உலகத்தை மாற்ற நீங்கள் பயன்படுத்தக்கூடிய சக்தி வாய்ந்த ஆயுதம், கல்வி.

+2

SAIVEERA CHEMISTRY MINIMUM STUDY MATERIAL

CONTENTS

- **CHAPTERWISE BOOK BACK & BOOK INSIDE IMPORTANT QUESTIONS WITH ANSWERS**
- **CHAPTERWISE BOOK BACK ONE MARKS**

Prepared By
Saiveera Academy, Coimbatore

UNIT – 4 TRANSITION AND INNER TRANSITION ELEMENTS

1.What are transition metals? Give four examples

IUPAC defines transition metal as an element whose atom has an incomplete d sub shell or which can give rise to cations with an incomplete d sub shell.

Example : Fe , Cu , Ni , CO

2.What are actinides? Give three examples

- The fourteen elements following actinium ,i.e., from Thorium (Th) to Lawrentium (Lr) are called actinoids. **Ex:** Actnium , Thorium , Uranium

3.Describe the preparation of potassium dichromate

1. It is prepared from **chromate ore.**
2. The ore is concentrated by **gravity separation.**
3. It is then mixed with excess sodium carbonate and lime and roasted in a reverberatory furnace.

$$\mathbf{4FeCr_2O_4 + 8\,Na_2CO_3 + 7\,O_2 \xrightarrow{900-1000^{\circ}C} 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2 \uparrow}$$

4. The roasted mass is treated with water to separate soluble sodium chromate from insoluble iron oxide.
5. The yellow solution of sodium chromate is treated with concentrated sulphuric acid which converts sodium chromate into sodium dichromate.

$$\mathbf{2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2CrO_7 + Na_2SO_4 + H_2O}$$

6. The above solution is concentrated to remove less soluble sodium sulphate. The resulting solution is filtered and further concentrated.
7. It is cooled to get the crystals of $Na_2SO_4.2H_2O$.
8. The saturated solution of sodium dichromate in water is mixed with KCl and then concentrated to get crystals of NaCl.
9. It is filtered while hot and the filtrate is cooled to obtain $K_2Cr_2O_7$ crystals.

4. What is lanthanide contraction and what are the effects of lanthanide contraction?

Lanthanide contraction

As we move across 4f series, the atomic and ionic radii of lanthanoids show gradual decrease with increase in atomic number. This decrease in ionic size is called lanthanoid contraction.

Effects of lanthanide contraction

1. Basicity differences

As we from Ce^{3+} to Lu^{3+},the basic character of Ln^{3+} ions decrease. Due to the decrease in the size of Ln^{3+} ions, the ionic character of $Ln-OH$ bond decreases (covalent character increases) which results in the decrease in the basicity.

2. Similarities among lanthanoids:

In the complete f - series only 10 pm decrease in atomic radii and 20 pm decrease in ionic radii is observed because of this very small change in radii of lanthanoids, their chemical properties are quite similar.

5. What are interstitial compounds? Write down their properties

An interstitial compound or alloy is a compound that is formed when small atoms like hydrogen, boron, carbon or nitrogen are trapped in the interstitial holes in a metal lattice. They are usually non-stoichiometric compounds **Example:** TiC,

Properties of interstitial compounds?

(i) They are hard and show electrical land thermal conductivity

(ii) They have high melting points higher than those of pure metals

(iii) Transition metal hydrides are used as powerful reducing agents

(iv) Metallic carbides are chemically inert.

6.Compare lanthanides and actinides

s.no	Lanthanoids	Actinoids
1	Differentiating electron enters in **4f orbital**	Differentiating electron enters in **5f orbital**
2	**Binding energy** of 4f orbitals are **higher**	**Binding energy** of 5f orbitals are **lower**
3	They show **less tendency** to form complexes	They show **greater tendency** to form complexes
4	Most of the lanthanoids are **colourless**	Most of the actinoids are coloured.
5	They do **not form oxo cations**	They do **form oxo cations** such as UO_2^{2+}

7.Transition metals show high melting points why?

