2010

CHEMISTRY

(Major)

Paper : 1.1

(Physical Chemistry)

Time : 3 hours

The figures in the margin indicate full marks for the questions

Candidates ***eligible*** *for Internal Assessment shall answer only one part each from Question Nos. 1 and 2 along with the rest of the questions* (*Marks* : 65)

Candidates ***not eligible*** *for Internal Assessment shall answer only two parts each from Question Nos. 1 and 2 along with the rest of the questions* (*Marks* : 75)

1. *(a)* State the most important postulates of the kinetic-molecular theory. Do they have any practical significance? Comment on the way the molecular speeds are distributed for *(i)* hydrogen, nitrogen and carbon dioxide at 300 K and for *(ii)* oxygen at 100 K, 500 K and 800 K. 5

(b) Define the compressibility factor of a gas. How can it be used to describe the deviation from ideal behaviour? 5

(c) Obtain an expression for the collision frequency in a mixture of two ideal gases. 5

(d) How does thermal conductivity of an ideal gas change with temperature? Obtain an expression for the thermal conductivity on the basis of the kinetic-molecular theory. 5

2. (a) Distinguish among closed, isolated and open thermodynamic systems. The enthalpy change for the formation of NOCl(g) from the gaseous elements is 51·71 kJ/mol at 298 K. If the gases are ideal, calculate internal energy change. 5

(b) Derive general expressions for E(thermal) of ideal monatomic, diatomic, linear polyatomic and non-linear polyatomic gases. 5

(c) If a sample of gas is allowed to expand at constant temperature against atmospheric pressure, *(i)* does the gas do work on its surroundings; *(ii)* is there heat transfer between the system and the surroundings; *(iii)* what is ΔE for the process? A non-ideal gas is heated slowly and the gas expands reversibly at a constant pressure of 760 mm from a volume of 1385 cm^3 to 1875 cm^3. Find the work done in joules. 5

(Continued)

(d) For each of the following out whether each of the ΔU and ΔH is positive, z

(i) Reversible melting and 0 °C

(ii) Reversible adiabat an ideal gas

(iii) Adiabatic expansio into vacuum

3. Answer any *five* of the follo

(a) Calculate the entrop 1·00 mol of water unde vaporization and fusio 0 °C respectively. As enthalpy changes for fusion of water 40·656 kJ/mol and 6·

(b) State how the entropy heat capacity. Calcul change for the reve 1·00 mol of ethane 1500 K at constant that

$$C_p = 5 \cdot 351 + 177 \cdot$$

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(c) What are the characteristics of a spontaneous process? State how the entropy will change in case of *(i)* freezing of ethanol, *(ii)* dissolving glucose in water, *(iii)* evaporation of bromine from a bromine solution at room temperature and *(iv)* cooling nitrogen gas from 373 K to 273 K.

(d) State and explain Nernst heat theorem. What is the most important application of the third law of thermodynamics?

(e) In the relation $\Delta G = \Delta H - T\Delta S$, state the conditions when ΔG can be positive or negative. Obtain the relation between the equilibrium constant and the standard Gibbs energy change.

(f) Of the following pairs, which has higher chemical potential?

(i) H_2O (l) at 298 K, 1 atm and H_2O (g) at 298 K, 1 atm

(ii) H_2O (s) at 273 K, 1 atm and H_2O (l) at 273 K, 1 atm

(iii) H_2O (s) at 268 K, 1 atm and supercooled H_2O (l) at 268 K, 1 atm

(iv) Glucose (s) at 298 K, 1 atm and glucose (aq.) at 298 K, 1 atm

Give brief reason in each case.

(Continued)

(g) Calculate ΔG for compression of 30·0 g 1·0 atm to 100·0 atm variations in V with p

4. Answer any *two* of the follo

(a) Clearly state Ostwald's law. Show how these l to predict the behaviou a real solution.

(b) What are abnor properties? Give exa solutions show positi deviations from ideal properties of mixing solvent?

(c) The vapour pressure o is 1074·6 mm. Find th at the same temperatu sucrose solution in approximation you ha

(d) Define 'activity' coefficients'. State how depend on *(i)* concer perature and *(iii)* pres

(e) Discuss qualitatively liquid water. Why ar important?

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

(a) What do you mean by zero-order and pseudo-order reactions? Give examples.

(b) Obtain the integrated rate expression for a first-order reaction and draw a graph to show variation of the concentration of the reactant with time.

(c) For a homogeneous reaction $aA + bB + cC + ... = eE + fF + ...$, obtain the complete rate expression. Show that the rate is an intensive property that depends on T, p and concentration.

(d) Show, indicating the principle involved, how an expression for the concentration of the final product can be obtained for a consecutive reaction of the type $A \rightarrow B \rightarrow C$. How do the concentrations of A, B and C change with time?

(e) How does the reaction rate depend on temperature? Show how Arrhenius plot of a reaction can be obtained. What is the significance of the pre-exponential factor?

(f) Discuss the kinetics of thermal decomposition of ethanol.

(g) What are zeolites? Why are they important as catalysts? Give two examples where zeolites are used as catalysts.

(Continued)

6. Answer any *five* of the follo

(a) Define mobility of an io have different mobilitie

(b) State how the molar c strong electrolyte soluti concentration accordi Hückel-Onsager equati between the two pa qualitatively why the e higher concentrations.

(c) How many different typ exist? Describe the calomel electrode.

(d) Give an expression for t of an electrolyte solutio ionic strength of 0·05 m KCl and $Zn(NO_3)_2$.

(e) Define pK of acids and you arrange a numb respect of their pK examples.

(f) Describe a concentra transference.

