2018

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 the following as directed : 1×7=7

(a) State True or False :

"Gases can be liquefied by applying pressure at any temperature."

(b) Find the critical volume of helium gas ($b = 0{\cdot}01927\ dm^3\ mol^{-1}$).

(c) If c_0 is the speed of light in vacuum and c is the speed of light in a medium, then what will be the expression for refractive index of the medium?

(d) Choose the correct answer :

At the same temperature, 0·01M solution of urea is isotonic with

(i) 0·01M NaCl solution

(ii) 0·01M $MgCl_2$ solution

(iii) 0·01M glucose solution

(iv) 0·01M sodium acetate solution

(e) Choose the correct answer :

If ΔT_b is the elevation in boiling point for an electrolytic solution and ΔT_b° is elevation of the boiling point for a non-electrolyte solution of the same concentration in the same solvent, then the van't Hoff factor is given by

(i) $\Delta T_b \times \Delta T_b^\circ$

(ii) $\Delta T_b^\circ / \Delta T_b$

(iii) $\frac{\Delta T_b - \Delta T_b^\circ}{2}$

(iv) $\Delta T_b / \Delta T_b^\circ$

(f) Define molar conductivity of an electrolytic solution.

(g) Give the condition for maximum buffer capacity of a buffer solution.

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

(a) For a monatomic ideal gas, show that the molar heat capacity at constant volume is 12·471 $JK^{-1}\,mol^{-1}$.

(b) A liquid *P* has half the surface tension of liquid *Q*. Again the density of liquid *P* is twice the density of liquid *Q*. If in a capillary tube *P* rises to 10·0 cm, what will be the rise of liquid *Q* in the same capillary tube when inserted identically at the same temperature?

(c) Define ideal solutions. Give the values of ΔV and $\Delta_{mix} H$ for an ideal solution.

(d) What are concentration cells? Give one suitable example of concentration cell with transference.

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

(a) *(i)* Give the postulates of kinetic molecular theory of gases. 3

(ii) Give the limitations of van der Waals equation of state. 2

(b) What is 'degrees of freedom' of a molecule? Calculate the various degrees of freedom of the following molecules : 2+3=5

(i) CO_2

(ii) H_2O

(c) (i) Give the principle of the stalagmometer method of determination of surface tension of a liquid. 3

(ii) The numbers of drops of water and an organic liquid in drop number method from a stalagmometer are 100 and 200 respectively. Calculate the surface tension of the organic liquid at 298 K. Given that at 298 K, the surface tension of water is $7 \cdot 28 \times 10^{-3}$ N m^{-1}, density of water is $1 \cdot 0$ kg dm^{-3} and density of the organic liquid is $0 \cdot 9$ kg dm^{-3}. 2

(d) (i) What is limiting molar conductivity? State the Kohlrausch law of the independent migration of ions. 2

(ii) The limiting molar conductances of Al^{3+} and SO_4^{2-} are 189 S cm^2 mol^{-1} and 160 S cm^2 mol^{-1} respectively. Calculate the limiting molar conductance of $Al_2(SO_4)_3$. 3

(Continued)

(e) (i) Define degree of dissociation of a weak electrolyte. 1

(ii) State Ostwald's dilution law. Explain the law with the help of a suitable example. 4

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

(i) Derive the equation of corresponding states. Justify why this equation can be considered as a generalized equation of state for a gas. 5

(ii) Derive an expression for osmotic pressure of a dilute solution from thermodynamic consideration. 5

(iii) What are transport properties of gas? Using kinetic theory, derive an expression for self-diffusion coefficient of a gas. 5

(iv) Discuss the construction of a calomel electrode. Explain the reaction taking place in the electrode. 5

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

(i) Define the terms collision cross-section and mean free path. 3

(ii) What are liquid crystals? Mention the uses of liquid crystals. 4

(iii) A solution, composed of 0·05*M* of an organic acid and 0·5*M* of its sodium salt, gives a pH of 5·5 at 298 K. Calculate the dissociation constant of the acid. 3

(iv) Explain the terms activity and activity coefficient. 2

(v) Discuss briefly about the structure of liquid crystals. 4

(vi) What is ionic strength of an electrolytic solution? Calculate the ionic strength of 0·01 mol kg^{-1} H_2SO_4 solution. 1+3=4