Due to greater number of unpaired d electrons for metallic bonding .

8. What is Bayer's reagent and write down its use

1. Cold dilute alkaline $KMnO_4$ is known as Bayer's reagent.

Use: It is used to oxidise alkenes into diols

9.Explain about Hume-Rothery rule to form a substitute alloy

1. The difference between the atomic radii of solvent and solute is less than 15%.
2. Both the solvent and solute must have the same crystal structure and valence and their electro negativity difference must be close to zero.

10.Why transition metals form complexes?

- They have a ability to donate an electron pair to form a coordinate covalent bond.
- They are small and highly charged and they have vacant low energy orbitals to accept an electron pair donated by other groups.

11. What is Chromyl chloride test

When potassium dichromate is heated with any chloride salt in the presence of Conc H_2SO_4, orange red vapours of chromyl chloride is evolved. This reaction is used to confirm the presence of chloride ion in inorganic qualitative analysis.

12. What are general electronic configuration of lanthanide and actinides?

Lanthanide - $[Xe]4f^{1-14}\ 5d^{0-1}\ 6s^2$

Actinide – $[Rn]5f^{0-14}\ 6d^{0-2}\ 7s^2$

13. What are the uses of potassium dichromate?

1. 1.It is used as a strong oxidizing agent.
2. It is used in dyeing and printing.
3. It used in leather tanneries for chrome tanning.
4. It is used in quantitative analysis for the estimation of iron compounds and iodides

14. What are Uses of potassium permanganate

1. It is used as a strong oxidizing agent.
2. It is used for the treatment of various skin infections and fungal infections of the foot.
3. It used in water treatment industries to remove iron and hydrogen sulphide from well water.
4. It is used as a Bayer's reagent for detecting unsaturation in an organic compound.

5. It is used in quantitative analysis for the estimation of ferrous salts, oxalates, hydrogen peroxide and iodides.

15.What is Zeigler Natta catalyst ? Ans write down its use.

Zeigler Natta catalyst - A mixture of $TiCl_4$ and trialkyl aluminium

Use: Polymerization

16.Calculate the equivalent weight of $KMnO_4$ in (i) acid medium (ii) basic medium (iii) neutral medium

(i) Equivalent weight of $KMnO_4$ in acid medium $= \frac{\text{Molecular weight of } KMnO_4}{\text{no of mols of electrons transferred}} = \frac{158}{5} = 31.6$

(ii) Equivalent weight of $KMnO_4$ in basic medium $= \frac{\text{Molecular weight of } KMnO_4}{\text{no of mols of electrons transferred}} = \frac{158}{1} = 158$

(iii) Equivalent weight of $KMnO_4$ in neutral medium $= \frac{\text{Molecular weight of } KMnO_4}{\text{no of mols of electrons transferred}} = \frac{158}{3} = 52.67$

SAIVEERA	MINIMUM STUDY MATERIAL	CHEMISTRY

UNIT – 7 CHEMICAL KINETICS

1.Define average rate and instantaneous rate.

Average rate : It is defined as change in concentration of a reaction or product of a chemical in a given interval of time

$$\text{Average rate} = \frac{\text{Change in concentration of reactants or products}}{\text{time intrerval}}$$

Instantaneous rate : The rate of the reaction, at a particular instant during the reaction is called the instantaneous rate

2.Derive integrated rate law for a zero order reaction A ⟶ product

A reaction in which the rate is independent of the concentration of the reactant over a wide range of concentrations is called as zero order reactions

A ⟶ product

Rate law

rate = $k[A]^o$

$\frac{-d[A]}{dt} = k\ (1)$ where $[A]^o = 1$

$-d[A] = k\ dt$ **..... (1)**

Integrate the equation (1) between the limits of $[A_o]$ at t = 0 and [A] at t = t ,

