2022

CHEMISTRY

(Honours)

Paper : CHE–HC–3016

(Inorganic Chemistry–II)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

1. Answer ***any seven*** of the following questions : 1×7=7

   (i) Find the Valence Electron Count of B_5H_9.

   (ii) Explain why *LiI* is soluble in water whereas *LiF* is only slightly soluble.

   (iii) Melting point of $BeCl_2$ (405°C) is much less than that of $CaCl_2$ (782°C). Why ?

   (iv) Why is F_2 highly reactive ?

(v) Iodine is almost insoluble in water, but it readily dissolves in aqueous solution of *KI*. Explain.

(vi) I^- is a soft base. (*True/False*)

(vii) A decrease in lattice energy favours decreased solubility, but a decrease in hydration energy favours increased solubility. (*True/False*)

(viii) *LiOH* is more basic than *NaOH*. (*True/False*)

(ix) $2XeF_6(s) + 3SiO_2(s) \rightarrow$

(x) $B_2H_6 + 2(CH_3)_3N \rightarrow$

(xi) $ZnCl_2 + 2N_2O_4 \rightarrow$

(xii) What is a levelling solvent?

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

(i) Applying Wade's rule, predict and draw the structure of $2\text{-}CB_5H_9$.

(ii) Arrange the following oxoacids of chlorine in decreasing order of their acid strengths. Write justification for your choice.
$HClO_4$, $HClO_3$, $HClO_2$, $HClO$

(iii) Bond strengths of $F\text{-}F$ in F_2 and $O\text{-}O$ in H_2O_2 are very weak. Why?

(iv) List the following in order of increasing solubility in water. Give justification.
LiF, KF, CsF, RbF, NaF

(v) Compare $[Be(H_2O)_4]SO_4$ and $[Mg(H_2O)_6]SO_4$. Be^{2+} has only four coordinated water molecules whereas Mg^{2+} has more than four coordinated water molecules. Explain.

(vi) Arrange the following compounds in ascending order of their solubility in water. Give explanations.
AgF, AgCl. AgBr, AgI

(vii) What is inert pair effect?

(viii) A large number of acids can be studied in which solvent — ammonia or water. Why?

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

(i) Briefly discuss bonding and structure of XeF_6. 2½+2½=5

(ii) What is diagonal relationship? Write *any four* similar properties of *Be* and *Al*. 1+4=5

(iii) Write *any five* differences between lithium and other group 1 elements.

(iv) Briefly discuss the reactions of lithium (*Li*) with water, dinitrogen and dioxygen.

(v) Briefly discuss hydrometallurgy with the help of a suitable example.

(vi) What is borazine? Describe its structure and bonding. 1+4=5

(vii) (a) State the Pauling's rules for determination of strength of mononuclear oxoacids.

(b) Use the Pauling's rule to state which is the stronger acid — H_2SO_4 or H_2SO_3.

(c) Pauling's rule is useful in detecting structural anomalies. Explain. 2+1+2=5

(viii) Describe the Mond's process for extraction and purification of Nickel.

4. Answer ***any three*** of the following questions : 10×3=30

(i) Discuss about the following Ellingham diagram. What will be the minimum temperature for reduction of *MgO* by carbon? Write the reduction reaction of *MgO* by carbon at this temperature. 5+2+3=10

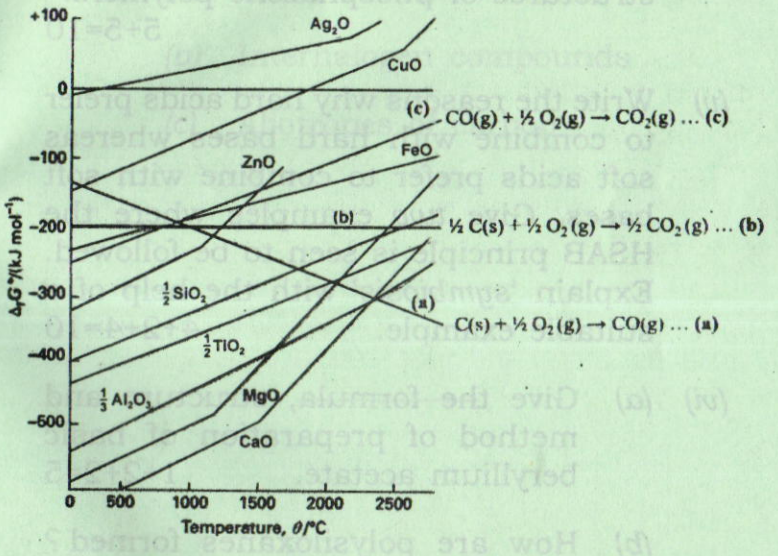


Fig. Ellingham diagram for the reduction of various metal oxides.