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

(i) What is buffer capacity of a buffer solution? Explain the term buffer action with the help of a suitable example. 1+4=5

(ii) Define electrode potential. Calculate the single electrode potential at 298 K of a half-cell for zinc electrode dipped in 0·01*M* $ZnSO_4$ solution. Given

$$E^{\circ}_{Zn^{2+}|Zn} = -0.763 \text{ volt}$$ 1+4=5

(Continued)

(iii) What are fuel cells? Write the electrode reactions of hydrogen-oxygen fuel cell. Calculate the standard e.m.f. of hydrogen-oxygen fuel cell. Mention one use of fuel cell. 1+2+2+1=6

(iv) Explain briefly how equilibrium constant can be calculated from the measurement of standard electrode potential. 4

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(Organic Chemistry)

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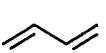
1. Answer any *seven* questions : 1×7=7

(a) Explain, why β-keto acids like $RCOCH_2CO_2H$ readily decarboxylate on heating.

(b) Indicate which reagent is expected to be more nucleophilic toward CH_3Br in ethanol and why :

$p\text{-}NO_2C_6H_4O^-$ or $p\text{-}CH_3C_6H_4O^-$

(c) Predict the major product :



(d) How would the pK_a values of ammonium ions change if they were determined in a solvent less polar than water?

(e) Arrange the following classes of compounds in decreasing order of boiling point considering that they have same number of carbon atoms :

Carboxylic acids, Amides, Ketones, Nitriles

(f) Semicarbazide has two NH_2 groups, but only one of them forms an imine. Explain.

(g) Which tautomeric form of 2,4-pentanedione is more stable in—

(i) water;

(ii) hexane?

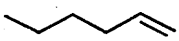
(h) The reaction of an alkene with Br_2 does not require a Lewis acid but the reaction of benzene does. Why?

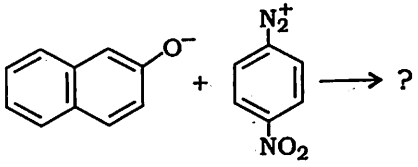
2. Answer any *four* questions : 2×4=8

(a) With the help of an example, bring out the difference between a chiral centre and a stereogenic centre.

(b) Ketones do not undergo Knoevenagel reaction with malonic acid or its esters. Why?

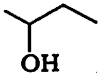
(c) What products would you expect from the following reactions? 1×2=2

(i)  + NBS $\xrightarrow{\text{peroxide}}$?

(ii) 

(d) Account for the fact that acetals are stable to bases but are readily hydrolyzed by acids. 2

(e) How would you employ organometallic reagents to make the following compounds? 1×2=2

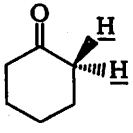
(i) 

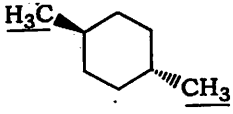
(ii) 

3. Answer any *two* from *(a)*, *(b)* and *(c)* and any *one* from *(d)* and *(e)* : 5×3=15

(a) Compare the relative stabilities of chair, boat and twist-boat conformations of cyclohexane. 5

(b) (i) Indicate whether the underlined atoms or groups are homotopic, enantiotopic or diastereotopic : 2





(ii) Using 2,3,4-trihydroxyglutaric acid, point out the stereogenic, non-stereogenic, chirotopic and achirotopic carbons. 3

(c) (i) Which conformer is favoured in ethylene glycol and why? 1½

(ii) Which conformer is favoured in 1,2-dibromoethane and why? 1½

(iii) Butane has chiral conformers, yet it is optically inactive. Explain. 2

(d) Provide evidences for aromatic electrophilic substitutions involving—

(i) π-complex;

(ii) σ-complex.

