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CHEMISTRY CONCENTRATE

ADSORPTION & ITS ISOTHERMS

METICULOUS ANALYSIS
AROMATICITY, GROUP DIRECTIVE INFLUENCE AND ELECTROPHILIC SUBSTITUTION

CONCEPT MAP
CHEMICAL KINETICS

TOUCH UPS
p-BLOCK ELEMENTS
SURFACE CHEMISTRY

JUVENILEZ
RAINBOW *EMF AND NERNST EQUATION*
AMPLIFIER *PERIODIC PROPERTIES*
GOLDEN OLDIES *HYDROCARBONS*

NOBLE PRIZE WINNER 2016

JEAN-PIERRE SAUVAGE
FRANCE

SIR J. FRASER STODDART
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NETHERLANDS

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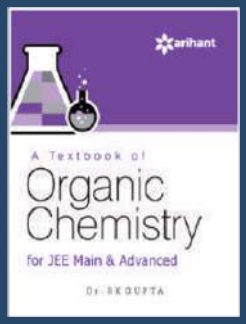

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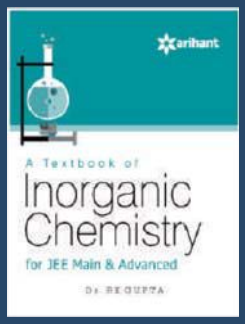

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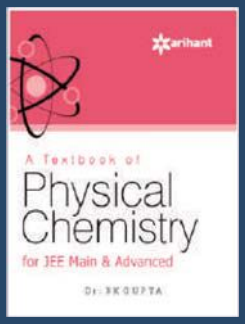

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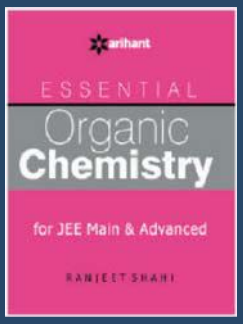

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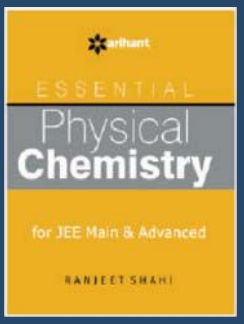

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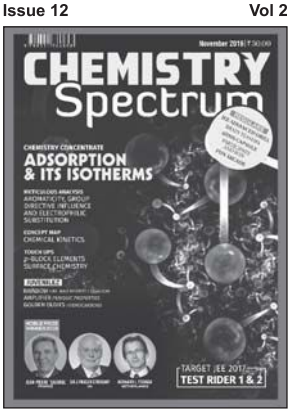
Issue 12 **Vol 2**



Dear Aspirants,

By now your studies would be in full swing as the season of examinations is approaching. Hope you had a gala festival time and a good break to enjoy. The month of November begins with different vibes altogether. Pinkish winters, new energies, overflowing enthusiasm and increased confidence levels give altogether a different feel of life.

Molecules are produced in the cooler region of space when individual atom or ions happen to collide and make bonding with each other. Such molecules are not seen in stars as their bonds would not survive at high temperatures of stars. Even the electrons of atoms does not retained at such huge temperatures. Thus, the matter there exists as plasma of ionized atoms and unbound electrons. The application of molecules for the betterment of human race was the main agenda of shown by the Noble prize winners of 2016. The invention of **Molecular Motors** is really amazing. Peculiar functioning at the molecular level can't be imagined by all. It is the capability of very few highly creative human beings like **Dan Aykroyd** who said –

"You look at the floor and see the floor. I look at the floor and see the molecules"

After the month of festivals, it is the beginning of study time for all of you. We have also planned something special for you like **Test Rider** and **Medi Quest** to make your task achievable. We will enhance the same from next issue onwards. The spectrum team will be anxiously waiting for the feed backs and comments.

Good luck

Contents

NOBEL PRIZE WINNER 2016 (02)

CHEMISTRY CONCENTRATE
Adsorption & Its Isotherms (03)

TEST RIDER 1 (11)

TEST RIDER 2 (17)

EXPLICATION SERIES :
Elements How they were Discovered (20)

JEE ADVANCED DRILL (22)

GOLDEN OLDIES : Hydrocarbons (29)

AIIMS CAPSULE (32)

AMPLIFIER : Periodic Properties (36)

IUPAC IDOLISER
Nomenclature of Organic Compounds Part 6 (38)

CONCEPT MAP (40)

METICULOUS ANALYSIS :
Aromaticity, Group Directive Influence and Electrophilic Substitution (42)

RAINBOW : EMF and NERNST Equation (54)

MEDI QUEST (58)

BRAIN TEASERS (63)

FUN ARCADE (68)

MASTER THE NCERT :
General Principles and Processes of Isolation of Elements (70)

TOUCH UP XI : *p*-Block Elements (74)

TOUCH UP XII : Surface Chemistry (76)

QUIZZER (80)

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NOBEL PRIZE WINNERS 2016

*The Nobel Prize in Chemistry 2016 is awarded to **Jean-Pierre Sauvage, Sir J. Fraser Stoddart** and **Bernard L. Feringa** for their development of molecular machines that are a thousand times thinner than a hair strand. This is the story of how they succeeded in linking molecules together to design everything from a tiny lift to motors and minuscule muscles.*

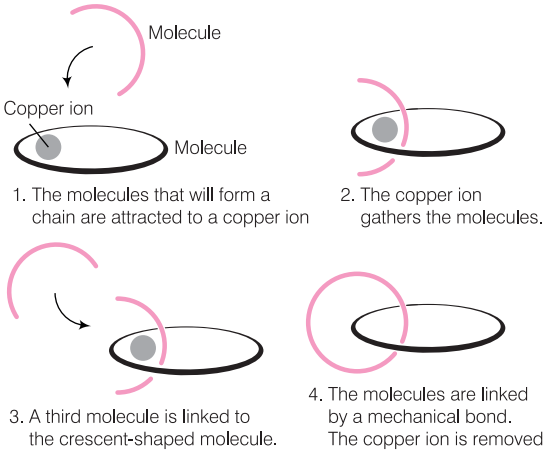
MECHANICALLY INTERLOCKED MOLECULES

In the mid-20th century, as part of efforts to build increasingly advanced molecules, chemists were attempting to produce molecular chains in which ring-shaped molecules were linked together. The person who succeeded would not just create an amazing new molecule, but also a new type of bond. Normally, molecules are held together by strong covalent bonds in which atoms share electrons. The dream was to instead create ***mechanical bonds,*** where molecules are interlocked without the atoms interacting directly with each other.

In the 1950s and 1960s, several research groups reported that their test tubes contained molecular chains, but the major breakthrough came in 1983. Using an ordinary copper ion, a French research group, led by chemist Jean-Pierre Sauvage, took control of the molecules.

JEAN-PIERRE SAUVAGE GATHERS MOLECULES AROUND A COPPER ION

Using the photochemical complex as a model, his research group constructed one ring-shaped and one crescent-shaped molecule so that they were attracted to a copper ion as shown in the figure below –



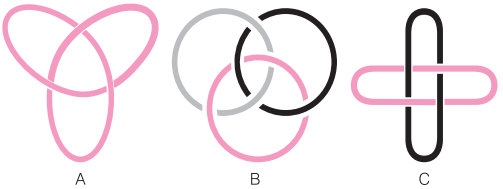
1. The molecules that will form a chain are attracted to a copper ion

2. The copper ion gathers the molecules.

3. A third molecule is linked to the crescent-shaped molecule.

4. The molecules are linked by a mechanical bond. The copper ion is removed

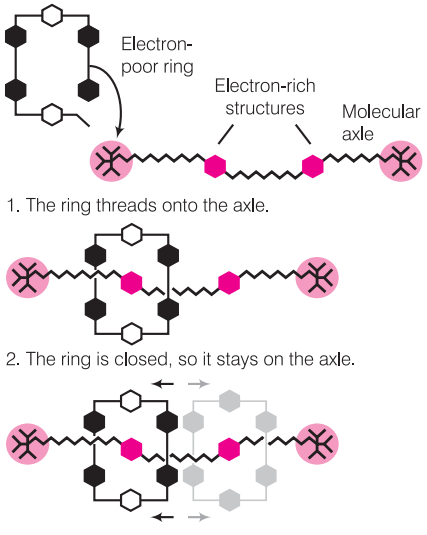
The copper ion provided a kind of cohesive force that held the molecules together. Likewise, he created many molecules as shown below.



Sauvage soon realised that molecular chains (called catenanes, from the Latin word for chain, catena) were not only a new class of molecule, but that he had also taken the first step towards creating a molecular machine. In order for a machine to perform a task, it must consist of several parts that can move in relation to each other. The two interlocking rings fulfilled this requirement

FRASER STODDART THREADS A MOLECULAR RING ONTO A MOLECULAR AXLE

Fraser Stoddart developed an open ring that lacked electrons, and a long rod, or axle, that had electron-rich structures in two places. When the two molecules met in a solution, electron-poor was attracted to electron-rich, and the ring threaded onto the axle. In the next step, the research group closed the opening in



1. The ring threads onto the axle.

2. The ring is closed, so it stays on the axle.

3. The ring jumps between the electron-rich areas of the axle when heat is added.

To be Continued at Page 73

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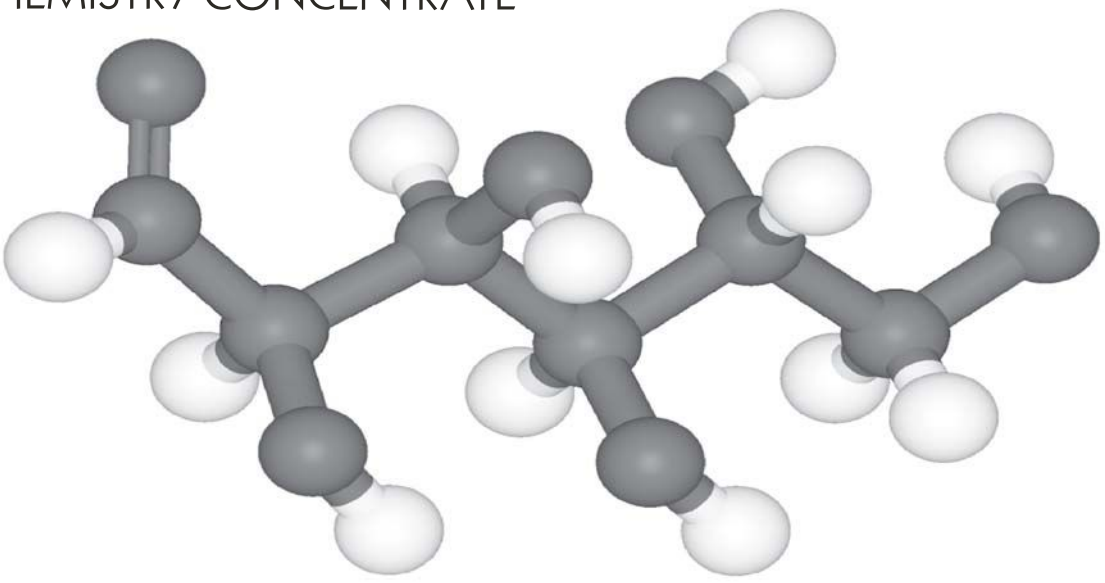
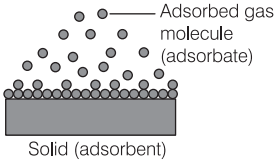


ADSORPTION & ITS ISOTHERMS

Adsorption

It is defined as the accumulation of molecular species at the surface rather than in the bulk of a solid or liquid. The molecular species that accumulates at the surface is called **adsorbate** and the solid on the surface of which accumulation occurs is called **adsorbent**. Thus, adsorption is a surface phenomenon.

Adsorption is a spontaneous process, i.e. there is decrease in free energy during the process. It is an exothermic process.



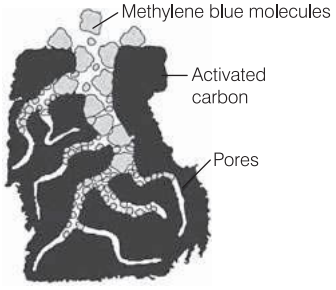
Adsorption of gas molecules over solid surface

The solids, in particular finely divided state, have larger surface area. Thus, show the property of adsorption to a larger extent than liquids.

The common adsorbents are **charcoal** (obtained by removing water and other volatile constituents from vegetable and animal), **silica gel** (prepared by heating a mixture of sodium silicate and 10% of HCl at 50°C), metals such as Ni, Cu, AgO, Au, Pt and colloids.

Some examples of adsorption are

(i) When finely divided charcoal is stirred into a dilute solution of methylene blue, the dye molecules are adsorbed by the charcoal particles. As a result, the colour of the solution, decreases appreciably.



(ii) In the presence of silica gel, the air becomes dry, i.e. loses moisture.

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Adsorption *vs* Absorption

There is one more term namely absorption which sound similar to adsorption. But both of these terms have different meanings as given below.

Differences between Adsorption and Absorption

	Adsorption		Absorption
(i)	It involves accumulation of molecular species at the surface only. Thus, it is a surface phenomenon.	(i)	It involves distribution of molecular species, more or less uniformly, throughout the bulk of the solid or liquid. Thus, it a bulk phenomenon.
(ii)	It is a rapid process and equilibrium is attained in a short time.	(ii)	It is a slow process and equilibrium is attained slower than in case of adsorption.

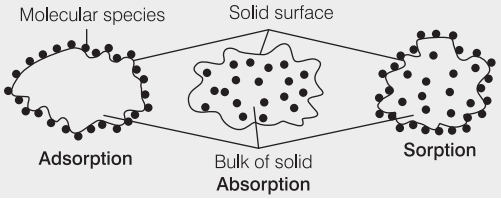
Example 1 When 0.2 g of animal charcoal is mixed with half litre of acetic acid solution and shaken for 30 min then concentration of solution will

(a) increases *(b)* decreases *(c)* remains same *(d)* None of these

Sol. ***(b)*** Concentration of acetic acid decreases because some of the acetic acid is adsorbed by charcoal.

Teacher's NOTE

- Both adsorption and absorption often take place side by side. Thus, it is difficult to distinguish between these two processes.
  For e.g. when a chalk stick is dipped into the ink, the surface of the chalk stick attains the colour of the ink. This is due to adsorption of coloured molecules of ink onto the surface of chalk stick.
  But side by side these molecules go deeper into the stick due to absorption.
- To avoid this difficulty, Mc Bain introduced the general term **sorption**. Sorption includes both the processes. e.g. dyes get adsorbed and absorbed both in cotton fibres, i.e. sorption takes place.

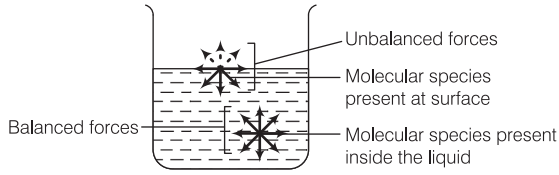


Reasons for Molecular Species to get Adsorbed on Solid and Liquid Surfaces

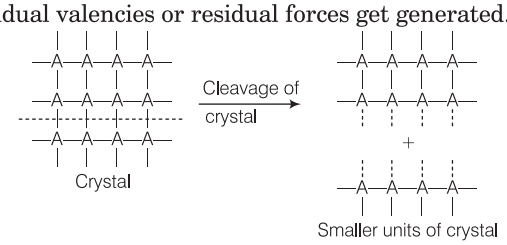
The phenomenon of adsorption arises due to the presence of residual (unbalanced) forces at the surface of liquid or solid body.

In case of liquids, the molecules inside the liquid gets equally attracted by the other molecular species from all the directions. Thus, the net force experienced by the molecules inside the liquid is zero. But at the surface of the liquid, molecules are attracted inwards only by the other molecular species present into the bulk due to residual forces. The upper exposed surface of these molecules experience lesser intermolecular forces due to lesser molecular density in gaseous phase. This creates an imbalance in forces acting over these molecules.

In order to balance these forces, molecules at the surface have tendency to adsorb over other species from the environment. In simpler words, you can say, adsorption occurs at the surface of liquid.



In case of solids, these residual forces arises due to unbalanced valence forces of atoms at the surface. These unbalanced forces arises due to cleavage of big crystal into smaller units. As a result of cleavage, residual valencies or residual forces get generated.



Example 2 Spontaneous adsorption of a gas on solid surface is an exothermic process, because [IIT 2008]

(a) ΔH increases for system *(b)* ΔS increases for gas
(c) ΔS decreases for gas *(d)* ΔG increases for gas

Sol. ***(c)*** $\Delta G = \Delta H - T\Delta S$

As gas is adsorbed on surface of solid, entropy decreases, so $\Delta S < 0$. Therefore, for $\Delta G < 0$, ΔH must be negative.

Teacher's NOTE

- The residual forces are responsible for attracting the adsorbate species on its surface. The extent of adsorption is proportional to the surface area per unit mass of adsorbent.
- During adsorption, there is always decrease in residual forces of the surface which appears as heat.
- When adsorption occurs, the molecular species that gets adsorbed, changes from less ordered to more ordered state (as freedom of movement of molecular species gets decreased). Thus, **entropy change, becomes negative in adsorption process.**
- For spontaneous process, at constant temperature and pressure, ΔG should be negative. On the basis of thermodynamic equation, $\Delta G = \Delta H - T\Delta S$, ΔG can be negative if ΔH is sufficiently negative because $-T\Delta S$ is positive. As adsorption is exothermic process, i.e. ΔH is negative, a combination of the values makes ΔG negative.

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Types of Adsorption

Types of adsorption can be divided into two categories.

(A) **On the Basis of Concentration of Adsorbate on the Surface of Adsorbent** : Adsorption is of two types

(i) **Positive adsorption** The concentration of the adsorbate is more on the surface of adsorbent than its concentration in bulk, e.g. when a concentrated solution of KCl is shaken with blood charcoal, it shows positive adsorption i.e. concentration of KCl is more on blood charcoals surface than in bulk.

(ii) **Negative adsorption** The concentration of the adsorbate is less on the surface of adsorbent than its concentration in bulk.

e.g. when a dilute solution of KCl is shaken with blood charcoal, it shows negative adsorption, i.e., concentration of KCl is more in bulk than on the blood charcoal surface.

(B) **On the Basis of Nature of Force Existing Between Adsorbate and Adsorbent.**

Adsorption is of two types. We shall discuss these two types of adsorption by comparing different properties which are given in the following table.

S. No.	Property	Physical adsorption	Chemical adsorption
(i)	Binding force between adsorbate and adsorbent	It is caused by weak intermolecular van der Waals' forces.	It is caused by strong chemical bonds.
(ii)	Specificity	As van der Waals' forces are universal (does not depend on the nature of gas), so the surface of adsorbent does not show strong attraction for a particular gas. Thus, it is not specific.	As chemical bonds are not universal, (depends on the nature of the gas), so the surface of adsorbent shows strong attraction for a particular gas, e.g. O_2 is adsorbed on metals forming oxides while H_2 is adsorbed by transition metals with unpaired *d*-orbitals forming hydrides. Thus, it is highly specific.
(iii)	Reversibility	It is generally reversible, the gas adsorbed can be removed by reversing the conditions of the temperature and pressure.	It is generally irreversible.
(iv)	Heat of adsorption	As it involves weak van der Waals' forces so, heat of adsorption is quite low ($20-40$ kJ mol^{-1}).	As it involves chemical bond formation, so heat of adsorption is high ($40-400$ kJ mol^{-1}).
(v)	Effect of temperature	It occurs at low temperature. The extent of adsorption, decreases with increase in temperature.	It occurs at all temperature. The extent of adsorption, first increases with increase in temperature and then decreases after a certain temperature.
(vi)	Activation energy	It does not involve appreciable activation energy.	It requires high activation energy.
(vii)	Effect of pressure	It requires high pressure. Decrease in pressure causes desorption (adsorbate on surface of adsorbent goes back to the bulk or environment).	It also requires high pressure. Decrease in pressure does not cause desorption.
(viii)	Number of layers of adsorbate	It forms multilayers of adsorbate species on adsorbent surface under high pressure.	It forms unimolecular layer of adsorbate species on adsorbent surface under high pressure.
(ix)	Surface area	It increases with increase in surface area of adsorbent.	It also increases with increase in surface area of adsorbent.

Note

- In general, the more liquefiable a gas (i.e. a gas with high critical temperature), the more readily it will be adsorbed on adsorbents surface.
- The amount of adsorption of gas on same mass of charcoal follows the following order.
  $SO_2(T_C = 157°C) > CH_4(T_C = -83°C) > H_2(T_C = -120°C)$
- Easily liquefiable gases, such as NH_3, HCl, Cl_2, SO_2, ... etc., are readily adsorbed than the permanent gases such as O_2, N_2, H_2 etc.

Example 3 Methylene blue, from its aqueous solution, is adsorbed on activated charcoal at 25°C. For this process, the correct statement is **[JEE advanced 2013]**

(a) the adsorption requires activation at 25°C
(b) the adsorption is accompanied by a decrease in enthalpy
(c) the adsorption increases with increase of temperature
(d) the adsorption is irreversible

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Sol. ***(b)*** It is physical adsorption and does not require activation. Thus, (a) is incorrect.

Physical adsorption takes place with decrease in enthalpy thus, exothermic change. i.e. $\Delta H < 0$ thus, (*b*) is correct.

Exothermic reaction is favoured at low temperature, thus (c) is incorrect. Physical adsorption is always reversible, thus (d) is incorrect.

Example 4 The correct statement(s) pertaining to the adsorption of a gas on a solid surface is (are) [IIT JEE 2011]

(a) Adsorption is always exothermic

(b) Physisorption may transform into chemisorption at high temperature

(c) Physisorption increases with increasing temperature but chemisorption decreases with increasing temperature

(d) Chemisorption is more exothermic than physisorption, however it is very slow due to higher energy of activation

Sol. ***(a, b, d)***

(a) In the process of adsorption, a bond is formed between adsorbate and adsorbent, hence always exothermic.

(b) Physisorption is caused by weak intermolecular van der Waals' forces while chemisorption is caused by strong chemical bonds. In order to form strong chemical bonds, physisorption requires high temperature. Therefore, a physisorption may transform into chemisorption but only at high temperature.

(c) It is wrong statement as at higher temperature, physically adsorbed substance starts desorbing.

(d) In physical adsorption, van der Waals' force hold the adsorbate and adsorbent together which is a weak electrostatic attraction. In chemisorption, strong chemical bond binds the adsorbate to the adsorbent. Therefore, chemisorption is more exothermic than physical adsorption.

Adsorption Isotherms

At constant temperature, the variation of the amount of gas adsorbed by the solid adsorbent with pressure, can be expressed by means of a curve. This curve is called adsorption isotherm at a particular temperature.

Here, we are going to discuss two such isotherms.

(A) Freundlich Adsorption Isotherm

Freundlich proposed an empirical relation between the quantity of gas adsorbed by unit mass of solid adsorbent, and pressure of the gas at a particular temperature.

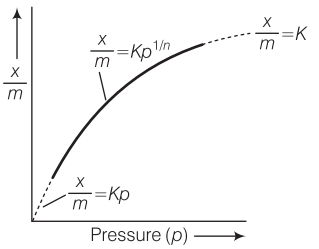
According to him, at constant temperature.

$$\frac{x}{m} = Kp^{1/n} \qquad \ldots(i)$$

Where, x = amount of adsorbate,

m = amount of adsorbent, p = pressure,

K and n are constants which depend on the nature of gas and adsorbent at a given temperature.



Interpretation of Freundlich Isotherm

From the above graph, following informations can be obtained.

(i) **At Very Low Pressure**

The graph is nearly straight line and at these pressures

$$\frac{x}{m} \propto p \text{ or } \frac{x}{m} = Kp$$

(ii) **At Intermediate Range of Pressure**

The graph is curved and $\frac{x}{m} \propto p^{1/n}$ or $\frac{x}{m} = Kp^{1/n}$

(iii) **At Very High Pressure**

The graph become parallel to x-axis which shows that extent of adsorption is independent of pressure, i.e.

$$\frac{x}{m} \propto p^0 \text{ or } \frac{x}{m} = K$$

At high pressure when saturation point is reached, logarithm of Eq. (i) is

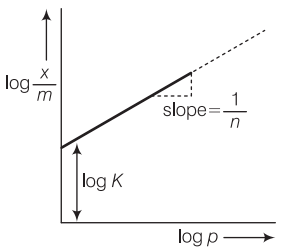
$$\log \frac{x}{m} = \log K + \frac{1}{n} \log p \qquad \ldots(ii)$$

On comparing Eq. (i) with straight line equation

$$y = mx + c$$

We get,

$y = \log \frac{x}{m}$, $m = \frac{1}{n}$, $x = \log p$ and $c = \log K$



Limitations of Freundlich Isotherm

- Concept of Freundlich isotherm is purely empirical.
- It is not applicable at high pressure.
- It does not consider the role of surface area of adsorbent in the process of adsorption.
- It is applicable only for physical adsorption as it considers multimolecular layer of adsorption.
- It is unable to explain, constant adsorption at higher pressures.

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Example 5 In an adsorption experiment, a graph between $\log\left(\frac{x}{m}\right)$ *versus* $\log p$ was found to be linear at angle of 45°. The intercept on $\log\left(\frac{x}{m}\right)$ axis was found to be 0.3010, calculate the amount of gas adsorbed per gram of charcoal under a pressure of 0.25 atm.

(a) 0.25 *(b)* 1.00
(c) 0.75 *(d)* 0.50

Sol. ***(d)*** This problem is based upon Freundlich isotherm,

According to Freundlich isotherm,

$$\frac{x}{m} = K p^{1/n}$$

or $$\log\frac{x}{m} = \log K + \frac{1}{n}\log p$$

$\because$ Plot of $\log\frac{x}{m}$ *versus* $\log p$ is linear with slope $\frac{1}{n}$

and intercept $\log K$.

Thus, $$\frac{1}{n} = \tan\theta$$

$\Rightarrow$ $$\frac{1}{n} = \tan 45° \text{ or } \frac{1}{n} = 1$$

or $$n = 1$$

$$\log K = 0.3010$$

or $$K = \text{antilog}(0.3010) = 2$$

$\therefore$ $$\frac{x}{m} = K p^{1/n} = 2(0.25)^1 = 0.50$$

Example 6 On the basis of physical adsorption theory, which equation represents Freundlich adsorption isotherm?

(a) $\log\frac{x}{m} = \log K + \frac{1}{n}\log p$

(b) $\frac{x}{m} = K(p)^{1/n}$

(c) $\frac{x}{m} = Kp$, at low pressure

(d) All of the above

Sol. ***(d)*** According to Freundlich adsorption isotherm,

$$\frac{x}{m} = K(p)^{1/n}$$

Taking logarithm of both sides;

$$\log\frac{x}{m} = \log K + \frac{1}{n}\log p$$

At low pressure, $$\frac{x}{m} \propto p$$

$\Rightarrow$ $$\frac{x}{m} = Kp$$

At high pressure, $\frac{x}{m} \propto p^0 \Rightarrow \frac{x}{m} = K$

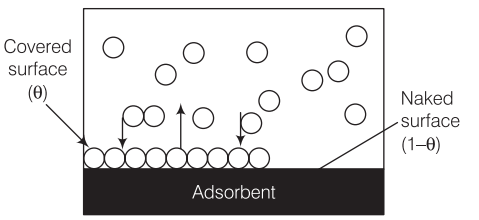
Biofiltration
An Application of Adsorption

- Biofiltration is a method that is used in water treatment process. This method effectively remove organic matter that can't be removed from water and biologically treated sewage effluent in conventional sewage treatment.
- The biofiltration method mainly relies on the activities of the microorganisms that are present into filter media.
- The activities of microbes determine the performance of biofiltration.
- Microbes adsorb organic matter present in water and produce energy. Thereby, save the nutrients sources present in the feed water.
- Moreover, biological filtration is economical and safe for environment.
- Biofiltration is more suitable than other treatment methods in terms of removing organic matter.

(B) Langmuir Adsorption Isotherm

The Freundlich isotherm is modified by Langmuir, he postulated following assumptions for adsorption.

- Surface of solid is made up of elementary sites. Each site can adsorb one gas molecule, i.e. the layer of gas adsorbed on the solid adsorbent is one molecule thick.
- These elementary sites are identical and each site has same affinity for the gas molecules.



$$\theta = \frac{\text{Number of adsorbed sites}}{\text{Total number of adsorption sites available}}$$

- Adsorption of a gas molecule at a particular site is independent, i.e. it does not depend on whether the neighbouring sites are adsorbed or not.
- The adsorbed gas behave ideally in the vapour phase.
- The adsorbed molecules do not move around the surface, i.e. these are fixed at their positions.
- Dynamic equilibrium exists on the surface of adsorbent, i.e. two opposite processes (adsorption and desorption) takes place simultaneously on the surface of adsorbent.

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According to Langmuir, the degree of adsorption is directly proportional to θ, i.e. the fraction of surface area covered,

$$\frac{x}{m} \propto \theta = K\theta$$

or
$$\frac{x}{m} = \frac{K' p}{1 + Kp} \quad \ldots(i)$$

where, K and K' are constants.

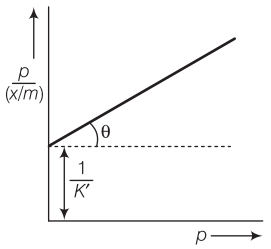
The relation (i) is called Langmuir adsorption isotherm.

Equation (i) can also be written as

$$\frac{p}{(x/m)} = \frac{1}{K'} + \left(\frac{K}{K'}\right)p$$

It is of the form $y = mx + c$, but it is not passing through the origin.

Here, $p/(x/m) = y,\ x = p,\ c = \frac{1}{K'}$, slope $= \frac{K'}{K}$



Interpretation of Langmuir Isotherm

Let us, consider the mathematical relation

$$\frac{x}{m} = \frac{K' p}{1 + Kp}$$

Case I When Pressure is Very High

$$1 + Kp \simeq Kp$$

or
$$\frac{x}{m} = \frac{K' p}{Kp} = \frac{K'}{K} = \text{constant}$$

Thus, at high pressure, the degree of adsorption approaches to a limiting value.

Case II When Pressure is Very Low

$$1 + Kp \simeq 1$$

or
$$\frac{x}{m} = K' p$$

Thus, degree of adsorption is directly proportional to pressure

Case III When Pressure is Moderate

$$\frac{x}{m} = Kp^{1/n} \text{ (Freundlich isotherm)}$$

where, $\frac{1}{n}$ lies between 0 to 1.

Success of Langmuir Isotherms

- It explains physisorption as well as chemisorption.
- It gives better results than Freundlich isotherm.

Limitation of Langmuir Isotherm

It does not hold good at high pressures.

Teacher's NOTE

The Langmuir adsorption isotherm is restricted to the formation of unimolecular layer of gas molecules on the surface of solids. However, it was suggested that there is possibility of multimolecular layer of gas molecules on the surface of the solids rather than single layer. On this basis Brunauer, Emmelt and Teller proposed a new theory known as BET theory.

Example 7 1g of charcoal adsorbs 100mL of 0.5M CH_3COOH to form a mono layer and thereby the molarity of acetic acid is reduced to 0.49M. Calculate the surface area of the charcoal adsorbed by each molecule of acetic acid.

(Surface area of charcoal $= 3.01 \times 10^2 m^2/g$) [IIT 2007]

(a) $2.5 \times 10^{-19} m^2$
(b) $2.5 \times 10^{-17} m^2$
(c) $5 \times 10^{-17} m^2$
(d) $5 \times 10^{-19} m^2$

Sol. (d) *Thinking process*

- *Area (A) occupied by a single molecule of acid can be calculated as,* $A = \frac{\text{Total area}}{\text{Number of molecules adsorbed}}$
- *Total area is already given in the problem, so you have to calculate number of molecules adsorbed.*
- *Number of molecules adsorbed* (N_a) *can be calculated as,*

N_a = Number of molecules of acid adsorbed × Avogadro's number

Initially, number of moles of acetic acid present

$$= \frac{MV}{1000} = \frac{0.5 \times 100}{1000} = 0.05$$

(where M = Molarity, V = Volume (mL))

Number of moles of acetic acid left

$$= \frac{0.49 \times 100}{1000} = 0.049$$

Thus, number of moles of acetic acid adsorbed

$$= 0.05 - 0.049 = 0.001 \text{ mole}$$

Number of molecules of acid adsorbed

$$= 0.001 \times 6.023 \times 10^{23}$$
$$= 6.023 \times 10^{20}$$

$$\therefore \quad A = \frac{3.01 \times 10^2}{6.023 \times 10^{20}}$$
$$= 5 \times 10^{-19} m^2$$

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Smart Practice

1. If x is the amount of adsorbate and m is the amount of adsorbent, which of the following relation is not related to adsorption process?

(a) $\frac{x}{m} = p \times T$ (b) $\frac{x}{m} = f(p)$ at constant T

(c) $\frac{x}{m} = f(T)$ at constant p (d) $p = f(T)$ at constant $\frac{x}{m}$

2. Which of the following statements is not correct regarding the adsorption of a gas on surface of a solid?

(a) Enthalpy and entropy change is negative

(b) Adsorption is specific and selective phenomenon

(c) On increasing temperature, adsorption increases progressively

(d) All of the above

3. At the high pressure, Langmuir adsorption isotherm takes the form

(a) $\frac{x}{m} = \frac{K'p}{1 + Kp}$ (b) $\frac{x}{m} = \frac{K'}{K}$

(c) $\frac{x}{m} = K'p$ (d) $\frac{m}{x} = \frac{K}{K'} + \frac{1}{K'p}$

4. Which among the following statements are correct with respect to adsorption of gases on a solid.

I. Freundlich adsorption isotherm fails at low pressure.

II. The extent of adsorption is equal to $Kp^{1/n}$ according to Freundlich isotherm.

III. The extent of adsorption is equal to $\frac{(1 + Kp)}{K'p}$ according to Langmuir isotherm.

IV. The extent of adsorption is equal to $\frac{K'p}{(1 + Kp)}$ according to Langmuir isotherm

Where, K' and K are constants and p is pressure

(a) I and III (b) I and IV (c) II and III (d) II and IV

5. A plot of $\log \frac{x}{m}$ *versus* $\log p$ for the adsorption of a gas on a solid gives a straight line with slope equal to

(a) $-\log K$ (b) n (c) $\frac{1}{n}$ (d) $\log K$

6. 50 mL of 1M oxalic acid is shaken with 0.5 g of wood charcoal. The final concentration of the solution after adsorption is 0.5 M. Amount of oxalic acid adsorbed per gram of charcoal is

(a) 3.45g (b) 3.15g (c) 6.30g (d) None of these

7. Silica garden is developed by setting of coloured ions in the voids of silicates. It is a case of

(a) adsorption (b) absorption

(c) sorption (d) None of these

8. The adsorption of a dye from a solution on charcoal is governed by Freundlich's isotherm in which $\frac{1}{n} = 2$ and $K = 6.8$. If 10 g of charcoal is shaken with 0.1M solution of the dye, equilibrium concentration of the solution will be (concentration of the dye, is taken, in millimoles/cc and the amount adsorbed is taken in millimoles/g).

