calculate the relative molar concentration of Zn^{2+} and Fe^{2+} ions at which the overall cell e.m.f. becomes zero.

Given $E^{\circ}_{Fe^{2+}, Fe} = -0{\cdot}440\,V$ and $E^{\circ}_{Zn^{2+}, Zn} = -0{\cdot}760\,V$ 4

(iii) Deduce an expression for the e.m.f. of the concentration cell with transference. 6

(iv) The e.m.f. of cell with transference

$$Ag \mid AgCl\,(s) \mid HCl\,(a^{+} = 0{\cdot}1751) \,||\, HCl\,(a^{+} = 0{\cdot}09048) \mid AgCl\,(s) \mid Ag$$

at 298 K is 0·02802 volt. The corresponding cell without transference has an e.m.f. of 0·1696 volt. Calculate the transference number of H^{+} ion and the value of the liquid junction potential. 4

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2017

CHEMISTRY

(Major)

Paper : 2.1

(Physical Chemistry)

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Answer in brief : 1×7=7

(a) Find an expression for the kinetic energy of *n*-mole gas from kinetic theory equation.

(b) State for which of the following gases the value of the compressibility factor is always greater than 1.

(i) H_2

(ii) N_2

(iii) CO_2

(iv) CH_4.

(c) Find the SI unit of the van der Waals constant a.

(d) State when the surface tension of a liquid vanishes.

(e) The critical temperatures of NH_3 and CO_2 are 405·5 K and 304·10 K respectively. State which of these two gases will liquefy first when cooling is started from 500 K to lower temperature.

(f) Out of aluminium and silver containers, state which one will be more suitable to store 1 M HCl, given that

$E^{\circ}_{Al^{3+}|Al} = -1 \cdot 66\,V$ and $E^{\circ}_{Ag^{+}|Ag} = 0 \cdot 80\,V$

(g) Find the correct answer :

The transference number of an ion

(i) is always positive

(ii) is always negative

(iii) can be positive as well as negative

(iv) is always zero

2. Answer the following questions : 2×4=8

(a) Deduce the expression for the most probable speed from Maxwell's expression for distribution of molecular speeds.

(b) Discuss the effect of temperature on viscosity of a liquid.

(c) The molar conductances at infinite dilution of NaOH, NaCl and $BaCl_2$ are $2 \cdot 48 \times 10^{-2}$, $1 \cdot 27 \times 10^{-2}$ and $2 \cdot 8 \times 10^{-2}\ S\ m^2\ mol^{-1}$ respectively. Find the molar conductance at infinite dilution of $Ba(OH)_2$.

(d) The dissociation constant of acetic acid at a certain temperature is $1 \cdot 6 \times 10^{-5}$. Find pK_a value.

3. Answer any *three* of the following questions : 5×3=15

(a) Deduce the expressions for critical constants P_c, T_c and V_c in terms of the van der Waals constants. Can a van der Waals gas be liquified for which the value of van der Waals constant a is zero? 4+1=5

(b) Define vapour pressure of a liquid. Explain a method of measurement of vapour pressure of a liquid. 1+4=5

(c) (i) What is meant by the laminar flow of liquid in a tube? 1

(ii) Explain the Ostwald's viscometer method of determination of viscosity of a liquid. 4

(d) Define transport number of ions. In a Hittorf cell, a solution of HCl is electrolyzed using Pt-electrodes. After electrolysis, the mass of HCl in the cathode compartment is found to be 0·14 g, while the initial mass of HCl in the same compartment before electrolysis was 0·155 g. During electrolysis, the mass of Ag deposited in the coulometer, connected in the same circuit is found to be 0·252 g. Find transport numbers of both the ions. 1+4=5

(e) Discuss about the Debye-Hückel theory of strong electrolyte that leads to the Debye-Hückel-Onsager equation. 5

4. (a) Answer *either* [*(i), (ii)* and *(iii)*] *or* [*(iv), (v)* and *(vi)*] :

(i) State and explain the principle of equipartition of energy. 2

(ii) Explain how the molar heat capacities at constant volume and constant pressure of ideal gas can be calculated using the principle of equipartition of energy. 5

(iii) The specific heat of a gas at constant volume is $0 \cdot 3138\ JK^{-1}\ g^{-1}$ and that at constant pressure is $0 \cdot 523\ JK^{-1}g^{-1}$. Calculate molecular mass of the gas. Determine the number of atoms in its molecule. 2+1=3

(iv) By considering pressure and volume correction terms, derive the van der Waals equation of state for n moles of real gas. 5

(v) Discuss the effect of temperature on the distribution of molecular speeds of a gas. Give graphical representations to show this effect. 3

