has two chiral centres.

(b) Arrange the following carbanions in order of their increasing stability (no explanation needed).

$\overset{\ominus}{C}H_3$, $(CH_3)_2\overset{\ominus}{C}H$, $CH_2 = CH - \overset{\ominus}{C}H_2$,  1+1

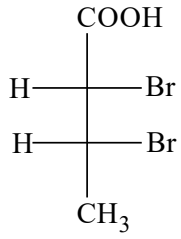
11. (a) Write down the structures of the following compounds :

(i) (*E*) – Acetophenone oxime

(ii) (*Z*, *E*) – Hepta – 2,4 – diene

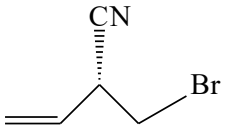
(iii) Erythro–2–bromo–3–chlorobutane in Newman projection formula.

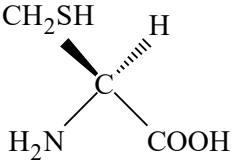
(b) Convert the given Fischer projection of the following molecule into staggered Newman and eclipsed sawhorse projection formulae. 3+2



12. (a) Draw the Fischer projection formula of 2, 3, 4-trihydroxy-pentanedioic acid [COOHCH(OH)CH (OH)CH(OH)COOH] and show the pseudoasymmetric centre in the structure you have drawn, indicating the R/S/r/s descriptors of C – 2, C – 3 and C – 4 centres.

(b) Assign R/S descriptors to the following compounds mentioning priority of the ligands around the chiral centre :

(i) 

; (ii) 

3+2

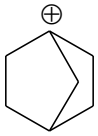
13. (a) Calculate the specific rotation of a mixture of *R*– and *S*– acid with 30% e.e. with respect to the *R*–isomer. [It is given that specific rotation of the pure *S*–isomer is –24°].

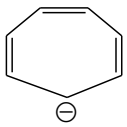
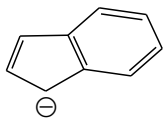
(b) Indicate symmetry elements present in

(i) *meso*– Tartaric acid (in staggered conformation)

(ii) 2– Chloropropane 3+2

14. (a) Which one is more stable in each of the following pairs and why?

(i) $(Me_3C)_3\overset{\oplus}{C}$ and 

(ii)  and 

(iii) $Ph_2\dot{C}H$ and $Me_2\dot{C}H$

(b) What do you mean by nucleophilic carbene? Illustrate with one example. 3+2

15. (a) Which of the following species behave as (i) nucleophile, (ii) electrophile, (iii) both, (iv) Neither

$$\ddot{N}H_3,\ H_2C{=}O,\ CH_3-C{\equiv}N,\ CH_4,\ \overset{\oplus}{N}O_2,\ I^{\ominus}$$

(b) (+) EtCH(Me)COPh loses optical activity during deuteration with D_2O/NaOH. – Explain. 3+2