$-\int_{[A_0]}^{[A]} d\,[A] = k \int_0^t dt$

$[A_o] - [A] = kt$

$\mathbf{k} = \frac{[A_0] - [A]}{t}$

3. Derive integrated rate law for a first order reaction A ⟶ product

Reaction in which rate of the reaction depends on the concentrations of one of the reactant only is called first order reaction

A ⟶ Products

Rate = k [A]

$\frac{-d[A]}{dt} = k\,[A]$

$\frac{-d[A]}{[A]} = k\ dt$

Integrate the above equation between the limits of $[A_o]$ at t = 0 and [A] at t = t ,

$-\int_{[A_o]}^{[A]} \frac{d[A]}{[A]} = k \int_0^t dt$

$\ln \frac{[A_o]}{[A]} = kt$ **.....(1)**

This equation is in natural logarithm. To convert it into usual logarithm with base 10, we have to multiply the term by 2.303

$k = \frac{2.303}{t} \log \frac{[A_o]}{[A]}$ **.....(2)**

4.Define half life of a reaction. Show that for a first order reaction half life is independent of initial concentration.

The half life of a reaction is defined as the time required for the reactant concentration to reach one half its initial value.

For first order reaction rate constant

$k = \frac{2.303}{t} \log \frac{[A_o]}{[A]}$ **.....(1)**

when $t = t_{½}$; $[A] = \frac{[A_o]}{2}$

$k = \frac{2.303}{t_{1/2}} \log 2$

$t_{½} = \frac{0.6932}{k}$ secs**.....(2)**

From (2) half life of the first order reaction does not contain any initial concentration term
Hence proved.

5.**What is an elementary reaction? Give the differences between order and molecularity of a reaction.**

Elementary reaction : Each and every single step in a reaction mechanism is called an elementary reaction.

Order of reaction	Molecularity of reaction
It is sum of the power of concentration terms involved in experimentally determined rate law	It is total number of reactant species involved in an elementary step
It can be zero or fractional or integer	It is always whole number, cannot be zero or fractional number
It is assigned for a overall reaction	It is assigned for each elementary step of mechanism

6. Differences between rate and rate constant of a reaction:

Rate of a reaction	Rate constant of a reaction
It represents the speed at which the reactants are converted into product at any instant	It is a proportionality constant
It is measured as decrease in the concentration of the reactants or increase in the concentration of products.	It is equal to the rate of reaction, when the concentration of each of the reactants in unity
It depends on the initial concentration of reactants.	It does not depends on the initial concentration of reactants.

7.Write the rate law for the following reactions.

(a) A reaction that is $\frac{3}{2}$ order in x and zero order in y.

(b) A reaction that is second order in NO and first order in Br_2.

(a) Rate $= k[x]^{\frac{3}{2}}[y]^0$

(b) $2NO + Br_2 \rightarrow 2NOBr$, Rate $= k[NO]^2[Br_2]$

8. Write Arrhenius equation and explains the terms involved.

$$k = Ae^{\frac{-E_a}{RT}}$$

A = Frequency factor or Arrhenius factor, E_a = Activation energy, R = gas constant
T = temperature, k = rate constant

9.Identify the order for the following

(i) Rusting of Iron **(ii) Radioactive disintegration of U_{92}^{238}**

(iii) 2A + 3B → Products ; rate $= k[A]^{1/2}[B]^2$

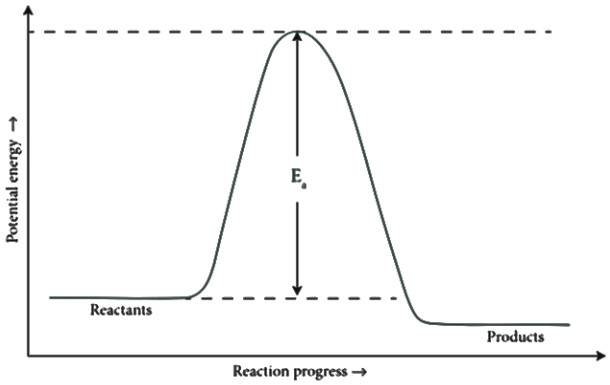
(i) First order reaction

(ii) Radioactive disintegration Follows first prder reaction

(iii) 2A + 3B → Products ; rate $= k[A]^{1/2}[B]^2$ Order $= \frac{1}{2} + 2 = 2.5$

10.Explain the effect of catalyst on reaction rate with an example.