(ii) What are clays? Discuss the structure of kaolinite clay. Write the general chemical formula of zeolites. Write *any two* applications of zeolites. 1+3+2+4=10

(iii) How are fullerenes synthesized? Discuss the structures of C_{60} and C_{70} fullerenes. Write the number of peaks that appear in the ^{13}C NMR spectra of C_{60} and C_{70}. 2+3+3+1+1=10

(iv) Write about the allotropes of phosphorus. Discuss the synthesis and structures of phosphazene polymers. 5+5=10

(v) Write the reasons why hard acids prefer to combine with hard bases whereas soft acids prefer to combine with soft bases. Give *two* examples where the HSAB principle is seen to be followed. Explain '*symbiosis*' with the help of a suitable example. 4+2+4=10

(vi) (a) Give the formula, structure and method of preparation of basic beryllium acetate. 1+2+2=5

(b) How are polysiloxanes formed? Distinguish between Silicon fluids and silicon rubbers. 2+3=5

(vii) (a) What are MDFs? Prepare a synthesis of *any one* MDF and give its structure. Mention *one* important application of MDF. 1+3+1=5

(b) What is the expected geometry of $[BrF_6]^-$ and $[IF_6]^-$. Explain the similarity or difference in their geometry. 5

(viii) Write short notes on : ***(any two)*** 5+5=10

(a) Pseudohalogens

(b) Interhalogen compounds

(c) Allotropes of carbon

(h) How can you carry out the following conversions ? 1+4+1+4=10

(a) Cyclohexanone to ε-Caprolactam

(b) Benzil to Benzilic acid

Write the reactions involved and propose mechanisms for each of the conversions.

Total number of printed pages–12

3 (Sem–3/CBCS) CHE HC 2

2022

CHEMISTRY

(Honours)

Paper : CHE–HC–3026

(Organic Chemistry–II)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

1. Answer the following questions ***(any seven)*** : 1×7=7

(a) What are the reagents used in Bouveault-Blanc reduction reaction ?

(b) Why thiols are also called as mercaptans ?

(c) Why are oxiranes reactive in comparison to other cyclic ethers ?

(d) Name *two* acids which can cleave an ether linkage.

(e) Why it is more advantageous to use thionyl chloride in place of phosphorous pentachloride in the preparation of acid chlorides ?

(f) What is saponification ?

(g) Draw the orbital diagram of a S_N2 transition state.

(h) Arrange the following in order of increasing nucleophilicity :

PhO^-, ^-OH, AcO^-, TsO^-

(i) Name *one* reagent that can convert an acid chloride to aldehyde.

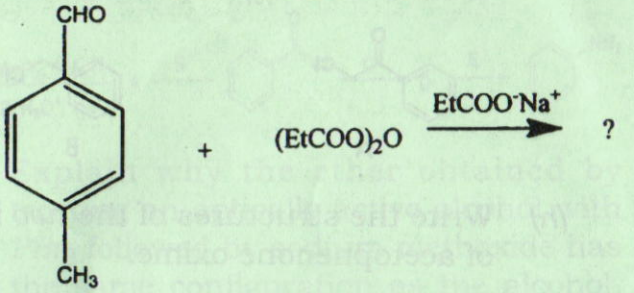
(j) Compound $A(C_5H_{10}O)$ forms a phenylhydrazone, gives negative Tollen's and iodoform test and can be reduced to pentane. What is the compound ?

(k) What is Fremy's salt ? Write its structure.

(l) Why don't *N*-nitrosoamines which form from secondary amines lead to diazonium ions ?

2. Answer the following questions : ***(any four)*** 2×4=8

(a) Predict the product obtained in the following reaction. Give the name of this reaction :



(b) What is cumene ? How is it being utilized for the synthesis of phenol ?

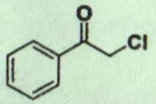
(c) If propionyl chloride is added to one equivalent of methylamine, only a 50% yield of *N*-methylpropanamide is obtained. If, however, the acyl chloride is added to two equivalents of methylamine, the yield of *N*-methyl-propanamide is almost 100%. Explain.

(d) Propose a synthesis of *n*-propylbenzene using organolithium compound.

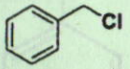
(e) Explain why a Claisen condensation product is not obtained from ester such as ethyl benzoate.

(f) What do you mean by stabilized ylides ? Give an example.

(g) Of the two compounds A and B shown below, which one is more reactive towards I^- in S_N2 conditions and why ?