(a) 0.02 M (b) 0.03 M

(c) 0.05 M (d) 0.04 M

9. Which of the following is not a characteristic of chemisorption?

(a) Adsorption is irreversible

(b) ΔH is the order of 400 kJ

(c) Adsorption is specific

(d) Adsorption increases with increase in surface area

10. Adsorption of gases on solid surface is generally exothermic because [IIT 2007]

(a) enthalpy is positive (b) entropy decreases

(c) entropy increases (d) free energy increases

11. Rate of physisorption increases with [IIT 2006]

(a) decrease in temperature (b) increase in temperature

(c) decrease in pressure (d) decrease in surface area

12. In an experiment, the volume of nitrogen gas at 1 atm and 0°C required to cover 1g of silica gel is found to be 0.129 dm^3. Calculate the surface area of the gel if each nitrogen molecule occupies an area of 16.2×10^{20} m^2 [Similar as asked in IIT 2007]

(a) 475.92 m^2 (b) 561.74 m^2

(c) 475.92 cm^2 (d) 561.74 cm^2

13. For adsorption of gas on solid surface, the plots of $\log\left(\frac{x}{m}\right)$ *vs* $\log p$ is linear. The slope of this plot is equal to

(a) K (b) $\log K$

(c) $\ln K$ (d) $\frac{1}{n}$ (n being integer)

14. According to Langmuir adsorption isotherm, at very high pressure, the amount of gas adsorbed.

(a) First increases, then decreases with increase in pressure

(b) Decreases with increase in pressure

(c) Increases with increase in pressure

(d) Reaches a constant limiting value

15. In Langmuir's model of adsorption of a gas on a solid surface

(a) the rate of dissociation of adsorbed molecules from the surface does not depend on the surface covered

(b) the adsorption at a single site on the surface may involve multiple molecules at the same time

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(c) the mass of gas striking a given area of surface is proportional to the pressure of the gas
(d) the mass of gas striking at a given surface area is independent of the pressure of the gas

16. Which of the following type of adsorptions, forms multilayers during adsorption?
(a) Physical adsorption
(b) van der Waals' adsorption
(c) Freundlich adsorption
(d) All of the above

17. Which of the following statements is/are correct?
(a) Langmuir adsorption is highly specific
(b) van der Waals' adsorption is reversible
(c) Both (a) and (b) are exothermic
(d) All are correct

18. Which of the following statements is not true?
(a) Both physisorption and chemisorption are exothermic
(b) Physisorption takes place with decrease of free energy whereas the chemisorption occurs with increase of free energy
(c) Physisorption requires low activation energy whereas chemisorption requires high activation energy
(d) The magnitude of chemisorption increases and that of physisorption decreases with rise in temperature

19. In an experiment, 200 mL of 0.5 M oxalic acid is shaken with 10g of activated charcoal and filtered. The concentration of the filterate is reduced to 0.4M. The amount of adsorption $\left(\frac{x}{m}\right)$ is

(a) 0.9 (b) 1.8
(c) 0.18 (d) 0.09

20. For a gas-solid system, classical adsorption isotherm is applicable. If mg of solid adsorbs xg of gas at pressure p, which of the following plots will give a straight line?

(a) $\frac{x}{m}$ *vs* p (b) $\frac{p}{x/m}$ *vs* p
(c) $\log\frac{x}{m}$ *vs* $\log p$ (d) $\log\frac{x}{m}$ *vs* p

21. The rate of chemisorption
(a) increases with decrease in temperature
(b) increases with increase in temperature
(c) increases with decrease in pressure of the gas
(d) is independent of pressure of the gas

22. Which among the following statements is false?
(a) Adsorption may be monolayered or multilayered.
(b) Particle size of adsorbent will not affect the amount of adsorption
(c) Increase of pressure increases the amount of adsorption
(d) Increase of temperature may decrease the amount of adsorption

23. Which of the following gets adsorbed greatly by activated charcoal?
(a) SO_2 (b) CO_2
(c) NO_2 (d) Water vapours

24. At equilibrium position in the process of adsorption
(a) $\Delta H > 0$ (b) $\Delta H = T\Delta S$
(c) $\Delta H > T\Delta S$ (d) $\Delta H < T\Delta S$

25. Pd can adsorb hydrogen atoms in the space between its atoms. This process is called
(a) absorption (b) desorption
(c) adsorption (d) chemisorption

26. Which of the following is incorrect about adsorption?
(a) The residual forces are responsible for attracting the adsorbate species on its surface
(b) When adsorption occurs, the molecular species that gets adsorbed comes from less ordered to more ordered state
(c) During adsorption, there is always decrease in residual forces of the surface
(d) All are incorrect

27. Sorption is term used when
(a) adsorption takes place
(b) absorption takes place
(c) Both adsorption and absorption take place
(d) desorption takes place

28. Desorption process occurs when
(a) temperature is increased
(b) temperature is decreased
(c) pressure is increased
(d) concentration is increased

29. Which of the following relations is/are correct related to Freundlich adsorption isotherm?

I. $x/m = K$ (at high pressure)

II. $\frac{x}{m} = K\,p^{1/n}$ (at intermediate pressure)

III. $\frac{x}{m} = K\,p^{n}$ (at low pressure)

(a) All are correct (b) All are incorrect
(c) I and II are correct (d) III is correct

30. The heat of adsorption in physisorption lie in the range (kJ mol^{-1}).
(a) 40 – 400 (b) 40 – 100
(c) 10 – 400 (d) 1 – 10

Answers

1. (a)	**2.** (c)	**3.** (b)	**4.** (d)	**5.** (c)
6. (d)	**7.** (a)	**8.** (b)	**9.** (b)	**10.** (b)
11. (a)	**12.** (b)	**13.** (d)	**14.** (d)	**15.** (c)
16. (d)	**17.** (d)	**18.** (b)	**19.** (c)	**20.** (c)
21. (b)	**22.** (b)	**23.** (d)	**24.** (b)	**25.** (d)
26. (d)	**27.** (c)	**28.** (a)	**29.** (c)	**30.** (c)

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JEE MAIN

(PAPER ONE PREP UP)

HALF TEST 1

(XI SYLLABUS) FULLY SOLVED

Mock Questions from Class XIth Syllabus with Complete Solutions

INSTRUCTIONS

- This test consists of 30 questions and each question is allotted 4 marks for correct response.
- Candidates will be awarded marks as stated above for correct response of each question. 1/4 marks will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
- There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted according as per instructions.

1. For the reaction, $A(g) + B(g) \longrightarrow C(g) + D(g)$, ΔH° and ΔS° are respectively, – 29.8 kJ mol^{-1} and – 0.100 kJ K^{-1} mol^{-1} at 298 K. The equilibrium constant for the reaction at 298K is

(a) 1 *(b)* 10 *(c)* 1.0×10^{-10} *(d)* 1.0×10^{10}

2. The group of molecules having identical shape is

(a) PCl_5, IF_5, XeO_2F_2 *(b)* BF_3, PCl_3, XeO_3

(c) ClF_3, $XeOF_2$, XeF_3^+ *(d)* SF_4, XeF_4, CCl_4

3. Which of the following pairs of compounds are positional isomers?

(a) $CH_3—CH_2—CH_2—\overset{\overset{O}{\|}}{C}—CH_3$ and $CH_3—CH_2—\overset{\overset{O}{\|}}{C}—CH_2—CH_3$

(b) $CH_3—CH_2—CH_2—CH_2—CHO$ and $CH_3—CH_2—CH_2—\overset{\overset{O}{\|}}{C}—CH_3$

(c) $CH_3—CH_2—CH_2—\overset{\overset{O}{\|}}{C}—CH_3$ and $CH_3—\underset{\underset{CH_3}{|}}{CH}—CH_2—CHO$

(d) $CH_3—CH_2—\overset{\overset{O}{\|}}{C}—CH_2—CH_3$ and $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH—CH_2—CHO$

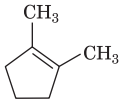
4. $A + 2B + 3C \rightleftharpoons AB_2C_3$

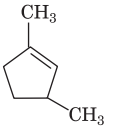
Reaction of 6.0g of A, 6.0×10^{23} atoms of B and 0.036 mole of C yields 4.8 g of compound AB_2C_3. If the atomic masses of A and C are 60 and 80 u, respectively, the atomic mass of B is (Avogadro's number = 6×10^{23}).

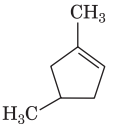
(a) 50 u *(b)* 60 u

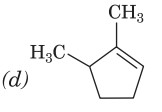
(c) 70 u *(d)* 40 u

5. Which compound would give 5-keto-2-methyl hexanal upon ozonolysis?

(a) 

(b) 

(c) 

(d) 

6. A dilute aqueous solution of Na_2SO_4 is electrolysed using platinum electrodes. The products at the anode and cathode respectively are

(a) O_2 and H_2 *(b)* $S_2O_8^{2-}$ and Na

(c) O_2 and Na *(d)* $S_2O_8^{2-}$ and H_2

7. Identify a reagent from the following list which can easily distinguish between 1-butyne and 2-butyne

(a) bromine, CCl_4 *(b)* H_2, Lindlar catalyst

(c) dil. H_2SO_4 *(d)* ammonical $CuCl_2$ solution

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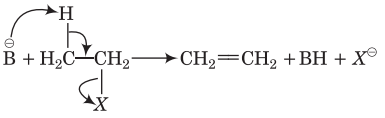
8. An aqueous solution of 6.3 g oxalic acid dihydrate is made upto 250 mL. The volume of 0.1N NaOH required to completely neutralise 10 mL of this solution is
(a) 40 mL *(b)* 20 mL
(c) 10 mL *(d)* 4 mL

9. The best indicator for detection of end point in titration of a weak acid and a strong base is
(a) methyl orange (3 to 4)
(b) methyl red (5 to 6)
(c) bromothymol blue (6 to 7.5)
(d) phenolphthalein (8 to 9.6)

10. The species that does not contain peroxide ion is
(a) PbO_2 *(b)* H_2O_2
(c) SrO_2 *(d)* BaO_2

11. β-elimination reaction is carried out with base ($\bar{B}$) as shown below?



The following bases are used for above reaction.
I. RO^- II. NO_3^-
III. $RCOO^-$ IV. CN^-
V. $\bar{O}H$

The decreasing order of reactivity for the above elimination is
(a) I > V > IV > III > II
(b) IV > V > II > I > III
(c) V > I > II > III > IV
(d) III > I > IV > V > II

12. The geometries of XeF_4, XeO_4 and XeO_2F_2 respectively are
(a) tetrahedral, square pyramidal and square planar
(b) square pyramidal, square planar and tetrahedral
(c) square planar, tetrahedral and trigonal bipyramidal
(d) tetrahedral, square planar and square pyramidal

13. Mixture *X* with 0.02 mole of $[Co(NH_3)_5SO_4]Br$ and 0.02 mole of $[Co(NH_3)_3Br]SO_4$ was prepared in 2L of solution. *X* reacts with two different compounds as follows:
1L of mixture '*X*' + excess $AgNO_3 \longrightarrow$ '*Y*'
1L of mixture '*X*' + excess $BaCl_2 \longrightarrow$ '*Z*'
The number of moles of '*Y*' and '*Z*' are respectively.
(a) 0.01, 0.01 *(b)* 0.02, 0.01
(c) 0.01, 0.02 *(d)* 0.02, 0.02

14. Two oxides of a metal '*M*' contains 27.6% and 30% of oxygen, respectively. If the formula of the first oxide is M_3O_4, then that of the second is
(a) M_2O_3 *(b)* M_2O
(c) MO_2 *(d)* M_2O_4

15. Consider a titration of potassium dichromate solution with acidified Mohr's salt solution using diphenyl amine as an indicator. The number of moles of Mohr's salt required per mole for dichromate is
(a) 3 *(b)* 4 *(c)* 5 *(d)* 6

16. The solubility of metal hydrides depends on their nature, lattice enthalpy and hydration enthalpy of the individual ions. Among the fluorides of alkali metals, the lowest solubility of LiF in water is due to
(a) ionic nature of lithium fluoride
(b) high lattice energy
(c) high hydration enthalpy for lithium ion
(d) low ionisation enthalpy of lithium atom

17. In an experiment, the same amount of Zn is treated separately with excess of sulphuric acid and excess of sodium hydroxide. The ratio of volumes of hydrogen evolved is
(a) 1 : 1 *(b)* 1 : 2 *(c)* 2 : 1 *(d)* 9 : 4

18. In the analysis of 0.500 g sample of feldspar, a mixture of the chlorides of sodium and potassium is obtained, which weighs 0.1180 g. Subsequent treatment of the mixed chlorides with $AgNO_3$, gives 0.2451 g of AgCl. What is the percentage of a sodium oxide and potassium oxide in feldspar?
(a) 10.62% Na_2O, 3.58% K_2O *(b)* 3.58% Na_2O, 10.62% K_2O
(c) 10.62% Na_2O, 35.8% K_2O *(d)* 35.8% Na_2O, 10.62% K_2O

19. A 2 g of sample containing sodium carbonate and sodium bicarbonate was heated to a temperature at which all the sodium bicarbonate in the sample was converted to Na_2CO_3, CO_2 and H_2O. The final weight of the sample after heating becomes 1.752 g. The percentage of Na_2CO_3 in the sample is
(a) 76% *(b)* 66% *(c)* 72% *(d)* 54%

20. Which of the following statements is correct?
(a) Increase in electronegativity down the group is accompanied by a decrease in non-metallic properties
(b) Electronegativity is inversely proportional to the metallic properties of elements
(c) Non-metals have less tendency to gain electron
(d) All of the above

21. Which of the following depicts the correct order of increasing size of given species?
(a) $S^{2-} < Cl^- < Ar < K^+ < Ca^{2+}$
(b) $Ca^{2+} < K^+ < Ar < Cl^- < S^{2-}$
(c) $Ar < Cl^- < S^{2-} < Ca^{2+} < K^+$
(d) $K^+ < Ca^{2+} < S^{2-} < Cl^- < Ar$

22. Consider the following statements about molecular orbital theory and identify the incorrect statement.
(a) The electrons in molecules are present in the various molecular orbitals as the electrons of atoms are present in the various atomic orbitals
(b) The atomic orbitals of comparable energies and proper symmetry combine to form molecular orbitals

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(c) In a molecular orbital an electron is influenced by two or more nuclei, depending upon the number of atoms in the molecule

(d) An atomic orbital is polycentric while a molecular orbital is monocentric

23. In which of the following pairs of molecules/ions both the species are not likely to exist?

(a) H_2^+, He_2^{2-} (b) H_2^-, He_2^{2-} (c) H_2^{2+}, He_2 (d) H_2, He_2^{2+}

24. Vinegar is used in food preservations. The main ingredient of vinegar is acetic acid that gives it a pungent taste. A sample of vinegar has 5 per cent V/V acetic acid. The density of acetic acid is 1.05g/mL. ($K_a = 1.75 \times 10^{-6}$)

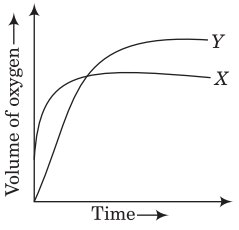
The molarity and pH of the above acetic acid solution is

(a) 0.875 M, 2.407 (b) 0.724 M, 3.100

(c) 0.875 M, 3.100 (d) 0.724 M, 2.407

25. Curve X on the graph given below, shows the volume of oxygen formed during the catalytic decomposition of a 1.0 mol/dm^3 solution of hydrogen peroxide.

$$2H_2O_2(aq) \longrightarrow O_2(g) + 2H_2O(l)$$



Which change would produce the curve Y?

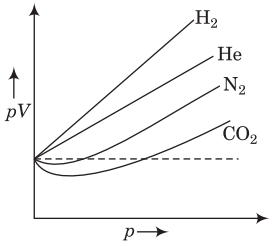
(a) Adding water

(b) Adding some 0.1 mol dm^{-3} hydrogen peroxide solution

(c) Using a different catalyst

(d) Lowering the temperature

26. Consider the following graph of pV *versus* p



Find out for which gases compressibility factor (Z) is greater than 1

(a) H_2 and N_2 (b) N_2, CO_2 and He

(c) He and CO_2 (d) H_2 and He

27. Match the items in Column I with its main significance listed in Column II.

Column I	Column II
A. Photon	p. Value is 4 for N-shell
B. Electron	q. Probability density
C. ψ^2	r. Always positive value
D. Principal quantum number (n)	s. Exhibits both momentum and wavelength

Codes

	A	B	C	D
(a)	p	q	r	s
(b)	s	s	q,r	p,r
(c)	p,q	r	s	q,s
(d)	p,q	q	q,r	p,s

28. Experimentally it was found that a metal oxide has formula $M_{0.98}O$. Metal M, present as M^{2+} and M^{3+} in its oxide. Fraction of metal which exists as M^{3+} would be

(a) 4.08% (b) 6.05%

(c) 5.08% (d) 7.01%

29. For complete combustion of ethanol,

$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$$

The amount of heat produced as measured in bomb calorimeter is 1364.47 kJ/mol at 25°C. Assuming ideality the enthalpy of combustion, ΔH, for the reaction will be [R = 8.314 kJ / mol]

(a) – 3810.21 kJ / mol

(b) – 3350.50 kJ / mol

(c) – 3858.67 kJ / mol

(d) – 3361.95 kJ / mol

30. The reaction of $CH_3CH{=}CH$–C$_6$H$_4$–OH with HBr gives

(a) $CH_3CHBrCH_2$–C$_6$H$_4$–OH

(b) $CH_3CHBrCH_2$–C$_6$H$_4$–Br

(c) CH_3CH_2CHBr–C$_6$H$_4$–OH

(d) CH_3CH_2CHBr–C$_6$H$_4$–Br

AMAZING REALITIES

Every hydrogen atom in your body is likely to be 13.5 billion years old, since they were created at the birth of the universe

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Answers with Explanation

1. (*a*) **Thinking process** *First calculate* ΔG° *with the help of following formula.*

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Then, calculate K_{eq} *with the help of following formula.*

$$\Delta G^\circ = -RT \ln K_{eq}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= -29.8 - 298\,(-0.100)$$

$$= -29.8 + 29.8$$

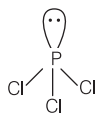
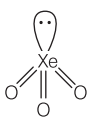
$$\Delta G^\circ = 0 \quad \text{or} \quad 0 = -RT \ln K_{eq}$$

or $$\ln K_{eq} = 0 \quad \text{or} \quad K_{eq} = e^0 = 1$$

2. (*c*) **Strategy** *Generally, the molecules in which same number of atoms and lone pairs are attached to the central atom, possess same shape.*

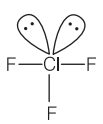
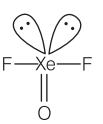
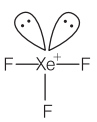
For option (a) Atoms attached to the central atom are different. So, we will check this option in the last if needed.

For option (b) Atoms attached to the central atom are same, so we will check for lone pairs.

Molecule	Lone pair
	Zero
	One
	One

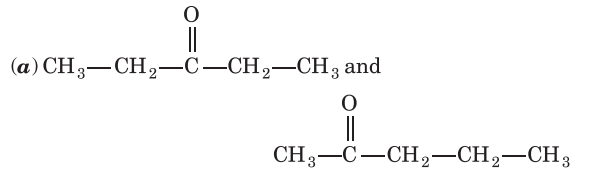
Hence, option (b) is incorrect.

For option (c), Atoms attached to the central atom are same. Again, we will check for lone pairs.

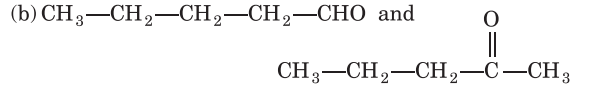
Molecule	Lone pair	Shape
	Two	T-shaped
	Two	T-shaped
	Two	T-shaped

Hence, option (c) is correct.

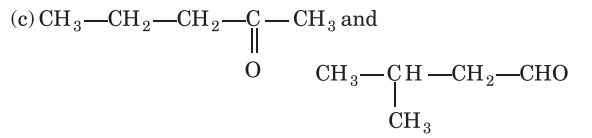
We don't need to check option (d) because of saving time purpose.

3. (*a*) 

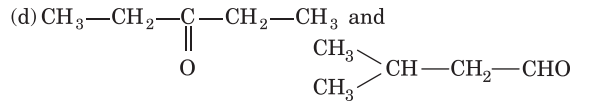
are positional isomers

(b) 

are functional isomers

(c) 

are functional isomers

(d) 

are functional isomers

4. (*a*) $A + 2B + 3C \longrightarrow AB_2C_3$

Given, 6.0 g of A, 6.0×10^{23} atoms of B and 0.036 mole of C yields 4.8 g of compound AB_2C_3.

Atomic mass of A = 60 u

Atomic mass of C = 80 u

$$\text{Mole of } A = \frac{6}{60} = \frac{1}{10} = 0.1 \text{ mole}$$

$$\text{Mole of } B = \frac{6.0 \times 10^{23}}{6.023 \times 10^{23}} = 1 \text{ mole}$$

Mole of C = 0.036 mole

According to reaction,

$$\underset{0.1\text{ mole}}{A} + \underset{0.2\text{ mole}}{2B} + \underset{0.3\text{ mol}}{3C} \rightleftharpoons \underset{0.1\text{ mole}}{AB_2C_3}$$

But we have only 0.036 mole of C

Thus, C is limiting reagent

So, 0.036 mole of C produces $\left(\frac{0.036}{3}\right)$ mole of AB_2C_3

$$\text{So, mole of } AB_2C_3 = \frac{\text{Mass}}{\text{Molecular mass}}$$

$$0.012 = \frac{4.8}{\text{Molecular mass of } AB_2C_3}$$

So, molecular mass of AB_2C_3 = 400 g mol^{-1}

Atomic mass of A + 2 × atomic mass of B + 3 × atomic mass of C = 400

$$60 + 2B + 3 \times 80 = 400$$

So, atomic mass of B = 50 u

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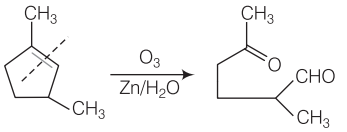
5. (*b*)



5-keto-2-methylhexanal

6. (*a*) Electrolysis of aqueous Na_2SO_4, gives $H_2(g)$ at cathode and $O_2(g)$ at anode.

7. (*d*) Ammonical $CuCl_2$, forms red precipitate with terminal alkynes. It can be used to distinguish terminal alkynes from internal alkynes

$$CH_3—CH_2—C\equiv C—H + CuCl_2 \xrightarrow{NH_3(aq)} CH_3—CH_2—C\equiv \bar{C}\,Cu^+$$

Red ppt.

8. (*a*) Normality of oxalic acid solution

$$= \frac{\text{Mass of oxalic acid (in g)}}{\text{Equivalent mass of oxalic acid}} \times \frac{1000}{\text{Volume of solution (in L)}}$$

Equivalent mass of oxalic acid dihydrate $\left(\begin{matrix}COOH\\|\\COOH\end{matrix}\cdot 2H_2O\right)$

$$= \frac{126}{2} = 63$$

∴ Normality of oxalic acid solution

$$= \frac{6.3}{63} \times \frac{1000}{250}$$

$$= 0.4\,N$$

Now, we know that,

At neutralisation point,

$$\underset{\text{Oxalic acid}}{(N_1V_1)} = \underset{\text{Sodium hydroxide}}{(N_2V_2)}$$

$$\therefore \quad 0.4 \times 10 = 0.1 \times V_2$$

or $\quad V_2 = 40\,mL$

9. (*d*) When a weak acid (H*X*) is titrated against a strong base NaOH, basic salt (Na*X*) is present at the end point. This makes end point slightly basic with pH around 8. Hence, phenolphthalein, changes its colour in this pH range, would be the best choice of indicator to detect the end point.

10. (*a*) In PbO_2, Pb is in + 4 oxidation state and oxygen is in–2 oxidation state. In all other cases, peroxide ion (O_2^-) is present.

11. (*a*) The reagent should be strong Bronsted base.

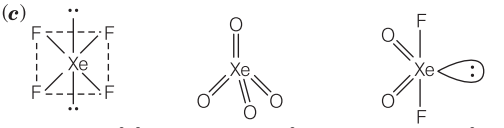
Acidic order $HNO_3 > RCOOH > HCN > H_2O > ROH$

Basic order $NO_3^- < RCOO^- < CN^- < \bar{O}H < RO^-$

Hence, decreasing order of basicities for β-elimination is

I > V > IV > III > II.

12. (*c*)



Hybridisation-sp^3d^2 Geometry-square planar

Hybridisation-sp^3 Geometry-tetrahedral

Hybridisation-sp^3d Geometry-trigonal bipyramidal or *see-saw*

13. (*a*) ∵ In 2L solution, there are 0.02 mole of Br^- ions and 0.02 mole of SO_4^{2-} ions present.

∴ 1 L solution of '*X*' will contain 0.01 mole of Br^- and 0.01 mole of SO_4^{2-} ions.

Hence, '*Y*' = 0.01 mole AgBr, '*Z*' = 0.01 mole $BaSO_4$

14. (*a*) Let '*x*' be the atomic mass of Metal '*M*'

In the oxide M_3O_4,

the mass of '*M*' = 72.4 and that of 'O' = 27.6

$$\therefore \quad M_{\frac{72.4}{x}}O_{\frac{27.6}{16}} = M_3O_4;\ \frac{72.4}{x} : \frac{27.6}{16} = 3:4$$

$$\therefore \quad x = 56$$

For second oxide, the mass of '*M*' = 70 and that of 'O' = 30

$$\therefore \quad M_{\frac{70}{56}}O_{\frac{30}{16}} = M_{1.25}O_{1.875} = M_1O_{1.5} \text{ 'or' } M_2O_3$$

15. (*d*) The redox reaction between potassium dichromate and Mohr's salt is given as

$$6\,Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6\,Fe^{3+} + 2Cr^{3+} + 7H_2O$$

16. (*b*) Due to small sizes of Li^+ and F^- ions, lattice enthalpy becomes much higher than hydration enthalpy. Hence, LiF is least soluble among the alkali metal fluorides.

17. (*a*) Reaction of Zn with excess of sulphuric acid is given as

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow$$

Reaction of Zn with excess of sodium hydroxide is given as,

$$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2\uparrow$$

Hence, the ratio of volumes of H_2 evolved in both the cases is 1 : 1.

18. (*b*) Suppose amount of NaCl in the mixture = *x* g

∴ The amount of KCl in the mixture = (0.118 – *x*) g

$$\underset{58.5\text{ g}}{NaCl} + AgNO_3 \longrightarrow \underset{143.5\text{ g}}{AgCl} + NaNO_3$$

∵ 58.5 g of NaCl gives 143.5 g of AgCl

∴ *x* g of NaCl will give $\left(\frac{143.5 \times x}{58.5}\right)$ g AgCl

Similarly,

AgCl obtained from KCl = $\frac{143.5 \times (0.118 - x)}{74.5}$ g

But on treatment of mixed chlorides with $AgNO_3$ 0.2451 g of AgCl is formed.

$$\left(\frac{143.5 \times x}{58.5}\right)g + \left(\frac{143.5 \times (0.118 - x)}{74.5}\right)g = 0.2451\,g$$

∴ $x = 0.0338$ g (Amount of NaCl)

$(0.118 - x) = 0.0842$ g (Amount of KCl)

Now,

$$\underset{117\text{ g}}{2NaCl} \longrightarrow \underset{62\text{ g}}{Na_2O}$$

$$0.0338\text{ g} \qquad \frac{0.0338 \times 62}{117}\,g = 0.0179\,g$$

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$\therefore$ Per cent of $Na_2O = \left(\frac{0.0179 \times 100}{0.5}\right)\% = 3.58\%$

and $\underset{149\text{ g}}{2KCl} \longrightarrow \underset{94\text{ g}}{K_2O}$

$0.0842\text{ g} \qquad \frac{0.0842 \times 94}{149}\text{ g} = 0.0531\text{ g}$

$\therefore$ Per cent of $K_2O = \frac{0.0531 \times 100}{0.5} = 10.62\%$

19. (*b*) The chemical reaction occured after heating the sample can be written as

$$\underset{(2 \times 84)\text{ g}}{2\,NaHCO_3(s)} \longrightarrow \underset{\underbrace{44\text{g} \quad 18\text{g}}_{=62\text{ g}}}{Na_2CO_3(s) + CO_2 + H_2O}$$

$= 168\text{ g}$

Here, the weight loss by the sample is due to evolution of CO_2 and H_2O.

$\therefore$ Weight of CO_2 and H_2O evolved

$= (2 - 1.752)\text{ g} = 0.248\text{ g}$ 62 g of CO_2 and H_2O are produced by 168 g of $NaHCO_3$

$\therefore$ 0.248 g of CO_2 and H_2O are produced by $\left(\frac{168}{62} \times 0.248\right)$ g of $NaHCO_3$.

$\therefore$ Weight of $NaHCO_3$ in the sample = 0.672 g

Weight of $Na_2CO_3 = (2 - 0.672)\text{ g} = 1.328\text{ g}$

$\therefore$ Per cent of $Na_2CO_3 = \left(\frac{1.328 \times 100}{2}\right)\% = 66.4\% \simeq 66\%$

20. ***(b)*** Decrease in electronegativity from top to the bottom in a group is accompained by a decrease in non-metallic properties. Non-metals have strong tendency to gain electrons. Also, electronegativity is related to the metallic properties of elements and is inversely proportional to the metallic properties of elements.

21. ***(b)*** In the given set the species with same number of shell and same number of electrons but different number of protons are present. Thus, greater the electron to proton ratio (e/Z), greater will be the size of isoelectronic species.

Hence, the increasing order of the size of given species is

$$Ca^{2+} < K^+ < Ar < Cl^- < S^{2-}$$

$$e/Z \text{ value}: \quad \frac{18}{20} < \frac{18}{19} < \frac{18}{18} < \frac{18}{17} < \frac{18}{16}$$

22. (*d*) An atomic orbital is monocentric while a molecular orbital is polycentric.

23. (*c*) **Key concept** *Species having zero or negative bond order does not exist.*

For $H_2^{2+}(1 + 1 - 2 = 0) = \sigma 1s^0$

Bond order = 0

For $He_2\ (2 + 2 = 4) = \sigma 1s^2, \sigma^* 1s^2$

$\Rightarrow$ Bond order $= \frac{2 - 2}{2} = 0$

$\therefore H_2^{2+}$ and He_2 both does not exist.

24. (*a*) We have sample of vinegar which has 5% V/V acetic acid, i.e. if vinegar is 100 mL then 5mL acetic acid present in it.

Volume of $CH_3COOH = 5$ mL

Density = 1.05 g/mL

We know, $d = \frac{m}{V} = \frac{m}{5\text{ mL}}$

$1.05\text{ g/mL} \times 5\text{ mL} = m$

$\therefore$ Molarity $= \frac{m}{\text{Molecular weight}} \times \frac{1000}{V\text{ (mL) of solution}}$

$= \frac{1.05 \times 5}{60} \times \frac{1000}{100} = 0.875\text{ M}$

Molarity $= 0.875\text{ M} = C$

We know, $pH = -\frac{1}{2}\log K_a - \frac{1}{2}\log C$

$= -\frac{1}{2}\log\ (1.75 \times 10^{-5}) - \frac{1}{2}\log(0.875)$

$= -\frac{1}{2}\ (0.2430 - 5) - \frac{1}{2}(-0.0580)$

$= 2.3785 + 0.029 = 2.407$

25. ***(b)*** The change would produce the curve Y, when we add some more 0.1 mol dm^{-3} hydrogen peroxide solution.

26. ***(d)*** The deviation of gases from ideal gas behaviour is represented in the form of compressibility factor, $Z = \frac{pV}{nRT}$

For ideal gases $Z = 1$

For H_2 and He, $pV > nRT$ at all the pressures.

Hence, $Z > 1$.

27. (*b*) A. Photon shows dual nature, i.e. it shows particle nature as well as wave nature. Hence, it exhibits both momentum and wavelength.

B. Electron also shows dual nature. Thus, it also exhibit both momentum and wavelength.

C. ψ^2 represents probability density and always has positive values.

D. Principal quantum number $n = 4$ for N-shell

$$\begin{matrix} K & L & M & N \\ 1 & 2 & 3 & 4 \end{matrix} \quad n =$$

It always has positive values.

28. (*a*) Metal oxide = $M_{0.98}O$

If 'x' ion of M are in + 3 state, then

$$3x + (0.98 - x) \times 2 = 2$$

$$x = 0.04$$

So, the percentage of metal in + 3 state would be

$$\frac{0.04}{0.98} \times 100 = 4.08\%$$

29. (*c*) Given reaction is,

$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2\,CO_2(g) + 3\,H_2O(l)$$

$\Delta E = -1364.47$ kJ / mol

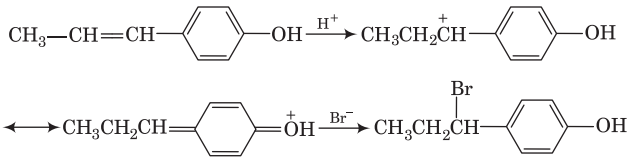
For the reaction the value of $\Delta n_g = -1$

$\therefore \quad \Delta H = \Delta E + \Delta n_g RT$

$= -1364.47 + (-1)(8.314)(300)$

$\Delta H = -3858.67$ kJ / mol

30. (*c*) Electrophilic addition on C = C is governed by stability of carbocation



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(PAPER TWO SCALE UP)

HALF TEST 1

(XI SYLLABUS)

WITH ANSWER KEY

Mock Questions from Class XIth syllabus to inhance Your Problem Solving Skills

INSTRUCTIONS

- This test consists of 30 questions and each question is allotted 4 marks for correct response.
- Candidates will be awarded marks as stated above for correct response of each question. 1/4 marks will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
- There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted according as per instructions.

1. Identify the incorrect statement from the following regarding heavy water. [JEE Main 2016]

(a) It reacts with CaC_2 to produce C_2D_2 and $Ca(OD)_2$

(b) It is used as a coolant in nuclear reactors

(c) It reacts with Al_4C_3 to produce CD_4 and $Al(OD)_3$

(d) It reacts with SO_3 to form deuterated sulphuric acid (D_2SO_4)

2. An organic compound contains C, H and S. The minimum molecular weight of the compound containing 8% sulphur is [JEE Main 2016]
(Atomic weight of S = 32 amu).

(a) 300 g mol^{-1} *(b)* 400 g mol^{-1}

(c) 200 g mol^{-1} *(d)* 600 g mol^{-1}

3. Which physical property of dihydrogen is wrong? [JEE Main 2015]

(a) Odourless gas *(b)* Tasteless gas

(c) Colourless gas *(d)* Non-inflammable gas

4. For the equilibrium, $A(g) \rightleftharpoons B(g)$, ΔH is -40 kJ mol^{-1}. If the ratio of the activation energies of the forward (E_f) and reverse (E_b) reaction is 2/3 then [JEE Main 2015]

(a) $E_f = 80$ kJ mol^{-1}, $E_b = 120$ kJ mol^{-1}

(b) $E_f = 60$ kJ mol^{-1}, $E_b = 100$ kJ mol^{-1}

(c) $E_f = 30$ kJ mol^{-1}, $E_b = 70$ kJ mol^{-1}

(d) $E_f = 70$ kJ mol^{-1}, $E_b = 30$ kJ mol^{-1}

5. A piston filled with 0.04 mole of an ideal gas, which expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37°C. As it does so, it absorbs 208 J of heat. The values of q and w for the process will be [JEE Main 2013]

(a) $q = +208$ J, $w = -208$ J *(b)* $q = -208$ J, $w = -208$ J

(c) $q = -208$ J, $w = +208$ J *(d)* $q = +208$ J, $w = +208$ J

6. Among Al_2O_3, SiO_2, P_2O_3 and SO_2, the correct order of acidic strength is

(a) $Al_2O_3 < SiO_2 < SO_2 < P_2O_3$

(b) $SiO_2 < SO_2 < Al_2O_3 < P_2O_3$

(c) $SO_2 < P_2O_3 < SiO_2 < Al_2O_3$

(d) $Al_2O_3 < SiO_2 < P_2O_3 < SO_2$

7. The bond dissociation energy of B—F in BF_3 is 646 kJ mol^{-1} whereas that of C—F in CF_4 is 514 kJ mol^{-1}. The correct reason for higher B—F bond dissociation energy as compared with that of C—F is

(a) stronger σ-bond between B and F in BF_3 as compared with that between C and F in CF_4

(b) significant $p\pi$-$p\pi$ interaction between B and F in BF_3, whereas there is no possibility of such interaction between C and F ions in CF_4

(c) lower degree of $p\pi$-$p\pi$ interaction between B and F in BF_3 than that between C and F in CF_4

(d) smaller size of B-atom as compared with that of C-atom

8. A real gas behaves ideally at temperature T, its volume is related to van der Waals' constants a and b by the expression as

(a) $V = \dfrac{n^2a}{a - nRTb}$ *(b)* $V = \dfrac{n^2a}{a + nRTb}$

(c) $V = \dfrac{nba}{a - RTb}$ *(d)* $V = \dfrac{nba}{a + RTb}$

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9. Which of the following statements is not correct for dispersion force of atoms/molecules?