(vi) Calculate the diameter of an oxygen molecule at 298·15 K at the pressure of 101·325 kPa. Given that van der Waals constant $b = 3 \cdot 183 \times 10^{-2}\ dm^3\ mol^{-1}$ for the gas. 2

(b) Answer *either* [*(i)*, *(ii)* and *(iii)*] *or* [*(iv)*, *(v)* and *(vi)*] :

(i) Explain how the van't Hoff factor will vary in case of NaCl solution in water. 2

(ii) Using the concept of chemical potential, show that the elevation of boiling point of a binary dilute solution containing non-volatile, non-electrolyte solute is proportional to the molal concentration of the solution. 5

(iii) A solution containing 3·975 g of sulphur in 100 g of CS_2 boils at 319·67 K. The boiling point of pure CS_2 is 319·30 K and $\Delta H_{vap} = 27 \cdot 78 \text{ kJ mol}^{-1}$. Calculate the molar mass of sulphur in carbon disulphide. 3

(iv) State Raoult's law of ideal solutions. Give its mathematical form explaining the terms involved in it. 2

(v) Using the concept of chemical potential, show that the relative lowering of vapour pressure of a binary dilute solution containing non-volatile non-electrolyte solute is equal to the mole fraction of the solute. 5

(vi) The vapour pressures of pure liquids *A* and *B* at 300 K are 200 mm of Hg and 500 mm of Hg respectively. Calculate the mole fraction in the vapour and liquid phases of a solution of *A* and *B* when the equilibrium total vapour pressure of the binary solution is 350 mm of Hg at the same temperature. Assume that the solution and its vapour behave ideally. 3

(c) Answer *either* [*(i)*, and *(ii)*] *or* [*(iii)* and *(iv)*] :

(i) Define ion mobility. Deduce the relationship between ion mobility and molar conductance. 6

(ii) For the cell reaction

$$Zn\,(s) + Fe^{2+}\,(aq) \rightleftharpoons Zn^{2+}\,(aq) + Fe\,(s)$$

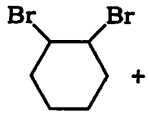
(f) (i) Outline the steps involved in the complete Hofmann degradation of piperidine. 2

(ii) Write the reaction involved in a Chugaev reaction and propose a mechanism. 3

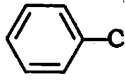
(iii) Why is nitromethane acidic? 1

(iv) Identify the products in the following reactions (major product only) : 4

(1) $CH_3NO_2 + HCHO \xrightarrow{NaOH,\ H_2O} A$

(2)  $+ KI \xrightarrow{Ethanol} B$

(3) $H_3C\ C{\equiv}C\ CH_3 + HCl \longrightarrow C$

(4)  $\xrightarrow[2)\ H_2O_2,\ H_2O,\ NaOH]{1)\ (BH_3)_2,\ THF} D$

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2017

CHEMISTRY

(Major)

Paper : 2·2

(Organic Chemistry)

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Answer the following questions : 1×7=7

(a) Arrange the following in order of decreasing electron releasing ability :

—OH, —OR, —NH_2, —NHR

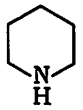
(b) Define specific rotation.

(c) Which compounds are used to make the following acetal?

(d) How can you protect a carbonyl group?

(e) What are the topicities of the hydrogen atom of the —CH_2— group and faces of $>C{=}O$ group in benzyl methyl ketone?

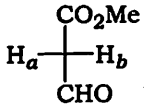
(f) What would you expect to be the site of (i) protonation and (ii) deprotonation if the given compound is to be treated with an appropriate acid or base?

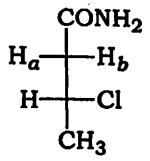


(g) How is the octane rating of gasoline determined?

2. Answer the following questions : 2×4=8

(a) Identify homotopic, enantiotopic and diastereotopic hydrogens (if any) :

(i) 

(ii) 

(b) Calculate the percent of each enantiomer of an unknown (*X*) if the specific rotation of (+)—*X* is +110° and the specific rotation of the mixture is +30°.

(c) A bromine radical is less reactive and more selective than a chlorine radical. Explain.

(d) Draw the *cis*-oid and *trans*-oid conformations of 2*E*, 4*E*-hexadiene and of 2*E*, 4*Z*-hexadiene.