A



B

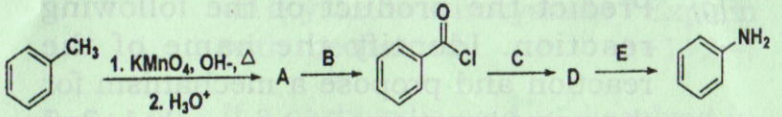
(h) Write the structures of the *two* isomers of acetophenone oxime.

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

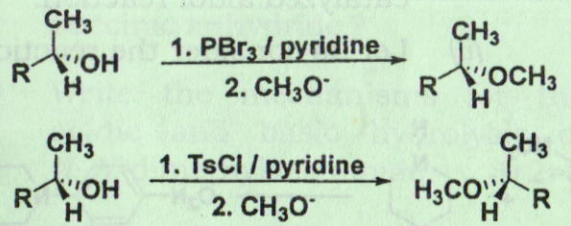
(a) What is Swern oxidation ? What is the active species that helps in the oxidation process ? Explain the mechanism by considering a suitable example. 1+1+3=5

(b) What are arene sulfonic acids ? Why they are much stronger than comparably substituted carboxylic acids ? Write the reaction for *any one* method of synthesis of arene sulphonic acid ? How can they be converted to sulphonyl chlorides ? 1+2+1+1=5

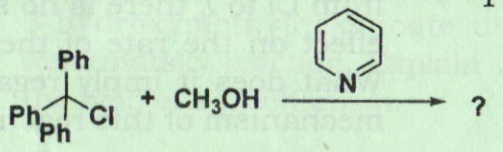
(c) The reaction sequence given below shows how a methyl group on a benzene ring can be replaced by an amino group. Identify the missing reagents and intermediates with proper justification.



(d) Explain why the ether obtained by treating an optically active alcohol with PBr_3 followed by sodium methoxide has the same configuration as the alcohol, whereas the ether obtained by treating the alcohol with tosyl chloride followed by sodium methoxide has a configuration opposite that of the alcohol.

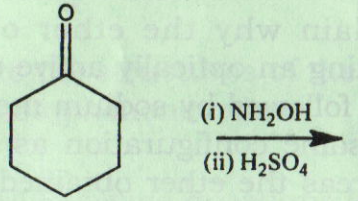


(e) Complete the following reaction and propose a mechanism for the same : 1+4=5



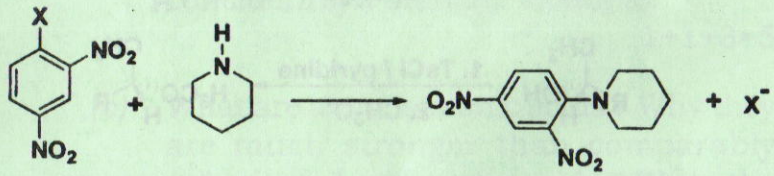
(f) Write the steps involved in a Benzyne mechanism. Provide evidence *(any one)* in support of the proposed mechanism. 3+2=5

(g) Predict the product of the following reaction. Identify the name of the reaction and propose a mechanism for the name reaction. 1+1+3=5



(h) (i) Propose a mechanism for acid catalyzed aldol reaction. 3

(ii) Let us consider the reaction



When the substituent *X* is changed from *Cl* to *I*, there is no significant effect on the rate of the reaction. What does it imply regarding the mechanism of this reaction ? 2

4. Answer following questions : ***(any three)*** 10×3=30

(a) (i) Write a reaction for the preparation of an acyl azide. How can you convert an acyl azide to isocyanate ? Explain with mechanism. 1+1+2=4

(ii) If a carboxylic acid is dissolved in isotopically labelled methanol ($CH_3{}^{18}OH$) and an acid catalyst is added, where will the label reside in the product ? Explain. 3

(iii) Write a reaction for the formation of succinic anhydride in the presence of acetic anhydride. How does acetic anhydride help in the formation of succinic anhydride ? 3

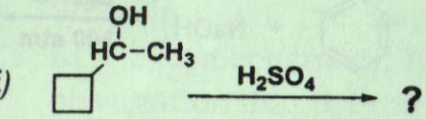
(b) (i) Write the mechanisms for the acidic and basic hydrolysis of *N, N*-dimethylacetamide. 3+2=5

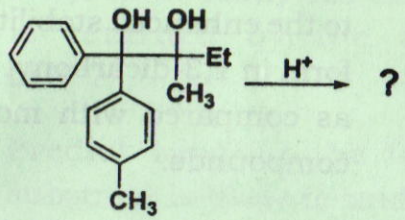
(ii) Why nucleophilic addition of the organozinc compound does not occur to the ester group in Reformatsky reaction ? How can you prepare 3-hydroxymethylhexanoate using Reformatsky reaction. Explain with the help of a mechanism. 5