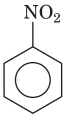
(a) The dispersion force exist in all type of molecules, whether neutral or polar

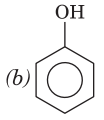
(b) Of the dipole-dipole, dipole-induced dipole and dispersion forces, the major contribution in the van der Waals' interaction comes from dipole-dipole interaction

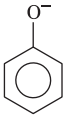
(c) The increasing dispersion forces are reflected in the physical properties of molecules

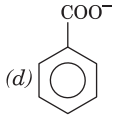
(d) The dispersion force increases with increase in the number of electrons and molar mass of atom/molecule

10. Which of the following compounds/ions has maximum electron density in the ring?

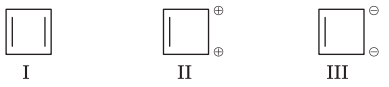
(a) 

(b) 

(c) 

(d) 

11. Which of the following species is/are anti-aromatic?



(a) Only I *(b)* Only II

(c) Only II *(d)* Both II and III

12. If θ is the angle made by orbital angular momentum with the *z*-axis, then the quantum number *l* and *m* of an atom are related to each other through the expression

(a) $m = l\cos\theta$ *(b)* $m = \{l(l+1)\}\cos\theta$

(c) $l = m\cos\theta$ *(d)* $m = \sqrt{l(l+1)}\cos\theta$

13. An unsaturated hydrocarbon *X* gives white precipitate with Tollen's reagent. If *X* is gaseous in nature, what is the molecular formula of it?

(a) C_3H_6 *(b)* C_2H_4

(c) C_2H_2 *(d)* C_4H_8

14. Match the following columns.

	Column I (Quantity)		**Column II** (Formula)
A.	Magnetic moment	p.	$mh/2\pi$
B.	Spin angular momentum	q.	$\sqrt{n(n+2)}$ BM
C.	Orbital angular momentum	r.	$\sqrt{s(s+1)}\,\frac{h}{2\pi}$
D.	*Z* component of orbital angular momentum	s.	$\sqrt{l(l+1)}\,\frac{h}{2\pi}$

Codes

	A	B	C	D		A	B	C	D
(a)	q	r	s	p	*(b)*	p	q	r	s
(c)	s	p	q	r	*(d)*	r	q	p	s

15. Identify the wrong statement among the following

(a) CFCs are responsible for ozone layer depletion

(b) Greenhouse effect is responsible for global warming

(c) Ozone layer does not permit I.R radiation from the sun to reach the earth

(d) Acid rain is mostly happened because of oxides of 'N' and 'S'

16. What is the oxidation state/number of silicon in zeolite $[Na_2Al_2Si_4O_{12}]$ and tremolite $[Ca_2Mg_5(OH)_2(Si_4O_{11})_2]$, respectively?

(a) +4, + 3 *(b)* +4, + 4+ *(c)* +2, + 2 *(d)* +3, + 4

17. In the reaction,

$$2Al(s) + 6HCl(aq) \longrightarrow 2Al^{3+}(aq) + 6Cl^{-}(aq) + 3H_2(g)$$

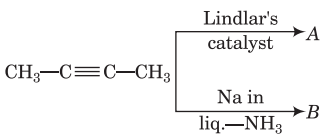
(a) 6 L HCl(*aq*) is consumed for the production of every 3L, $H_2(g)$

(b) 33.6 L $H_2(g)$ is produced regardless of temperature and pressure for every mole of Al that reacts

(c) 67.2 L $H_2(g)$ at STP is produced for every mole of Al that reacts

(d) 11.2 L $H_2(g)$ at STP is produced for every mole of HCl(*aq*) consumed

18.

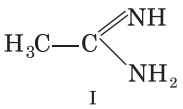


In the above reaction *A* and *B*, respectively are

(a) cis and *trans* but-2-ene *(b) trans* and *cis* but-2-ene

(c) Both *cis* but-2-ene *(d)* Both *trans* but-2-ene

19. The correct order of basicities of the following compounds



I

$CH_3CH_2NH_2$ II

$(CH_3)_2NH$ III

CH_3CONH_2 IV

(a) II > I > III > IV *(b)* III > I > II > IV

(c) I > III > II > IV *(d)* I > III > IV > II

20. Consider the following statements

I. Cs^+ is most hydrated than other alkali metal.

II. Among the alkali metals, Li has the highest melting point.

III. Li is the strongest reducing agent because of low ionisation enthalpy.

IV. Li is the strongest reducing agent because of the high ionisation potential is compensated by high hydration enthalpy.

V. Li is resembled to Al.

Choose whether the above statements are true (T) or false (F)

	I	II	III	IV	V		I	II	III	IV	V
(a)	F	T	F	T	F	*(b)*	T	T	F	T	F
(c)	F	F	F	T	F	*(d)*	T	T	T	F	F

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21. Which of the following represents, sp^2—sp^2—sp—sp hybridisation?

(a) CH_2 with CH

(b) CH with CH

(c) CH with CH_2

(d) CH_2 with CH_2

22. Which of the following is not the correct combination of names for isomeric alcohols with molecular formula $C_4H_{10}O$ is/are?

(a) *tert*-butanol and 2-methylpropan-2-ol

(b) *tert*-butanol and 1,1-dimethylethan-1-ol

(c) *n*-butanol and butan-1-ol

(d) *iso*-butyl alcohol and 2-methylpropan-1-ol

23. 5.5 g of a mixture of $FeSO_4 \cdot 7H_2O$ and $Fe_3(SO_4)_3 \cdot 9H_2O$ requires 0.1 N $KMnO_4$ solution for complete oxidation. Calculate the number of mole of $Fe_2(SO_4)_3 \cdot 9H_2O$ in the mixture.

(a) 0.0045 (b) 0.15

(c) 0.0952 (d) 1.52

24. 4.0 g of ideal gas is filled in a bulb having volume 10 dm^3 at a constant temperature, T and constant pressure, p. If 0.8 g gas is removed from the bulb to maintain the original pressure at $(T + 125)$ K temperature, what would be the value of T for a gas having molar mass 40 g/mole.

(a) 500 K

(b) 500°C

(c) 773 K

(d) 773°C

25. According to kinetic theory of gases.

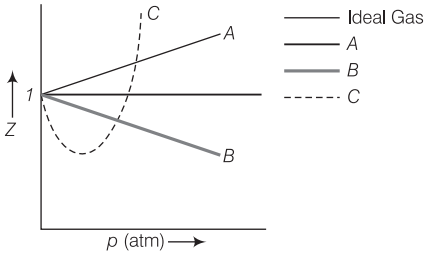
(a) The pressure exerted by a gas is proportional to mean square velocity of the molecules

(b) The pressure exerted by the gas is proportional to the root mean square velocity of the molecules

(c) The root mean square velocity is inversely proportional to the temperature

(d) The mean translational kinetic energy of molecule is directly proportional to the absolute temperature

26. The given graph represents the variation of Z (compressibility factor $(Z) = \frac{pV}{nRT}$) *versus* p, for three real gases A, B and C. Identify the only incorrect statement.



(a) For the gas A, $a = 0$ and its dependence on p is linear at all pressures

(b) For the gas B, $b = 0$ and its dependence on p is linear at all pressures

(c) For the gas C, which is typical real gas for which neither a nor $b = 0$, by knowing the minima and the point of intersection, with $Z = 1$, a and b can be calculated

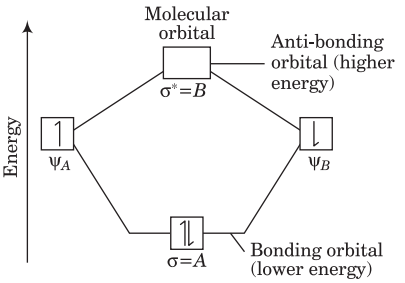
(d) At high pressure, the slope is positive for all real gases

27. Two buffers (X and Y) of pH 4.0 and 6.0, respectively are prepared from acid HA and the salt NaA. Both buffers are 0.50 M in HA. What would be the pH of the solution obtained by mixing equal volumes of the two buffers? $(K_a = 1.0 \times 10^{-5})$

(a) 5.703 (b) 6.279

(c) 7.629 (d) 7.502

28. Consider the following energy diagram for molecular orbital theory. Identify A and B.



	A	B
(a)	$\Psi_A + \Psi_B$	$\Psi_A - \Psi_B$
(b)	$\Psi_A - \Psi_B$	$\Psi_A + \Psi_B$
(c)	$\Psi_A - \Psi_B$	$\Psi_A - \Psi_B$
(d)	$\Psi_A + \Psi_B$	$\Psi_A + \Psi_B$

29. Calculate ΔG° for the conversion of oxygen to ozone, $\frac{3}{2}O_2(g) \rightleftharpoons O_3(g)$ at 298 K, if K_p for this conversion is 2.47×10^{-29}.

(a) 163.288 kJ/mol (b) –163.288 kJ/mol

(c) 163.288 J/mol (d) – 163.288 J/mol

30. Which of the following compounds exhibits stereoisomerism?

(a) 2-methylbutene-1 (b) 3-metylbutyne-1

(c) 3-methylbutanoic acid (d) 2-methylbutanoic acid

Answers

1. (b)	2. (b)	3. (d)	4. (a)	5. (a)
6. (d)	7. (b)	8. (c)	9. (b)	10. (c)
11. (a)	12. (d)	13. (c)	14. (a)	15. (c)
16. (b)	17. (d)	18. (a)	19. (c)	20. (a)
21. (a)	22. (b)	23. (a)	24. (a)	25. (d)
26. (b)	27. (a)	28. (a)	29. (a)	30. (d)

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EXPLICATION SERIES

Elements How They were Discovered Part 6
ZINC AND ANTIMONY

We have read about mercury and phosphorus in October 2016 issue. Now in this issue, we are going to read some interesting things about zinc and antimony. They show many advantages and disadvantages in our daily life. Like, zinc is an essential mineral that keeps the body's enzymes humming while antimony alloys are used in making typeface for clear, sharp printing. They also cause serious health problems on healthy consumption.

Zinc

- The name 'zinc' originates from the Latin word denoting leucoma or white deposit. Some scholars relate zinc to the German word *Zink*, which means lead.
- Zinc compounds have been known to mankind from ancient times. It's best known mineral was calamine (zinc carbonate). Upon calcination it yielded zinc oxide which was widely used, for instance, for treating eye diseases.
- Zinc oxide is comparatively easily reduced to free metal. It was obtained in a metal state much later than copper, iron, tin and lead.
- Zinc was first recognised as a metal in India and waste from zinc smelter at Zawar, in Rajasthan. These wastes were testified to the large scale on which it was refined during the period 1100 to 1500.
- Before metallic zinc was isolated, its ores were used for making brass (an alloy of zinc and copper). Brass was known in Greece, Rome, India and China.
- In the 10-11th centuries the secret of zinc production was lost in Europe. As a result of this, zinc had to be imported from India and China. It is believed that China was the first country to produce zinc on a large scale.
- The production process was extremely simple. Earthen ware filled with calamine were tightly closed and piled into a pyramid. The gaps between the pots were filled with coal and the pots were heated to red hot. After cooling the pots, where zinc vapours condensed were broken and metal ingots were extracted.
- Europeans rediscovered the secret of zinc production in the 16th century when zinc had already been recognised as independent metal.
- During 17th and 18th centuries many chemists and metallurgists worked on methods of zinc extraction. A great deal of credit should go to *A*. Marggraf who published, a large treatise, *Methods of Extraction of zinc from its native mineral calamine*. He also found that lead ores from Rammelsberg (Germany) contained zinc. That zinc could be obtained from sphalerite, natural zinc sulphide.
- According to current research, zinc's role in life can't be understated. Infact, the element appears to be crucial component of the meeting between sperm and egg.

Antimony

- The compounds of antimony had been known since ancient time. There is a 5000 years old antimony vase at the Louvre in Paris.
- Some scholars say that metallic antimony was used in South Babylon for making vessels about 3400 year B.C.
- There are several interpretations of the Latin name of antimony (*antimonium*). Most likely it originates from the Greek word *antimonos*, which means "an enemy of solitude", and underlines simultaneous occurrence of antimony and other minerals.
- The Roman author Pliny used the name stibium in the first century A.D. The modern symbol of antimony, Sb, comes from the word stibium.
- One of the antimony minerals, stibnite (Sb_2S_3), was used in Egyptian cosmetics for four or five thousands years ago as a black eyeliner.
- The name "antimony" is derived from two Greek words: '*anti*' and '*monos*' which means 'not alone'. This name was given because antimony is rarely found native; it is usually found in the combination of sulphur or with heavier metals such as copper, lead and silver.
- In antiquity antimony was confused with lead. It was only in chemical literature of the Renaissance period that antimony was given a sufficiently accurate description. For example, G. Agricola clearly pointed out that antimony is a metal, different from other metals.
- Basilius valentinus devoted to antimony a whole treatise, *Triumphal Carriage of Antimonium*, in which he described the uses of antimony and its compounds.
- Antimony was also used in making coloured glazes for beads and glassware.
- Today, antimony is primarily used in alloys ceramics, glass, plastics and flame retardant materials.
- The manufacture of lead storage batteries, like the ones used in cars and trucks, account for about one fifth of all the antimony used each year.
- A small amount of antimony is also used in making transistors, electrical devices such as computer games, pocket calculators etc.
- Antimony and its compounds are dangerous to human health. In low levels, these materials can irritate the eyes and lungs while at higher levels these can cause lung, heart, liver or kidney damage. At very high doses, they can cause death.

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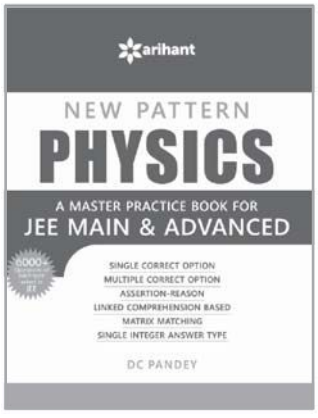

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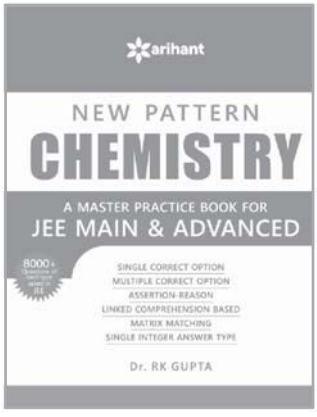

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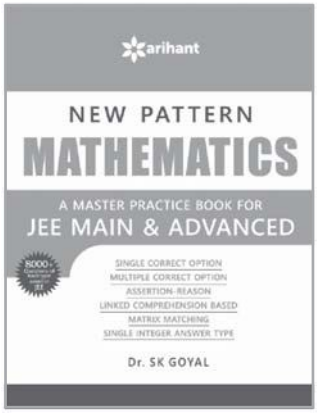

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A collection of 30 innovative problems on JEE Advanced pattern from complete syllabus

Single Answer Correct Type

1. There are three naturally occuring isotopes of carbon : ^{12}C, ^{13}C and ^{14}C.
If atomic weight of carbon, in a sample containing two isotopes ^{12}C and ^{13}C, is 12.01112, find the per cent abundance of ^{13}C. (Atomic weights of ^{12}C and ^{13}C are 12.0000 and 13.0034, respectively).
(a) 1.108 *(b)* 98.891 *(c)* 1.910 *(d)* 99.981

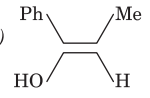
2. The increasing order of atomic radii of the following group 13 elements is [JEE Advanced 2016]
(a) Al < Ga < In < Tl *(b)* Ga < Al < In < Tl
(c) Al < In < Ga < Tl *(d)* Al < Ga < Tl < In

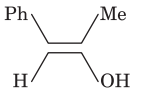
3. Phenol associates in benzene to a certain extent to form dimers. A solution containing 2.0×10^{-2} kg of phenol in 1.0 kg of benzene has freezing point depression of 0.69 K. Calculate the degree of association of phenol. (K_f for benzene = 5.12 K molal^{-1})
(a) 0.367 *(b)* 0.464 *(c)* 0.929 *(d)* 0.734

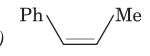
4. Consider the following reaction sequence,

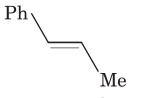
$$Ph{-}C{\equiv}C{-}Me \xrightarrow{B_2H_6,\ THF} A \xrightarrow{CH_3COOH} B$$

Identify the compound B

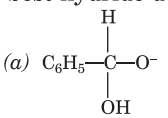
(a) 

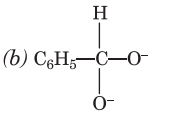
(b) 

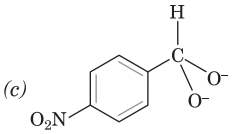
(c) 

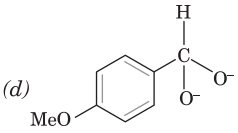
(d) 

5. In Cannizzaro's reaction, the intermediate which is best hydride donor is

(a) 

(b) 

(c) 

(d) 

One or More than One Option Correct Type

6. The crystalline form of borax has [JEE Advanced 2016]
(a) tetranuclear $[B_4O_5(OH)_4]^{2-}$ unit
(b) all boron atoms in the same plane
(c) equal number of sp^2 and sp^3 hybridised boron atoms
(d) one terminal hydroxide per boron atom

7. Choose the correct statement(s) for the applications of electrochemical series.
(a) The metal which has high negative standard reduction potential, readily loses the electrons and converts into cation
(b) Metals like Fe, Pb, Sn, Ni, Co, etc., which lie a little down in series, do not react with cold water
(c) Metals like, Cu, Ag and Au which lie below the hydrogen, are less reactive and do not evolve hydrogen from water
(d) Metals having values of reduction potential between 0.0 V to –2.0 V, are moderately electronegative

8. The correct statement(s) about O_3 is/are [JEE Advanced 2013]
(a) O—O bond lengths are equal
(b) thermal decomposition of O_3 is endothermic
(c) O_3 is diamagnetic in nature
(d) O_3 has a bent structure

9. Phenol is less acidic than
(a) acetic acid *(b)* *p*-methoxy phenol
(c) *p*-nitrophenol *(d)* ethanol

10. Which of the following statements about the zeolites is/are true?
(a) These are used as cation exchangers
(b) Some of the SiO_4^{4-} units are replaced by AlO_4^{5-} and AlO_6^{9-} ions in zeolite
(c) These have open structure which enables them to take up small molecules
(d) Zeolites are alumino silicates having three dimensional structures

11. The properties that show similar trends down the group among the elements from group 1 to 17, is/are
(a) metallic character
(b) reactivity
(c) electronegativity
(d) melting and boiling points

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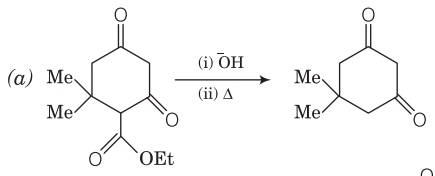
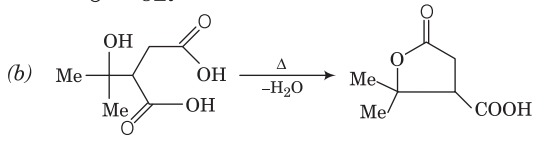
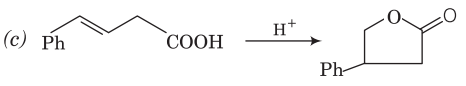
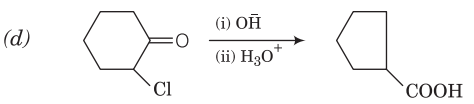
12. Which of the following reactions is/are correct?

(a) 

(b) 

(c) 

(d) 

13. In corundum, oxide ions are arranged in hcp array and the aluminium ions occupy $\frac{2}{3}$rd of the octahedral voids.

Choose the correct option(s) regarding this statement.

(a) Number of tetrahedral voids for each oxide ion $(N_t) = 2$

(b) Number of octahedral voids for each oxide ion $(N_o) = 2$

(c) Formula of the compound is Al_2O_3

(d) Number of Al^{3+} ions for each oxide is $\frac{3}{2}$

Integer Type

14. 29.2% (w/W) HCl stock solution has density of 1.25 g mL^{-1}. The molecular weight of HCl is 36.5 g mol^{-1}. The volume (mL) of stock solution required to prepare a 200 mL solution of 0.4 M HCl is [JEE Advanced 2012]

15. In 1 L saturated solution of AgCl $[K_{sp}(AgCl) = 1.6 \times 10^{-10}]$, 0.1 mole of CuCl $[K_{sp}(CuCl) = 1.0 \times 10^{-6}]$ is added. The resultant concentration of Ag^+ in the solution is 1.6×10^{-x}. The value of 'x' is [JEE Advanced 2011]

16. An intimate mixture of ferric oxide, Fe_2O_3 and aluminium Al, is used in solid fuel rockets. Calculate the fuel value in kcal/cc to the nearest integer. Heats of formation and densities are as follows :

$\Delta H_f(Al_2O_3) = -399$ kcal mol^{-1};

$\Delta H_f(Fe_2O_3) = -199$ kcal mol^{-1}

Density of Fe_2O_3 = 5.2 g/cc; Density of Al = 2.7 g/cc

17. The reaction involved in oxidation of iodide ion by persulphate ion is given below :

$$I^- + S_2O_8^{2-} \longrightarrow I_3^- + SO_4^{2-}$$

If the rate of disappearance of $S_2O_8^{2-}$ ions is 1.5×10^{-3} Ms^{-1}. Find the average rate (in the multiple of 10^{-3} Ms^{-1}) of formation of SO_4^{2-} ions.

18. An organic compound X on analysis gives 24.24% carbon and 4.04% hydrogen. Further, sodium extract of 1.0 g of X gives 2.90 g of AgCl with acidified $AgNO_3$ solution. The compound X may be represented by two isomeric structures, Y and Z. Y on treatment with $aq \cdot KOH$ gives a dihydroxy compound, while (Z) on similar treatment gives ethanol. How many carbon atoms contained by molecular formula of X.

19. AlF_3 is not soluble in anhyd. HF but soluble in KF. How many of the following statements is/are correct?

I. AlF_3 dissolves in ionic KF due to the formation of complex, $K_3[AlF_6]$

II. Anhyd. HF being weak acid does not dissociate into appreciable extent

III. AlF_3 dissolves in ionic KF due to the formation of complex $K_4[AlF_6]$

IV. Anhyd. HF being strong acid dissociates completely to larger extent

20. The atoms present in 10 g of an α-active radioisotope are disintegrating in a sealed container. In one hour, the helium gas collected at STP is 11.2 cm^3. Calculate the half-life (in years) of the radioisotope to the nearest integer.

21. If molar solubility of $Ni(CN)_2$ in a buffer solution of pH equal to 3 is 3.6×10^{-x} M. Find out the value of 'x' $(K_{sp} = 3 \times 10^{-23}, K_a(HCN) = 4 \times 10^{-10})$.

Comprehension I

Two moles of a perfect gas undergo the following process :

I. A reversible isobaric expansion from (1.0 atm, 20.0 L) to (1.0 atm, 40.0 L).

II. A reversible isochoric change of state from (1.0 atm, 40.0 L) to (0.5 atm, 40.0 L).

III. A reversible isothermal compression from (0.5 atm, 40.0 L) to (1.0 atm, 20.0 L).

22. Calculate the total work (w) and the total heat change (q) involved in the above process.

(a) –620.72 J and –620.77 J

(b) –620.72 J and 620.77 J

(c) –600.77 J and 600.77 J

(d) 600.77 J and –600.77 J

23. What will be the values of ΔU (in J), ΔH and ΔS (in J/K) respectively for overall process?

(a) 600.77, – 600.77 and 600.77

(b) 620.72, 620.72 and 0

(c) 620.72, – 620.72 and 620.72

(d) All have zero value

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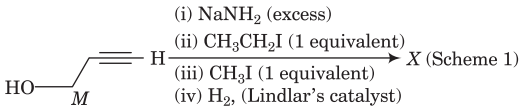
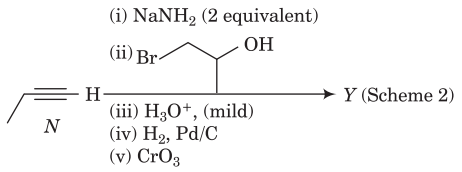
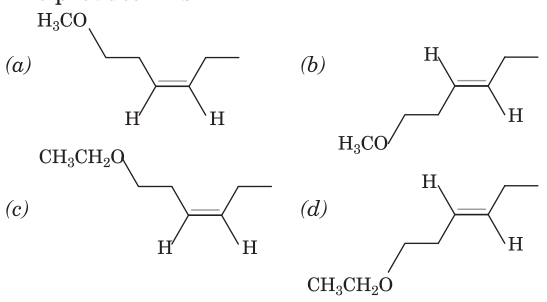
Comprehension II

Schemes 1 and 2 describe sequential transformation of alkynes *M* and *N*. Consider only the major products formed in each step for both schemes.





24. The product *X* is



25. The correct statement with respect to product *Y* is

(a) it gives positive Tollen's test and is a functional isomer of *X*

(b) it gives a positive Tollen's test and is a geometrical isomer of *X*

(c) it gives a positive iodoform test and is a functional isomer of *X*

(d) it gives a positive iodoform test and is a geometrical isomer of *X*

Comprehension III

Due to small size and high electronegativity, fluorine does not form oxyacid while all other halogens (Cl_2, Br_2 and I_2) form four series of oxyacids named as hypohalous acid, halous acid, halic acid and perhalic acid, respectively. Fluorine forms only hypofluorous acid.

It is obtained by passing F_2 over ice at 273 K

$$F_2 + H_2O \overset{273\ K}{\rightleftharpoons} \underset{\text{Hypofluorous acid}}{HOF} + HF$$

26. What is the correct decreasing order of acidic strength of the following?

HOCl(I), HOBr(II) and HOI(III)

(a) I > II > III *(b)* III > II > I

(c) II > I > III *(d)* I > III > II

27. What is the correct increasing order of acidic strength of the following oxyacids?

$$\underset{I}{HOCl}, \underset{II}{HClO_2}, \underset{III}{HClO_3}, \underset{IV}{HClO_4}$$

(a) IV < III < II < I *(b)* I < II < III < IV

(c) IV < II < III < I *(d)* I < III < II < IV

Matrix Match Type

28. Match the thermodynamic processes given under Column I with the expression given under Column II. [JEE Advanced 2015]

Column I	Column II
A. Freezing of water at 273 K and 1 atm.	p. $q = 0$
B. Expansion of 1 mole of an ideal gas into a vacuum under isolated conditions.	q. $W = 0$
C. Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container.	r. $\Delta S_{sys} < 0$
D. Reversible heating of $H_2(g)$ at 1 atm from 300 K to 600 K, followed by reversible cooling to 300 K at 1 atm.	s. $\Delta U = 0$
	t. $\Delta G = 0$

Codes

	A	B	C	D		A	B	C	D
(a)	r,t	p,q,s	p,q,s	p,q,s,t	*(b)*	p,t	q,s	r,s	s,t
(c)	t,s	r,q,t	p,s	p,q	*(d)*	s,q	q,s	p,t,s	t,r

29. Match the Column I which represents the name of crystal defect with Column II representing characteristics of crystal defects.

Column I	Column II
A. Schottky defect	p. Displacement of ions from lattice site to interstitial site.
B. Frenkel defect	q. Unpaired electron trapped in anionic vacancies.
C. F-centre	r. An atom/ion in a crystal is replaced by another chemical species present in the compound.
D. Antisite defect	s. Equal number of cations and anions are missing from crystal lattice.
	t. Density does not change.

Codes

	A	B	C	D		A	B	C	D
(a)	s	p,t	q,t	r,t	*(b)*	s,p	t,q	t	r
(c)	q,t	s,p	r	t	*(d)*	p	q,r	s	t

30. Match the following Columns.

Column I (Molecule)	Column II (Shape)
A. PCl_3	p. Square planar
B. BCl_3	q. T-shape
C. ClF_3	r. Trigonal pyramidal
D. XeF_4	s. *See-saw*
	t. Trigonal planar

Codes

	A	B	C	D		A	B	C	D
(a)	s	q	p	r	*(b)*	r	t	q	s
(c)	r	t	q	p	*(d)*	q	s	r	t

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Answers with Explanation

1. ***(a)*** Let x be the per cent abundance of ^{13}C then per cent abundance of $^{12}C = 100 - x$

Given, atomic weight of carbon in sample = 12.01112

$$\therefore \quad 12.01112 = \frac{(12.0000)(100 - x) + (13.0034)x}{100}$$

or $\quad 1201.112 = 1200.000 - 12.00000\,x + 13.0034\,x$

or $\quad 1.112 = 1.0034\,x$

or $\quad x = 1.108\%$

2. ***(b)*** As we move down the group, atomic radius increases but due to poor shielding of *d*-orbital electrons in Ga, atomic radius of Ga is smaller than that of Al.

Thus, the correct increasing order is Ga < Al < In < Tl.

3. ***(d)*** Given, mass of phenol (solute), $w_2 = 2.0 \times 10^{-2}$ kg

$k_f = 5.12\ \text{K molal}^{-1}$

Mass of benzene (solvent), $w_1 = 1.0$ kg

$\Delta T_f = 0.69$ K

Now as we know, $\Delta T_f = ik_f m$

(where, m = molality of solution)

$$\therefore \quad \Delta T_f = \frac{i \times k_f \times w_2 \times 1000}{M_2 \times w_1};$$

(M_2 = molecular mass of solute)

$$\text{or} \quad 0.69 = \frac{i \times 5.12 \times 2.0 \times 10^{-2} \times 1000}{M_2 \times 1.0}$$

or M_2 (observed) = 148.4 i g mol^{-1}

M_2 (calculated) for C_6H_5OH

$= 12 \times 6 + 1 \times 5 + 16 + 1 = 94$ g mol^{-1}

On equating M_2(observed) and M_2 (calculated) we get,

$148.4i = 94$

$$\text{or} \quad i = \frac{94}{148.4} = 0.633$$

Now, $\quad 2C_6H_5OH \rightleftharpoons (C_6H_5OH)_2$

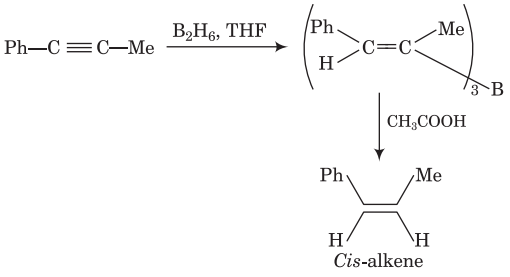
Initial moles	1 mol	0
Moles after association	$1 - \alpha$	$\alpha / 2$

Total moles after association $= 1 - \alpha + \frac{\alpha}{2} = 1 - \frac{\alpha}{2}$

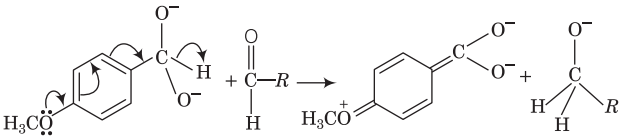
Therefore, $i = \frac{1 - \alpha/2}{1}$

or $\quad \alpha = 2(1 - i) = 2(1 - 0.633) = 0.734$

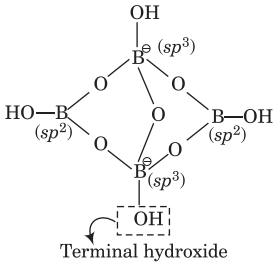
4. ***(c)*** **Key concept** Hydroboration reaction first gives R_3B and then with CH_3COOH, it gives *cis*-alkene.



5. ***(d)*** **Key concept** Electron donating group at *ortho*/*para*-position, promotes hydride transfer.



6. ***(a, c, d)*** $Na_2B_4O_7 \cdot 10\,H_2O$ (borax) is made of two tetrahedral and two triangular units, and is written as $Na_2[B_4O_5(OH)_4] \cdot 5H_2O$

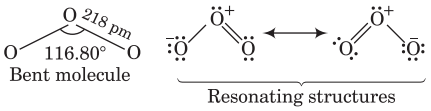


- Thus, it has tetranuclear unit $[B_4O_5(OH)_4]^{2-}$
- Two sp^2 and two sp^3-hybridised B-atoms.
- Each boron has one —OH group
- Due to different hybridisations, boron atoms lie in different planes.

Thus, options (a), (c) and (d) are correct.

7. ***(a, b)*** Metals having values of reduction potentials between 0.0V to – 2.0 V, are moderately electropositive. Al, Zn, Fe, Ni, Co.... etc., belong to this group.

8. ***(a, c, d)*** The O —O bond lengths in O_3 are equal due to resonance.



Since, all electrons are paired, therefore, O_3 is diamagnetic in nature.

9. ***(a, c)*** Phenol is less acidic than acetic acid. Nitro group at *para*-position of phenol, exerts electron withdrawing effect which results increase in acidic strength of phenol.

Therefore, phenol is less acidic than *p*-nitrophenol.

- Methoxy group at *para*-position, exerts electron donating effect, which results decrease in acidic strength of phenol.
- Ethanol is a weaker acid than phenol due to resonance stabilisation in phenoxide ion.

Hence, increasing order of acidic strength will be.
ethanol < *p*-methoxy phenol < phenol < *p*-nitrophenol < acetic acid.

10. ***(a, c, d)*** Zeolites have SiO_4 and AlO_4 tetrahedrons linked together in a three dimensional open structure in which four or six membered ring predominates. Due to open chain structure, these have cavities and can take up water and other small molecules.

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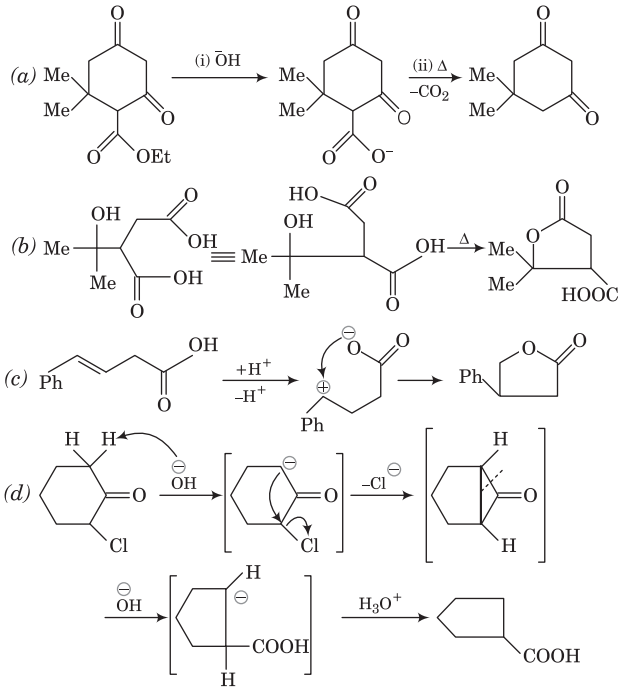
11. ***(a, c)*** Metallic character and electronegativity always follow the similar trends down the group among the elements of group 1 to 17.

12. ***(a, b, c, d)***



13. ***(a, c)*** In hcp arrangement of oxide ion,

Number of octahedral voids for each oxide ion $(N_o) = 1$

Number of tetrahedral voids for each oxide ion $(N_t) = 2$

$\because N_t = 2 \times N_o$

$\therefore Al^{3+}$ occupies only $\frac{2}{3}$rd of octahedral voids

Thus, the number of Al^{3+} for each oxide ion $= \frac{2}{3}$ or the ratio of oxide ion to aluminium ion = 3 : 2

Thus, formula is Al_2O_3.

14. ***(8)*** Mass of HCl in 1.0 mL stock solution

$$= 1.25 \times \frac{29.2}{100} = 0.365\ g$$

Mass of HCl required for 200 mL 0.4 M HCl

$$= \frac{200}{1000} \times 0.4 \times 36.5 = 0.08 \times 36.5\ g$$

$\because$ 0.365 g of HCl is present in 1.0 mL of stock solution.