Draw the energy profile diagram for both the mechanisms. 4+1

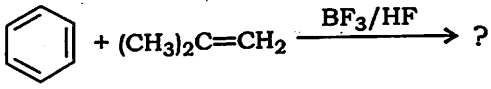
(e) (i) What do you mean by partial rate factor? How is it calculated? 1+1=2

(ii) The chlorination of toluene by using chlorine in aqueous acetic acid takes place 344 times faster than does the same reaction of benzene. The product ratio is 59·9% *ortho*-, 0·3% *meta*- and 39·8% *para*-chlorotoluene. Calculate the partial rate factors for the reaction. 3

(Continued)

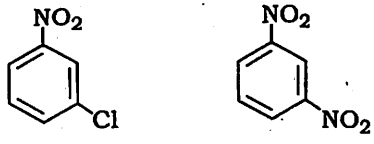
4. Answer either *(a) or (b)* and any *two* from *(c), (d), (e)* and *(f)* : 10×3=30

(a) *(i)* Write the product obtained for the reaction given below and propose a mechanism for the same : 1+3=4



(ii) Nitration of *N,N*-dimethyl aniline gives mainly the *m*-nitro derivative when concentrated nitric and sulphuric acids are used but mainly the *o*- and *p*-nitro derivatives in less acidic conditions. Why? 2

(iii) Indicate the position(s) of major monoelectrophilic substitution of each of the following compounds and account for the same : 2



(iv) When nitrations of aromatic substrates are carried out, nitronium ion is said to act as an electrophile. Provide two evidences in support of formation of the nitronium ion. 2

(b) (i) What happens when methyl picrate is allowed to react with potassium ethoxide? Propose a mechanism for the reaction and justify with evidences. 1+2+1=4

(ii) Account for the observation that nucleophilic substitution of chlorobenzene takes place through a benzyne mechanism whereas nucleophilic substitution of chloronitrobenzenes proceeds via the addition-elimination sequence. 3

(iii) Why is S_N1 mechanism common to diazonium compounds? Provide evidence in support of the reversible nature of the first step of the mechanism. 3

(c) (i) Why is propene more reactive towards electrophilic addition than ethene? Explain. 2

(ii) Propose a mechanism for the formation of *meso*-1,2-dibromostilbene by the addition of bromine to 2-stilbene in nitromethane. 3

(iii) What is decarboxylation? What product(s) is/are formed by the decraboxylation of 2-methylbutanoic acid? 2

(Continued)

(iv) How can the compound $HOCH_2CH_2NH_2$ be prepared, starting with a carbonyl compound with one fewer carbon atom than the desired product? 2

(v) What do you mean by reductive amination? 1

(d) (i) How can you convert cyclohexene to *trans*-1,2-cyclohexane diol? Propose a mechanism for the reaction. 3

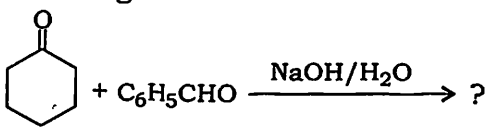
(ii) Compound *A* ($C_{10}H_{16}$) takes up 2 mols of hydrogen on catalytic hydrogenation. Ozonolysis gives two diketones, *B* ($C_6H_{10}O_2$) and *C* ($C_4H_6O_2$). Propose a reasonable structure (or structures) of *A*. 2

(iii) Account for the fact that aliphatic α-chloroamines hydrolyse even more rapidly than the related α-chloroethers. 3

(iv) How can you prepare pentan-1-ol from pentene? Write the reaction. 2

(e) (i) Although an aryl group is usually found to be electron-withdrawing relative to alkyl, aromatic aldehydes tend to be less reactive than aliphatic aldehydes. Explain. 2

(ii) Predict the major product and propose a mechanism for the reaction given below : 3



(iii) Using the Hell-Volhard-Zelinsky reaction, propose a synthetic route for the preparation of alanine. 2

(iv) Give a chemical method to distinguish three isomeric amines having the molecular formula C_3H_9N. 3

(f) (i) Propose a mechanism for the benzoin condensation reaction. What role does cyanide ion play in this reaction? 3+1=4

(ii) Grignard reagents fail to form addition compounds with olefins. Why? 2

(iii) Distinguish between phenol and benzyl alcohol using chemical methods. 2

(iv) Diazonium salts can be used to prepare heterocyclic compounds. What happens when *o*-phenylene-diamine is diazotized? Write the reaction. 2

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