

2022

CHEMISTRY

PAPER-I

Time Allowed — 3 Hours

Full Marks — 200

*If the questions attempted are in excess of the prescribed number, only the questions attempted first up to the prescribed number shall be valued and the remaining ones ignored.*

*Answers may be given either in English or in Bengali but all answers must be in one and the same language.*

### Section-I

This Section comprises 15 questions in three Groups.

Answer any ten questions taking at least three questions from each Group.

#### Group-A

1. How the four Quantum Numbers signify the state of an electron in H atom? 4
2.  $\text{ICl}_2^-$  is linear but  $\text{NH}_2^-$  is bent.— Justify. 4
3. Among the following which is stronger base  $(\text{H}_3\text{Si})_2\text{O}$ ,  $(\text{H}_3\text{C})_2\text{O}$ ? Explain. 4
4. Aqueous solution of  $\text{SbCl}_3$  turns turbid. — Explain. 4
5.  $E^\circ$  values for  $\text{Zn}^{+2}/\text{Zn}$  and  $\text{Ag}^+/\text{Ag}$  half cells are  $-0.763 \text{ V}$  and  $+0.799 \text{ V}$  respectively. Calculate the  $E^\circ_{\text{cell}}$  value in Volt. 4

#### Group-B

6. Explain why the distance between two successive hkl planes for a cubic system cannot be  $a/\sqrt{7}$  where  $a$  is the length of the edge of the cube. 4
7. Calculate the ratio of final to initial wall collision frequency for an ideal gas if pressure is doubled at constant density. 4
8. Calculate the inlet pressure required to maintain a flow rate of  $9.5 \times 10^5 \text{ Lh}^{-1}$  of nitrogen at 293 K flowing through a pipe of length 8.50 m and diameter 1.00 cm. The pressure of the gas as it leaves the tube is 1.00 bar. The volume of the gas is measured at that pressure. Given  $\eta = 1.76 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$  at 293 K. 4
9. Does the equilibrium constant depend on the stoichiometry of the chemical reaction? “ $K_p$  is independent of pressure at constant temperature for all gaseous reaction” — Justify or contradict. 2+2=4

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## Group-B

3. (a) Write down the Maxwell function for distribution of molecular speeds in three dimensions in the 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  $T$ . Estimate the ratio of the most probable speeds in two cases. 2+2+2=6
- (b) One mole of an ideal gas is expanded adiabatically but irreversibly from  $V_1$  to  $V_2$  and no work is done.
- (i) Does the temperature of the gas change?
- (ii) What is  $\Delta S$  for the gas and the surroundings? 4
- (c) Write down the van der Waal's equation in the virial form. Hence deduce the expression for the Boyle temperature from the second virial coefficient. 4
- (d)  $N_2$  and  $O_2$  combine at a given temperature to produce NO. At equilibrium, the yield of NO is  $x\%$  by volume. If  $x = \sqrt{Kab} - \frac{K(a+b)}{4}$  where  $K$  is the equilibrium constant of the reaction at the given temperature and ' $a$ ' and ' $b$ ' are the volume percentages of  $N_2$  and  $O_2$  respectively in the initial pure mixture, what should be the initial composition of the reaction mixture in order that maximum yield of NO is ensured? 6
- (e) Why is it difficult to blow a balloon initially, but becomes easier afterwards? (Consider the balloon as a bubble).  
Find the change in surface energy when two identical Hg droplets of diameter 1.5 mm merge isothermally to form one drop. [ $\gamma$  of Hg = 490 dyne  $cm^{-1}$ ] 2+3=5
- (f) For the ideal gas reaction  $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ , state with reasons, how the equilibrium is affected when each of the following changes is made in the above equilibrium mixture at 25°C.
- (i) He(g) is added at constant  $T$  and  $V$ .
- (ii) He(g) is added at constant  $T$  and  $P$ . 2+3=5
- (g) What do you mean by residual entropy? 3
- (h) Al crystallises with a face centered cubic lattice. The inter ionic distance (shortest) in a unit cell of Aluminium is 2.86 Å. Calculate the density of Al. (Atomic weight of Al = 27).  
Show that in an orthorhombic unit cell, the separation of the  $hkl$  planes will be reduced by a factor of ' $n$ ' if all three Miller indices are multiplied by that factor.