$\therefore$ 0.08 × 36.5 g HCl will be present in stock solution

$$= \left(\frac{0.08 \times 36.5}{0.365}\right) mL = 8.0\ mL$$

15. ***(7)*** It is a case of simultaneous solubility of salts with a common ion. Here, solubility product of CuCl is much greater than that of AgCl, it can be assumed that Cl^- in solution comes mainly from CuCl.

$$[Cl^-] = \sqrt{K_{sp}(CuCl)} = 10^{-3}\ M$$

Now, for AgCl, $K_{sp} = 1.6 \times 10^{-10}$

$$= [Ag^+][Cl^-] = [Ag^+] \times 10^{-3}$$

$$\Rightarrow [Ag^+] = 1.6 \times 10^{-7}$$

16. ***(4)*** $Fe_2O_3(s) + 2Al(s) \longrightarrow Al_2O_3(s) + 2Fe(s)$

$$\Delta H_r^\circ = \Delta H_f^\circ (\text{products}) - \Delta H_f^\circ (\text{reactants})$$

$$= -399 - (-199) = -200\ kcal$$

Mass of reactants

$$= (56 \times 2)\ g + (16 \times 3)\ g + (27 \times 2)\ g$$

$$= 214 g$$

$$\text{Fuel value/gram} = \frac{200}{214} = 0.93\ kcal\ g^{-1}$$

$$\text{Volume of reactants} = \frac{160}{5.2} cc + \frac{54}{2.7} cc = 50.77\ cc$$

$$\therefore \text{Fuel value/cc} = \frac{200}{50.77} = 3.94\ kcal\ cc^{-1}$$

$$\simeq 4\ kcal\ cc^{-1}$$

17. ***(3)*** The balanced equation is

$$3I^- + S_2O_8^{2-} \longrightarrow I_3^- + 2SO_4^{2-}$$

$$\text{Rate of reaction} = -\frac{1}{3}\frac{d[I^-]}{dt} = -\frac{d[S_2O_8^{2-}]}{dt} = \frac{1}{2}\frac{d[SO_4^{2}]}{dt}$$

or $$-\frac{d[S_2O_8^{2-}]}{dt} = 1.5 \times 10^{-3}\ Ms^{-1}$$

$\therefore$ $$\frac{d[SO_4^{2-}]}{dt} = 2 \times 1.5 \times 10^{-3} = 3 \times 10^{-3}\ Ms^{-1}.$$

18. ***(2)*** Per cent of Cl in X

$$= \frac{35.5}{143.5} \times \frac{\text{Mass of AgCl}}{\text{Mass of } X} \times 100$$

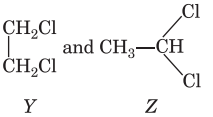
$$= \frac{35.5}{143.5} \times \frac{2.90}{1.0} \times 100$$

$$= 71.74\%$$

Now, we can calculate empirical formula of X by the following table

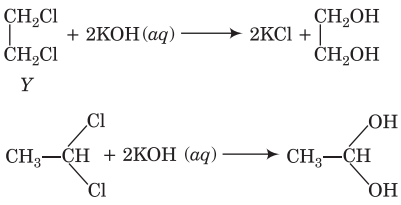
S. No	Element	Mole ratio/atomic mass	Simple mole ratio	Empirical formula
1	C	24.24 / 12 = 2.02	2.02 / 2.02 = 1	CH_2Cl
2	H	4.04 / 1 = 4.04	4.04 / 2.02 = 2	
3	Cl	71.74 / 35.5 = 2.02	2.02 / 2.02 = 1	

Since, Y isomer of the compound X, gives a dihydroxy compound, hence X must have two Cl-atoms in its molecule. Thus, the molecular formula of X is $C_2H_4Cl_2$. The possible isomers of $C_2H_4Cl_2$ are



Y Z

The reactions given by Y and Z are



19. ***(2)*** Statements I and II are correct.

$$AlF_3 + 3KF(aq) \longrightarrow K_3[AlF_6]$$

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20. ***(2)*** Given, amount of radioactive isotope = 10 g

Atoms present in 10 g of radio isotope

$= 10 \times 6.023 \times 10^{23}$ atoms $= 6.023 \times 10^{24}$ atoms

22400 cm^3 of helium contains = 6.023×10^{23} atoms

11.2 cm^3 of helium will contain

$$= \left(\frac{6.023 \times 10^{23}}{22400} \times 11.2\right) \text{atoms}$$

$= 3.01 \times 10^{20}$ atoms

One He-atom is obtained by disintegration of one atom of radioisotope, the total number of atoms of radioactive isotope which get disintegrated in 1 h = 3.01×10^{20} or 0.0003×10^{24}.

The number of atoms of the radioactive isotope left after 1h,

$N = (6.023 \times 10^{24} - 0.000301 \times 10^{24})$

$= 6.0227 \times 10^{24}$

Using, $\lambda = \frac{2.303}{\lambda} \log \frac{N_0}{N}$

$$\lambda = \frac{2.303}{t} \log \frac{6.023 \times 10^{24}}{6.0227 \times 10^{24}}$$

$= 2.303 \times 2.1632 \times 10^{-5}$

$= 4.982 \times 10^{-5}\ hr^{-1}$

$$t_{1/2} = \frac{0.693}{\lambda} = \frac{0.693}{(4.982 \times 10^{-5} \times 24 \times 365)} = 1.58\ yr$$

≈ 2 yr

21. ***(4)*** $Ni(CN)_2 + 2H^+ \rightleftharpoons Ni^{2+} + 2HCN$

Here, K is given as $\frac{K_{sp}}{K_a^2} = \frac{3 \times 10^{-23}}{(4 \times 10^{-10})^2}$

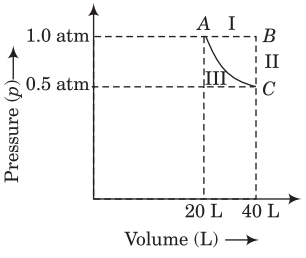
$= 1.875 \times 10^{-4}$

or $K = 1.875 \times 10^{-4} = \frac{s(2s)^2}{[H^+]^2}$

$4s^3 = 1.875 \times 10^{-10}$; $[(H^+) = 10^{-3}M]$

or $s = 3.6 \times 10^{-4}M$

22. ***(a)*** **Key concept** For cyclic process, $W = q$



Here, AB = isobaric expansion (I)

BC = isochoric change (II)

CA = isothermal compression (III)

Total work done,

$W = W_{A \longrightarrow B} + W_{B \longrightarrow C} + W_{C \longrightarrow A}$

$= -p(V_2 - V_1) + 0 + 2.303\, nRT \log \frac{V_3}{V_1}$

$= -1 \times (40 - 20) + 0 + 2.303\, p_1V_1 \times \log \frac{V_3}{V_1}$;

$(\because p_1V_1 = nRT)$

$= -20 + 2.303 \times 1 \times 20 \log \frac{40}{20} = -6.13$ L atm

$= -(6.13 \times 101.26)$ J $(\because 1$ L atm $= 101.26$ J$)$

$= -620.72$ J

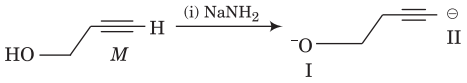
$W = q$ (For cyclic process)

$\therefore \quad q = -620.72$ J

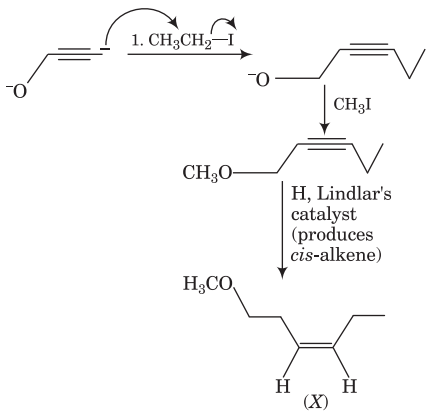
23. ***(d)*** As the overall process is cyclic, so, $\Delta U = 0$, $\Delta H = 0$ and $\Delta S = 0$.

24. ***(a)*** **Thinking process** *This problem can be solved by using the concept of nucleophilic substitution reaction, oxidation reaction and reduction reaction including strength of nucleophile and regioselectivity.*

Reaction of scheme 1 can be completed as



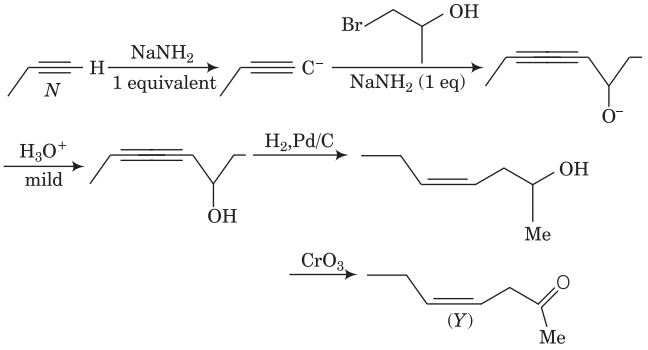
Among two naked nucleophilic groups I and II, II is more nucleophilic and will react selectively as follows:



Hence, using the concept of regioselectivity we come on the conclusion that final product is correctly represented by structure (a).

25. ***(c)*** **Thinking process** *This problem can be solved by using the concept of iodoform test and functional isomerism.*

Iodoform test The compound containing —$COCH_3$ or —CH(OH) group will undergo iodoform test.



Thus, X and Y are functional isomers of each other and Y gives iodoform test due to the presence of CH_3CO group as indicated.

Hence, correct choice is (c).

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26. ***(a)*** **Key concept** For oxyacids having same oxidation number of halogen atoms, acidic strength decreases with increase in atomic number of halogen atoms.

In HOCl, HOBr and HOI all the halogen atoms are in +1 oxidation state.

The increasing order of atomic number of halogen atoms is Cl < Br < I

Thus, the correct decreasing order of acidic strength of the given oxyacids will be

$$\underset{(I)}{HOCl} > \underset{(II)}{HOBr} > \underset{(III)}{HOI}$$

27. ***(b)*** **Key concept** For oxyacids of same halogen atom acidic strength increases with increase in oxidation number of halogen atom.

Oxyacid	Oxidation number of chlorine
$HOCl$	+1
$HClO_2$	+3
$HClO_3$	+5
$HClO_4$	+7

Thus, the correct increasing order is

$$\underset{(I)}{HOCl} < \underset{(II)}{HClO_2} < \underset{(III)}{HClO_3} < \underset{(IV)}{HClO_4}$$

28. ***(a)*** A. $H_2O(l) \longrightarrow H_2O(s)$ at 273 K and 1 atm

$\Delta H = -\text{ve} = q$

$\Delta S_{sys} < 0, \Delta G = 0$

$W \neq 0$ (as water expands on freezing)

$\Delta U \neq 0$

B. Free expansion of ideal gas,

$q = 0, W = 0$

$\Delta U = 0, \Delta S_{sys} > 0$

$\Delta G < 0$

C. Mixing of equal volume of ideal gases at constant pressure and temperature in an isolated container.

$q = 0, W = 0, \Delta U = 0$

$\Delta S_{sys} > 0$

$\Delta G < 0$

D. $H_2(g)$ 300K $\xrightarrow[\text{heating, 1 atm}]{\text{Reversible}}$ 600 K $\xrightarrow[\text{cooling, 1 atm}]{\text{Reversible}}$ 300 K

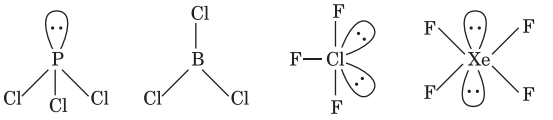
As system comes to its initial temperature, so ΔU, ΔG, W and q will be equal to zero.

Hence, the correct match is

A → r, t; B → p, q, s; C → p, q, s; D → p, q, s, t

29. ***(a)*** A ⟶ s; B ⟶ p, t; C ⟶ q, t; D ⟶ r, t

30. ***(c)*** A ⟶ r; B ⟶ t; C ⟶ q; D ⟶ p

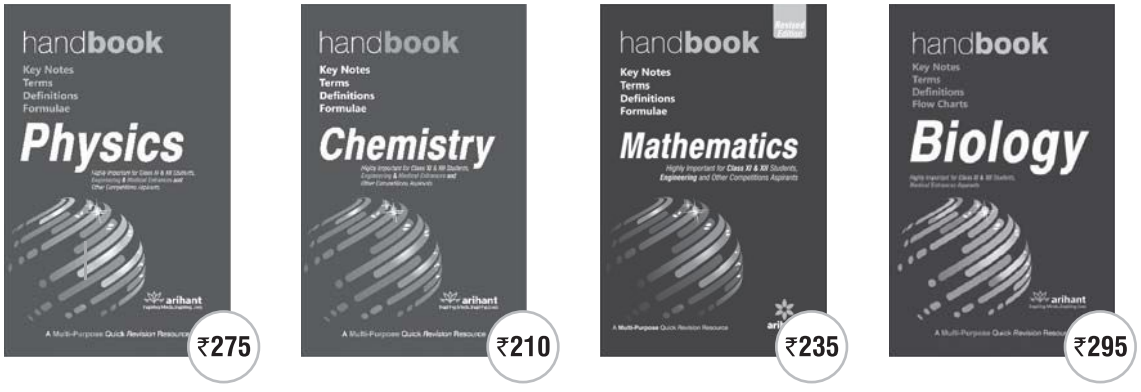


PCl_3–Trigonal pyramidal; BCl_3–Trigonal planar; ClF_3–T-shape; XeF_4–Square planar

HANDBOOKS

Multipurpose Revision Books **For Class XI, XII, Medical, Engineering & Other Competitive Exams** *having*

Key Notes | Terms | Definitions | Formulae



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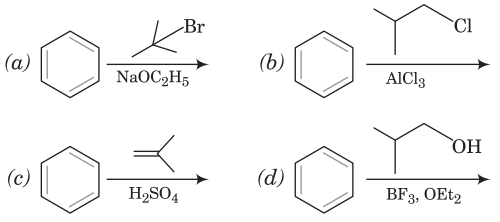
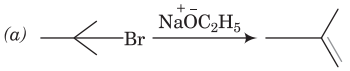
HYDROCARBONS

A collection of best asked questions from JEE to revise your concepts

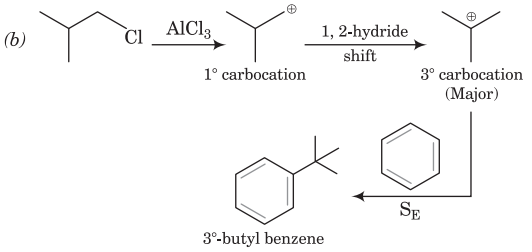
1. Among the following reactions, which gives *tert*-butyl benzene as the major product?
[JEE Advanced 2016]

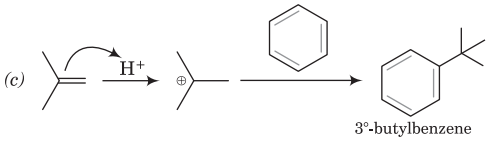


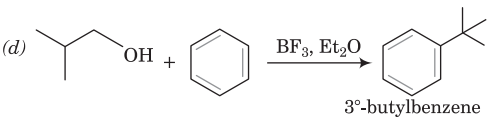
(b, c, d)



$C_2H_5O^-$ (a strong nucleophile) shows E1 reaction to form *iso*-butene as the major product.



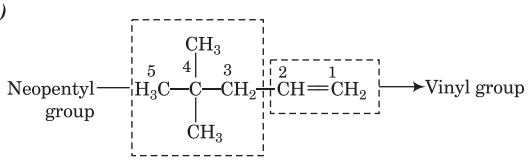




2. The hydrocarbon with seven carbon atoms containing a neopentyl and a vinyl group is
[JEE Main 2016]

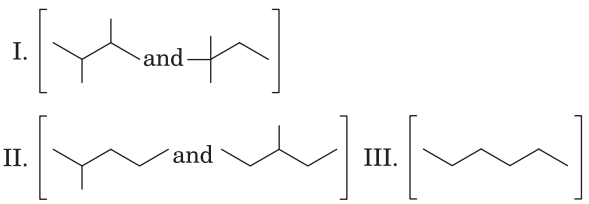
(a) 4, 4- dimethylpentene *(b)* 2,2-dimethyl-4-pentene
(c) *iso*-propyl -2-butene *(d)* 2,2-dimethyl-3-pentene

(a)



4, 4-dimethylpentene

3. Isomers of hexane, based on their branching, can be divided into three distinct classes, as shown in the figure.
[JEE Advanced 2014]



The correct order of their boiling points is
(a) I >II> III *(b)* III> II> I
(c) II > III > I *(d)* III > I > II

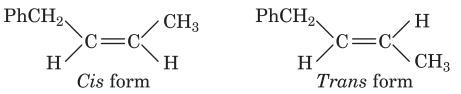
(b) Key concept *More the branching in an alkane, lesser will be its surface area and lesser will be the boiling point.*
On moving III to I, i.e. III → II → I.
- Branching increases
- Surface area decreases
- Boiling point decreases

Hence, the correct order of their boiling points is III> II > I.

4. Which of the following compounds will exhibit geometrical isomerism?
[JEE Main 2015]

(a) 1-phenyl-2-butene *(b)* 3-phenyl-1-butene
(c) 2-phenyl-1 butene *(d)* 1, 1-diphenyl-1-propane

(a) Key concept *A compound must contain two different groups to the doubly bonded carbon atom in order to exhibit geometrical isomerism.*



1-phenyl-2-butene

All the doubly bonded carbon atoms contain two different groups. Thus, 1-phenyl-2-butene exhibit geometrical isomerism.

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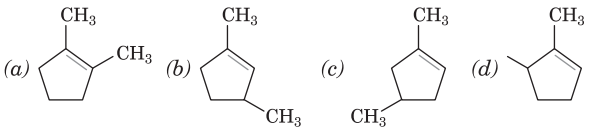
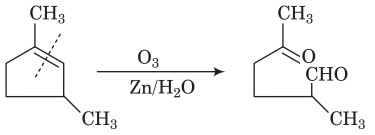
5. Which compound would give 5-keto-2-methyl hexanal upon ozonolysis? **[JEE Main, 2015]**



(b)



5-keto-2-methylhexanal

Short trick *In order to determine correct compound, take all the compounds one by one mentioned in the problem, break double bond and attach oxygen atom to the both breakage parts. Now, name the compound according to IUPAC rules and match this name with the asked name in the problem.*

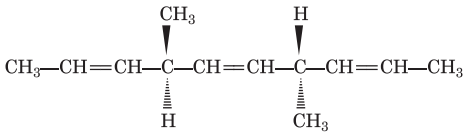
6. The major organic compound formed by the reaction of 1, 1, 1-trichloroethane with silver powder is **[JEE Main 2014]**

(a) acetylene (b) ethene
(c) 2-butyne (d) 2-butene

(c) The reaction is

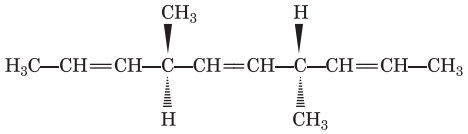
$$CH_3-C(Cl_3)C-CH_3 + 6Ag + Cl_3C-CH_3 \longrightarrow \underset{\text{2-butyne}}{CH_3-C\equiv C-CH_3} + 6AgCl$$

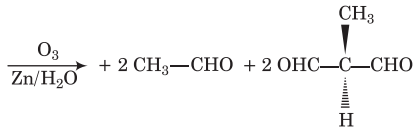
7. The number of optically active products obtained from the complete ozonolysis of the given compound is **[JEE Main 2012]**



(a) 0 (b) 1 (c) 2 (d) 4

(a) Ozonolysis of the given triene occur as follows:





Since, none of the above dial is chiral, therefore no optically active product is obtained.

8. The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and an alkyne. The bromoalkane and alkyne respectively are **[JEE Advanced 2010]**

(a) Br CH_2 $CH_2CH_2CH_2CH_3$ and $CH_3CH_2C\equiv CH$
(b) $BrCH_2CH_2CH_3$ and $CH_3CH_2CH_2C\equiv CH$
(c) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_3C\equiv CH$
(d) $BrCH_2CH_2CH_2CH_3$ and $CH_3CH_2C\equiv CH$

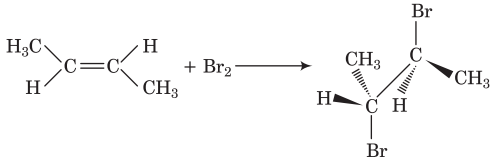
(d) $CH_3-CH_2-C\equiv CH \xrightarrow{NaNH_2} CH_3-CH_2-C\equiv C^{\ominus}$

$CH_3CH_2C\equiv C^{\ominus} + Br-CH_2CH_2CH_2CH_3 \longrightarrow \underset{\text{3-octyne}}{CH_3CH_2-C\equiv C-CH_2CH_2CH_2CH_3}$

9. The number of stereoisomers obtained by bromination of *trans*-2-butene is **[JEE Advanced 2007]**

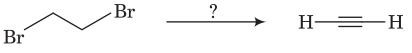
(a) 1 (b) 2 (c) 3 (d) 4

(c) Br_2 undergoes anti-addition on C = C as



Meso isomer

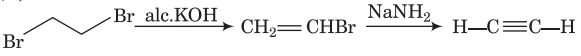
10. The reagent(s) for the following conversion,



is/are **[JEE Advanced 2007, 3M]**

(a) alcoholic KOH
(b) alcoholic KOH followed by $NaNH_2$
(c) aqueous KOH followed by $NaNH_2$
(d) Zn / CH_3OH

(b)



11. The total number of cyclic isomers possible for a hydrocarbon with the molecular formula C_4H_6 is **[JEE Advanced 2010]**

(5) Thinking process

- *To find out total number of possible cyclic isomers, first calculate DBE (Double Bond Equivalent).*

$$DBE = C - \frac{H}{2} + \frac{N}{2} + 1$$

where, C = *total number of carbon atoms*
H = *total number of hydrogen atoms*
N = *total number of nitrogen atoms*

- *The value of DBE equals to the sum of ring and π -bonds present in the compound.*
- *Draw the other possible minimum carbon containing rings and draw different isomers for different rings.*

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12. $CH_3—CH=CH_2 + NOCl \longrightarrow P$; Identify the adduct. [JEE Advanced 2006, 3M]

(a) $CH_3—\underset{Cl}{CH}—\underset{NO}{CH_2}$ (b) $CH_3—\underset{NO}{CH}—\underset{Cl}{CH_2}$

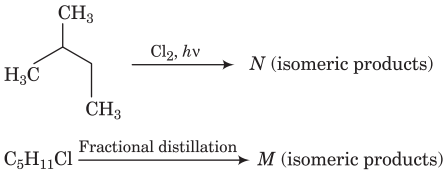
(c) $CH_3—CH_2—\underset{NO}{\overset{Cl}{CH}}$ (d) $\underset{NO}{CH_2}—CH_2—\underset{Cl}{CH_2}$

(a) Key concept NOCl *undergoes electrophilic addition on alkene as*

$$NOCl \longrightarrow \overset{+}{N}=O + Cl^-$$

$$CH_3—CH=CH_2 + \overset{+}{N}O \longrightarrow CH_3—\overset{+}{C}H—\underset{NO}{CH_2} \xrightarrow{Cl^-} CH_3—\underset{Cl}{CH}—\underset{NO}{CH_2}$$

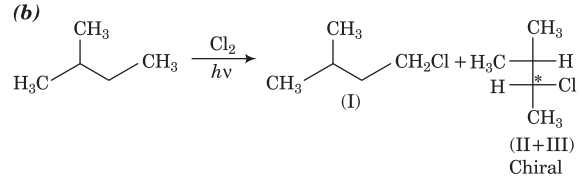
13.

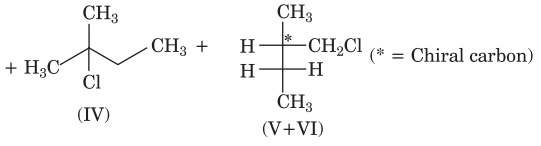


What are *N* and *M*? [JEE Advanced 2006]

(a) 6, 6 (b) 6, 4 (c) 4,4 (d) 3,3

(b)

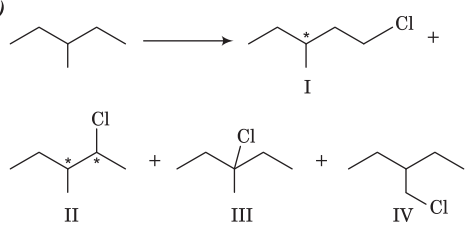




Since, fractional distillation cannot separate enantiomers (II + III and V+ VI), therefore, $M = 4$ and $N = 6$

14. The maximum number of isomers (including stereoisomers) that are possible on mono-chlorination of the following compound is $CH_3CH_2CH(CH_3)CH_2CH_3$ [JEE Advanced 2010]

(8)

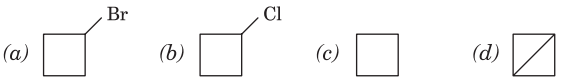


I has one chiral carbon = two isomers.

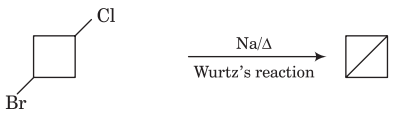
II has two chiral carbons and no symmetry = four isomers.

III and IV have no chiral carbon, no stereoisomers.

15. 1-bromo-3-chlorocyclobutane when treated with two equivalents of Na, in the presence of ether which of the following will be formed? [JEE Main 2006]



(d) Key concept *This reaction is an example of Wurtz's reaction.*



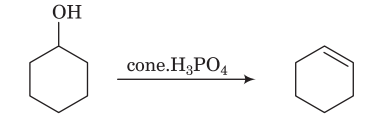
1-bromo-3-chlorocylobutane

16. Cyclohexene is best prepared from cyclohexanol by which of the following? [JEE Main 2008]

(a) con H_3PO_4 (b) conc $HCl/ZnCl_2$

(c) con HCl (d) conc HBr

(a) Key concept *Cyclohexanol on treatment with concentrated* H_3PO_4 *undergoes, acid catalysed dehydration, giving cyclohexene.*

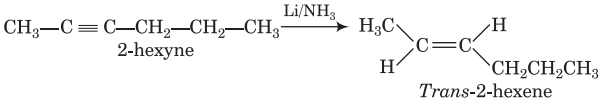


Cyclohexanol Cyclohexene

17. 2-hexyne gives *trans*-2-hexene on treatment with [JEE Main 2009]

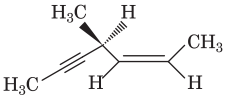
(a) Li/NH_3 (b) $Pd/BaSO_4$ (c) $LiAlH_4$ (d) Pt/H_2

(a) Key concept *Alkynes on treatment with alkali metals in liquid ammonia, gives trans hydrogenation product.*



Trans-2-hexene

18. Hydrogenation of the adjoining compound in the presence of poisoned palladium catalyst gives



[JEE Main 2007]

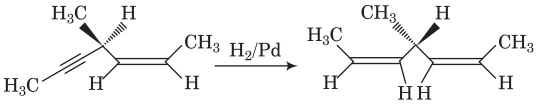
(a) an optically active compound

(b) an optically inactive compound

(c) a racemic mixture

(d) a diastereomeric mixture

(b) Key concept *Hydrogenation with poisoned palladium brings about cis-hydrogenation of alkyne and does not affect double bonds.*



(optically inactive)

To be Continued at Page 35

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ASSERTION & REASON ZONE

A practice set of best assertion and reason problems for medical entrances from complete syllabus.

Directions (Q. Nos. 1-30) In the following questions a statement of Assertion followed by a statement of Reason is given. Choose the correct answer out of the following choices.

(a) Both Assertion and Reason are true and Reason is the correct explanation of the Assertion

(b) Both Assertion and Reason are true but Reason is not the correct explanation of the Assertion

(c) Assertion is true but Reason is false

(d) Both Assertion and Reason are false

1. **Assertion (A)** Fe^{3+} can be used for coagulation of As_2S_3 sol.
Reason (R) Fe^{3+} reacts with As_2S_3 to give Fe_2S_3. [AIIMS 2016]

2. **Assertion (A)** Reaction with molecularity equal to or greater than 3 are rare.
Reason (R) The probability of simultaneous collision is low in case of a reaction involving three or more reacting species.

3. **Assertion (A)** When we plot a graph of the square of wave function *versus* distance of electron from the nucleus, for 2*s*-orbital then the graph approaches to zero on distance axis twice.
Reason (R) For 2*s*-orbital there exists two nodal surfaces.

4. **Assertion (A)** Atoms with completely filled and half-filled subshells are stable.
Reason (R) Completely filled and half-filled subshells have symmetrical distribution of electrons and have maximum exchange energy. This leads to more stability of the atom.

5. **Assertion (A)** The electrolysis of NaCl solution gives $H_2(g)$ at cathode and $Cl_2(g)$ at anode.
Reason (R) Cl_2 has higher oxidation potential than H_2O.

6. **Assertion (A)** Haemoglobin is an oxygen carrier.
Reason (R) Oxygen binds as O_2^- to Fe of haemoglobin. [AIIMS 2013]

7. **Assertion (A)** Increasing order of bond dissociation energy for Cl_2, O_2 and N_2 is shown as $Cl_2 < O_2 < N_2$
Reason (R) The bond dissociation energy is directly proportional to bond order.

8. **Assertion (A)** A common salt is sometimes appears yellow instead of being purely white.
Reason (R) NaCl suffers from Frenkel defect.

9. **Assertion (A)** The rates of bromination of C_6H_6 and C_6D_6 are the same in the presence of $FeBr_3$ as a catalyst.
Reason (R) C—H and C—D bond fission are involved in the rate determining step in their corresponding reaction mechanisms.

10. **Assertion (A)** The order of a reaction can be fractional value.
Reason (R) The order of a reaction cannot be written from balanced equation of a reaction.

11. **Assertion (A)** Reactants having different allotropic forms or physical states have different enthalpies during the course of reaction.
Reason (R) Different allotropic forms are held by forces of different attraction strengths.

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12. **Assertion (A)** Pure NaCl is recovered from sea water by passing dry HCl gas over crude salt.
Reason (R) The ionic products preceeds its solubility product due to the addition of HCl.

13. **Assertion (A)** Glycerol is purified by distillation under reduced pressure.
Reason (R) Glycerol is a trihydric alcohol. [AIIMS 2013]

14. **Assertion (A)** If helium is allowed to expand in vacuum, it will liberate heat.
Reason (R) The inversion temperature of helium is very low.

15. **Assertion (A)** Aluminium is obtained by high temperature reduction of alumina with carbon.
Reason (R) Alumina reacts with carbon to form aluminium carbide which decomposes at high temperature to form aluminium while carbon is oxidised to CO.

16. **Assertion (A)** Benzaldehyde is less reactive than ethanol towards nucleophilic attack.
Reason (R) All the carbon atoms of benzaldehyde are sp^2-hybridised.

17. **Assertion (A)** CO and CN are referred as π-acid ligands.
Reason (R) In CO and CN, vacant π-type orbitals are present. [AIIMS 2009]

18. **Assertion (A)** The O – O bond length in H_2O_2 is shorter than that in O_2F_2.
Reason (R) H_2O_2 is an ionic compound.

19. **Assertion (A)** NO_3^- is planar while NH_3 is pyramidal.
Reason (R) N in NO_3^- has sp^2 and in NH_3 has sp^3-hybridisation.

20. **Assertion (A)** Rate of a reaction doubles, when concentration of reactant is doubled in a first order reaction.
Reason (R) On increasing the concentration, rate constant of reaction increases.

21. **Assertion (A)** The order of reactivity of alkenes, $(CH_3)_2\underset{(I)}{C}=CH_2, CH_3\underset{(II)}{CH}=CH_2, CH_2\underset{(III)}{=}CH_2$ when subjected to acid catalysed hydration is I > II > III.
Reason (R) Here, reactivity increases as the number of electron releasing group increases.

22. **Assertion (A)** At room temperature, the eclipsed and staggered forms of ethane cannot be isolated.
Reason (R) Both the conformers are equally stable.

23. **Assertion (A)** A heavier gas takes more time for diffusion.
Reason (R) At a given temperature, the rate of diffusion of a gas is inversely proportional to the square root of its density.

24. **Assertion (A)** Wolframite impurity is separated from tin stone (SnO_2) by magnetic separation.
Reason (R) Tin stone is ferromagnetic and is attracted by the magnet.

25. **Assertion (A)** Mercury vapour is shining silvery in appearance.
Reason (R) Mercury is a metal with shining silvery appearance. [AIIMS 2007]

26. **Assertion (A)** Complexes of MX_6 and MX_5L type (X and L are unidentate) do not show geometrical isomerism.
Reason (R) Geometrical isomerism is not shown by complexes of coordination number 6.

27. **Assertion (A)** 2,2-dimethylpropanal give Cannizzaro reaction with conc.NaOH
Reason (R) Cannizzaro is a disproportionation reaction.

28. **Assertion (A)** Starch is a polymer of α-glucose. It is hydrolysed to glucose by enzyme amylase.
Reason (R) Starch has two components which are amylose and amylopectin.

29. **Assertion (A)** A solid has rigidity but liquids do not.
Reason (R) The intermolecular forces are very strong in solid.

30. **Assertion (A)** Hydrolysis of sucrose results a change in the sign of optical rotation from dextro (+) to laevo (–).
Reason (R) Sucrose on hydrolysis gives fructose and glucose.

CHEMISTRY IN action!

New Environment Friendly Solar cells

Plastic solar cells, or organic photovoltaics, are popular because they are lightweight, flexible, transparent and inexpensive to manufacture. This makes them useful to multiple applications. Unfortunately, the halogen-containing solvents used in their manufacture are an obstacle to large-scale commercialisation. These solvents play key role in making sure that the solar cell's morphology, or structure, maximises its energy efficiency; however, they are environmentally hazardous. Additionally, the use of these harsh chemicals requires a controlled environment, which adds to production costs. Scientists have created an efficient, semi-printed plastic solar cell without the use of environmentally hazardous halogen solvents. These solar cells can be manufactured at room temperature, which has implications for large-scale commercial production. In this new solar cell *o*-methylanisole (*o*-MA) is used as the solvent. *o*-MA is a commonly used flavoring agent in foods, and is nontoxic to humans.

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Answers with Explanation

1. *(b)* Fe^{3+} can be used for coagulation of As_2S_3 solution because As_2S_3 is negatively charged sol and hence, it can be coagulated by Fe^{3+}, which is positively charged.

2. *(a)* The major conditions for a reactions to occur, are proper orientation of reacting species and effective collision between them. In case of more than three species chances of obeyance of these conditions are rare.

3. *(c)* When we plot a graph of ψ^2 *versus* r for $2p$-orbital the graph touches the r axis twice.
The first time when it crosses the nucleus and the second time when it crosses the single nodal plane available in $2p$-orbital.
Also, the number of nodal plane available in $2s$-orbital $= (2-1) = 1$

4. *(a)* The extra stability of half-filled and fully-filled subshells can be explained in terms of symmetry and exchange energy. All the orbitals of the same subshell are either completely filled or half-filled have more symmetrical distribution of electrons. Consequently, their shielding to one another is relatively small and the electrons are more strongly attracted by the nucleus.
This leads to more stability of the atom.

5. *(c)* Cl_2 has higher reduction potential than H_2O but has lower discharge potential on account of over potential of O_2.

6. *(c)* O_2 binds to Fe of haem part to form oxyhaemoglobin. One molecule of haemoglobin (Hb) binds with four molecules of O_2.

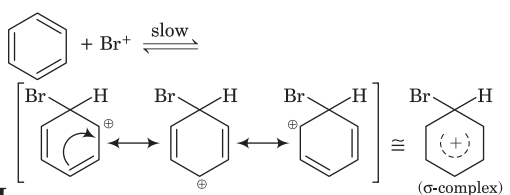
7. *(a)* Bond orders of N_2, O_2 and Cl_2 are 3, 2, and 1, respectively.

8. *(c)* In the crystal lattice of NaCl, a missing negative ion is filled with an electron as F-centre. The presence of F-centre imparts colour to the common salt.

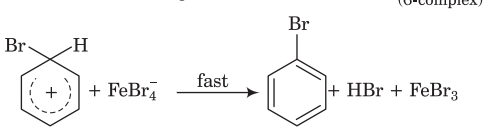
9. *(c)* Bromination of benzene proceeds through following mechanism:

Step I $Br_2 + FeBr_3 \overset{\text{fast}}{\rightleftharpoons} FeBr_4^- + Br^+$

Step II



Step III



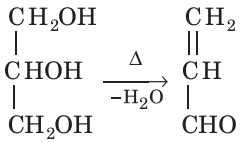
Step II is the slowest and rate determining step and no kinetic isotopic effect is observed when H is replaced by D. Since, C—H or C—D bond fission is not involved in the rate determining step, therefore, rate of bromination of C_6H_6 and C_6D_6 is same.

