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3 (Sem-3/CBCS) CHE HC 1

2023

CHEMISTRY

(Honours Core)

Paper : CHE-HC-3016

(Inorganic Chemistry-II)

Full Marks : 60

Time : Three hours

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

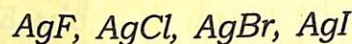
1. Answer the following as directed: $1 \times 7 = 7$
 - (a) Name the graph of Gibbs Energy (ΔG) versus Temperature (T) for the formation of oxide of metal.
 - (b) "Group-I elements gets oxidized easily"
– State whether *True* or *False*.
 - (c) Write the structural formula of borazine.
 - (d) What is "basicity of an acid"?

Contd.

- (e) Which one of the following species is conjugate base of OH^- ?
 (i) H_2O
 (ii) O^{2-}
 (iii) O_2
 (iv) O_2^{2-}
- (f) "The name inert gas is improper" – Explain the statement.
- (g) Calculate the hardness of Al^{3+} for the ionization energy, 119.99 eV and electron affinity 28.45 eV.

2. Answer the following : $2 \times 4 = 8$

- (a) Describe the structure of boric acid.
- (b) What is inert pair effect? Arrange the stability of +1 oxidation states of Ca^+ , Al^+ , In^+ and Tl^+ in their increasing order.
- (c) Applying Wade's rule, predict and draw the structure of CB_5H_9 .
- (d) Arrange the following compounds in ascending order of their solubility in water.



Give explanation.

3. Answer **any three** of the following :

$5 \times 3 = 15$

- (a) Briefly discuss the bonding and structure of diborane. 5

- (b) What is diagonal relationship? Write *any four* similar properties of Be and Al. $1+4=5$
- (c) Discuss the Mond's process used in metal refining.
- (d) What are polyhalides? Give example. How they are different from Interhalogen Compounds? $1+1+3=5$
- (e) Write constructing properties of the borazine and benzene.

4. Answer **any three** of the following :

$10 \times 3 = 30$

- (a) What is Allotropism? Name Different allotropes of carbon. Discuss bonding in graphite. Explain the high thermal and electrical conductivity of graphite. What is intercalation compounds? Give examples. $2+2+2+2+1+1=10$
- (b) (i) What happens when Xenon is heated in presence of fluorine? How the amount of fluorine affect the nature of product? $2+2=4$
- (ii) Discuss the bonding in XeF_6 . 4
- (iii) Complete the following reaction
 $\text{XeF}_6 + \text{H}_2\text{O} \rightarrow ?$
 $3\text{XeF}_6 + 6\text{H}_2\text{O} \rightarrow ?$ 2

- (c) (i) Give the formula, structure and method of preparation of basic beryllium acetate. 1+2+2=5
- (ii) How are poly siloxanes formed? Distinguish between silicon fluids and silicon rubbers. 2+3=5
- (d) Write notes on : (**any two**) 5+5=10
- (i) Pseudohalogens
- (ii) Pasting process
- (iii) Catenation
- (e) (i) State the Pauling's rules for determination of strength of mononuclear oxoacids. 3
- (ii) Arrange the following in order of descending acid strengths in aqueous solution –
 HClO_4 , HOCl , HClO_3 , HClO_2
Give explanation. 3
- (iii) Pauling's rule is useful in detecting structural anomalies, explain. 2
- (iv) What is symbiosis? Explain. 2
- (f) What is silicates? Explain the bonding and structure of SiO_4^{4-} unit using hybridization. What are different types of silicates? Give their structure. 1+4+3+2=10

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3 (Sem-3/CBCS) CHE HC 2

2023

CHEMISTRY

(Honours Core)

Paper : CHE-HC-3026

(Organic Chemistry-II)

Full Marks : 60

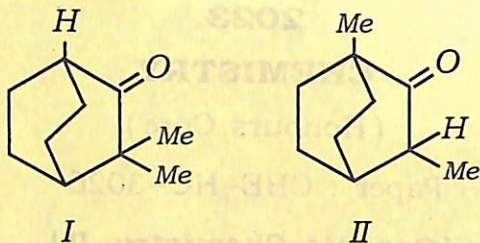
Time : Three hours

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

1. Answer the following questions : $1 \times 7 = 7$
- (a) Arrange the following in increasing order of basicity
 $(CH_3)_2CHO^\ominus$, PhO^\ominus , CH_3O^\ominus , $\overset{\ominus}{OH}$
- (b) Draw the energy profile diagram of $E|CB$ mechanism of β -elimination reaction.