1. In the presence of a catalyst, the energy of activation is lowered and hence, greater number of molecules can cross the energy barrier and change over to products, thereby increasing the rate of the reaction.



Example

- ✓ To the solution containing 0.1N oxalic acid solution, 0.1N $KMnO_4$ solution and 5 ml of 2N dilute H_2SO_4 , addition of few crystals of manganese sulphate to that solution pink color of solution fades up
- ✓ In this case $MnSO_4$ acts as a catalyst and increases the rate of oxidation of oxalic acid

11. Explain pseudo first order reaction with an example.

Second order reaction can be altered to a first order reaction by taking one of the reactants in large excess, such reaction is called pseudo first order reaction

Acid hydrolysis of an ester,

$$CH_3COOCH_3(aq) + H_2O \xrightarrow{H^+} CH_3COOH\,(aq) + CH_3OH$$

If the reaction is carried out with the large excess of water, there is no significant change in the concentration of water during hydrolysis. i.e.,concentration of water remains almost a constant.

12. Define activation energy

In order to react, the colliding molecules must possess a minimum energy called activation energy. The molecules that collide with less energy than activation energy will remain intact and no reaction occurs.

13. Paracetamol prescribed to take once in 6 hours.Justify this statement

- ✓ Paracetamol is a well known anti-pyretic and analgesic that is prescribed in cases of fever and body pain. Paracetamol has a half-life of 2.5 hours within the body i.e.the plasma concentration of a drug is halved after 2.5 hrs.
- ✓ After 10 hours (4 half-lives)only 6.25 % of drug remains. Based on such studies the dosage and frequency will be decided.
- ✓ So it is usually prescribed to take once in 6 hours depending upon the conditions.

14. Give examples of zero and first order reaction

Examples of zero order reaction

1.Photochemical reaction between H_2 & I_2

2. Decomposition of N_2O on hot platinum surface

3. Iodination of acetone in acid medium is zero order with respect to iodine.

Examples for the first order reaction

(i) Decomposition of dinitrogen pentoxide

(ii) Decomposition of thionylchloride

(iii) Decomposition of the H_2O_2 in aqueous solution

(iv) Isomerisation of cyclopropane to propene.

UNIT – 13 ORGANIC NITROGEN COMPOUNDS

1.Write down the possible isomers of the $C_4H_9NO_2$ give their IUPAC names

Chain isomerism

$CH_3CH_2CH_2CH_2NO_2$ and $CH_3CH(CH_3)CH_2NO_2$

1-nitrobutane

2-methyl-1-nitropropane

Position isomerism

$CH_3CH_2CH_2CH_2NO_2$ and $CH_3CH(NO_2)CH_2CH_3$

1-nitrobutane

2-nitrobutane

Functional isomerism

$CH_3CH_2CH_2CH_2NO_2$ and $CH_3CH_2CH_2CH_2 - O - N = O$

1-nitrobutane butyl nitrile

2.Identify compounds A , B , C in the following sequence of reactions

i. $\mathbf{C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow{HNO_2/273\ K} B \xrightarrow{C_6H_5OH} C}$

ii. $\mathbf{C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow{NH_3} C}$

iii. $\mathbf{CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow{OH^-/Partial\ hydrolysis} B \xrightarrow{NaOH+Br_2} C}$

i. $C_6H_5NO_2 \xrightarrow{Fe/HCl} C_6H_5NH_2 \xrightarrow{HNO_2/273\ K} C_6H_5N_2Cl \xrightarrow{C_6H_5OH} C_6H_5 - N = N - C_6H_5 - OH$