(g) Write short notes on :

(i) Dry cells

(ii) Corrosion and its

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2010

CHEMISTRY

(Major)

Paper : 1.2

(Organic Chemistry)

Time : 3 hours

The figures in the margin indicate full marks for the questions

Candidates ***eligible*** *for Internal Assessment shall answer from* PART—I *only* (*Marks* : 65)

Candidates ***not eligible*** *for Internal Assessment shall answer both from* PART—I *and* PART—II (*Marks* : 75)

PART—I

(*Marks* : 65)

1. Answer any *four* of the following : 1×4=4

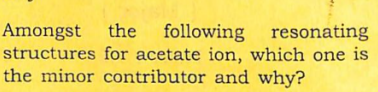
(a) Arrange the following bonds in the increasing order of bond lengths :

C—H ; O—H ; N—H

(b) Why does neopentane melt at a higher temperature (–16·8 °C) than pentane (–129·8 °C)?

(c) Of ethanol and dimethyl ether (functional group isomers), which one will have a higher boiling point and why?

(d) Amongst the following resonating structures for acetate ion, which one is the minor contributor and why?

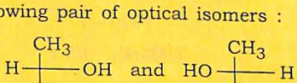


(e) Which one of the two, ethanol and ethane thiol is a stronger acid?

(f) Why is acetic acid a stronger acid than propanoic acid?

2. (a) Draw and label the *E,Z*-isomers of 1-chloro-2-methyl-pent-1-ene. 1

(b) Give the *R* and *S* designations to the following pair of optical isomers : 1



(c) Draw the Newman projection formula for the staggered conformation of the compound

$$CHOCH(OH)CH(OH)CH_2OH$$

with $C_2—C_3$ bond as the projected bond. 1

(*Continued*)

(d) Draw the chair conforma methyl-4-*t*-butyl cycloh identify the more stable i

Or

Draw the chair conf *cis*-1,3-dimethyl cycloh comment on its optical a

(e) What is a racemic mixtu method for the resolution mixture with a suitable e

Or

What are diastereomers? answer with suitable exa

3. (a) Give the products in reactions (any *four*) :

(i) $RCH{=}CHR \xrightarrow{OsO_4} A$

(ii) $CH_3COOH \xrightarrow[/H^+]{EtOH} C$

(iii) $RCOOH \xrightarrow{PCl_5} E \xrightarrow{Pd/Boil}$

(iv) $CH_3NO_2 + PhCHO \xrightarrow{^-OH}$

(v) $RCHOHR \xrightarrow[\Delta]{[(CH_3)_3CO]_3A}$

(b) Why is acetylenic hydrogen acidic in nature? Give one reaction showing the acidic nature of acetylenic hydrogen. 2

(c) Describe how starting from Ag-carboxylate, an alkyl bromide can be synthesised. 2

Or

What happens when—

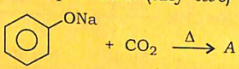
(i) glycerol is heated with $KHSO_4$;

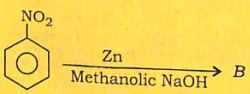
(ii) propanoic acid is treated with P/Br_2?

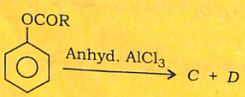
(d) Describe how you can distinguish among 1°, 2° and 3° amines. 2

4. Answer any *four* of the following : 2×4=8

(a) Give the products (any *two*) :

(i) 

(ii) 

(iii) 

(*Continued*)

(b) What is *ortho*-effect? basis, why nearly all benzoic acids are stron benzoic acid.

(c) Explain why electrophi in naphthalene prefe place in position 1 than

(d) Amongst phenol and identify the stronger reason for that.

(e) Write short note on (an

(i) Friedel-Crafts alkyla

(ii) Benzoin condensati

5. Answer any *five* of the follow

(a) What is allylic bromin the allylic brominatior succinimide and discuss support of the free radic reaction.

(b) What is Walden inversi evidence in suppor inversion.

(c) What is an epoxidation reaction? Give its mechanism. Illustrate with a suitable example, how a *trans*-diol could be synthesised from an alkene through epoxidation.

(d) Write the two empirical rules which govern the orientation in the elimination reactions of an unsymmetrical substrate. Provide explanations for these rules.

(e) What is *syn*-elimination? Discuss a pyrolytic *syn*-elimination reaction with the mechanism.

(f) Write short notes on (any *two*) :

(i) Aldol condensation

(ii) Reformatsky reaction

(iii) Knoevenagel reaction

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

(a) What are σ- and π-complexes in the context of electrophilic aromatic substitution? Illustrate your answer with suitable examples. Draw an energy profile diagram for electrophilic aromatic substitution on benzene ignoring the formation of the π-complex.

(*Continued*)

(b) What is the interme mechanism in aromat substitution? Illustrate with a suitable example

(c) What do you understand intermediates? How doe establishment of benzyn aromatic nucleophilic su

(d) What is an organolithiu a general method of an organolithium reage Complete the followin reactions showing intermediates and prod

(i) Ph-Br $\xrightarrow[THF]{Li}$ *A* $\xrightarrow{PhC}$

(ii)  $\xrightarrow[(C_2H_5)_2O/-78\ ^\circ]{(CH_3)_2CuLi}$

PART—II

(*Marks* : 10)

(In lieu of Internal Assessment)

7. Answer any *five* of the following : 2×5=10

(a) Draw the tautomers of acetoacetic ester. Identify the stable form and explain why it is more stable than the other form.

(b) Define enantiotopic and diastereotopic hydrogens. Give examples.

(c) What happens when benzaldehyde is treated with a strong base?

(d) Starting from nitrobenzene, how can you synthesise *p*-dinitrobenzene?

(e) Explain why the nitro group is *m*-directing in aromatic electrophilic substitution.

(f) Explain why *N*-ethylamine is more basic than *N*-methylamine.

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