Contd.

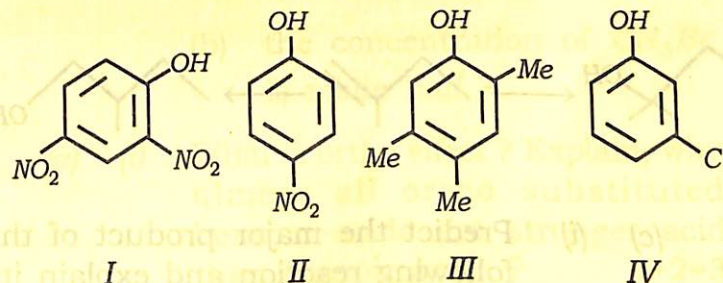
- (c) Which one of the following bridged bicyclic compounds will exhibit Keto-Enol tautomerism.



- (d) DMF and DMSO favours S_N2 reaction although they are polar solvents. Explain.
- (e) Potassium - *t*-butoxide is a widely used base in organic reactions but the corresponding sodium compound is unknown. Give reason.
- (f) Why is thioethanol more acidic than ethanol ?
- (g) Name the reagent that can be used to convert Cis-2-butene to racemic 2,3-butanediol.

2. Answer the following questions : $2 \times 4 = 8$

- (a) Arrange the following compounds in increasing boiling point and give reason for your answer.
n-hexanol, *n*-butanol and *t*-butanol
- (b) Between $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ and $\text{CH}_3\text{OCH}_2\text{Cl}$, which would react faster in S_N1 solvolysis. Explain.
- (c) The phenols shown have approximate pK_a value of 4, 7, 9 and 11. Suggest with explanation which pK_a value belong to which phenol :



- (d) Arrange the following carboxylic acid derivatives in order of increasing reactivity towards hydrolysis reaction and justify your answer :



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

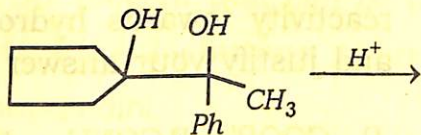
(a) Write the mechanism of Benzoin condensation. Explain why *p*-dimethylaminobenzaldehyde fails to undergo benzoin condensation but when mixed with benzaldehyde the condensation occurs. 3+2=5

(b) (i) Explain why alcohols are weaker acids than phenols but phenols are stronger nucleophiles. 2

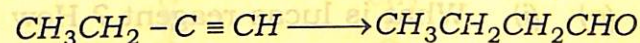
(ii) Provide the required reagents and conditions for the following conversion : $1\frac{1}{2} \times 2 = 3$



(c) (i) Predict the major product of the following reaction and explain its formation mechanistically. 3

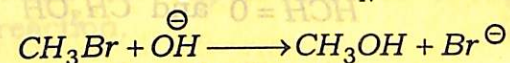


(ii) How do you carry out the following conversion ? 2



(d) (i) Why are vinylic and aryl halides unreactive towards both S_N1 and S_N2 reactions ? 3

(ii) The rate equation of S_N2 reaction



$$\text{Rate} = k[CH_3Br][OH^-]$$

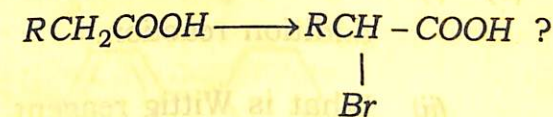
What type of changes are expected in the rates of the reaction if

(a) the concentration of each of the reactants is made double ?

(b) the concentration of CH_3Br is made half ?

(e) (i) What is ortho effect ? Explain, why almost all ortho substituted benzoic acids are stronger acid than benzoic acids ? 1+2=3

(ii) How can you convert : 2



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

(a) (i) What is Lucas reagent ? How is it used to distinguish between 1°, 2° and 3° alcohols ? 1+2=3

(ii) Methyl chloromethyl ether is readily hydrolysed by water to HCHO and CH_3OH but $\text{CH}_3\text{OCH}_2\text{CH}_2\text{Cl}$ does not. Explain. 2