A – Aniline B – Benzene diazonium chloride C – p – hydroxy azobenzene

ii. $C_6H_5N_2Cl \xrightarrow{CuCN} C_6H_5CN \xrightarrow{H_2O/H^+} C_6H_5COOH \xrightarrow{NH_3} C_6H_5CONH_2$

A – Cyanobenzene B – Benzoic acid C – Benzamide

iii. $CH_3CH_2I \xrightarrow{NaCN} CH_3CH_2CN \xrightarrow{OH^-/Partial\ hydrolysis} CH_3CONH_2 \xrightarrow{NaOH+Br_2} CH_3NH_2$

A – Ethyl cyanide B – Acetamide C – Methyl amine

3.Write short notes on the following

i. Hofmann's bromide reaction ii. Gabriel phthalimide synthesis iii. Carbylamine reaction.
iv Mustard oil reaction v. Coupling reaction vi. Gomberg reaction vii.Sandmeyer reaction
viii. Gattermann reaction ix.Thrope Nitrile Condensation

i Hofmann's bromide reaction

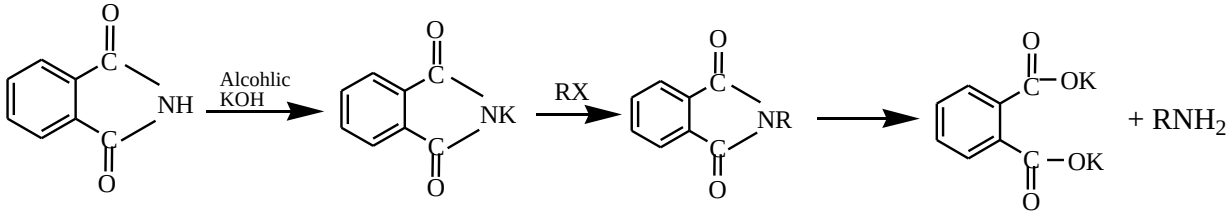
When Amides are treated with bromine in the presence of aqueous or ethanolic solution of KOH, primary amines with one carbon atom less than the parent amides are obtained.

$$\mathbf{RCONH_2 \xrightarrow{Br_2/KOH} RNH_2 + K_2CO_3 + KBr + H_2O}$$

ii. Carbylamine reaction

$$C_2H_5NH_2 + CHCl_3 + 3KOH \xrightarrow{yields} C_2H_5NC + 3KCl + 3H_2O$$

iii.Gabriel phthalimide synthesis



iv. Mustard oil reaction

$$CH_3 - NH_2 + CS_2 \longrightarrow CH_3 - NH - \overset{\overset{S}{\|}}{C} - SH \xrightarrow{HgCl_2} CH_3\text{-}N = C = S + HgS + 2HCl$$

v.Coupling reaction

Benzene diazonium chloride reacts with electron rich compounds like phenol to form brightly coloured azo compounds

$$C_6H_5N_2Cl \xrightarrow{C_6H_5OH} C_6H_5 - N = N - C_6H_5 - OH$$

vi.Gomberg reaction

Benzene diazonium chloride reacts with benzene in the presence of sodium hydroxide to give biphenyl. This reaction in known as the Gomberg reaction.

vii. Sandmeyer reaction

- On mixing freshly prepared solution of benzene diazonium chloride with cuprous halides(chlorides and bromides), aryl halides are obtained.

$$C_6H_5N_2Cl \xrightarrow{Cu_2Cl_2/HCl} C_6H_5Cl + N_2$$

viii. Gattermann reaction

- Conversion of benzene diazonium chloride into chloro / bromo arenes can also be effected using hydrochloric / hydrobromic acid and copper powder.

$$C_6H_5N_2Cl \xrightarrow{Cu/HCl} C_6H_5Cl + N_2$$

ix.Thrope Nitrile Condensation

Self condensation of two molecules of alkyl nitrile (containing a–H atom) in the presence of sodium to form iminonitrile

4. What are the test to identify primary amine?

1) Carbylamine test
2) Mustard oil reaction

Carbylamine test

Aliphatic (or) aromatic primary amines react with chloroform and alcoholic KOH to give isocyanides (carbylamines), which has an unpleasant smell

Mustard oil reaction

When primary amines are treated with carbon disulphide (CS_2), N - alkyldithio carbamic acid is formed which on subsequent treatment with $HgCl_2$, give an alkyl isothiocyanate

5.How will you distinguish between primary secondary and tertiary alphatic amines.