Although NaCl and KCl have same crystalline structures, reflection from (111) planes is present in NaCl crystal but that is missing in KCl crystal. — Explain. 2+2+3=7

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4. (a) Represent graphically (by P-V curve) the behaviour of a typical van der Waals' gas at three different temperatures  $T \gg T_c$ ,  $T = T_c$  and  $T < T_c$ . Justify that the condition

$$\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 \text{ serve to give the critical constants.} \quad 5$$

- (b) For the process  $H_2O$  (liquid)  $\rightarrow H_2O$  (vapour),  $\Delta H_{vap} = 40.52 \text{ kJ mol}^{-1}$  at  $100^\circ\text{C}$  and 1 atm pressure. Assuming ideal behavior of the vapour phase, calculate  $w$ ,  $\Delta U$ ,  $\Delta S$  and  $\Delta G$  for the process. 5

- (c) "Joule-Thompson experiment is an isenthalpic process" — Justify or criticize the statement.

Prove that: 
$$\mu_{JT} = \frac{1}{C_p} \left[ T \left( \frac{\partial V}{\partial T} \right)_P - V \right]$$

where  $\mu_{JT}$  is the Joule-Thompson coefficient. Hence explain 'inversion temperature'.

2+3+2=7

- (d) What is the highest order that can be observed in Bragg's reflection from a crystal of interplanar distance  $2\text{\AA}$  by X-ray having wavelength 100 pm?

From the following data, determine the type of cubic lattice to which the system belong:

Edge length 286 pm, Density  $7.86 \text{ g cm}^{-3}$ , Molar mass  $55.85 \text{ g mol}^{-1}$ . 3+4=7

- (e) Show that according to the simple kinetic molecular theory of gases, the viscosity coefficient is

(i) independent of pressure. Give a physical explanation of why this should be so.

(ii) directly proportional to average velocity of a definite amount of gas at definite temperature. 4+3=7

- (f) State whether each of the following properties increases or decreases as intermolecular attraction increases:

Surface tension of a liquid, Viscosity of a liquid, Viscosity of a gas.

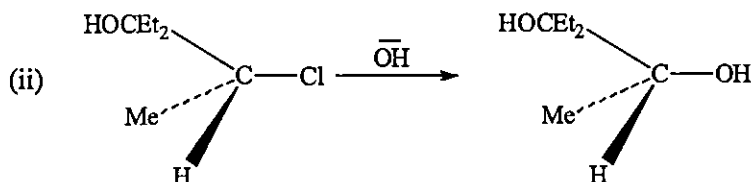
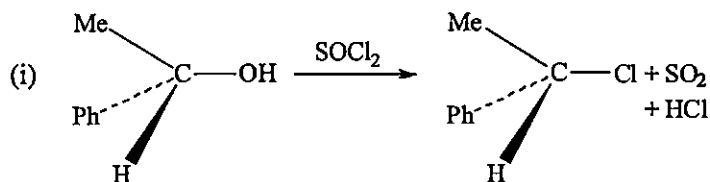
The limb of a vertical U-tube having internal dimensions of 1 mm and 2 mm respectively, is partially filled with a liquid. What is the difference in levels of the liquid? 3+3=6

- (g) The value of  $K_p$  for the reaction  $NH_3(g) \rightleftharpoons \frac{3}{2}H_2(g) + \frac{1}{2}N_2(g)$  is  $1.36 \times 10^{-3}$  at 298 K.

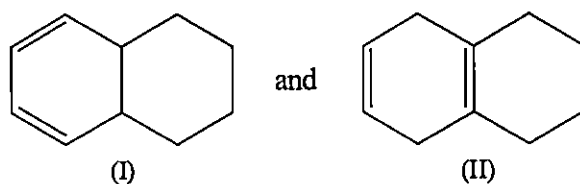
Determine the corresponding value of  $K_c$ . 3

(d) Suggest the mechanism of the following reactions:

5×2=10



(e) How would you distinguish between the two compounds by UV spectroscopic studies? 3



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