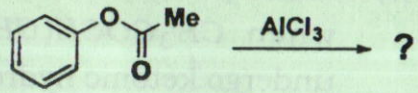
(c) (i) Compound **A** ($C_7H_{11}Br$) is treated with magnesium in ether to give **B** ($C_7H_{11}MgBr$), which reacts violently with D_2O to give 1-methylcyclohexene with a deuterium atom on the methyl group **C**. Reaction of **B** with acetone (CH_3COCH_3) followed by hydrolysis gives **D** ($C_{10}H_{18}O$). Heating **D** with concentrated H_2SO_4 gives **E** ($C_{10}H_{16}$), which decolorizes two equivalents of Br_2 to give **F** ($C_{10}H_{16}Br_4$). **E** undergoes hydrogenation with excess H_2 and a *Pt* catalyst to give iso-butylcyclohexane. Determine the structures of compounds **A** through **F**, and show your reasoning throughout. 7

(ii) When ethylene oxide is treated with anhydrous *HBr* gas, the major product is 1,2-dibromoethane. When ethylene oxide is treated with concentrated aqueous *HBr*, the major product is ethylene glycol. Explain these observations. 3

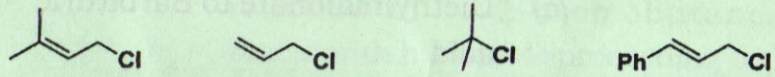
(d) Predict the products of the following transformations and justify your answer with mechanism : 3+4+3=10

(i) 

(ii) 

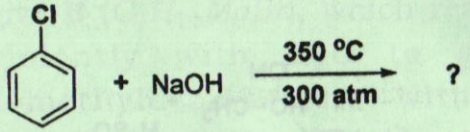
(iii) 

(e) (i) Arrange the following in decreasing order of hydrolysis in 50% aqueous *EtOH* at 45°*C*. 2



(ii) Propose a mechanism for acid catalyzed hemiacetal formation from aldehyde and ethanol. 3

(iii) Complete the reaction. Propose a mechanism for the same clearly mentioning the steps involved. 5



(f) (i) Suggest *one* factor that contributes to the enhanced stability of the enol form in 1,3-dicarbonyl compounds as compared with monocarbonyl compounds. 2

(ii) What products will be obtained when $CH_3COCH(CH_3)COOC_2H_5$ undergo ketonic hydrolysis ? Write the reactions involved. 2

(iii) Write the reactions involved in the conversion of *(any two)* 2+2=4

(a) Diethylmalonate to Barbituric acid

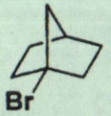
(b) Ethylacetoacetate to Crotonic acid

(c) Ethylacetoacetate to Heptan-2-one

(iv) Between organolithium and Grignard reagent which one is more reactive and why ? 2

(g) (i) Write in detail the steps involved in a S_N1 mechanism. Explain the observation that the rate of the S_N1 reaction of many *RX* derivatives is retarded by the addition of X^-? 3+1=4

(ii) Predict whether the following substrate is likely to undergo S_N1 and/or S_N2 reaction or neither ? Explain. 3



(iii) Use *either* Wedge formula *or* Fischer projection to show the reaction of *S*-2-bromobutane reacts with hydroxide proceeding by S_N2 mechanism ? 2

(iv) Which is a better nucleophile and why 1

$n^-C_4H_9O^-$, $t^-C_4H_9O^-$?

(ii) How is the phase rule applied in the preparation of freezing mixture? 3

(h) (i) What are consecutive reactions? Give one example. 3

(ii) Discuss the kinetics of a consecutive reaction to obtain the concentration of product. Show how the concentrations of different species involved in a consecutive reaction vary with time. 5+2=7

Total number of printed pages–8

3 (Sem–3 /CBCS) CHE HC 3

2022

CHEMISTRY

(Honours)

Paper : CHE–HC–3036

(Physical Chemistry III)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

(Symbols used signify their usual meaning)

1. Answer ***any seven*** of the following as directed : 1×7=7

(a) Define phase of a system.

(b) For a one-component system, maximum number of phases that can exist in equilibrium is three.
*(State true **or** false)*

(c) The order of a chemical reaction at $300K$ is 1. The order of the reaction at $600K$ will be

(i) 0
(ii) 1
(iii) 1·5
(iv) 2 *(Choose the correct option)*

(d) For a *nth* order reaction which of the following relations is correct ?