10. *(b)* The order of a reaction is determined experimentally and it depends upon the concentration change of reactant.

11. *(a)*

12. *(c)* The ionic product of NaCl exceeds its solubility product due to the addition of HCl and it is precipitated as pure NaCl. It is further purified by crystallisation.

13. *(b)* Glycerol is trihydric alcohol. It is purified by its distillation under reduced pressure because it decomposes below its boiling point to form a foul smelling compound acrolein.



Acrolein

14. *(a)* Helium shows heating effect at room temperature as it possesses very low values of inversion temperature.

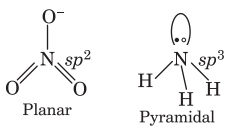
15. *(d)* Aluminium is extracted by high temperature electrolytic reduction of Al_2O_3 to which fluorspar and cryolite have been added. Al_2O_3 reacts with carbon at high temperatures to form Al_4C_3 which does not decompose.

16. *(b)* Due to electron withdrawing effect of carbonyl group of benzaldehyde, electron density of benzene ring decreases. As a result of which density on carbonyl group increases. Hence, carbonyl carbon of benzaldehyde is less reactive towards nucleophilic attack.

17. *(a)* The ligands having vacant π -type orbitals have a tendency to receive back donated π-electrons.
Thus, these are called π-acid ligands or π-acceptor ligands, e.g. CO and CN have lone pair as well as π or π^*-orbitals which take part in the formation of π-bond with central metal atom as observed in case of carbonyls.

18. *(d)* The O—O bond length is shorter in O_2F_2 than in H_2O_2 due to higher electronegativity of F-atom.
H_2O_2 is a covalent compound.

19. *(a)*



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20. *(c)* For first order reaction,
Rate $(r) = k[A]$
when concentration of A doubles rate becomes

$$r' = k_2[2A] = 2r$$

Hence, rate also doubles. But for a given reaction rate constant is independent of concentration of reactant.

21. *(a)* The order of reactivity of given alkene (when subjected to acid catalysed hydration) is III < II < I.

Correct Reason The relative rates of hydrogenation as the number of electron releasing group increases.

The reactivity of alkenes is however, also related to the following factors.
(i) Steric effect
(ii) Hyperconjugation
(iii) Heat of combustion

22. *(c)* **Correct Reason** Eclipsed and staggered conformations are interconvertable at room temperature. Since, the energy difference between these two conformations of ethane is not so large, so the eclipsed and staggered conformation interconvert rapidly. Thus, it is impossible to isolate these forms at room temperature.

23. *(a)* Rate of diffusion $\propto \sqrt{\frac{1}{\text{Molecular mass}}}$. Hence, lighter gas molecules move rapidly than heavier gas molecules.

24. *(c)* Wolframite is ferromagnetic and is attracted by the magnet.

25. *(d)* Mercury vapour are invisible as no metallic bonding is possible in vapour state. So, both Assertion and Reason are incorrect.

26. *(b)* **Correct explanation**: Complexes of the type MX_6 and MX_5L do not show geometrical isomerism because change of position of ligands gives the same arrangement.

27. *(b)* **Correct explanation** 2, 2 dimethylpropanal does not contain α-H and hence in presence of conc. alkali it undergoes Cannizzaro reaction.

28. *(b)*

29. *(a)* A solid has rigidity but liquids do not.
It is because in solids, the intermolecular forces are very strong and predominate over thermal energy but in liquids, these forces are no longer strong enough.

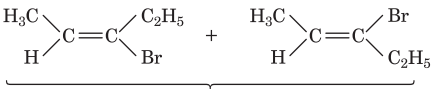
30. *(b)* Sucrose, which is dextrorotatory, on hydrolysis gives laevorotatory fructose (– 92.4°) and dextrorotatory glucose (+ 52.5°). Hence, the final product is laevorotatory.

Continued from Page 31

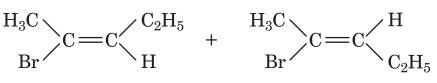
19. The number of structural and configurational isomers of a bromo compound, C_5H_9Br, formed by the addition of HBr to 2-pentyne respectively are
[JEE Main 2008]

(a) 1 and 2 *(b)* 2 and 4 *(c)* 4 and 2 *(d)* 2 and 1

(b) $CH_3—C\equiv C—CH_2CH_3 + HBr$



Geometrical isomers



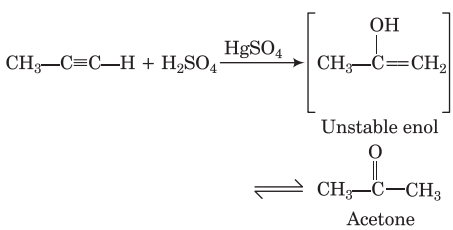
Geometrical isomers

Therefore, two structural and four configurational isomers are formed.

20. When propyne is treated with $aq \cdot H_2SO_4$ in the presence of $HgSO_4$, the major product is
[JEE Main 2006]

(a) propanal
(b) propylhydrogen sulphate
(c) acetone
(d) propanol

(c) **Key concept** *Alkynes undergo Markownikoff's addition of water in the presence of* $H_2SO_4/HgSO_4$



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AMPLIFIER

PERIODIC PROPERTIES

Innovative problems targetted to improve your conceptual learning.

1. *What is the difference between effective nuclear charge (Z_{eff}) and actual nuclear charge (Z)?*

Actual nuclear charge (Z) Actual nuclear charge or the nuclear charge is the total positive charge of all the protons present in the nucleus. It has same value as the atomic number.

Effective nuclear charge, (Z_{eff}) A single electron species is attracted by the actual nuclear charge. But in a many electron species, each electron is simultaneously attracted to the nucleus and repelled by the other electrons. Thus, we can treat each electron individually as though it was moving in the net electric field created by the nucleus and the electron density of the other electrons. We can view this net electric field as if it results from a single positive charge located at the nucleus, called the **effective nuclear charge** (Z_{eff}).

2. *Is only effective nuclear charge is responsible for increase in atomic radius on moving down a group?*

On moving down the group, nuclear charge and shielding effect both increases. But the increase in shielding effect is much higher than the increase in nuclear charge. Hence, the attraction between the nucleus and valence electron, decreases and atomic radius increases.

3. *The atomic radius decreases as we move from left to right in a period. But radius of noble gases is highest in their respective periods, why?*

Nobles gases are present in monoatomic form. Thus, radius of noble gases is only van der Waals' radius. Since, van der Waals' radius is always larger than the covalent radius, therefore the radius of noble gases is highest in their respective periods.

4. *Two sign conventions are used for electron affinity. Why?*

The electron affinity (EA) of an element is the energy change when an electron is added to a gaseous atom to form a unit negative charged ion. Thus, the atom which has higher tendency to accept electrons, will show higher negative value of electron affinity. On the other hand, the atom with least tendency to accept electron will show positive value of electron affinity.

$$F(g) + e^- \longrightarrow F^-(g)\ \Delta E = EA = -328\ kJ\ mol^{-1}$$

[He] $2s^2\ 2p^5$ (Incomplete octet) Less stable → [He] $2s^2\ 2p^6$ (Complete octet) More stable

$$Ne(g) + e^- \longrightarrow Ne^-(g)\ EA > 0\ kJ\ mol^{-1}$$

[He] $2s^2\ 2p^6$ (Complete octet) More stable → [He] $2s^2, 2p^6, 3s^1$ (Incomplete octet) Less stable

5. *Does electronegativity has any unit?*

Yes, electronegativity has the unit of energy. To understand more, you can simply consider Mulliken scale. According to which,

$$\text{Electronegativity } (\chi) = \frac{\text{Ionisation enthalpy (IE)} + \text{electron gain enthalpy } (\Delta H_{eg})}{2}$$

As, ionisation enthalpy and ΔH_{eg} both have units of energy, so electronegativity must have unit of energy. It was very difficult to understand behaviour of atoms on the basis of these energy values. So, Pauling considered F (the most electronegative element) as the standard element and arbitrarily assigned an electronegativity of 4. Assuming electronegativity of hydrogen to be 2.1, he calculated electronegativities of other elements also.

6. *Are electronegativity and electron affinity, same properties regarding to atoms/molecules?*

Electronegativity and electron affinity are two different properties. Electronegativity is concerned with the combined atoms in a molecule while electron affinity is concerned with an isolated gaseous atom.

7. *Generally, electron gain enthalpy, decreases on moving down a group, but F has less negative electron gain enthalpy than Cl, why?*

The electron gain enthalpy of F is less negative than that of Cl because F has small size and greater interelectronic repulsion than Cl.

8. *Consider the following outer electronic configuration of two elements X and Y, respectively.*

$X = 5d^1, 6s^2$; $Y = 4f^1, 5d^1, 6s^2$

Predict to which block(s) the above elements belong?

Block is shown by that orbital which receives the last electron. If any of the *d*-orbital is incomplete, i.e. the last electron enters in it, then the element belongs to *d*-block. Similarly, if *d* and *f* both the orbitals are partially filled, the element generally belongs to *f*-block. However, if *f*- and *d*-orbitals are completely filled and last electron enters in *s*- or *p*-orbital, then the block of the element is *s* or *p*.

Thus, $5d^1, 6s^2$, (*X*) belongs to *d*-block and $4f^1, 5d^1, 6s^2$ (*Y*) belongs to *f*-block.

9. *Why the second electron affinity of halogens is zero?*

The outer shell electronic configurations of halogens is ns^2, np^5. A halogen can accept only one electron in order to get stable closed shell configuration of *np*-shell. Now, further addition of another electron is not possible. Thus, second electron affinity of halogens is zero.

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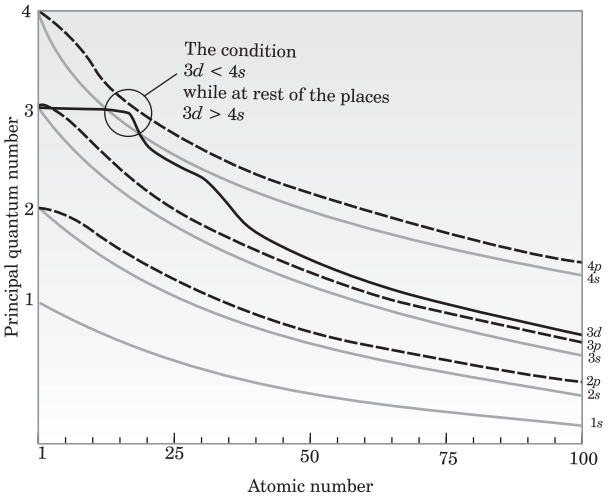
10. *On the basis of symmetry, $(n-1)d^4ns^2$ and $(n-1)d^9ns^2$ configurations are less stable. These configurations immediately change over to the corresponding more stable $(n-1)d^5ns^1$ and $(n-1)d^{10}ns^1$ configurations. We all know, that $(n-1)$ d-orbitals are of higher energy (less stable) as compared to ns-orbitals (more stable), according to Aufbau principle. Then why electron jumps from more stable ns to less stable $(n-1)$d-orbital?*

› It can be explained on the basis of energy diagram which is given below. (Considering 4*s* and 3*d* orbitals.)



It is clearly visible in above diagram that in general the energy of 3*d*-orbital > 4*s*-orbital except around atomic number 24 and 29 where it follows the condition of Aufbau principle i.e., energy 3*d* < 4*s*. Thus electrons can easily transit from 4*s* of more energy to 3*d* orbital of lesser energy and more stability.

11. *All the transition elements are d-block elements, but all d-block elements are not transition elements. Explain.*

› The elements in which the last electron enters into any of the five *d*-orbitals of their respective penultimate shells are called d-**block elements**.

As, the last electron enters in *s*-orbital in case of Zn, Cd, Hg and Cn. So these elements cannot be regarded as *d*-block elements. Because of this, these elements should be regarded as s-**block elements**.

But properties of these elements resemble more with the *d*-block elements than *s*-block elements. Thus, on the basis of properties, all transition elements are *d*-block elements, but on the basis of electronic configurations all *d*-block elements are not transition elements.

12. *The compound M—O—H can act either as an acid or a base depending upon the ionisation enthalpy of the element. Justify by taking elements (M) of the third period of the periodic table.*

› When the ionisation enthalpy of the element *M* is low, it has a strong tendency to loose electron, i.e. to get oxidised into M^+.

As a result *M*—O bond of *M*—OH compound will break to produce M^+ and $\bar{O}H$ ions and hence, the compound *M*—OH acts as a base.

$$MOH \longrightarrow M^+ + \bar{O}H$$

Now, in general, ionisation enthalpy increases from left to right in a period or you can say basic character decreases in the same order. Thus, NaOH is the strongest base, followed by $Mg(OH)_2$ while $Al(OH)_3$ is the weakest base.

On the other hand, if the ionisation enthalpy of the element *M* is high, it has little tendency to get converted into M^+ ion.

Instead, the compound, *M*—OH ionises to give H^+ ions and hence the compound *M*—OH behave as an acid. Thus, $Al(OH)_3$ is strongest acid among NaOH, $Mg(OH)_2$ and $Al(OH)_3$.

13. *All halogens are non-metals though iodine exhibits a metallic cluster, why?*

› As the ionisation energy decreases down the group so *I* has the lowest value of ionisation energy among halogens. Thus, iodine shows some electropositive or metallic character and forms metallic cluster.

14. *Why metallic character increases while non-metallic character decreases in a group from top to bottom.*

› On going from top to bottom in a group, atomic size increases with increase in atomic number. As a result, tendency of elements to give up electrons also increases, i.e. metallic character increases while non-metallic character decreases.

15. *First ionisation energy of nitrogen is higher than that of oxygen, why?*

› Electronic configurations of outermost shell of nitrogen and oxygen are ns^2np^3 and ns^2np^4, respectively. 3*p*-subshell is half-filled in case of nitrogen which is relatively stable as compare to the oxygen ($3p^4$). Oxygen will give its outermost electron from 3*p*-orbital more easily in order to come in more stable half-filled electronic configuration. Thus, more energy will be required in case of nitrogen for removal of electron from 3*p*-orbital.

16. *Consider the following ionisation energy data (in kJ mol^{-1}) for an element X.*

$IE_1 = 400$ $IE_2 = 800$
$IE_3 = 1500$ $IE_4 = 19000$
$IE_5 = 20{,}200$ $IE_6 = 22{,}500$

Determine the outermost electronic configuration of element on the basis of above data.

› As you can see, there is a sudden high jump in energy after third ionisation energy. Thus, the element must acquire half-filled or fully-filled electronic configuration after the removal of three electrons. Thus, the outermost electronic configuration of element must be ns^2np^1.

To be Continued at Page 56

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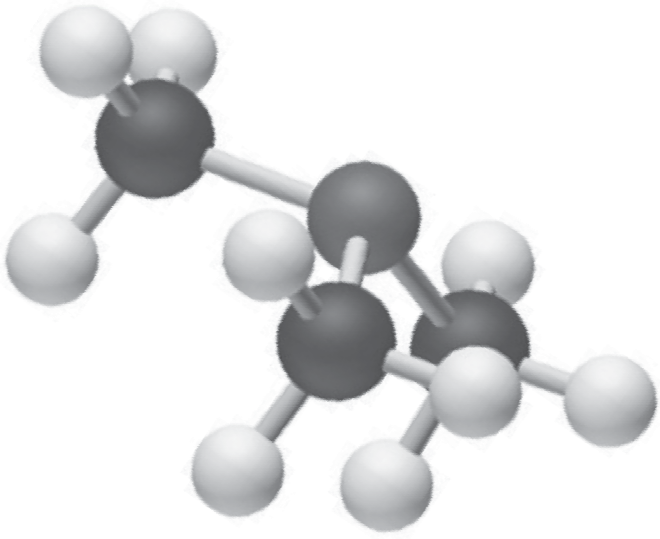

NOMENCLATURE OF ORGANIC COMPOUNDS

PART 6

This section is targetted to provide an insight of IUPAC nomenclature of organic and inorganic compounds through questions as every year atleast 1-2 questions are asked on IUPAC nomenclature in all the competitive exams and boards.

Naming of Organic Compounds with One Type of Functional Group

- We have learned naming of substituted hydrocarbons in October 2016 issue.
- Now, we are going to learn naming of organic compounds with different functional groups. In this issue, we shall consider only one functional group containing organic compounds.
- The 2°-suffixes are used to indicate functional group in the IUPAC names of organic compounds.

Prefix and Suffix of Various Functional Groups
(As given under the 1993 recommendations of IUPAC)

S.No.	Class	Formula	Prefix	Suffix
1.	Acid halides	$-\overset{\overset{O}{\|\|}}{C}-X$, $-(\overset{\overset{O}{\|\|}}{C})-X$ where, X = halogen	Halocarbonyl- —	–carbonyl halide –oyl halide
2.	Alcohols, phenols	—OH	Hydroxy–	–ol
3.	Aldehydes	—CHO —(C)HO	Formyl–	–carbaldehyde –al
4.	Amides	$-CONH_2$ —(C)O—NH_2	Carbamoyl–	–carboxyamide –amide
5.	Amines	$-NH_2$	Amino–	–amine
6.	Carboxylic acids	—COOH —(C)OOH	Carboxy– —	–carboxylic acid –oic acid
7.	Ethers	—O*R*	(*R**)-oxy	–
8.	Esters derivatives (of carboxylic acids)	—COO*R* —(C)OO*R*	(*R**)-oxy-carbonyl (*R**)-oxycarbonyl	(*R**)... carboxylate (*R**)...oate
9.	Imines	=NH =N*R*	Imino- (*R**)-imino	–imine
10.	Ketones	>(C)=O	Oxo	–one
11.	Nitriles	—C≡N —(C)≡N	Cyano- —	–carbonitrile –nitrile
12.	Sulphonic acid	$-SO_2-OH$	Sulpho-	–sulphonic acid
13.	Thiols	—SH	Sulphanyl-	–thiol

*In the above table *R* designates any alkyl group and C-atom in ( ) means when it is included in the main chain while C-atom without ( ) means when it is not included in the main chain.

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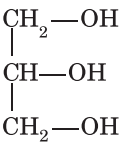
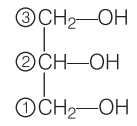
Example 1

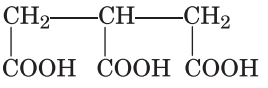


Sol. **Rule** *The alcohols containing two or three —OH groups are named as alkanediols and alkanetriols, respectively. The '–e' of the corresponding alkane name is retained in such cases.*

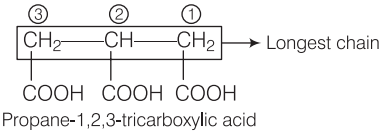


Propane-1,2,3-triol

Example 2

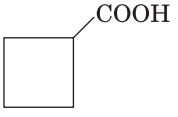


Sol. **Rule** *If an unbranched chain is directly linked to more than two carboxylic groups, these carboxylic groups are named from the parent hydrocarbon by substitutive use of a suffix like carboxylic acid.*

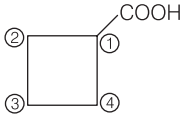


Propane-1,2,3-tricarboxylic acid

Example 3

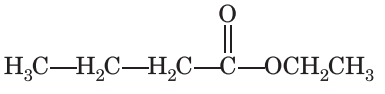


Sol. **Rule** *Due to the presence of cyclic hydrocarbon, difficulty lies in inclusion of C-atom of functional group within the longest possible chain. Hence, the suffix used is carboxylic acid and not the oic acid.*



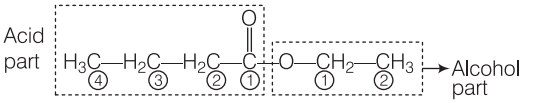
Cyclobutane carboxylic acid

Example 4



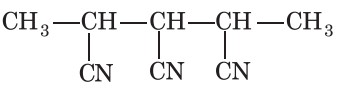
Sol. **Rule**

- *Alkyl group present after key oxygen atom of alcohol part, is written as alkyl.*
- *The rest of all the carbon atoms before key oxygen, i.e. of acid part are written as alkanoate.*

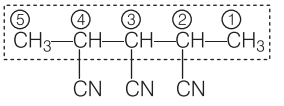


Ethyl butanoate

Example 5

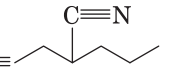


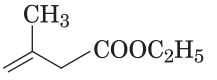
Sol. **Rule** *The rule is same as mentioned in the example 2. Here, the suffix used is carbonitrile.*

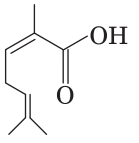


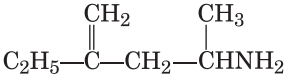
Pentane-2,3,4-tricarbonitrile

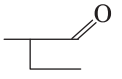
Practice Problems

(i) 

(ii) 

(iii) 

(iv) 

(v) 

Practice Problems Answers

(October 2016 Issue)

(i) 2-chloro-4, 4-dimethylhexane
(ii) 2-chloro-3-ethylpenta-1, 4-diene
(iii) 3-bromo-2-chloro-5-methyloctane
(iv) 1-chloro-7-(1-chloromethyl)-1, 8-dibromooctane
(v) 3-(1,1-dichloromethyl)-4-(1,1,1-trichloromethyl) hexane
(vi) 4-(2-bromo-1-chloroethyl)-5-(1,1-dichloroethyl) octane

AMAZING REALITIES

Ozone, is created in nature by lightning. When it strikes, the lightning cracks oxygen molecules in the atmosphere into radicals which reform into ozone. The smell of ozone is very sharp, often described as similar to that of chlorine. This is why you get that "clean" smell sensation after a thunderstorm.

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The area of chemistry that is concerned with the speeds or rates of reactions is called **chemical kinetics**.

CONCE your Rev CHEMICAL

❶ RATE OF A CHEMICAL REACTION

- It is defined as the change in concentration of a reactant or product per unit time.
  For a general reaction,
  $$R \longrightarrow P$$
  $$\text{Rate of reaction, } (r) = -\frac{\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$$
- Negative sign indicates decrease in concentration of reactant with time.
- Positive sign indicates increase in concentration of product with time.

Ⓐ UNIT OF RATE OF A CHEMICAL REACTION

- For reactions in liquid medium, unit of r is mol $L^{-1}s^{-1}$.
- For reactions in gaseous medium, unit of r is atm^{-1}.

Ⓑ TYPES OF RATE OF REACTION

(a) **Average rate** Change in molar concentration of either reactant(s) or product(s) in unit time.

(b) **Instantaneous rate** Rate of a reaction at any instant of time. It is equivalent to small change in concentration (dx) in small interval of time (dt).

Ⓒ FORMULAE RELATED TO THE RATE OF A REACTION

- For a general reaction,
  $$aA + bB \longrightarrow cC + dD$$
  $$\text{Rate } (r) = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$
- **Average rate** $(r_{av}) = -\frac{\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$
- **Instantaneous rate** (r_{ins})
  $$= \lim_{\Delta t \to 0} -\frac{\Delta[R]}{\Delta t} = -\frac{d[R]}{dt};$$
  $[R]$ = concentration of reactant
  $d[R]$ = Change in the concentration of reactant in infinitesimally small interval of time dt.

Ⓓ FACTORS AFFECTING THE RATE OF A REACTION

- **Concentration of reactants** It is directly proportional to the rate of reaction.
- **Nature of the reactants** Physical state of reactants
  $$\underset{\text{Decreasing rate of reaction}}{\text{Gaseous state} > \text{Liquid state} > \text{Solid state}}$$
- **Physical size of the reactants** In solids, rate increases with decrease in particle size because in powdered state, particles possess larger surface area.
- **Temperature** Generally for most of the reactions rate becomes double for every 10°C rise in temperature.
- **Presence of catalyst** Positive catalyst increases, however negative catalyst decreases the rate of a reaction.

❷ RATE EXPRESSION AND RATE CONSTANT

For a general reaction,
$$aA + bB \longrightarrow cC + dD$$
$$\text{Rate} = k[A]^a\,[B]^b \qquad \ldots(i)$$

- Eq. (i) is known as **rate expression**.
- K is known as rate constant.
- The value of rate constant is independent of concentration of reactants and varies only with temperature. Larger the value of K, faster is the reaction.

❸ MOLECULARITY OF A REACTION

It is defined as the number of species of reactants actually taking part in a single rate determining step of a chemical reaction.

Reactions

Unimolecular	Bimolecular	Trimolecular
Involves participation of only one molecule	Involves participation of two molecules	Involves participation of three molecules
$O_2F_2 \rightleftharpoons O_2 + F_2$	$2HI \longrightarrow H_2 + I_2$	$2NO + Cl_2 \longrightarrow 2NOCl$

Note *In case of complex reactions slowest step (which is the rate determining step) of the reaction decides molecularity of the reaction.*
Molecularity of a reaction is always a whole number (except zero) and never a fraction.
The value of molecularity does not exceed more than three as probability of colloiding more than three molecules in a single step, is almost negligible.

❹ ORDER OF A REACTION

- It is defined as the sum of the exponents (powers) of the molar concentrations of the reactants in the experimentally determined rate expression.

Ⓐ METHODS OF DETERMINATION OF ORDER OF REACTION

ⓐ INITIAL RATE METHOD

In this method, the order of a reaction is determined by varying the concentration of one of the reactants, while keeping others constant, e.g. $aA + bB \longrightarrow$ Product
$$r = k[A]^a\,[B]^b$$
If $[B]$ remain constant, $r = k'[A]^a$, where $k' = k[B]^b$
The value of a can be determined by inspecting the rate at different concentrations of A.

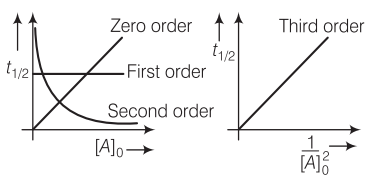
ⓑ INTEGRATION METHOD

Also called hit and trial method. In this method, different values of $[A]_0$, $[A]_t$ and t are determined experimentally and substituted in rate equation of various order.

ⓒ HALF-LIFE METHOD

It is also called fractional change method. For a reaction of nth order, $t_{1/2} \propto 1/([A]_0)^{n-1}$ or $\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{[A_0]_2}{[A_0]_1}\right)^{n-1}$

Taking log on both sides and on solving we get,
$$n = 1 + \frac{\log[(t_{1/2})_1/(t_{1/2})_2]}{\log([A_0]_2/[A_0]_1)}$$

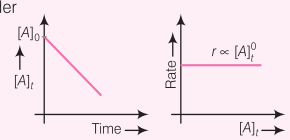
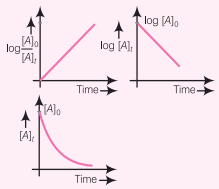
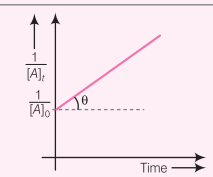
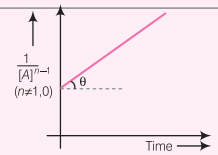


$t_{av} = \frac{1}{k}$ and for first order reaction, $t_{av} = 1.44\,t_{1/2}$

❺ INTEGRATED RATE LAWS

These laws are the approach to determine rate law and rate co

DIFFERENT INTEGRATED LAWS F

Order of reaction	Graphs	Rate expressio
Zero order		$[A]_t = [A]_0 - k$
First order reaction		$[A]_t = [A]_0 e^{-kt}$, $K = \frac{2.303}{t}\log$ $K = \frac{2.303}{t}\log$ gaseous reacti time required to 1/nth of a react $t = \frac{2.303}{K}\log$
Second order reaction		(i) $Kt = \left[\frac{1}{[A]_t} -$ both reactants initial concentra (ii) $k = \frac{2.303}{t(a-b)}$ $(a > b)$ when bo have different c
nth order reaction		$Kt = \frac{1}{n-1}\left[\frac{1}{}\right.$ $n \neq 1$ (First orde is order of the r

ⓓ GRAPHICAL METHOD

In this method, the order of reaction can be known by plotting a graph between $\log(dx/dt)$ *versus* $\log[A]_t$ or $\log(a - x)$.

Note There are some reactions which also shows fractions and negative order.
$r = k\,[CO]^2\,[Cl_2]^{1/2}$
e.g. $CO + Cl_2 \longrightarrow COCl_2$; order = 2.5
$2O_2 \longrightarrow 3O_2$; $r = k\,[O_3]^2\,[O_2]^{-1}$,
Order with respect to O_2 is -1

❻ PSEUDO FIRST ORDER REACTIONS

Under certain conditions, some second order reactions are approximated to first order kinetics. These type of reactions are called pseudo first order reaction.

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PT MAP
ision Tool
KINETICS

nstant by using calculus.

OR DIFFERENT ORDERS OF REACTION

on	Half-life ($t_{1/2}$)	Unit of rate constant	Examples
	$\frac{[A]_0}{2k}$	$mol\,L^{-1}s^{-1}$	Photochemical reaction, enzyme catalysed reactions etc.
$\frac{[A]_0}{[A]_t}$ $\frac{p_0}{p_0 - p_x}$ (for on) o complete tion, $\frac{n}{n-1}$	$\frac{0.693}{K}$	s^{-1}	Radioactive disintegration, regeneration of bacteria etc.
$\frac{1}{[A]_0}$ when have same ation $\log\frac{b(a-x)}{a(b-x)}$ oth reactants oncentration	$\frac{1}{K[A]_0}$	$mol^{-1}\,L\,s^{-1}$	Saponification reaction.
$\frac{1}{[A]_0^{n-1}}$ er) when 'n' reaction	$\frac{2^{n-1}-1}{K(n-1)[A]_0^{n-1}}$ $(n \neq 1)$	$(mol\,L^{-1})^{1-n}s^{-1}$	**Note** Here $[A]_0$ and $[A]_t$ are, respectively the initial concentration and concentration after time t of the reactant.

e.g. During the hydrolysis of ethyl acetate, when excess of water is taken, concentration of water does not get altered much during the course of reaction. So, the rate depends mainly on the concentration of ethylacetate only. Thus, the order of the reaction is taken to be 1 by considering concentration of ethyl acetate only.

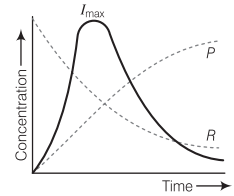
❼ REACTION INVOLVING TWO FIRST ORDER CONSECUTIVE STEPS

In reactions which involve two consecutive first order steps, take place as follows:

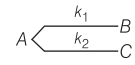
$$R \xrightarrow{K_1} I \quad \text{Ist step;} \quad I \xrightarrow{K_2} P \quad \text{IInd step}$$

I = Intermediate

The concentration profiles of reactant, intermediate and product are shown in the graph.



❽ PARALLEL FIRST ORDER REACTION

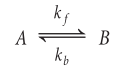


Rate constant $k = k_1 + k_2$

$$\frac{d[B]}{dt} = k_1[A];\ \frac{d[C]}{dt} = k_2[A];\ \frac{d[A]}{dt} = k[A]$$

At any instant, $\frac{[B]}{[C]} = \frac{k_1}{k_2}$

❾ REVERSIBLE REACTION
(First order opposed by first order)



Rate of reaction

= Rate of forward reaction – Rate of backward reaction

$$(k_f + k_b)t = \ln\left[\frac{x_{eq}}{x_{eq} - x}\right];\ \text{where } x_{eq} = \frac{k_f[A]_0}{[k_f + k_b]}$$

x and x_{eq} are concentrations of product formed or concentrations or reactant decomposed, at time 't' and at equilibrium respectively.

❿ DEPENDENCE OF TEMPERATURE ON RATE OF REACTION

The dependence of temperature on rate of a reaction is summarised by Arrhenius.

Ⓐ ARRHENIUS EQUATION

$$k = Ae^{-E_a/RT}$$

where, k = Rate constant,
R = Gas constant, E_a = Activation energy,
A = Pre-exponential factor, T = Temperature

Ⓑ ACTIVATION EQUATION

The minimum amount of energy required by the reactant species in order to take part in a chemical reaction, thereby undergoing effective collisions for a reaction to take place is called activation energy (E_a).

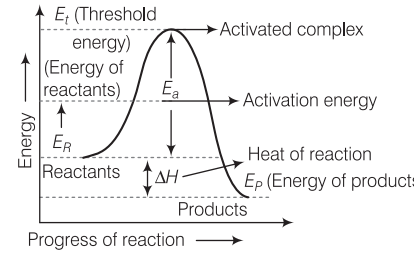
- Activation energy is always positive, whether the reaction is exothermic or endothermic.
- A positive catalyst decreases E_a value and increases rate of reaction
- A negative catalyst increases E_a value and decreases rate of reaction.
- If k_1 and k_2 are the rate constants at temperatures T_1 and T_2 respectively, then ($T_2 > T_1$).

$$\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right](T_2 > T_1)$$

Note Catalyst neither alter the Gibbs free change (ΔG) nor enthalpy change (ΔH) of the reaction. It proceeds *via* alternate path by altering the potential energy barrier.

⓫ ACTIVATED COMPLEX THEORY

According to Arrhenius, during the course of a reaction, first reactant molecules form an unstable intermediate (activated complex). The life-time of this intermediate is very short, it breaks up to form products.

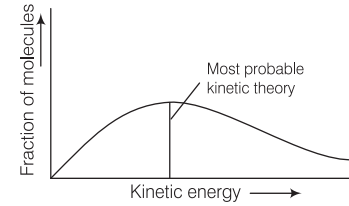


Reaction profile diagram

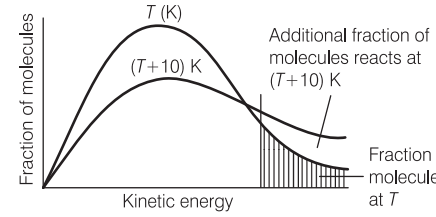
⓬ COLLISION THEORY OF CHEMICAL REACTIONS

Ⓐ MOST PROBABLE KINETIC ENERGY

- According to Maxwell and Boltzmann statistics, the most probable kinetic energy is the energy possessed by large fraction of molecules.



- Often rate of a reaction increases by a factor of 2 by increasing 10 K in temperature.



Ⓑ POSTULATES OF COLLISION THEORY FOR BIMOLECULAR GASEOUS REACTIONS

- The reaction between the molecules, occurs only when they collide with each other in proper orientations.
- Only those collisions lead to product formation in which molecules acquire greater energy than the activation energy.
- For an effective collision, the colliding molecules must possess threshold energy. This threshold energy is acquired by the molecules as a result of interchanges of energies.
- An activation energy is supplied to the molecules for attaining this threshold energy. During collisions, this energy is acquired by the molecules as a result of interchange of energies. The rate (r) of a reaction in terms of collision frequency is given as, $r = Z_{AB}\,e^{-E_a/RT}$
  where, Z_{AB} refers to the collision frequency of reactants A and B, $e^{-E_a/RT}$ represents the fraction of molecules with energy either equal to or greater than E_a.
- For an effective collision, probability or steric factor has to be introduced in the above equation for proper orientation of colloiding molecules. Rate (r) = $pZ_{AB}\,e^{-E_a/RT}$

⓭ KINETICS OF ENZYME ACTION

- An enzyme is normally a protein molecule, that catalyses a wide range of reactions in our body. An enzyme is specific for a particular reaction.
- The enzyme interacts with the reactant (substrate) at a specific location present in enzyme called active site and forms enzyme-substrate complex, which is a non-covalent interaction. The substrate is converted into product at the active site, forming enzyme product complex.
- Finally the enzyme leaves the product and is bound to another substrate till the completion of reaction.

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Sanjay Sharma

AROMATICITY, GROUP DIRECTIVE INFLUENCE AND ELECTROPHILIC SUBSTITUTION

Coverage of Special Topics for JEE Advanced

Aromaticity

- The term aromaticity has come from the Latin word *aroma* which means fragrance (pleasant odour). In simple words, the compounds with characteristic fragrances are known as **aromatic compounds**. The group of aromatic hydrocarbons are known as **arenes**.
- Technically, aromaticity is associated with special stability of certain completely conjugated cyclic compounds. A major contribution to this stability comes from the delocalisation of π-electrons in these compounds. Conjugation also imparts some special properties that are characteristics of them only.
- Aromaticity is usually described by molecular orbital (MO) terminology. Regarding this the most appreciated work has done by Huckel.

Huckel Rule for Aromaticity

- Huckel applied MO calculations on monocyclic systems, (C_nH_n) containing $n\pi$-electrons. This results in aromatic stability with the presence of $(4n + 2)\pi$ electrons in a closed shell. Here, n is an integer.
- According to Huckel, a compound to be aromatic should follow the conditions given below.