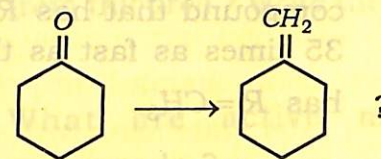
(iii) Picric acid liberates CO_2 from aqueous Na_2CO_3 but phenol does not. Explain. 2

(iv) Give the products of Reimer-Tiemann reaction on *p*-Cresol. Explain the reaction with mechanism. 3

(b) (i) Write the mechanism of Michael addition reaction. 3

(ii) What is Wittig reagent ? 1

(iii) How will you convert



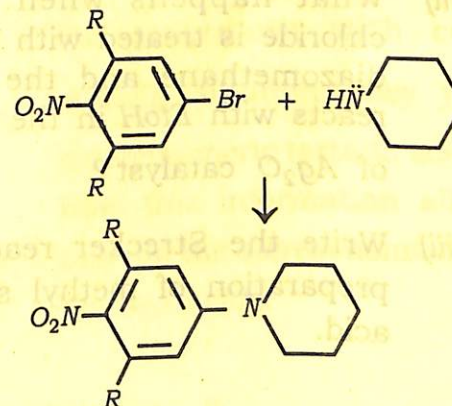
Write the mechanism of the reaction involved. 3

(iv) Write the significance of Wittig reaction. 2

(v) What do you mean by ylides ? 1

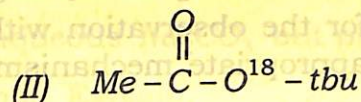
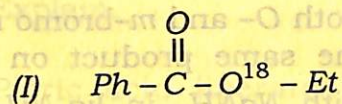
(c) (i) Both *O*- and *m*-bromo anisole give the same product on treatment with NaNH_2 in liq. NH_3 . Account for the observation with appropriate mechanism. 5

(ii) Write down the mechanism of the following reaction :



Account for the fact that the compound that has $R = H$ reacts 35 times as fast as the one that has $R = CH_3$. 3+2=5

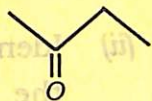
- (d) (i) Give the mechanism of alkaline hydrolysis of the following ester in ordinary water (H_2O^{16}) and indicate the distribution O^{18} is the products in each case. 4



- (ii) What happens when an acid chloride is treated with excess of diazomethane and the product reacts with $EtoH$ in the presence of Ag_2O catalyst? 2
- (iii) Write the Strecker reaction for preparation of methyl sulphonic acid. 2

- (iv) How can CH_3CH_2SH be prepared from thiourea? Write the reactions. 2

- (e) (i) What are active methylene compounds? 1

- (ii) Convert EAA to  3

- (iii) 7-chloro cyclohepta-1, 3, 5-triene readily forms white $AgCl$ ppt. When boiled with $AgNO_3$ solution but 5-chlorocyclopenta-1, 3-diene does not give reason. 2

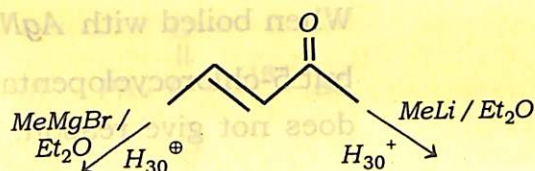
- (iv) Two dicarboxylic acids have the general formula $COOH - CH = CH - COOH$. On treatment with cold dil. $KMnO_4$ solution, they yield two diastereomeric tartaric acids. Show how this information allows one to write the stereochemical formula for two acids. 4

- (f) (i) When an alkyl halide is converted to a Grignard reagent then the carbon atom linked to halogen atom changes its polarity. Justify this statement with an example.

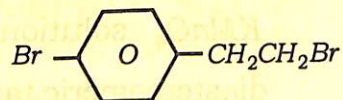
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- (ii) Identify the product/products for the following reaction and offer explanation :

3



- (iii) Write the Grignard reagent that is formed when



is treated with one mole of Mg in dry ether.

2

- (iv) Why Clemmensen reduction of 4-methyl-5-hydroxyhexan-3-one to 3-methylhexan-2-ol cannot be carried out ?

2

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3 (Sem-3/CBCS) CHE HC 3

2023

CHEMISTRY

(Honours Core)

Paper : CHE-HC-3036

(Physical Chemistry III)

Full Marks : 60

Time : Three hours

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

1. Answer the following as directed : $1 \times 7 = 7$

- (i) What is Eutectic Point ?
- (ii) Give one example of a consecutive reaction.
- (iii) What is adsorption isobar and adsorption isotherm ?