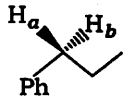
3. Answer the following questions (any *three*) : 5×3=15

(a) (i) Draw chair- and boat-forms of cyclohexane in Newman projection. 2

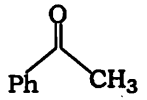
(ii) Explain why chair-form of cyclohexane is more stable than boat-form. 2

(iii) Which conformer of *n*-butane is more stable in the gaseous form? 1

(b) (i) Identify the indicated hydrogens as pro-*R* and pro-*S* : 1



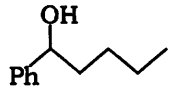
(ii) Identify which face (front or back) is Re face and Si face : 1



(iii) Define prostereogenic centre. State whether each carbon atom in chloroethene is prostereogenic or prochiral or both. 1+2

(c) Account for the observation that NaOH reacts with *p*-bromotoluene to give *m*- and *p*-cresols at 300 °C, while *m*-bromotoluene yields three isomeric cresols. (Use appropriate mechanism) 5

(d) (i) The drug ferripentol, shown below, is synthesized by the reaction between butylmagnesium bromide and an aldehyde. Draw the structure of the aldehyde and give the mechanism for the reaction : 3



(ii) Is a Grignard reagent formed when benzyl bromide is heated with magnesium metal in a mixture of diethyl ether and ethanol as the solvent? Explain. 2

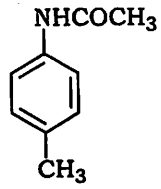
4. Answer the following questions [either *(a) or (b)* and any *two* from *(c), (d), (e)* and *(f)*] : 10×3=30

(a) (i) How can you account for the formation of a σ-complex when benzene undergoes electrophilic attack? 2

(ii) Provide two evidences in support of the arenium ion mechanism. 3

(iii) A chlorine atom is deactivating but *ortho-* and *para*-directing towards electrophilic aromatic substitution. Explain. 4

(iv) In a standard nitration reaction with HNO_3 and H_2SO_4, the following compound forms a single mono-nitration product. What is its structure? 1



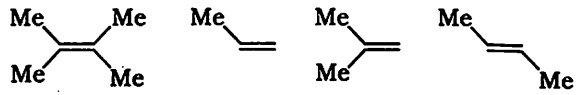
(b) (i) Provide an explanation for the observation that nucleophilic substitution on 4-bromo-2,6-dimethylnitrobenzene is considerably slower than on 4-bromonitrobenzene. 2

(ii) The rates of nucleophilic substitution of nitrohalobenzenes depend on the halogen displaced. What is the order of learning group ability of halogens in such reactions? Provide an explanation. 1+2

(iii) Give an example each of an ipso substitution and cine substitution. 1+1

(iv) The bromination of toluene by using bromine in aqueous acetic acid takes place 605 times faster than does the same reaction of benzene. The product ratio is 32·9% *ortho*-, 0·3% *meta*- and 66·8% *para*-bromotoluene. Calculate the partial rate factors for the reaction. 3

(c) (i) Arrange the following in order of decreasing reactivity towards bromination : 1



(ii) Show that addition of bromine to alkene is stereospecific. Write the mechanisms involved to justify the same. 4

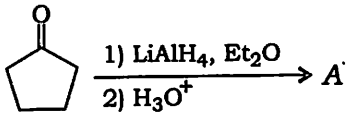
(iii) How can you carry out the conversion of an olefin to the *cis*-diol and *trans*-diol? Write the appropriate mechanisms. 5

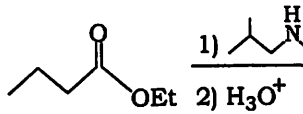
(d) (i) The α-hydrogen atoms of amides have pK_a values near 30. Account for the lower acidity of these hydrogen atoms as compared with the α-hydrogen atoms of esters. 2

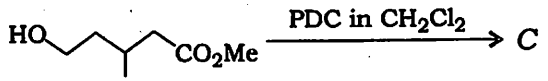
(ii) Propose a mechanism for the Claisen condensation reaction. 3

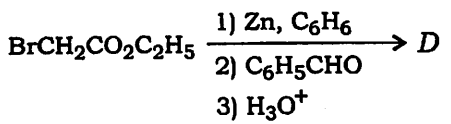
(Continued)

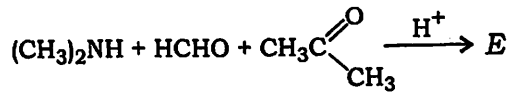
(iii) Identify the products in the following reactions [only the major product(s) is to be written] : 5

(1) 

(2) 

(3) 

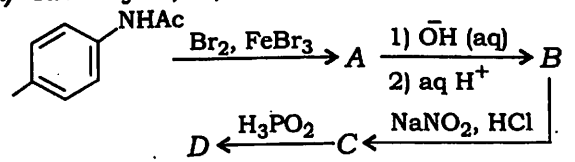
(4) 

(5) 

(e) (i) How can you detect for the presence of nitro- and amino-groups in *m*-nitroaniline? Write the reactions involved. 2

(ii) Aromatic electrophilic substitution on naphthalene is regioselective. Explain. 4

(iii) Identify *A*, *B*, *C* and *D* : 4



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