(i) $t_{\frac{1}{2}} \propto \frac{1}{a^{n-1}}$
(ii) $t_{\frac{1}{2}} \propto \frac{1}{a^{1-n}}$
(iii) $t_{\frac{1}{2}} \propto \frac{1}{a^{n+1}}$
(iv) $t_{\frac{1}{2}} \propto \frac{1}{a^{1+n}}$ *(Choose the correct option)*

(e) Give one example of parallel reaction.

(f) What is a negative catalyst ?

(g) Explain how physical adsorption is influenced by temperature.

(h) An iceberg is floating in a lake. Considering the lake, iceberg and atmosphere as a single system, determine the number of phases.

(i) Consider a heterogeneous system of p phases at equilibrium containing three components. Express degrees of freedom F of the system.

(j) Give one example of a reaction where order and molecularity are the same.

(k) Give *one* example of chemical adsorption process.

(l) What is meant by selectivity of a catalyst ?

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

(a) Can there be a 'quadruple point' on a phase diagram for a one-component system ? Give reason.

(b) Explain why solid-liquid equilibrium line has a negative slope.

(c) State and explain the steady state approximation.

(d) What is temperature coefficient of a reaction ?

(e) Describe the characteristics of a catalytic reaction.

(f) Discuss the factors on which adsorption of gas on solid depends.

(g) What are Zeolites ? Give one example of a reaction catalysed by a Zeolite catalyst.

(h) Explain pseudo-order reaction. Give example.

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

(a) Draw and interpret the phase diagram of water system.

(b) Derive Gibbs-Duhem-Margules equation.

(c) Deduce BET equation of adsorption.

(d) Consider the following Lindemann mechanism for the decomposition of a molecule A, in presence of a species M :

$A + M \xrightarrow{k_1} A^* + M$ (activation)

$A^* + M \xrightarrow{k_{-1}} A + M$ (deactivation)

$A^* \xrightarrow{k_2} P$ (decomposition)

Using the steady state approximation, derive the rate law for formation of products.

(e) What is chain reaction. Give the Rice-Herzfeld mechanism for the reaction

$$H_2 + Br_2 \longrightarrow 2HBr$$

Based on this mechanism derive the rate law for the formation of product.

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

(g) For adsorption of gases on solid surfaces, five general types of isotherms have been observed. Draw these isotherms.

(h) Explain a suitable method of experimental determination of order of a reaction.

4. Answer **any three** of the following questions : 10×3=30

(a) (i) Derive the integrated form of the Clausius-Clapeyron equation to show the variation of vapour pressure of a liquid with temperature. Give the graphical variation of log P with $\frac{1}{T}$. 5+1=6

(ii) At $300K$ and $350K$ the vapour pressure of a liquid are $1{\cdot}5\times10^5\ Nm^{-2}$ and $2{\cdot}0\times10^5\ Nm^{-2}$ respectively. Calculate the enthalpy of vaporization of the liquid. 4

(b) (i) State and explain the Nernst distribution law. Give the essential preconditions for the validity of the distribution law. With the help of suitable example, explain the limitations of the distribution law. 2+2+2=6

(ii) Thermodynamically derive the Nernst distribution law. 4

(c) (i) On the basis of hard sphere collision theory of reaction for elementary bimolecular gaseous reaction $A + B \rightarrow$ Products, find out an expression for Arrhenius pre-exponential factor, A. 6

(ii) Why the steric factor, p, had to be introduced into the expression for the rate constant using the collision theory? Discuss the physical significance of the steric factor. 4

(d) Give the assumptions of Langmuir adsorption theory. On the basis of these assumptions, deduce the Langmuir isotherm. Under what condition does the Langmuir isotherm reduce to the Freundlich isotherm? 3+5+2=10

(e) (i) Derive the integrated rate law for the reaction $A + B \rightarrow$ Products. 5

(ii) From the integrated rate law for the reaction $A + A \rightarrow$ Products, show that half-life time of the reaction is inversely proportional to the initial concentration of the reaction. 2

(iii) In a particular reaction the time required to complete half of the reaction was found to increase nine times when the initial concentration of the reactant was reduced to one-third. Determine order of the reaction. 3

(f) Give one example of enzyme catalysed reaction. Mention three characteristic features of enzyme catalysed reaction. Derive an expression for the rate of formation of product of an enzyme catalysed reaction using the Michaelis-Menten mechanism. How is the rate influenced by high substrate concentration? 1+3+5+1=10

(g) (i) What are solid solutions? Discuss briefly three types of solid solutions. Give examples. 1+3+3=7