Primary amine	Secondary amine	Tertiary amine
With HNO_2 forms alcohol.	With HNO_2 forms N-nitroso amine	With HNO_2 forms salt.
With $CHCl_3/KOH$ forms carbylamines	With $CHCl_3/KOH$ no reaction	With $CHCl_3/KOH$ no reaction
With CS_2 and $HgCl_2$ alkyl isothiocyanate is formed.	With CS_2 and $HgCl_2$ no reaction	With CS_2 and $HgCl_2$no reaction

6. How is chloropicrin is prepared?

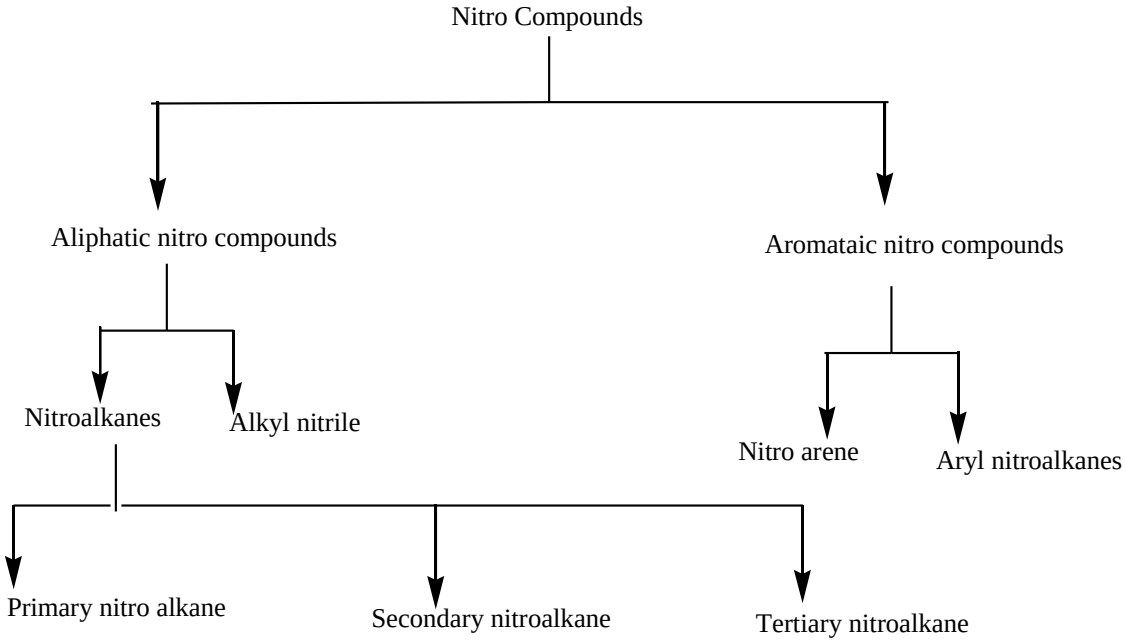
Primary and secondary nitroalkanes on treatment with Cl_2 or Br_2 in the presence of NaOH give halonitroalkanes.

$$CH_3NO_2 + 3Cl_2 \xrightarrow{NaOH} CCl_3NO_2 + 3HCl$$

7.What is Libermann's nitroso test,

Alkyl and aryl secondary amines react with nitrous acid to give N – nitroso amine as yellow oily liquid which is insoluble in water.

8. **Write down the classification of Nitro compounds**



9.Explain about reduction of nitrobenzene in different medium