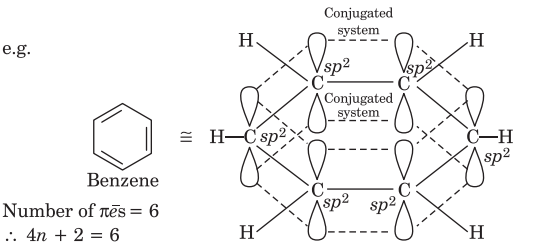
I. It must be cyclic and planar.

II. It must contain a conjugated system (a system of connected p-orbitals with delocalised electrons. In most of the cases this conjugated system can be visible with alternate presence of any two or more of the following

(a) π-bond (b) lone-pair
(c) negative or positive charge
(d) odd electron of free radical

III. It must contain $4n + 2$, number of π electrons, i.e. after solving $(4n + 2) = \pi$ electrons the value of n, must come out to be a positive integer or zero.

e.g.

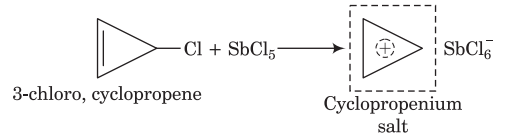


- The above compound is cyclic, planar (as each carbon is sp^2-hybridised, so all carbon and hydrogen atom will lie in a plane) and conjugated. Again, n value is 1 for this compound which is an integer.
- Since, it follows Huckel's rule, therefore it is an aromatic compound.

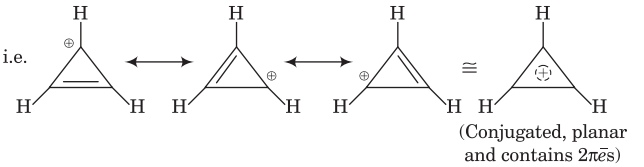
Aromaticity in Non-benzenoid Compounds

There are many compounds (except Benzene) which acquire aromaticity by losing or gaining electrons. They do so in order to gain lower energy state or stable state. We shall discuss about these compounds one by one as follow

(i) **Cyclopropene or Derivatives of Cyclopropene**



Delocalisation in cyclopropenium ion



There are 2π electrons taking part in conjugation. According to Huckel's rule, $4n + 2 = 2$, or $n = 0$. Thus, species is aromatic in nature.

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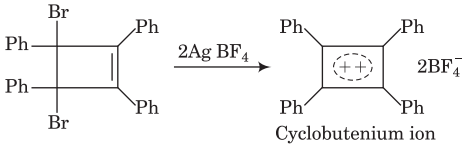
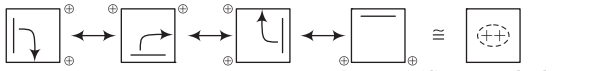
(ii) **Cyclobutene or Derivatives of Cyclobutene**



Delocalisation in cyclobutenium ion

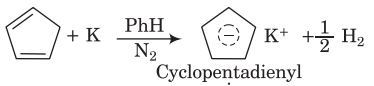


There are 2π electrons taking part in conjugation.

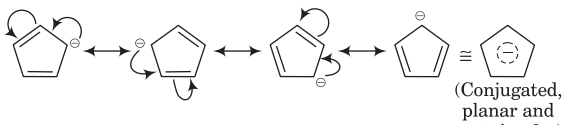
According to Huckel's rule, $4n + 2 = 2 \Rightarrow n = 0$

Thus, species is aromatic in nature.

(iii) **Cyclopentadiene or Derivatives of Cyclopentadiene**



Delocalisation in cyclopentadienyl anion



There are 6 electrons (4π electrons + 2 non-bonding electrons) taking part in conjugation.

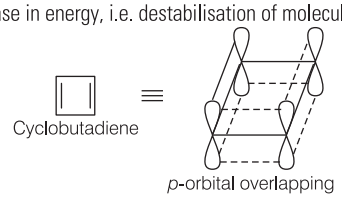
According to Huckel's rule,

$4n + 2 = 6 \Rightarrow n = 1$ (integer)

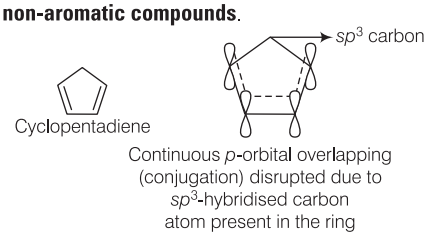
Thus, species is aromatic in nature.

Anti-aromatic and Non-aromatic Compounds

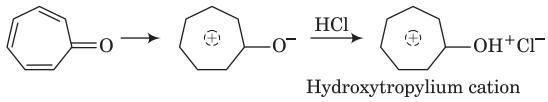
- The compounds that follow all the criteria of aromaticity but contains $4n\ \pi$ electrons instead of $(4n + 2)\pi$ electrons are called anti-aromatic compounds. These are called by this name because delocalisation of $4n\ \pi$ electrons in them results to increase in energy, i.e. destabilisation of molecule.



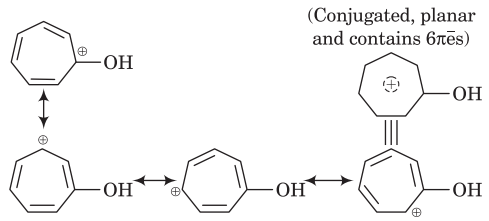
- The cyclic compounds in which conjugation is disrupted sufficiently are known as **non-aromatic compounds**.



(iv) **Cycloheptatriene, Tropone or Derivatives of Tropone**



Delocalisation in hydroxy tropylium cation.



There are 6π electrons taking part in conjugation.

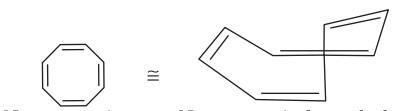
According to Huckel's rule,

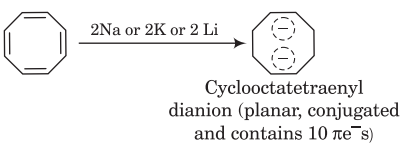
$4n + 2 = 6$

$\Rightarrow \quad n = 1$ (integer)

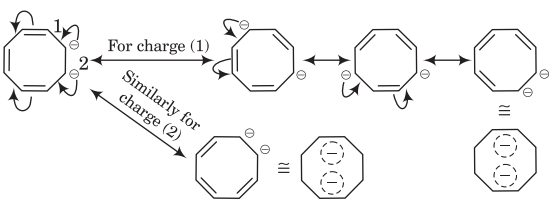
Thus, species is aromatic in nature.

(v) **Cyclooctatetraene or Derivatives of Cyclooctatetraene**





Delocalisation in cyclooctatetraenyl dianion



There are 10πe⁻s taking part in conjugation.

According to Huckel's rule

$4n + 2 = 10 \Rightarrow n = 2$ (integer)

Thus, species is aromatic in nature.

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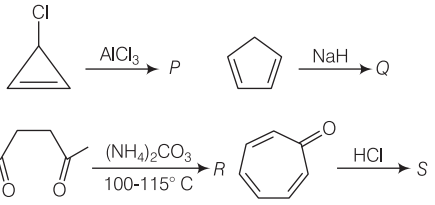
METICULOUS ANALYSIS

Example 1 Among *P*, *Q*, *R* and *S*, the aromatic compounds(s) is/are [JEE Advanced 2013]



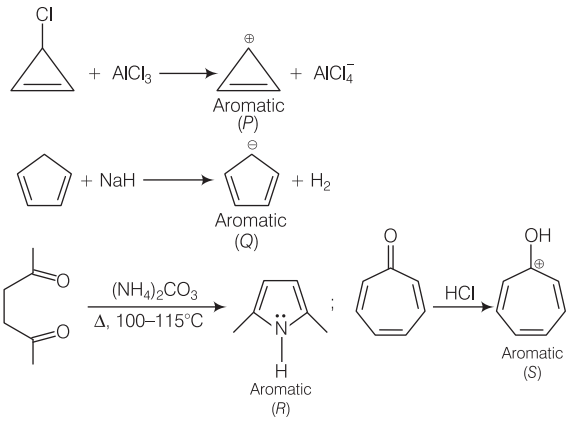
(a) *P* (b) *Q* (c) *R* (d) *S*

Sol. ***(a, b, c, d)*** An species is said to have aromatic character if

(i) ring is planar

(ii) their is complete delocalisation of π-electrons

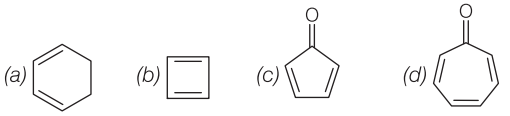
(iii) Huckel rule, i.e. $(4n + 2)\ \pi e^{-}s$ rule is followed where, *n* is an integer including zero.



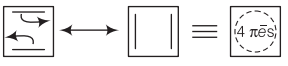
	n	(4*n* + 2)	π electrons
P	0	2	2
Q	1	6	6 (including lone pair)
R	1	6	6 (including lone pair on N)
S	1	6	6

In all cases there is complete delocalisation of π-electrons.

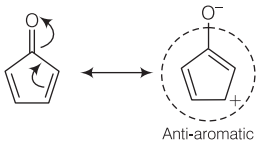
Example 2 Which of the following molecules, in pure form is/are unstable at room temperature? [JEE Advanced 2012]



Sol. ***(b, c)*** According to Huckel rule, the compounds which have $4n(n = 0, 1, 2, 3, \ldots)$ delocalised π-electrons in a close-loop are anti-aromatic and characteristically unstable. Compound in option *b* satisfy the criteria of anti-aromaticity as

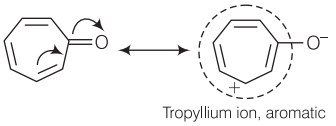


Compound in *option* 'c' is anti-aromatic in its resonance form



Compound in *option* 'a' has 4π-electrons which are also delocalised but do not constitute close loop, hence non-aromatic.

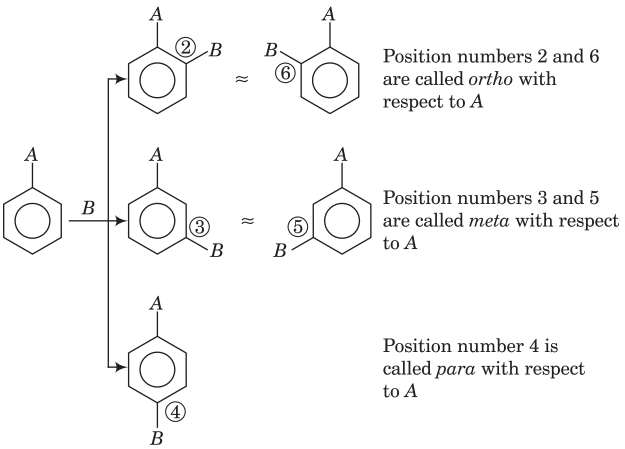
Compound in *option* 'd' is aromatic, characteristically stable.



Order of stability : Aromatic > Non-aromatic > Anti-aromatic

Directive Influence of Groups

- Since, all the six hydrogen atoms of benzene ring are equivalent, therefore when one group say *A* is introduced to the benzene ring, only one product is obtained.
- On the other hand, when a second substituent (say *B*) is introduced in a mono substituted benzene derivative. Following three isomeric disubstituted products are possible.



- However, experiments have shown that the group already present (*A* in the above case) on the benzene ring directs the new incoming group (*B* in the above case) either to *ortho* or *para* or *meta*-positions.

  This effect of group, already present on the ring is known as *directive influence of the group* or *orientation effect*.
- On the basis of above effect of the known groups in organic chemistry, these groups have been classified into two types.

  1. *Ortho* and *para* directing groups.
  2. *Meta* directing groups.

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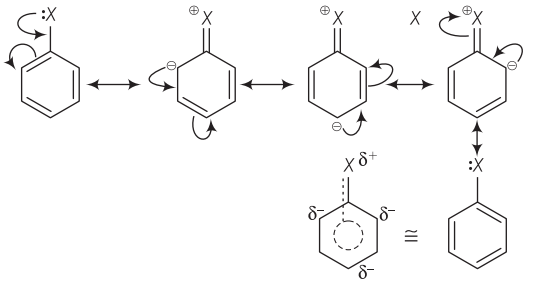
ortho and para directing groups (Ring activator)

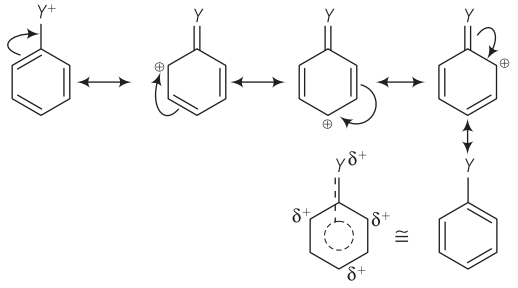
- These substituents increases electron density on the ring for further electrophilic substitution. That's why these are also called *ring activators*.
- In these groups, (except alkyl groups), the atom attached to the benzene ring contains atleast one lone pair of electrons.
- This unshared electron pair can undergo delocalisation by interaction with the π-electrons of the ring thereby causing an increased electron density at *o* and *p*-positions, respectively.



where, *X* is electron donating group.

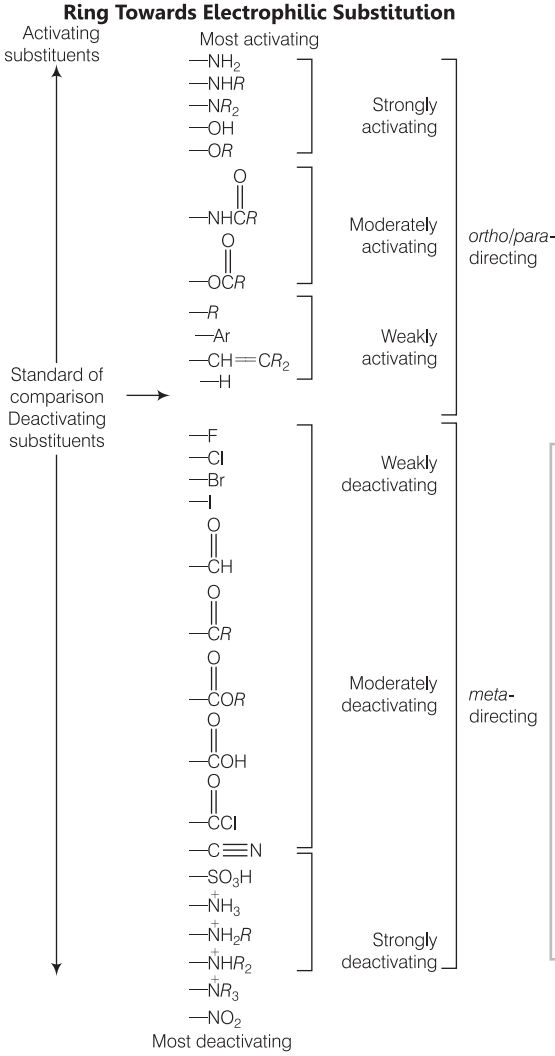
meta directing group (Ring deactivator)

- These substituents decreases electron density on the ring for further electrophilic substitution. That's why these are also called *ring deactivators*.
- In these groups, the atom attached to the benzene ring does not contain lone pair of electrons. It is either of a group of high electronegativity or a group with electron deficient nature. Thus, these groups pulls electrons from the benzene ring towards themselves. These groups withdraw electrons from *o* and *p*-positions leaving *m*-position some what electron rich. Hence, they give *m*-substituted product.



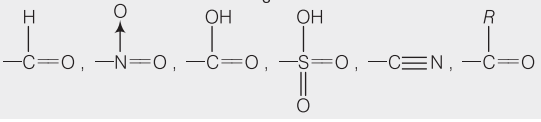
where, *Y* is electron withdrawing group.

Effect of Various Groups on the Reactivity of Benzene Ring Towards Electrophilic Substitution



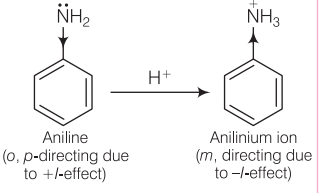
Teacher's NOTE

- The halogens are exception as these are *ortho* and *para* directing but ring deactivators. The *ortho* and *para* directive influence of halogens is attributed to their ability of donating lone pair while their ring deactivation influence is attributed to their high electronegativity (i.e. inductive effect)
- Of all the haloarenes, fluorobenzene deviates the benzene ring to the least extent towards further electrophilic substitution reactions. This is because the electron donating conjugation effect of *F* is only slightly outweighted by its electron withdrawing inductive effect.
- All the *meta*-directing groups possess a positive charge, e.g. $-\overset{+}{N}R_3$, or the key atom of the substituent is more electronegative atom than atoms attached to it

e.g. 

Effect on *o*, *p*-activating Nature of Aniline in Presence of Strong Acid

- $-NH_2$ group in aniline behaves as *o, p*-directing in aqueous solution but in presence of strong acids it mainly gives *m*-substituted product.
- The formation of *m*-substituted product can be explained by the fact that in presence of strong acid it forms anilinium ion. This ion exerts a strong-*I*-effect (or behaves as ring deactivator) due to the presence of positive charge on nitrogen atom (key atom). Thus, it mainly yield the *m*-substituted product.



- Further, in the anilinium ion, the lone pair of electrons on N-atom is involved in bond formation with hydrogen so $-\overset{+}{N}H_3$ group will not exert any conjugative effect.
- On the other hand, the formation of a small amount of *o* and *p*-substituted anilines in presence of strong acid is due to small residual concentration of free aniline (a very weak base).

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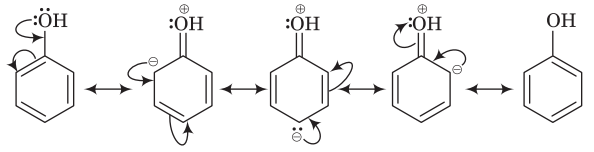
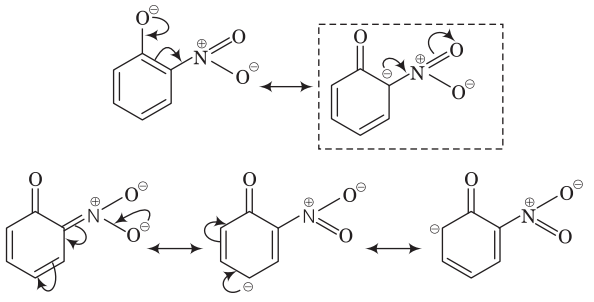
Effect of Ring Activating and Ring Deactivating Groups on Acidity of Benzoic Acid and Phenol

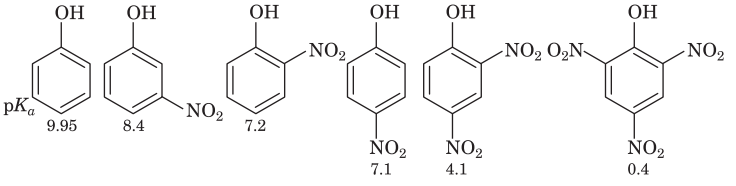
- Strength of an acid is indicated by K_a or pK_a value. Higher the value of K_a or lower the value of pK_a, stronger is the acid. e.g. The pK_a value of benzoic acid (4.20) is lower than that of phenol (9.95). Thus, benzoic acid is stronger acid than phenol.
- The acidic character of phenols is due to conjugation between lone pair of oxygen and benzene nucleus as shown below.



The positive charge on oxygen signifies the weakeing of O—H bond. In general, electron donating groups decrease acidity and electron withdrawing groups, increases the acidity of acids. e.g. presence of electron releasing group like —CH_3, —C_2H_5 over benzene nucleus destabilises the phenoxide ion. Thus, decreases the acidity of phenol. On the other hand presence of electron withdrawing groups like —NO_2, —CN etc., stabilises the phenoxide ion and thus increases the acidity of phenol.

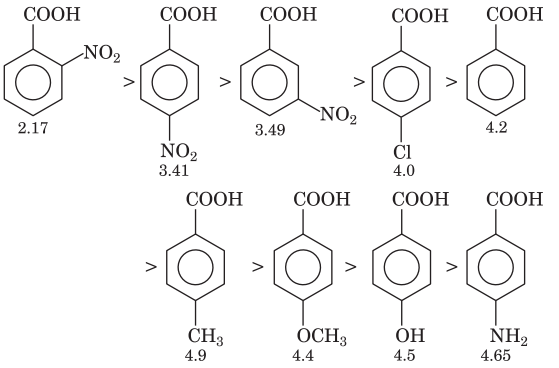


- If we compare pK_a values for different substituted phenols by electron withdrawing groups,



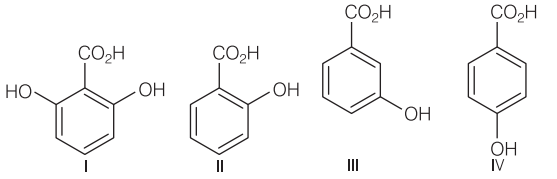
- The lesser acidic strength of *o*-substituted phenol over *p*-substituted one is very interesting. This is because of the symmetrical placement of substituent in *p*-isomer while rest other effects are exactly same in both.

Among substituted aromatic acids the strength decreases as follows



The highest acidic strength of *ortho* substituent can be explained *via ortho* effect. It is a special effect in which the substituent present at *ortho*-position disturbs the conjugation of first substituent (main group here —COOH) with the benzene nucleus. This in turn increases polarity of —OH bond and thus, release of H^+. In extreme cases *ortho* effect also involves H-bonding as asked in the problem given below.

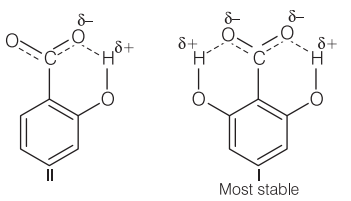
Example 3 The correct order of acidity for the following compounds is [JEE Advanced 2016]



(a) I > II > III > IV
(b) III > I > II > IV
(c) III > IV > II > I
(d) I > III > IV > II

Sol. ***(a)*** —OH *group displays both kinds of effect, an electron withdrawing acid strengthening inductive effect from the meta-position and an electron-releasing acid weakening resonance effect from the ortho and para-position (at this position, resonance effect overweighs the inductive effect). Thus, III > IV. However, o-hydroxybenzoic acid (II) is far stronger than the corresponding meta and para isomers as the carboxylate ion is stabilised by intramolecular H-bonding.*

2, 6-dihydroxybenzoic acid (I) forms carboxylate ion which is further stabilised by intramolecular H-bonding. Thus, correct order is I > II > III > IV.



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Example 4 Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds :

Benzene, toluene, chlorobenzene and nitrobenzene. [JEE Advanced 2006]

(a) I > II > III > IV (b) IV > III > II > I

(c) II > I > III > IV (d) II > III > I > IV

Sol. **(c)** **Thinking Process** *This problem can be solved by identifying activating and deactivating groups attached to the benzene ring.*

The reactivity in electrophilic substitution is greater in case of activating group than in case of deactivating group attached to the benzene ring.

Both chloro and nitro groups show deactivating behaviour in electrophilic aromatic substitution reaction. Also nitro group is stronger deactivating group. Methyl group acts as activating group in electrophilic aromatic substitution.

Hence, overall reactivity order is

nitrobenzene < chlorobenzene < benzene < toluene.

Electrophilic Substitution

In aromatic systems, situation is different from aliphatic systems due to high electron density on the aromatic ring. So, an electrophile (electron loving species) can attack at the ring more easily than nucleophile. Due to the presence of a very stable conjugated system benzene and other aromatic compounds have a stronger tendency to undergo substitution rather than addition to leave the aromatic ring intact. These reactions are extensively studied from the stand point of applications in organic synthesis.

Mechanisms of Aromatic Electrophilic Substitution (S_EAR) Reactions

These reactions proceed through the following three steps.

Step I **Release of Electrophile and Formation of Nu^- Catalyst Complex** (E^+) The generalised equation for this step is given below.

$E^+Nu^- + \text{Catalyst} \longrightarrow E^+ + Nu^-$ catalyst complex

The electrophiles for different electrophilic substitution reactions and formation of Nu^- catalyst complex are summarised in the following table.

The most common catalysts for electrophilic substitutions are **LEWIS ACIDS**.

Electrophilic substitution reaction	Reaction involved in the release of electrophile	Released electrophile	Nucleophilic catalyst complex
Halogenation	$X{-}X + AlX_3 \longrightarrow \overset{\delta+}{X}\cdots\overset{\delta-}{AlX_4}$	X^+	AlX_4^-
	$X{-}X + FeX_3 \longrightarrow \overset{\delta+}{X}\cdots\overset{\delta-}{FeX_4}$ $X{-}X + SnX_4 \longrightarrow \overset{\delta+}{X}\cdots\overset{\delta-}{SnX_5}$	X^+	FeX_4^-
	where, $X{-}X\,(X_2)$ Halogen molecule, i.e. substrates AlX_3, FeX_3 and SnX_4 are Lewis acids.	X^+	SnX_5^-
Nitration via nitrating mixture, i.e. $[H_2SO_4 + HNO_3]$	$H_2SO_4 \longrightarrow H^+ + HSO_4^-$ $H^+ + H{-}\ddot{O}{-}NO_2 \longrightarrow H{-}\overset{+}{O}(H){-}NO_2$ $H_2O + \overset{+}{N}O_2$	$\overset{+}{N}O_2$	
Sulphonation	$2H_2SO_4 \rightleftharpoons SO_3 + HSO_4^- + H_3O^+$	SO_3	
Friedal Craft alkylation, acylation or carboxylation	$Z{-}Cl + AlCl_3 \rightarrow \overset{\delta+}{Z}\cdots\overset{\delta-}{Cl}AlCl_3$ For alkylation, $Z = -CH_3$ For acylation $Z = -COCH_3$ For carboxylation $Z = -COOH$	$\overset{\delta+}{Z}$	$AlCl_4^-$
Formylation	$CO + HCl \rightleftharpoons H{-}\overset{O}{\overset{\|}{C}}{-}Cl$ $H{-}\overset{O}{\overset{\|}{C}}{-}Cl + AlCl_3 \rightleftharpoons$ $H{-}\overset{+}{\underset{O}{\overset{\|}{C}}} + AlCl_4^-$	$H{-}\overset{+}{\underset{O}{\overset{\|}{C}}}$	$AlCl_4^-$
Gattermann Synthesis	$HC{\equiv}N + HCl \rightleftharpoons H{-}\underset{Cl}{\overset{\|}{C}}{=}NH$ $H{-}\underset{Cl}{\overset{\|}{C}}{=}NH + AlCl_3 \rightleftharpoons$ $H{-}\overset{+}{C}{=}NH + AlCl_4^-$	$H{-}\overset{+}{\underset{NH}{\overset{\|}{C}}}$	$AlCl_4^-$

AMAZING REALITIES

A remarkable transition occurs in the properties of liquid helium at the temperature 2.17K (very close to absolute zero), called the "lambda point" for helium. Part of this liquid becomes a "superfluid"i.e., a zeroviscosity fluid which will move rapidly through any pore in the apparatus.

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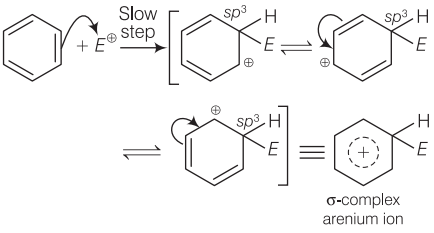
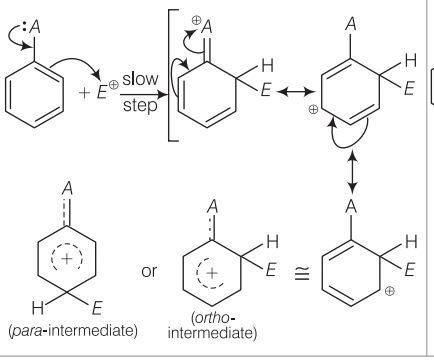
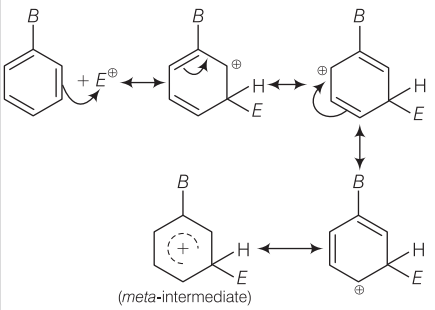
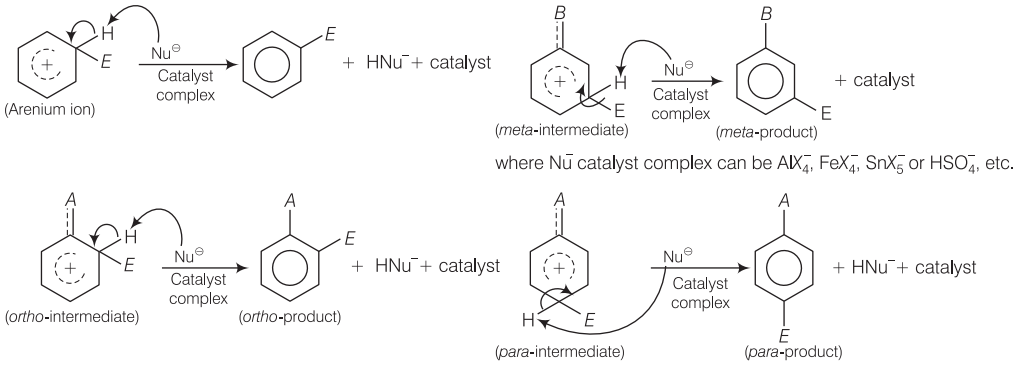
METICULOUS ANALYSIS

Step II **Formation of Carbocation Intermediate** (σ-complex) The electrophile attacks at benzene ring and forms σ-complex, in which one carbon becomes sp^3-hybridised. The mechanisms involved in the formation of σ-complex are given below :

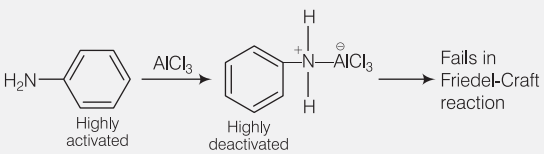
Benzene	Benzene ring with activating group (A)	Benzene ring with deactivating group (B)
		

Step III **The Nucleophilic Catalyst Complex of Step-I Abstracts Proton from σ-complex and releases catalyst .**



Teacher's **NOTE**

- Nitration can be conducted with nitric acid alone but the presence of a strong acid accelerates the reaction.
  The formation of $\overset{+}{N}O_2$ from nitric acid occurs by protonation and removal of water. H_2SO_4 is good at both of these jobs. First, it is a strong acid and second, it is a very good dehydrating agent.
- Nitronium salts such as nitronium tetrafluoroborate ($NO_2^+BF_3^-$), nitronium antimonypentafluoride ($NO_2^+SbF_5^-$) and nitronium hexafluorophosphate ($NO_2^+PF_6^-$) are also efficient nitrating agents under anhydrous conditions and in short reaction time.
- Friedal-Craft alkylation, in general, a very slow reaction. It is failed to occur at strongly deactivated ring like nitrobenzene. Similarly, in case of aniline, Lewis acid reacts with —NH_2 forming a salt which is highly deactivated



- In sulphonation, at high temperature, fuming H_2SO_4 (oleum) introduces second —SO_3H group at *m*-position (—SO_3H is *m*-directing and strong deactivating group).

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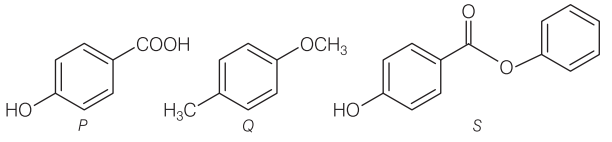
Aromatic Electrophilic Substitution in Case of Multi Substituted Benzenes

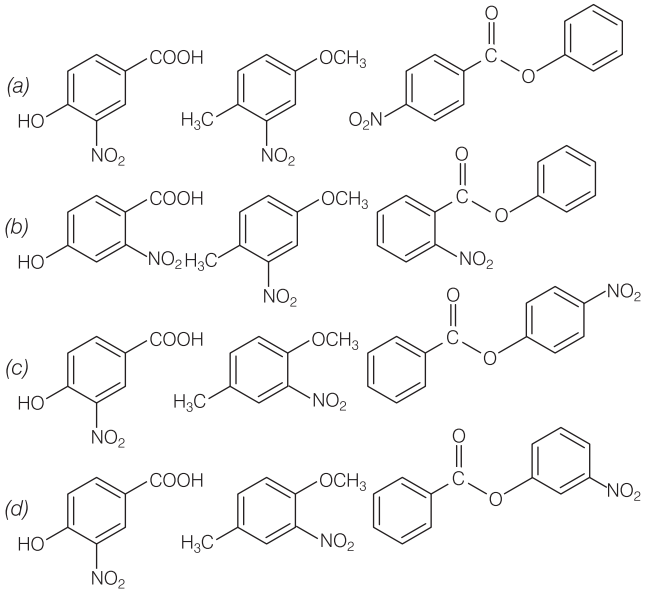
It becomes very confusing when there are two or more groups present on the benzene ring. To avoid this confusion, you may go through the following guidelines.

- If two groups (namely electron donating and electron withdrawing, respectively) present on the benzene ring then activating group have a larger influence than deactivating group at the position of the incoming electrophile. They do so because mesomeric effect (by activating groups) exerts a greater influence than inductive effect (by deactivating groups).
- If two groups are present at *meta*-position then the incoming E^+ avoids *para*-position due to steric effect.
- When both activating groups are present on the benzene ring, then electrophilic substitution takes place at *ortho*-position of more activating group.

Example 5 The compounds *P*, *Q* and *S* [IIT JEE 2010]

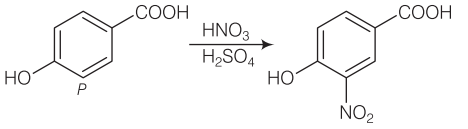


were separately subjected to nitration using HNO_3/H_2SO_4 mixture. The major product formed in each case respectively, is

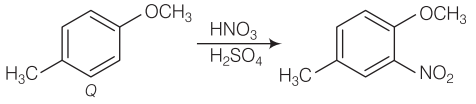


Sol. **(c)** For compound *P*, —OH is activating while —COOH is deactivating group in aromatic electrophilic substitution reaction.

Therefore, electrophile will attack at *ortho* position to the activating group. The reaction involved is given below.

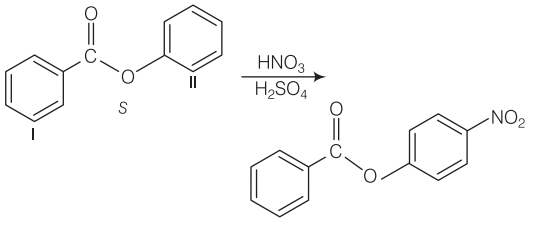


For compound *Q*, both —OCH_3 and —CH_3 are activating *ortho*/*para* directing groups, but —OCH_3 is stronger activator. Thus, electrophile will attack at *ortho* position of —OCH_3.

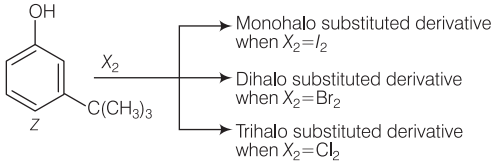


For compound *S*, ring II is activated (as oxygen is directly attached to the ring) while ring I is deactivated (as —CO group is directly attached to the ring).

Therefore, electrophile will attack at *para* position to the ring II, the less hindred position.