Contd.

- (iv) How many components are present in the following equilibria ?



- (v) What is autocatalysis ?
- (vi) A radioactive substance has $t_{1/2}$ of 6.93 min. Find its average life.
- (vii) Under what condition of pressure, would the Lindemann theory of unimolecular gaseous reaction show first-order kinetics ?

2. Answer the following questions : $2 \times 4 = 8$

- (i) Explain why the slope of vapour pressure *vs* temperature plot for solid-vapour equilibrium is steeper than the slope of liquid-vapour equilibrium.
- (ii) Why are zeolites suitable as catalysts for cracking and reforming reactions ?

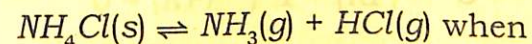
- (iii) If the reaction $\text{A} \rightarrow \text{Products}$ follows zero-order kinetics, show with the help of a diagram, how $[\text{A}]$ will change with time.

- (iv) The activation energy of a certain uncatalyzed reaction at 300 K is 76 kJ mol^{-1} . The activation energy is lowered to 57 kJ mol^{-1} by the use of a catalyst. By what factor is the rate of the catalysed reaction increased ?

3. Answer **any three** questions from the following : $5 \times 3 = 15$

- (i) Derive Gibbs' Phase rule. How is the number of component C calculated for systems involving ions and having some chemical reactions equilibrium among the constituents ? Evaluate the degrees of freedom for the following equilibrium

$$2 + 1 + 2 = 5$$



$$(a) \quad P_{\text{NH}_3} \neq P_{\text{HCl}}$$

$$(b) \quad P_{\text{NH}_3} = P_{\text{HCl}}$$

(ii) Draw and explain *five* general types of isotherms that have been observed during adsorption of gas on solid surface.

(iii) Draw and interpret the phase diagram for a two-component system involving simple eutectic.

(iv) What are chain reactions? Discuss the kinetics of $H_2 - Br_2$ chain reaction.

$$1+4=5$$

(v) Distinguish between order and molecularity of a reaction. Discuss *one* experimental method for the determination of the order of a reaction.

$$2+3=5$$

4. Answer **any three** questions from the following :

$$10 \times 3 = 30$$

(a) Give the assumptions of BET theory. On the basis of these assumptions, deduce the BET equation of adsorption.

$$3+7=10$$

(b) (i) Explain briefly the phase diagram for a two-component system with incongruent melting point. Explain the cooling curve for such a system.

$$5+2=7$$

(ii) Discuss the mutual solubility curve of a conjugate solution having upper critical solution temperature.

$$3$$

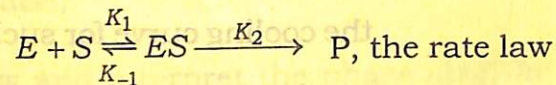
(c) What are the assumptions of Langmuir Isotherm? Derive Langmuir Adsorption Isotherm. Show that for adsorption of a gas with dissociation ($X_2 \rightarrow 2X$) the Langmuir adsorption isotherm becomes

$$\theta = \frac{(KP)^{1/2}}{1 + (KP)^{1/2}}$$

Draw the Langmuir Isotherms for with and without dissociation.

$$2+4+2+2=10$$

- (d) Discuss Enzyme catalysis with an example. For the Michaelis-Menten mechanism of enzyme action.



is given by

$$r = K_2 [E]_0 [S]_0 / [S]_0 + K_M$$

Where $K_M = K_2 + K_{-1}/K_1$ is Michaelis constant.

Answer the following :

- (i) Show that enzyme reaction is of first-order and zero-order with respect to low and high initial concentration of S respectively.
- (ii) What type of graph is expected between the rate and $[S]_0$?
- (iii) Show that if $K_2 \ll K_{-1}$, K_M represents the dissociation constant for ES.
- (iv) What is 'Turnover number' of an enzyme catalyst ? $3+2+2+2+1=10$

- (e) (i) 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 ?

- (ii) Write the mechanism of unimolecular reaction as proposed by Lindemann. Using this mechanism, deduce an expression for the rate of unimolecular reaction.

5+5=10

- (f) State and explain the Nernst Distribution Law. Under what conditions the law is valid ? How is the law derived from thermodynamic considerations ? Discuss the practical applications of the Nernst Distribution Law.

2+2+4+2=10