Example 6 The reactivity of compound *Z* with different halogens under appropriate conditions is given below



The observed pattern of electrophilic substitution can be explained by [JEE Advanced 2014]

(a) the steric effect on the halogen
(b) the steric effect of the *tert*-butyl group
(c) the electronic effect of the phenolic group
(d) the electronic effect of the *tert*-butyl group

Sol. **(a, b, c)**

- The steric effect of halogen, follows the order, $Cl_2 < Br_2 < I_2$
- The electronic effect of phenolic group directs the approaching electrophile towards *ortho* and *para*-positions.
- 3°-butyl group has large size so it causes steric effect around aromatic nucleus. On the basis of above factors the products of the given reactions are as follows

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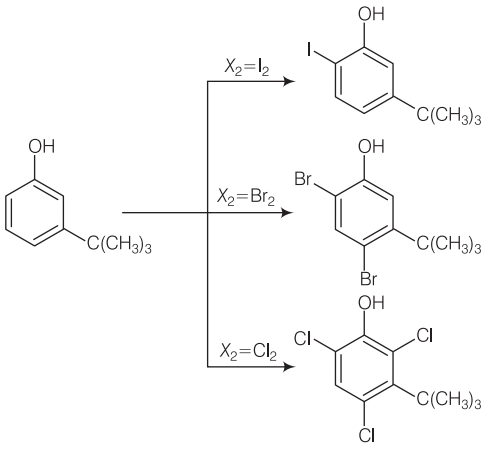


Hence, orientation in electrophilic substitution reaction is decided by

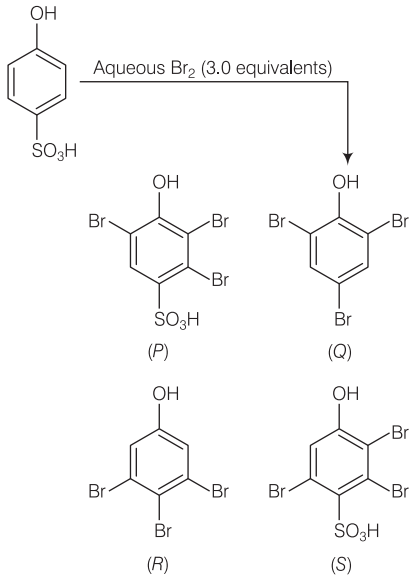
(a) The steric effect of the halogen

(b) The steric effect of the *tert*-butyl group

(c) The electromeric effect of the phenolic group

So, (a), (b) and (c) are correct choices.

Example 7 The major product(s) of the following reaction is/are **[JEE Advanced 2013]**



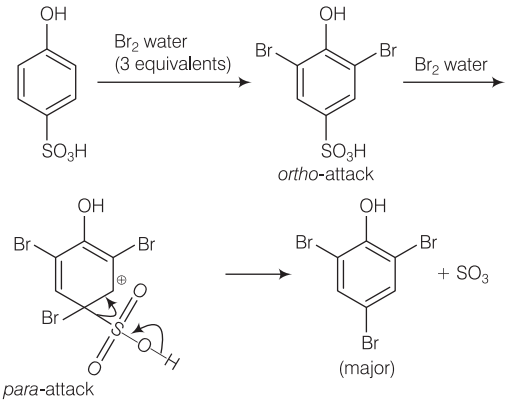
(a) *P*

(b) *Q*

(c) *R*

(d) *S*

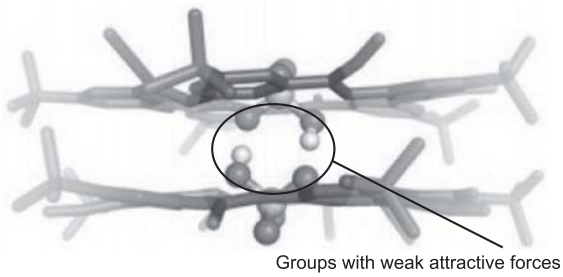
Sol. ***(b)*** **Thinking Process** —OH *group is activating group and is o and p-directing. Also* — SO_3H *is a better leaving group and is knocked out by* Br^-.



CHEMISTRY IN action

'Supramolecule' that could help reduce nuclear, agricultural waste

Researchers have provided the experimental proof for the existence of a chemical bond between two negatively charged molecules of bisulfate, or HSO_4. The existence of this structure i.e., a "supramolecule" with two negatively charged ions in dimer state was once regarded as impossible as it violates the 250 years old Coulomb's law. But the structural evidence shows that two hydroxy anions can in fact be chemically bonded. Here, the long-range repulsions between these anions are offset by short-range attractions as shown below



In molecular chemistry, two monomer molecules connected by a strong covalent bond are called a "dimer." (A polymer is a chain of many monomers.) In supramolecular chemistry, the dimers are connected by many weak non-covalent bonds. This new molecular structure has the potential applications to the safe storage of nuclear waste and reduction of chemicals that contaminate water.

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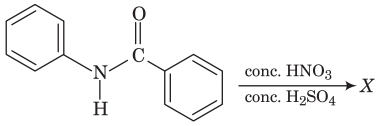
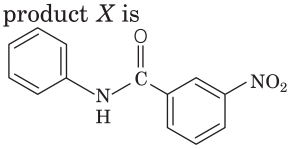
Smart Practice

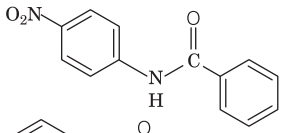
Single Answer Correct Type

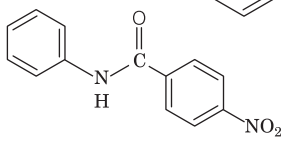
1. In the following reaction, [JEE Advanced 2007]

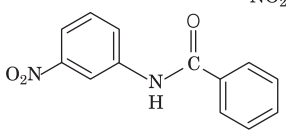


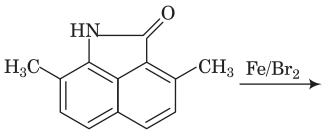
The product X is

(a) 

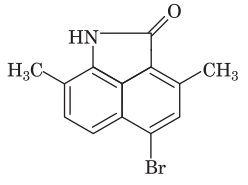
(b) 

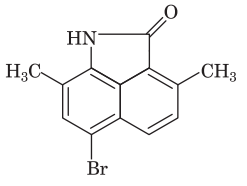
(c) 

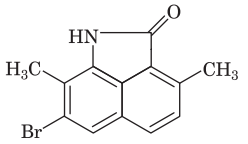
(d) 

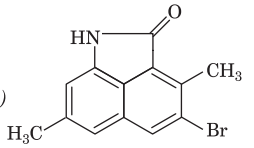
2. 

Product on monobromination of this compound is [IIT Mains 2009]

(a) 

(b) 

(c) 

(d) 

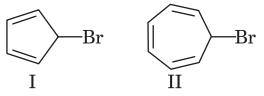
3. Among the following the compound that can be most readily sulphonated is [IIT JEE 2009]

(a) benzene (b) nitrobenzene
(c) toluene (d) chlorobenzene

4. Phenol reacts with bromine in carbon disulphide at low temperature to give

(a) *m*-bromophenol (b) *o*-and *p*-bromophenol
(c) *p*-bromophenol (d) 2, 4, 6-tribromophenol

5. Consider the following cyclic compounds. [JEE Advanced 2012]

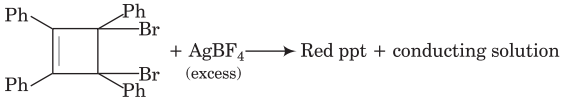


If these compounds undergo heterolytic fission of C—Br bonds, the preferred mode of decomposition would be

(a) Both decomposes to form Br^-
(b) Both decomposes to form Br^+
(c) I and II decompose to form Br^- and Br^+ respectively
(d) I and II decompose to form Br^+ and Br^- respectively

6. The following compound, when treated with excess of $AgBF_4$, gives a red precipitate leaving a highly conducting filterate, because

[Similar as asked in JEE Advanced 2013]



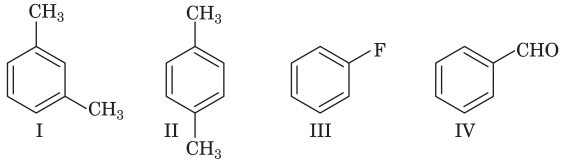
(a) A dianion aromatic system is formed
(b) A dication aromatic system is formed
(c) A covalent ditetrafluoroborate compound is formed
(d) An aromatic salt precipitate is formed which has red colour

7. When potassium metal is added to 1, 3, 5, 7-cyclo octatetraene, a highly conducting salt is formed without evolution of H_2 gas because

[Similar as asked in JEE Advanced 2013]

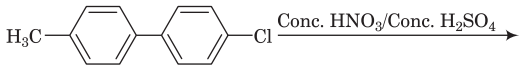
(a) reduction of cyclooctatetraene into anionic $C_8H_8^-$
(b) reduction of cyclooctatetraene into anionic $C_8H_8^{2-}$
(c) reduction of cyclooctatetraene into C_8H_{10}
(d) oxidation of cyclooctatetraene into $C_8H_8^{2+}$

8. What is the correct increasing order of reactivity of the following compounds towards electrophilic aromatic substitution reaction?



(a) I < II < III < IV (b) IV < III < II < I
(c) IV < III < I < II (d) III < IV < I < II

9. Consider the following reaction,



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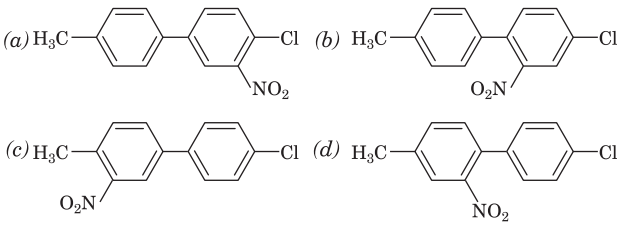
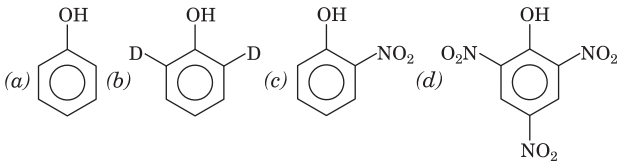
Which of the following is the product, obtained from the above reaction?



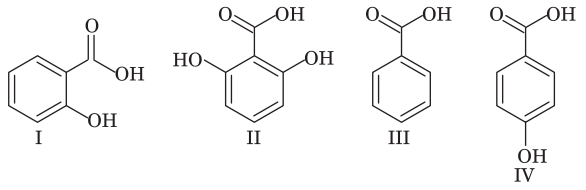
10. pK_a value is greater for

[Similar as asked in JEE Advanced 2016]



11. The order of K_b value of the following compounds is

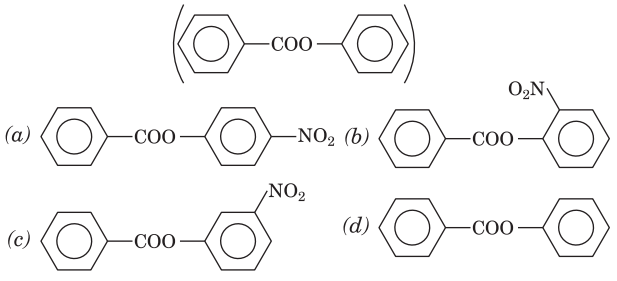
[Similar as asked in JEE Advanced 2016]



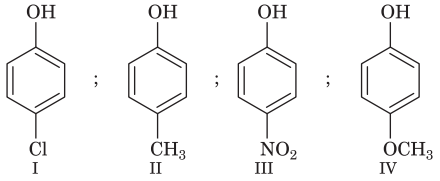
(a) II > I > IV > III (b) IV > III > I > II
(c) IV > I > III > II (d) III > IV > I > II

12. Which of the following is correct for the mononitration of phenyl benzoate?

[Similar as asked in JEE Advanced 2007]



13. Arrange the following compounds in the decreasing order of acidity. [IIT JEE 2013]



(a) II > IV > I > III (b) I > II > III > IV
(c) III > I > II > IV (d) IV > III > I > II

14. *o*-nitrophenol is less soluble in water than *p* and *m*-nitrophenols because

(a) *o*-nitrophenol is more steam volatile than those of *m* and *p*-isomers
(b) *o*-nitrophenol shows intramolecular H-bonding
(c) *o*-nitrophenol shows intermolecular H-bonding
(d) melting point of *o*-nitrophenol is lower than those of *m*-and *p*-isomers

More Than One Correct Type

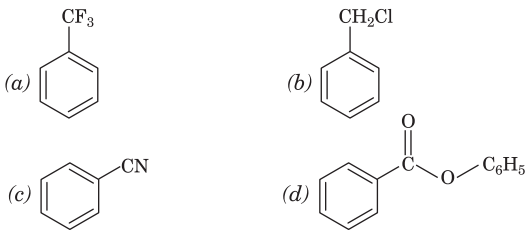
15. When nitrobenzene is treated with Br_2 in the presence of $FeBr_3$, the major product formed is *m*-bromonitrobenzene. Statements which related to obtain the *m*-isomer, are [IIT 2016]

(a) the electron density on *meta* position is more than that on *ortho* and *para*-positions
(b) the intermediate carbonium ion formed after initial attack of Br^+ at the *meta*-position is less destabilised
(c) loss of aromaticity occurs when Br^+ attacks at the *ortho* and *para*-positions and not at *meta*-position
(d) easier loss of H^+ to regain aromaticity from *meta*-position than from *ortho* and *para*-positions

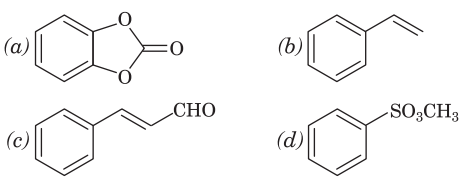
16. Which of the following statements is/are correct about chlorination of toluene?

(a) In chlorination of toluene, methyl group acts as an activating group
(b) In presence of $AlCl_3$, *ortho* and *para* chlorotoluenes are formed
(c) Once a chlorine atom is introduced into benzene ring, further chlorination at benzene ring becomes difficult as compared to the first chlorination
(d) Chlorination of toluene in presence of $AlCl_3$ is more difficult than benzene

17. The compound(s) that direct incoming electrophile predominantly at *meta*-position is/are



18. The compound(s) that undergo slower electrophilic substitution than benzene is/are



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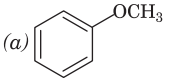
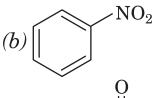
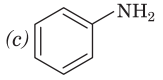
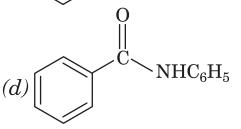
19. Which of the following compounds fail in Friedal-Craft alkylation reaction?

(a) 

(b) 

(c) 

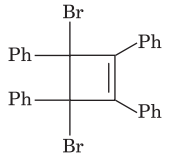
(d) 

20. Which of the following compounds is/are not aromatic in nature?

(a)

(b)

(c)

(d) 

21. Which of the following statements is/are true for ring activating groups?

(a) These groups increase electron density on aromatic ring for further electrophilic substitution

(b) In these groups, the atom attached to benzene ring, contains at least one lone pair

(c) These groups increase electron density at *o*-and *m*-positions

(d) These groups increase electron density at *o*-and *p*-positions.

22. Aromatic systems generally give aromatic substitution reactions because

(a) these systems have high electron density on the aromatic ring

(b) these systems have low electron density on the aromatic system

(c) these systems do not want to lose their stability due to aromaticity

(d) All of the above are correct

Comprehension Based Type

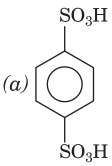
Paragraph I

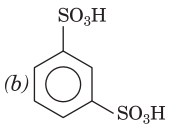
The displacement of proton from benzene ring by $—SO_3H$ group is known as sulphonation and the product is known as benzene sulphonic acid. It is carried out by heating benzene with conc. H_2SO_4.

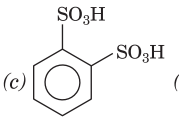
23. Which of the following electrophiles take part in sulphonation process?

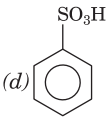
(a) SO_3 (b) H_2SO_4 (c) H_3O^+ (d) HNO_3

24. At high temperature, which of the following is obtained as major product?

(a) 

(b) 

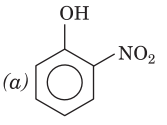
(c) 

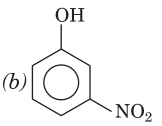
(d) 

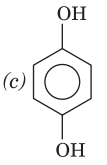
Paragraph II

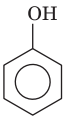
The acidic character of phenols is due to conjugation between lone pair of oxygen and benzene nucleus. The positive charge on oxygen signifies the weakening of O—H bond. Presence of electron releasing group over benzene nucleus destabilises the phenoxide ion, thus, decreases the acidity of phenol whereas presence of electron withdrawing groups stabilises the phenoxide ion and thus, increases the acidity of phenol.

25. Which of the following compounds is highly acidic?

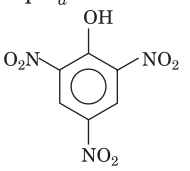
(a) 

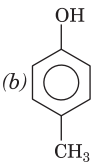
(b) 

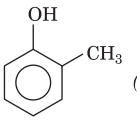
(c) 

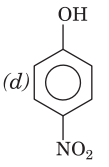
(d) 

26. The pK_a value is least for

(a) 

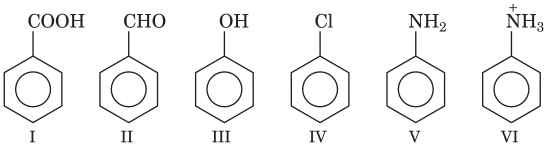
(b) 

(c) 

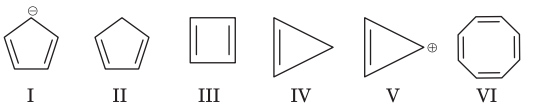
(d) 

Integer Type

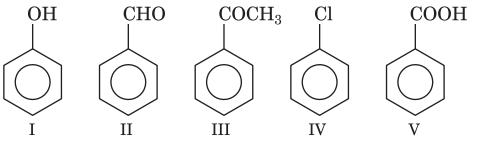
27. How many of the following compounds give *o* and *p*-products on electrophilic substitution?



28. How many of the following species are aromatic?



29. How many of the following compounds give *m*-substituted product on electrophilic substitution?



30. In order to cyclooctatetraene to be aromatic, how many electrons has to introduced by reacting it with metal?

Answers

1. (b)	**2.** (b)	**3.** (c)	**4.** (c)	**5.** (d)
6. (b)	**7.** (b)	**8.** (b)	**9.** (c)	**10.** (b)
11. (b)	**12.** (a)	**13.** (c)	**14.** (b)	**15.** (a,b)
16. (a,b,c)	**17.** (a,c)	**18.** (b,c,d)	**19.** (b,c)	**20.** (a,c,d)
21. (a,d)	**22.** (a,c)	**23.** (a)	**24.** (b)	**25.** (b)
26. (a)	**27.** (3)	**28.** (2)	**29.** (3)	**30.** (2)

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EMF AND NERNST EQUATION

Stepwise learning and Practice through Selective problems

1 Find the equilibrium constant for the reaction,
$Cu^{2+} + In^{2+} \rightleftharpoons Cu^{+} + In^{3+}$
Given that, $E^{\circ}_{Cu^{2+}/Cu^{+}} = 0.15$ V,
$E^{\circ}_{In^{2+}/In^{+}} = -0.40$ V, $E^{\circ}_{In^{3+}/In^{+}} = -0.42$ V
[IIT JEE 2009]

(a) 10^{10} (b) 10^{9} (c) 10^{11} (d) 10^{8}

(a) This problem can be solved stepwise as follows:

***Step* I** *Calculate, $E^{\circ}_{In^{3+}/In^{2+}}$ with the help of $E^{\circ}_{In^{2+}/In^{+}}$ and $E^{\circ}_{In^{3+}/In^{+}}$*

Given, $In^{2+} + e^{-} \longrightarrow In;\ E^{\circ}_{1} = -0.40$ V ...(i)

$In^{3+} + 2e^{-} \longrightarrow In^{+};\ E^{\circ}_{2} = -0.42$ V ...(ii)

Required reaction,

$In^{3+} + e^{-} \longrightarrow In^{2+};\ E^{\circ}_{3}$ ...(iii)

If we subtract Eq, (i) from Eq. (ii) we shall get Eq. (iii)

$\therefore \quad \Delta G^{\circ}_{3} = \Delta G^{\circ}_{2} - \Delta G^{\circ}_{1} = -n_1FE^{\circ}_{2} - (-n_2FE^{\circ}_{1})$

$= -2F(-0.42) + F(-0.40)$

or $\quad -FE^{\circ}_{3} = 2F(0.42) - 0.40F$ or $E^{\circ}_{3} = -0.44$ V

***Step* II** *Calculate E°_{cell} for the mentioned equation in the problem.*

Given equation,

$Cu^{2+} + In^{2+} \longrightarrow Cu^{+} + In^{3+}$

$E^{\circ}_{cell} = E^{\circ}_{(Cu^{2+}/Cu^{+})} - E^{\circ}_{(In^{3+}/In^{2+})}$

$= 0.15 - (-0.44) = 0.59$ V

***Step* III** *Calculate equilibrium constant from Nernst equation,*

$$E^{\circ}_{cell} = \frac{0.059}{n}\log K.$$

or $$\log K = \frac{nE^{\circ}_{cell}}{0.059} = \frac{1 \times 0.59}{0.059}$$

or $\log K = 10$ or $K = 10^{10}$

TRY THESE

1. For the cell reaction,

$Mg|Mg^{2+}(aq) \,||\, Ag^{+}(aq)\,|\,Ag$

Calculate the equilibrium constant at 25°C.

($E^{\circ}_{Mg^{2+}/Mg} = -2.37$ V and $E^{\circ}_{Ag^{+}/Ag} = 0.80$ V)

(a) 1.89×10^{107}
(b) 2.93×10^{108}
(c) 1.97×10^{106}
(d) 1.79×10^{104}

2. $Zn\,|\,Zn^{2+}(0.1M)\,||\,Fe^{2+}(0.01M)\,|\,Fe$

The emf of the above cell is 0.2905 V. Equilibrium constant for the cell reaction is

(a) $10^{0.32/0.059}$ (b) $10^{0.32/0.0295}$
(c) $10^{0.26/0.0295}$ (d) $10^{0.32/0.059}$

1. (a) **2.** (b)

2 Given below are the half-cell reactions,
$Mn^{2+} + 2e^{-} \longrightarrow Mn;\ E^{\circ} = -1.18$ V
$2(Mn^{3+} + e^{-} \longrightarrow Mn^{2+});\ E^{\circ} = +1.51$ V
The E° for $3Mn^{2+} \longrightarrow Mn + 2Mn^{3+}$ will be
[JEE Main 2014]

(a) – 2.69 V; the reaction will not occur
(b) – 2.69 V; the reaction will occur
(c) – 0.33 V; the reaction will not occur
(d) – 0.33 V; the reaction will occur

(a) ***Step* I** *Write down the formula involving calculation of E°_{cell}*, $E^{\circ}_{cell} = E^{\circ}_{R} - E^{\circ}_{P}$
where, E°_{R} and E°_{P} are standard reduction potentials of reactant and product, respectively.

***Step* II** *Find out E°_{R} and E°_{P} with the help of given data*

$Mn^{2+} + 2e^{-} \longrightarrow Mn;\ E^{\circ}_{R} = -1.18$ V ...(i)

$2(Mn^{3+} + e^{-} \longrightarrow Mn^{2+});\ E^{\circ}_{P} = 1.51$ V ...(ii)

As we required reduction potentials in the formula mentioned in step I, so reverse the Eq. (ii) to get reduction potential of reactant.

$2(Mn^{2+} \longrightarrow Mn^{3+} + e^{-});\ E^{\circ}_{R} = -1.51$ V

***Step* III** *Calculate E°_{cell}*

$E^{\circ}_{cell} = -1.18$ V $- 1.51$ V $= -2.69$ V

***Step* IV** *A reaction to occur in an electrochemical cell, E°_{cell} must be positive. Check out whether calculated E°_{cell} in step* III *is positive or not.*

As E°_{cell} comes out to be negative so reaction will not occur.

TRY THESE

1. The standard reduction potentials of Cu^{2+}/Cu and Cu^{2+}/Cu^{+} are 0.337 V and 0.153V, respectively. The standard electrode potential of Cu^{+}/Cu half-cell is

(a) 0.189 V (b) 0.827 V (c) 0.521 V (d) 0.490 V

2. The standard reduction potential data at 25°C is given below:

$E^{\circ}(Fe^{3+}/Fe^{2+}) = +0.77$ V ; $E^{\circ}(Fe^{2+}/Fe) = -0.44$ V;

$E^{\circ}(Cu^{2+}/Cu) = +0.34$ V ; $E^{\circ}(Cu^{+}/Cu) = +0.52$ V;

$E^{\circ}(O_2(g) + 4H^{+} + 4e^{-} \longrightarrow 2H_2O) = +1.23$ V

$E^{\circ}(O_2(g) + 2H_2O + 4e^{-} \longrightarrow 4OH) = +0.40$ V

$E^{\circ}(Cr^{3+}/Cr) = -0.74$ V; $E^{\circ}(Cr^{2+}/Cr) = +0.91$ V

Match E° of the redox pair in Column I with the values given in Column II and select the correct answer using the code given below the lists.
[JEE Advanced 2013]

Column I	Column II
A. $E^{\circ}(Fe^{3+}/Fe)$	p. – 0.18 V
B. $E^{\circ}(4H_2O \rightleftharpoons 4H^{+} + 4OH^{-})$	q. – 0.4 V
C. $E^{\circ}(Cu^{2+} + Cu \longrightarrow 2Cu^{+})$	r. – 0.04 V
D. $E^{\circ}(Cu^{3+}, Cu^{2+})$	s. – 0.83 V

Codes

	A	B	C	D
(a)	s	p	q	r
(c)	p	q	r	s

	A	B	C	D
(b)	q	r	s	p
(d)	r	s	p	q

1. (c) **2.** (d)

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3 For the following electrochemical cell at 298K,
$Pt(s) \mid H_2(g, 1\text{ bar}) \mid H^+(aq, 1\text{ M}) \parallel M^{4+}(aq), M^{2+}(aq) \mid Pt(s)$

$E_{cell} = 0.092\text{ V}$ when $\frac{[M^{2+}(aq)]}{[M^{4+}(aq)]} = 10^x$

Given, $E^\circ_{M^{4+}/M^{2+}} = 0.151\text{ V}$; $2.303\frac{RT}{F} = 0.059\text{ V}$

The value of x is [JEE Advanced 2016]

(a) – 2 (b) – 1 (c) 1 (d) 2

(d) ***Step I*** *Write down the two half-cell reactions involved in the electrochemical cell.*

Oxidation reaction at anode

$$H_2(g) \longrightarrow 2H^+(aq) + 2e^-;\ E^\circ_{SHE} = 0.00\text{ V}$$

Reduction reaction at cathode

$$M^{4+}(aq) + 2e^- \longrightarrow M^{2+}(aq);\ E^\circ_{M^{4+}/M^{2+}} = 0.151\text{ V}$$

Step II *Find out* E°_{cell}, $E^\circ_{cell} = E^\circ_{right} - E^\circ_{left}$

$$E^\circ_{cell} = E^\circ_{M^{4+}/M^{2+}} - E^\circ_{SHE}$$
$$= 0.151\text{ V} - 0\text{ V} = 0.151\text{ V}$$

Step III *Write down the net cell reaction,*

Net cell reaction is,

$$M^{4+}(aq) + H_2(g) \longrightarrow M^{2+}(aq) + 2H^+(aq);\quad E^\circ_{cell} = 0.151\text{ V} \ldots (i)$$

Step IV *Apply Nernst equation in Eq.* (i)

Nernst equation is,

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n}\log\frac{[M^{2+}][H^+]^2}{[M^{4+}]\,p_{H_2}} \quad \ldots(ii)$$

Step V *Put all the given values in Eq.* (ii) *and find out the value of* x $[H^+] = 1$ and $p_{H_2} = 1$ [Given]

Now, $E_{cell} = E^\circ_{cell} - \frac{0.059}{n}\log\frac{[M^{2+}]}{[M^{4+}]}$

$$0.092 = 0.151 - \frac{0.059}{2}\log 10^x,$$

[$\because$ Number of electron involved in electrode reaction, $n = 2$]

$$0.059 = \frac{0.059}{2}\log 10^x$$

$\therefore \quad \log 10^x = 2 \Rightarrow 10^x = \text{Antilog}(2), \quad x = 2$

TRY THESE

1. Consider the following cell,
$Zn|\,Zn(NO_3)_2(0.25\text{ M}) \parallel AgNO_3(0.1\text{ M}) \mid Ag$
The standard oxidation potential of zinc is 0.76V and of silver is – 0.80 V. Calculate the emf of the cell

(a) 0.52 V (b) 1.52 V (c) – 1.52 V (d) – 0.52 V

2. The standard reduction potentials of Cu^+/Cu and Ag^+/Ag electrodes are 0.337 V and 0.799 V, respectively. Construct a galvanic cell using these electrodes so that its standard emf should be positive. If the concentration of Cu^{2+} is 0.01M for what concentration of Ag^+, will the emf of the cell at 25°C, becomes zero?

(a) 1.5×10^{-7}M (b) 1.5×10^{-8} M
(c) 1.5×10^{-9} M (d) 1.5×10^{-10}M

1. (b) **2.** (c)

4 The emf of a cell corresponding to the reaction, $Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(0.1\text{M}) + H_2(g, 1\text{ atm})$ is 0.28V at 25°C.
Write the half-cell reactions and calculate the pH of the solution at the hydrogen electrode.
$E^\circ_{Zn^{2+}/Zn} = -0.76\text{ V}$; $E^\circ_{H^+/H_2} = 0$

(a) 7.7 (b) 8.6
(c) 6.8 (d) 7.9

(b) This problem can be solved stepwise as follow:

Step I *Write down the two half-cell reactions at cathode and anode respectively alongwith their electrode potential values*

At anode $Zn \longrightarrow Zn^{2+} + 2e^-;\ E^\circ = 0.76\text{ V}$ …(i)

At cathode $2H^+ + 2e^- \longrightarrow H_2(g);\ E^\circ = 0.00\text{ V}$ …(ii)

Step II *Write down the Nernst equation for the reaction mentioned in the given problem.*

$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(0.1\text{ M}) + H_2(g) \quad \ldots(iii)$$

$$E_{cell} = E^\circ_{cell} - \frac{0.0592}{2}\log\frac{[Zn^{2+}]}{[H^+]^2} \quad \ldots(iv)$$

Step III *For calculation of* E°_{cell} *use Eqs. (i) and (ii).*

As same number of electrons are involved in both Eqs. (i) and (ii). Hence, E°_{cell} for Eq. (iii) can be obtained by direct addition of electrode potentials from Eqs. (i) and (ii).

$\therefore \quad E^\circ_{cell} = (0.76 + 0.00)\text{ V}$
$= 0.76\text{ V}$

Step IV *Since, values of* E_{cell} *and* $[Zn^{2+}]$ *are given in the problem, therefore we can calculate* $[H^+]$ *from Eq. (iv) as*

$$0.28 = 0.76 - \frac{0.0592}{2}\log\frac{[0.1]}{[H^+]^2}$$

or $\frac{2(0.28 - 0.76)}{0.0592} = -[\log(0.1) - \log[H^+]^2]$

$$\left[\because \log\frac{A}{B} = \log A - \log B\right]$$

$$\frac{2(0.28 - 0.76)}{0.0592} = -[\log(0.1) - 2\log[|H|]^+]$$

$$[\because \log x^n = n\log x]$$

or $-\frac{0.96}{0.0592} = -[\log(0.1) + 2\text{pH}] \quad [\because -\log[H^+] = \text{pH}]$

or $16.21 = \log(0.1) + 2\text{pH}$

or $\text{pH} = 8.6$

TRY THESE

1. Consider the following cell reaction,
$2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l);\ E^\circ = 1.67\text{ V}$
At $[Fe^{2+}] = 10^{-3}$M, $p_{O_2} = 0.1$ atm and pH = 3, the cell potential at 25°C is [IIT JEE 2011]

(a) 1.47 V (b) 1.77 V (c) 1.87 V (d) 1.57 V

2. If the observed emf of an electrochemical cell
$Pt \mid H_2(1\text{ atm}) \mid H^+(3 \times 10^{-4}\text{M}) \parallel H^+(M_1) \mid H_2(1\text{ atm}) \mid Pt$ is 0.154V.
Calculate the value of pH.

(a) 0.917 (b) 1.219 (c) 8.173 (d) 8.917

1. (d) **2.** (a)

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5 The emf of the following cell depends on the difference of M^{2+} ions at the two electrodes.
$M|M^{2+}$(saturated solution of a sparingly soluble salt, MX_2) $||$ M^{2+} (0.001 mol dm^{-3}) $|$ M.
If emf of the cell at 298 K is 0.059V.
Find the solubility product, (K_{sp}, mol^3 dm^{-9}) of MX_2 at 298 K in the cell,
[take $(2.303 \times R \times 298)] / F = 0.059$ V. **[IIT JEE 2012]**
(a) 1×10^{-15} (b) 4×10^{-15} (c) 1×10^{-12} (d) 14×10^{-12}

(b) ***Step* I** *Write down the concentration cell.*
$M|M^{2+}$(saturated solution of a sparingly soluble salt, MX_2) $||$ M^{2+}(0.001 mol dm^{-3}) $|$ M.
***Step* II** *Write down the Nernst equation for concentration cell.*

$$E_{cell} = E^{\circ}_{cell} - \frac{2.303RT}{nF} \log \frac{[M^{n+}]_{concentrated}}{[M^{n+}]_{dilute}}$$

$$E_{cell} = E^{\circ}_{cell} - \frac{2.303RT}{nF} \log \frac{[M^{2+}]_{saturated}}{[M^{2+}]_{dilute}} \quad ...(i)$$

***Step* III** *Put all the given values in Eq.* (i)
Given, $[M^{2+}]_{dilute} = 0.001$ mol dm^{-3}
$E_{cell} = 0.059$ V
$T = 298$ K, $n = 2$
On putting all these values in Eq. (i), we get

$$0.059 = -\frac{0.059}{2} \log \frac{[M^{2+}]_{saturated}}{0.001} \quad ...(ii)$$

***Step* IV** *Find out value of* $[M^{2+}]$ *saturated.*
On solving Eq. (ii)

$$0.059 = -\frac{0.059}{2} \log \frac{[M^{2+}]_{saturated}}{0.001}$$

or $$-2 = \log \frac{[M^{2+}]_{saturated}}{0.001}$$

or $$\text{Antilog}(-2) = \frac{[M^{2+}]_{saturated}}{0.001}$$

$$0.01 = \frac{[M^{2+}]_{saturated}}{0.001}$$

or $[M^{2+}]_{saturated} = 10^{-5}$ mol / dm^3 = S(solubility)
***Step* V** Calculate solubility product by using the formula
$K_{sp} = (S)(2S)^2$

$$MX_2 \rightleftharpoons \underset{S}{M^{2+}} + \underset{2S}{2X^-}$$

$$K_{sp} = (S)(2S)^2 = (10^{-5})(2 \times 10^{-5})^2$$
$$= 4 \times 10^{-15} \text{ mol}^3 \text{ dm}^{-9}$$

TRY THESE

1. 0.1M KCl is 85% dissociated and 0.1M $AgNO_3$ is 82% dissociated. If emf of the cell, Ag|AgCl, (0.1 M) KCl $||$ (0.1M) $AgNO_3$| Ag is 0.45V. Calculate the solubility product of AgCl at 25°C.
(a) 1.7×10^{-9} (b) 1.7×10^{-10} (c) 1.7×10^{-8} (d) 1.7×10^{-11}

2. A silver electrode is dipped in the saturated solution of Ag_2SO_4. The potential difference between the silver electrode and the standard hydrogen electrode is found to be 0.711V. Determine $K_{sp}(Ag_2SO_4)$ ($E^{\circ}_{Ag^+|Ag} = 0.799$V).
(a) 1.705×10^{-4} (b) 1.692×10^{-3}
(c) 1.705×10^{-5} (d) 1.692×10^{-6}

1. (b) **2.** (c)

Continued from Page 37

17. Alkali metals are paramagnetic while alkaline earth metals are diamagnetic in nature. But when it come to their salts both alkali and alkaline metal salts show diamagnetic nature. Explain.

Alkali and alkaline earth metals have electronic configurations of valence shell, ns^1 and ns^2, respectively. Thus, alkaline earth metals do not have unpaired electron and are diamagnetic. But when alkali metals form bond with another atom, this unpaired electron is taken up by the another atom and M^+ is formed. Similarly, for alkaline metals two electrons are taken by the another atom.
Now, all the electrons are paired. Thus, their salts are diamagnetic in nature.

18. SO_3 is more acidic than SO_2. Why?

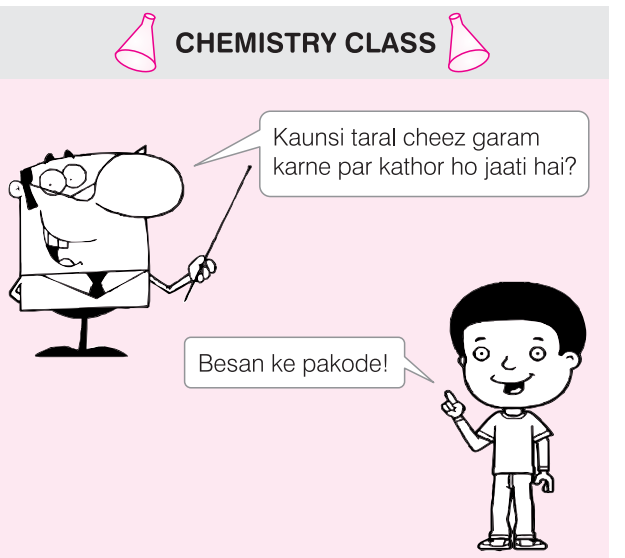
Oxygen is more electronegative than sulphur. Thus, increase in number of oxygen atoms cause more electropositive character on S-atom. As a result, acidic nature of that molecule will increase. In other words you can say that acidic nature of non-metal oxides increases with increase in number of oxygen atoms.

19. The number of lanthanoids and actinoids is 14 each in periodic table, Why?

In lanthanoids and actinoids, *f*-subshells are gradually filled by differentiating electrons and *f*-subshells can accommodate a maximum of 14 electrons. Thus, the number of lanthanoids and actinoids is 14 each in periodic table.

20. The value of second ionisation energy (IE_2) is always higher than that of first ionisation energy (IE_1) of an element, why?

The cation formed by removal of first electron from the atom has increased effective nuclear charge. As a result, valence electrons are more strongly attracted by nucleus and removal of second electron becomes difficult. Thus, IE_2 in always higher than IE_1 for an element.



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HALF TEST 1

(XI SYLLABUS) FULLY SOLVED

INSTRUCTIONS

- This test consists of 45 questions and each question is allotted 4 marks for correct response.
- Candidates will be awarded marks as stated above for correct response of each question. 1/4 marks will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
- There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted according as per instructions.

1. $\frac{K_p}{K_C}$ for the following reaction will be,

$$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$$

(a) RT *(b)* $1/RT$ *(c)* $1/\sqrt{RT}$ *(d)* $RT/2$

2. Predict the correct order of repulsion between different electron pairs.

(a) Lone pair- lone pair > bond pair-bond pair > lone pair -bond pair

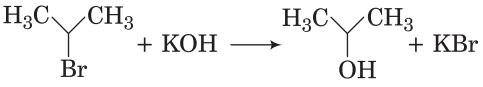
(b) Bond pair- bond pair> lone pair - bond pair > lone pair - lone pair

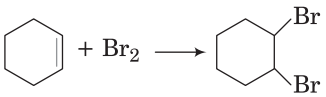
(c) Lone pair - bond pair > bond pair - bond pair > lone pair - lone pair

(d) Lone pair - lone pair > lone pair - bond pair > bond pair - bond pair

3. For the following reactions

I. $CH_3CH_2CH_2Br + KOH \longrightarrow CH_3CH{=}CH_2 + KBr + H_2O$

II. 

III. 

Which of the following statements is correct?

(a) I is elimination reaction, II is substitution reaction and III is addition reaction

(b) I is elimination, II and III are substitution reactions

(c) I is substitution, II and III are addition reactions

(d) I and II are elimination reactions and III is addition reaction

4. A mixture of gases contains H_2 and O_2 gases in the ratio of 1: 4 (w/w). What is the molar ratio of the two gases in the mixture?

(a) 1 : 4 *(b)* 4 : 1 *(c)* 16 : 1 *(d)* 2 : 1

5. The heat of formation is the change in enthalpy accompaying the formation of a substance from its elements at 298 K and 1 atm pressure. Since, the enthalpies of elements in their most stable states are taken to be zero, the heat of formation of compounds is

(a) Always negative

(b) Always positive

(c) Standard heat enthalpy of that compound

(d) Zero

6. A 400 mg of iron capsule contains 100 mg of ferrous fumarate, $(CHCOO)_2Fe$. The percentage of iron present in it, is approximately

(a) 33% *(b)* 25% *(c)* 14% *(d)* 8%

7. The molecular shapes of SF_4, CF_4 and XeF_4 are

(a) different with 1, 0 and 2 lone-pairs of electron on the central atom, respectively

(b) different with 0, 1 and 2 lone-pairs of electron on the central atom, respectively

(c) same with 1, 1 and 1 lone-pair of electron on the central atoms, respectively

(d) same with 2, 0 and 1 lone-pairs of electron on the central atom, respectively

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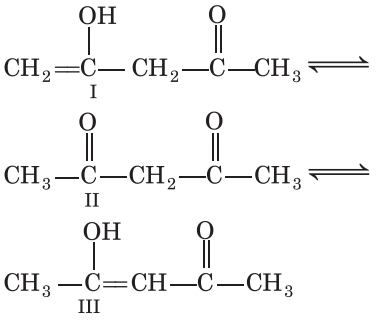
8. An organic compound *A* undergoes ozonolysis and produces equimolar mixture of acetone and propionaldehyde. Identify *A* from the following compounds

(a) 2-methyl-1-pentene *(b)* 1-pentene

(c) 2-pentene *(d)* 2-methyl-2-pentene

9. The order of stability of the following tautomeric compounds is [NEET 2013]



(a) I > II > III *(b)* III > II > I *(c)* II > I > III *(d)* II > III > I

10. The decreasing order of hydration enthalpies of earth metal ions is

(a) $Be^{2+} > Ba^{2+} > Ca^{2+} > Sr^{2+} > Mg^{2+}$

(b) $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} > Be^{2+}$

(c) $Be^{2+} > Ca^{2+} > Mg^{2+} > Ba^{2+} > Mg^{2+}$

(d) $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$

11. Pb(IV) compounds are strong oxidants whereas Ge(II) compounds are strong reductants. It can be because

(a) Pb is more electropositive than Ge

(b) ionisation potential of lead is less than that of Ge

(c) ionic radii of Pb^{2+} and Pb^{4+} are larger than those of Ge^{2+} and Ge^{4+}

(d) more pronounced inert pair effect in Pb than Ge

12. Kjeldahl's method can be used for the estimation of nitrogen in

(a) pyridine *(b)* $C_6H_5NO_2$

(c) $C_6H_5NHCOCH_3$ *(d)* $C_6H_5—N=N—C_6H_5$

13. The metallic sodium dissolves in liquid ammonia to form a deep blue coloured solution. This deep blue colour is due to the formation of

(a) solvated electron, $\bar{e}(NH_3)y$

(b) solvated atomic sodium, $Na(NH_3)y$

(c) Na^+ and Na^-

(d) $NaNH_2 + H_2$

14. 50 mL of each gas *A* and gas *B* takes 150 s and 200 s respectively for effusing through a pin hole under the similar conditions. If molecular mass of gas *B* is 36, the molecular mass of gas *A* will be

(a) 96 *(b)* 128 *(c)* 20.2 *(d)* 64

15. Which of the following has highest knocking property?

(a) Aromatic hydrocarbons

(b) Olefins

(c) Branched chain paraffins

(d) Straight chain paraffins

16. An organic compound of formula C_3H_7N was analysed for nitrogen by Duma's method. Calculate the volume of N_2 gas evolved at NTP from 2 g of substance.

(a) 405 mL *(b)* 342 mL *(c)* 392 mL *(d)* 100 mL

17. Number of moles of MnO_4^- required to oxidise one mole of ferrous oxalate completely in acidic medium will be

(a) 0.6 mole *(b)* 0.4 mole *(c)* 7.5 mole *(d)* 0.2 mole

18. Which of the following statements is incorrect about electromagnetic radiation?

(a) These can pass through vacuum as well as through any medium

(b) These have the same speed as that of light

(c) These waves possess significant value of wavelength ranging from 30 m to 10^{-12} m

(d) All are correct

19. An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If T_i is the initial temperature and T_f is the final temperature, which of the following statement is correct?

(a) $(T_f)_{irrev} > (T_f)_{rev}$

(b) $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process

(c) $(T_f)_{irrev} = (T_f)_{rev}$

(d) $T_f = T_i$ for both reversible and irreversible processes

20. When S in the form of S_8, is heated at 900 K, the initial pressure of 1 atm falls by 29% at equilibrium. This is because of conversion of some S_8 to S_2. Find the value of K_p for the reaction.

(a) 3.55 atm^3 *(b)* 4.55 atm^3 *(c)* 1.05 atm^3 *(d)* 2.55 atm^3

21. Calculate the pH of a solution which contains 100 mL of 0.1 M HCl and 9.9 mL of 1.0 M NaOH.

(a) 5.12 *(b)* 4.09 *(c)* 2.01 *(d)* 3.04

22. Match the following columns.

	Column I (Property)		Column II (Element)
A.	Highest valency	p.	Neon
B.	Highest electronegativity	q.	Nitrogen
C.	Highest ionisation enthalpy	r.	Caesium
D.	Largest size	s.	Fluorine
		t.	Chlorine

Codes

	A	B	C	D		A	B	C	D
(a)	r	p	q	t	*(b)*	t	s	r	q
(c)	q	s	p	r	*(d)*	r	s	q	p

23. Calculate the work done by 16 g of oxygen gas (assuming ideal behaviour) of molar mass 32 g mol^{-1} undergoing isothermal reversible expansion at 300 K from an initial volume 2.5 L to the final volume 25 L (in L atm). ($R = 8.2 \times 10^{-2}$ L atm K^{-1} mol^{-1})

(a) –56.64 J *(b)* –28.32 J *(c)* 113.28 J *(d)* 56.64 J

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24. The energy required to excite the electron in the atom from $n = 1$ to $n = 2$ when the ionisation enthalpy of hydrogen atom is 1.312×10^6 J mol^{-1} will be (in the unit of 10^5).

(a) 8.53 *(b)* 7.51 *(c)* 8.92 *(d)* 9.84

25. The decreasing order of reactivity towards electrophilic addition of the following is

I. $CH \equiv CH$

II. $CH_2 = CH_2$

III. $H_2C = CH—Cl$

IV.

(a) I > II> III > IV *(b)* II > I > III > IV

(c) IV > III > I > II *(d)* IV > III > II > I

26. Using MOT, compare O_2^+ and O_2^- species and choose the incorrect option.

(a) O_2^+ has higher bond order than O_2^-

(b) O_2^- is less stable

(c) O_2^+ is diamagnetic while O_2^- is paramagnetic

(d) Both O_2^+ and O_2^- are paramagnetic

27. The pair of compounds which cannot exists together in solution is

(a) $NaHCO_3$ and NaOH *(b)* $NaHCO_3$ and H_2O

(c) $NaHCO_3$ and Na_2CO_3 *(d)* Na_2CO_3 and NaOH

28. If two gases have the same value of a but different value of b (a and b are van der Waals' constants), then

(a) the gas having smaller value of b will occupy lesser volume

(b) the gas having smaller value of b has larger compressibility

(c) the gas having smaller value of b has lesser compressibility.

(d) Both (a) and (b)

29. The equilibrium constant for the reaction, $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$ at 298 K is 73. Calculate the value of the standard free energy change. ($R = 8.314$ JK^{-1} mol^{-1})

(a) 12.922 kJ mol^{-1} *(b)* –12.922 kJ mol^{-1}

(c) 10.632 kJ mol^{-1} *(d)* –10.632 kJ mol^{-1}

30. In environmental chemistry, the medium which is affected by a pollutant is called as the ……

(a) sink *(b)* slag

(c) solvent *(d)* receptor

31. What is the change in the oxidation state of Mn in the reaction of MnO_4^- with H_2O_2 in acidic medium?

(a) $7 \rightarrow 4$ *(b)* $6 \rightarrow 4$

(c) $7 \rightarrow 2$ *(d)* $6 \rightarrow 2$

32. Precipitate of CaF_2 ($K_{sp} = 1.7 \times 10^{-10}$) will be obtained, when equal volume of the following is mixed.

(a) 10^{-4} M Ca^{2+} ions and 10^{-4} M F^- ions

(b) 10^{-2} M Ca^{2+} ions and 10^{-8} M F^- ions

(c) 10^{-2} M Ca^{2+} ions and 10^{-3} M F^- ions

(d) 10^{-3} M Ca^{2+} ions and 10^{-5} F^- ions

33. When two ice cubes are pressed over each other, they unite to form one cube. Which of the following forces is responsible to hold them together?

(a) Dipole forces *(b)* van der Waals' forces

(c) Covalent forces *(d)* Hydrogen bond forces

34. Which of the following statements is wrong ?

(a) Using Lassaigne's test, nitrogen and sulphur present in organic compound can be tested

(b) Using Beilstein's test the presence of halogen in a compound can be tested

(c) In Lassaigne's filterate, the nitrogen, present in an organic compound is converted into NaCN

(d) In the estimation of carbon, an organic compound is heated with CaO in a combustion tube

35. Which of the following is aromatic?

(a) *(b)* *(c)* *(d)*

36. Which of the following can be used for the preparation of propane?

(a) $CH_3CH = CH_2 \xrightarrow[\text{(ii) } AgNO_3/NaOH]{\text{(i)}B_2H_6}$

(b) $CH_3CH_2CH_2Cl \xrightarrow[\text{(ii) } H_2O_2]{\text{(i)Mg/ether}}$

(c) $CH_3CH_2CH_2I \xrightarrow{\Delta}$

(d) $CH_3CH_2COONa \xrightarrow[\Delta]{NaOH(CaO)}$

37. Which of the following statements is incorrect with respect to S_N1 and S_N2 mechanisms for alkyl halide?

(a) A weak nucleophile and a protic solvent, increase the rate or favours S_N1 reaction.

(b) S_N1 reaction can be catalysed by some lewis acids.

(c) Competing reaction for an S_N2 reaction is rearrangement

(d) A strong nucleophile in an aprotic solvent increases the rate or favours S_N2 reaction

38. Among the following carbocations

I. $Ph_2\overset{+}{C}CH_2Me$

II. $PhCH_2CH_2\overset{+}{C}HPh$

III. $Ph_2CH\overset{+}{C}H_2$

IV. $Ph_2C(Me)\overset{+}{C}H_2$

The order of stability is

(a) IV > II > I > III *(b)* I > II > III > IV

(c) II > I> IV> III *(d)* I > IV > III > II

39. Which among of the following statements are true with respect to electronic displacement in a covalent bond?

I. Inductive effect operates through π- bond.

II. Resonance effect operates through σ- bond.

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III. Inductive effect operates through σ - bond.
IV. Resonance effect operates through π- bond.
(a) III and IV *(b)* I and II *(c)* II and IV *(d)* I and III

40. The best method for the separation of naphthalene and benzoic acid from their mixture is
(a) chromatography *(b)* crystallisation
(c) distillation *(d)* solvent extraction

41. Which of the following statements is not correct for biological functions of boron/boron compounds?
(a) It is an essential element in the nutrition of plants.
(b) Boric acid is extensively used as anti-bacterial.
(c) Aromatic organoborons are excellent insectisides
(d) Boron compounds are used in cancer therapy

42. The mass of potassium dichromate crystals required to oxidise 750 cm^3 of 0.6 M Mohr's salt solution is, (Given, molar mass; potassium dichromate = 294, Mohr's salt = 392)
(a) 0.49 g *(b)* 0.45 g *(c)* 22.05 g *(d)* 2.2 g

43. What is the minimum energy that photons must possess in order to produce photoelectric effect with platinum metal? The threshold frequency for platinum is $1.3 \times 10^{15} s^{-1}$.
(a) 3.6×10^{-13} erg *(b)* 8.2×10^{-13} erg
(c) 8.2×10^{-14} erg *(d)* 8.6×10^{-12} erg

44. Which of the following does not apply to metallic bond?
(a) Overlapping of valence orbitals
(b) Mobile valence electrons
(c) Delocalised electrons
(d) Highly directed bonds

45. For a cell reaction, (at 25°C)
$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$, the value of emf is 1 V.
If enthalpy of reaction is –197.5 kJ mol^{-1}, the change in standard molar entropy will be (in JK^{-1} mol^{-1})
(a) –11.5 *(b)* –15.1 *(c)* 11.5 *(d)* 15.1

Answers

1. (c)	**2.** (d)	**3.** (a)	**4.** (b)	**5.** (c)
6. (d)	**7.** (a)	**8.** (d)	**9.** (b)	**10.** (d)
11. (d)	**12.** (c)	**13.** (a)	**14.** (c)	**15.** (d)
16. (c)	**17.** (a)	**18.** (d)	**19.** (a)	**20.** (d)
21. (d)	**22.** (c)	**23.** (b)	**24.** (d)	**25.** (b)
26. (d)	**27.** (a)	**28.** (c)	**29.** (d)	**30.** (d)
31. (c)	**32.** (c)	**33.** (d)	**34.** (d)	**35.** (c)
36. (c)	**37.** (c)	**38.** (c)	**39.** (a)	**40.** (d)
41. (d)	**42.** (c)	**43.** (d)	**44.** (c)	**45.** (b)

Hints

1. $K_p = K_C (RT)^{\Delta n_g}$; $\Delta n_g = 1 - \frac{3}{2} = -\frac{1}{2}$.

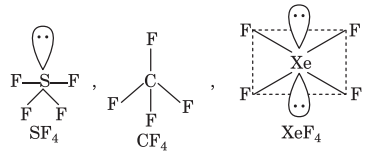
2. According to VSEPR theory, a lone pair occupies more space than a bond pair . It do so because it lies closer to the central atom.

4. Molar ratio $= \frac{\text{Number of moles of } H_2}{\text{Number of moles of } O_2}$

5. Standard enthalpy of formation of a compound is the change in the standard enthalpy when 1 mole of a compound is formed from the requisite amount of elements in their most stable state of aggregation at 1 bar pressure and 25°C.

6. Percentage of Fe in capsule
$= \frac{\text{Amount of Fe present in 100 g } (CHCOO)_2Fe}{400} \times 100$

7.



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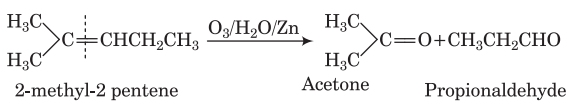

2-methyl-2 pentene Acetone Propionaldehyde

9. III is stabilised by conjugation and hydrogen bonding. I is less stable because double bond is not in conjugation with carbonyl group.

10. As the size increases, hydration enthalpy decreases.

11. Inert pair effect is more pronounced in heavier members like Pb.

12. Kjeldahl's method can not be used for the estimation of nitrogen in *azo* compounds and compounds containing nitrogen in the ring.

13. All alkali metals dissolve in liquid ammonia
$M + (x + y)NH_3 \longrightarrow M^+(NH_3)_x + \bar{e}(NH_3)y$
These electrons are excited to higher energy levels and the absorption of the photons occurs in the red region of the spectrum.
Thus, solution appears blue.

14. From Graham's law of effusion,
$\frac{r_B}{r_A} = \sqrt{\frac{M_A}{M_B}} = \frac{V_B\ t_A}{t_B.\ V_A}$

15. The knocking property of fuel, increases with decrease in octane number of a fuel.
The octane number, increases in the order.
Straight chain alkanes < branched chain alkanes < olefins < cycloalkanes < aromatic compounds.

16. Percentage of N in $C_3H_7N = \left(\frac{14}{57} \times 100\right)\%$
Percentage of N $= \frac{1}{8} \times \frac{\text{Volume of } N_2 \text{ at NTP}}{\text{Mass of substance}}$.

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17. $3MnO_4^- + 5C_2O_4^{2-} + 5Fe^{2+} + 24H^+ \longrightarrow 3Mn^{2+} + 10\,CO_2 + 5Fe^{3+} + 12H_2O$

19. Work done in reversible process is maximum.

20. $K_p = \dfrac{[p_{S_2}]^4}{[p_{S_8}]}$.

21.

	HCl +	$NaOH \longrightarrow$	$NaCl$ +	H_2O
Milliequivalent (M_{eq}) before reaction	$100 \times 0.1 = 10$	$9.9 \times 1 = 9.9$	0 9.9	0 9.9
M_{eq} after reaction	0.1	0		

$$[H]^+_{left} = \frac{0.1}{109.9}$$

$$pH = -\log [H^+]_{left}$$

23. $w_{rev} = -2.303\, nRT \log \dfrac{V_2}{V_1}$

$$n \text{ (Number of moles)} = \frac{\text{Mass (g)}}{\text{Molecular mass (g mol}^{-1})}$$

24. $E_1 = -1.312 \times 10^6 \text{ J mol}^{-1}$

$$E_2 = -\frac{1.312 \times 10^6 \times (1)^2}{(2)^2}$$

$$\Delta E = E_2 - E_1$$

25. The order of electrophilic addition (EA) is alkene > alkyne. But, if alkene has EWG (Electron withdrawing group), reactivity of alkenes become less than that of alkynes.

26. Molecules having odd number of electrons are paramagnetic in nature.

27. $NaHCO_3 + NaOH \longrightarrow \underset{\text{Neutral salt}}{Na_2CO_3} + H_2O$

28. For smaller value of b, volume correction $(V - nb)$ comes out to be large. So, molecules will show considerable volume which results in lesser compressibility.

29. $\Delta G^\circ = -2.303\, RT \log K$

30. Receptors, are the biotic or abiotic components, which affected adversely by the pollution.

31. $\underset{\text{OS of Mn} = +7}{2MnO_4^-}(aq) + 5H_2O_2(aq) + 16\,H^+(aq) \longrightarrow \underset{\text{OS of Mn} = +2}{2Mn^{2+}} + 5O_2(g) + 8H_2O$

32. For precipitation, ionic product should be greater than solubility product.

33. Ice has H-bonding therefore, when two ice cubes are pressed over each other, they unite to form one cube.

34. In the estimation of carbon , an organic compound is heated with CuO in a combustion tube.

35. For an species to be aromatic, it should obey the Huckel's rule. According to Huckel's rule, it should be cyclic, planar, conjugated and must contain $(4n + 2)$ π electrons.

36. Alkyl halides undergo reduction with red phosphorus and HI which results in the formation of alkane.

37. S_N1 reaction occurs through the formation of carbocation as intermediate. Hence, rearrangement occurs in S_N1 reaction and not in S_N2 reaction.

38. The order of stability of carbocations is,
3° benzylic > 2° benzylic > 2° carbocation >1° carbocation.

39. Inductive effect is a permanent effect which operates through σ- electrons while resonance involves delocalisation of π- electrons.

40. Both naphthalene and benzoic acid sublimes and are soluble in diethylether. When NaOH which is dissolved in water, is poured to ether mixture, benzoic acid forms sodium benzoate. Sodium benzoate is more soluble in water than ether and moves out of mixture.

41. Boron compounds are used in brain tumor therapy.

42. Mohr's salt is $FeSO_4.(NH_4)_2SO_4.6H_2O$ oxidisable part is only Fe^{2+}

$[Fe^{2+} \longrightarrow Fe^{3+} + e^-] \times 6$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$

43. The threshold frequency (ν_0) is the lowest frequency that photons may possess to produce photoelectric effect. The energy corresponding to this energy is the minimum energy (E).

$$E = h\nu_0$$

45. $\Delta G^\circ = -nFE^\circ$ also $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

Notice Board

JEE 2017 WITH NEW GUIDLINES

The Indian Institute of Technology_Madras will be conducting the Joint Entrance Examination (JEE) Advanced 2017. The dates for the main examination is not released by the CBSE yet.

The JEE cell at IIT Madras is in the process of finalising the events required for conducting the examination. Last year, IIT Guwahati conducted the JEE.

The Union Ministry of Human Resource Development (HRD Ministry) has decided that class 12th marks will not be a factor for determining rankings in JEE for admissions to engineering undergraduate courses from 2017. The present system of allotting 40% weightage to class 12th marks for determining ranks in JEE shall be dispensed.

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BRAiN TEASERS

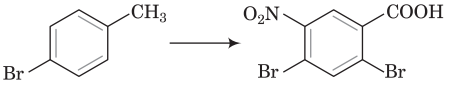
To boost up your rank in JEE Main and Advanced

1. The number of optically active stereoisomers of tartaric acid, (HOOC · CHOH · CHOH · COOH) is
(a) 4 *(b)* 2 *(c)* 1 *(d)* 3

2. A person is stuck to Antarctica in a shipwreck. He does not have any drinking water available. He finds an ethylene ($CH_2 = CH_2$) cylinder containing 4.2 g of ethylene. He decides to burn this ethylene to melt 1 kg of ice at −10°C. When a mole of ethylene is combusted, it releases 340 kcal of energy. Assuming, no heat is lost to the environment, the amount of water available for drinking is

[Given, specific heat capacity of ice = 2100 J kg^{-1} °C
Latent heat of fusion of ice at 0°C = 3.35×10^5 J kg^{-1}]
(a) 1 L
(b) 575 mL
(c) 990 mL
(d) It is not sufficient to melt the ice

3. The best sequence of reactions for the following conversion is [NSEC 2015]

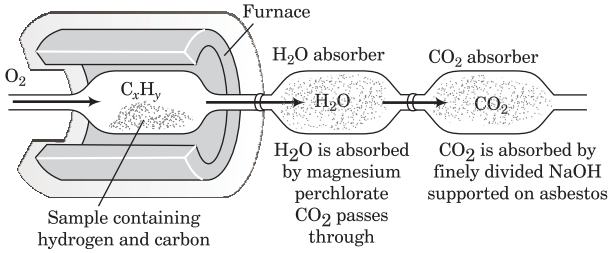


(a) (i) 1 mol $Br_2/FeBr_3$ (ii) $KMnO_4$, heat (iii) $HNO_3 + H_2SO_4$
(b) (i) $HNO_3 + H_2SO_4$ (ii) 1 mol $Br_2/FeBr_3$ (iii) $KMnO_4$, heat
(c) (i) $KMnO_4$, heat (ii) $HNO_3 + H_2SO_4$ (iii) 1 mol $Br_2/FeBr_3$
(d) (i) 1 mol $Br_2/FeBr_3$ (ii) $HNO_3 + H_2SO_4$ (iii) $KMnO_4$, heat

4. Caproic acid is responsible for the aroma of dirty gym socks and running shoes, contains carbon, hydrogen and oxygen. On combustion analysis, a 0.450 g sample of caproic acid gives 0.418 g of H_2O and 1.023 g of CO_2. What is the empirical formula of caproic acid?
(a) C_3H_6O *(b)* $C_6H_{12}O_2$
(c) C_2H_4O *(d)* $C_8H_{16}O_3$

5. You have been asked to determine the value of x in blue, hydrated copper (II) sulphate $CuSO_4 \cdot x H_2O$. For it, you have 1.023 g of the solid hydrated copper (II) sulphate. It is experimentally observed that after heating the solid thoroughly in a porcelain crucible, 0.654 g of nearly white, anhydrous copper (II) sulphate, $CuSO_4$ remains. The value of x per mole is
(a) 5 *(b)* 6 *(c)* 7 *(d)* 8

6. When 1.125 g of a liquid hydrocarbon, C_xH_y, was burned in an apparatus like shown in Fig. below.



3.447 g of CO_2 and 1.647 g of H_2O were produced. The molar mass of the compound was found to be 86.2 g/mol in a separate experiment. The molecular formula for the unknown hydrocarbon, C_xH_y is
(a) C_6H_{14} *(b)* C_5H_{12} *(c)* C_7H_{16} *(d)* C_8H_{18}

7. A 1.034 g sample of impure acid is dissolved in water and an acid-base indicator is added. The sample requires 34.47 mL of 0.485 M NaOH to reach the equivalence point. What is the mass of oxalic acid and what is its mass per cent in the sample?
(a) 0.553 g $H_2C_2O_4$ and 72.8% $H_2C_2O_4$
(b) 0.753 g $H_2C_2O_4$ and 72.8% $H_2C_2O_4$
(c) 0.553 g $H_2C_2O_4$ and 52% $H_2C_2O_4$
(d) 0.853 g $H_2C_2O_4$ and 52% $H_2C_2O_4$

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BRAIN TEASERS

8. How old is a fossil bone whose ^{14}C content is 15.0% of that living bone? Half-life of ^{14}C isotope is 5.73×10^3 yr

(a) 25488 yr *(b)* 15688 yr
(c) 388 yr *(d)* 6818 yr

9. 1, 2-dichloroethylene can exist in two forms

Choose the correct option(s).
(a) *A* is polar
(b) *B* is polar
(c) Both *A* and *B* are polar
(d) Neither *A* nor *B* is polar

10. Helium-filled balloons are used to carry scientific instruments high into the atmosphere. Suppose a balloon is launched when the temperature is 22.5°C and the barometric pressure is 754 mm of Hg. If the balloon's volume is 4.19×10^3 L (and no helium escapes from the balloon), what will be the volume at a height of 20 miles, where the pressure is 76.0 mm of Hg and the temperature is –33.0°C?

(a) 4.48×10^4L *(b)* 3.38×10^4L
(c) 5.55×10^3L *(d)* 5.53×10^4L

11. You are trying to determine, by experiment, the formula of a gaseous compound to replace chlorofluoro carbons in air. You have determined the empirical formula which is CHF_2, but now you want to know the molecular formula. To do this, you need the molar mass of the compound. You therefore, do another experiment and find that a 0.100 g sample of the compound exerts a pressure of 70.5 mm of Hg in a 256 mL container at 22.3°C. What is its molecular formula?

(a) $C_2H_2F_4$ *(b)* $C_3H_3F_6$ *(c)* $C_4H_4F_8$ *(d)* $C_5H_5F_{10}$

12. Consider the following reaction,

$$2Li(s) + 2D_2O(l) \longrightarrow 2LiOD(aq) + D_2(g)$$

What amount of D_2O (in moles) can be prepared from 0.125 g of Li metal in 15 mL of D_2O ($d = 1.11$ g/mL). If dry D_2 gas is captured in a 1450 mL flask at 22.0°C, what is the pressure of the gas in mm Hg? (Deuterium has an atomic weight of 2.0147 g/mol)
(a) 0.831 mole and 0.150 atm
(b) 0.725 mole and 0.150 atm
(c) 0.725 mole and 0.175 atm
(d) 0.735 mole and 0.175 atm

13. Sucrose, $C_{12}H_{22}O_{11}$, decomposes to fructose and glucose in acid solution with the rate law Rate = $k[C_{12}H_{22}O_{11}]$, $k = 0.216$ h^{-1} at 25°C.

What is the half-life of $C_{12}H_{22}O_{11}$ at this temperature. What amount of time is required for 87.5 per cent of the initial concentration of $C_{12}H_{22}O_{11}$ to decompose?
(a) 3.21 h and 9.63 h
(b) 4.21 h and 9.63 h
(c) 4.21 h and 3.21 h
(d) 4.21 h and 8.63 h

14. You put 925 mL of water (about 4 cupsful) in a pan at 100°C and the water slowly evaporates. How much energy must have been transferred as heat to vaporise the water?
(a) 3.00×10^3 kJ
(b) 2.00×10^3 kJ
(c) 4.00×10^3 kJ
(d) 5.00×10^3 kJ

15. Calculate the wavelength associated with an electron of mass $m = 9.109 \times 10^{-28}$ g that travels at 40 per cent of the speed of light.

(a) 6.07×10^{-12} m *(b)* 5.07×10^{-12} m
(c) 7.07×10^{-12} m *(d)* 8.08×10^{-12} m

CHEMISTRY IN action!

MOFs: New Hope for Carbonless Supercapacitor

Energy storage devices are called supercapacitors. These have become a hot area of research, in part because they can be charged rapidly and deliver intense bursts of power. All supercapacitors currently use components made of carbon, which require high temperatures and harsh chemicals to produce.

Now Researchers have for the first time developed a supercapacitor that uses no conductive carbon at all, and that could potentially produce more power than existing versions of this technology. These materials are called metal-organic frameworks, or MOFs, which are extremely porous, sponge-like structures. These materials have an extraordinary large surface area for their size, much greater than the carbon materials do. That is an essential characteristic for supercapacitors, whose performance depends on their surface area.

But MOFs have a major drawback for such applications i.e., they are not very electrically conductive, which is also an essential property for a material used in a capacitor. However the material did exhibit another needed characteristic for such electrodes, i.e., it conducts ions (atoms or molecules that carry a net electric charge) very well. This will help in creating the supercapacitor of our choice.

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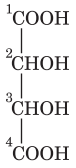
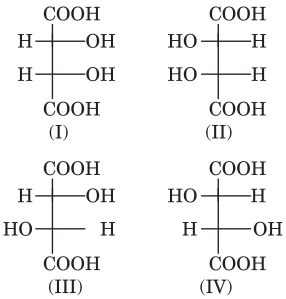
Answers with Explanation

1. ***(b)*** Tartaric acid contains two asymmetric carbon



atoms and thus, we assume there are $2^2 = 4$ stereoisomers which can be as follows



Though I and II seem to have different stereochemistry but in actual these are the same molecule. And further, there is a point of symmetry in the centre of I and II which means that the upper half and the lower half of the molecules is identical. Hence, these are optically inactive.

Optically inactive compounds with asymmetric C-atom are called *meso*-forms. This clearly shows that tartaric acid has only 3 stereoisomers, III and IV, the enantiomeric pair and the optically inactive *meso* I or *meso* II.

Hence, tartaric acid has only two optically active isomers, III and IV.

2. ***(b)*** $\underset{1\text{ mole}}{CH_2{=}CH_2} + 3O_2 \longrightarrow 2CO_2 + \underset{2\text{ mole}}{2H_2O} + 340\text{ kcal}$

Given, mass of ethylene = 4.2 g

Molar mass of ethylene = $2 \times 12 + 4 \times 1 = 28$ g

Moles of ethylene = $\frac{4.2\text{ g}}{28\text{ g}} = 0.15$ mole

Heat produced by 0.15 mole of ethylene

$= 340 \times 0.15 = 51$ kcal

$= 51 \times 4.184$ kJ

$= 213.384$ kJ

$= 213384$ J

Mass of ice = 1 kg, temperature of ice $(T_1) = -10°C$, $T_2 = 0°C$

$\Delta T_1 = T_2 - T_1 = 0°C - (-10°C)$

$= 10°C$

Heat required to raise the temperature of ice at $-10°$ to 0°C

$Q_1 = mC_{ice}\Delta T_1$

$= 1(\text{kg})(2100\text{ J kg}^{-1}\,°\text{C}) \times 10\,°\text{C}$

$= 21000$ J

Remaining heat after raising temperature of ice at $-10°C$ to 0°C = (213384 – 21000) J = 192384 J

Heat required to melt ice at 0°C to water at 0°C;

$Q_2 = mL_{ice}$

$= 1(\text{kg})(3.35 \times 10^5\text{ J kg}^{-1})$

$= 335000$ J

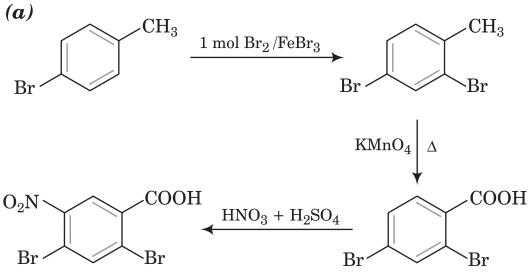
$\because$ 335000 J heat is consumed to melt 1000 mL (= 1000 g) of water

$\therefore$ 192384 J heat is consumed to melt = $\frac{1000}{335000} \times 192384$

$= 574.2805$ mL

$= 575$ mL of water.

3. ***(a)***



4. ***(a)*** You can solve this problem by going through the following steps :

Step I *Find the molar amounts of* C *and* H *in the sample.*

Moles of C

$= 1.023\text{ g of } CO_2 \times \frac{1\text{ mole of } CO_2}{44.01\text{ g } CO_2} \times \frac{1\text{ mole of C}}{1\text{ mole of } CO_2}$

$= 0.02324$ mol of C

Moles of H

$= 0.418\text{ g of } H_2O \times \frac{1\text{ mole of } H_2O}{18.02\text{ g of } H_2O} \times \frac{1\text{ mole of H}}{1\text{ mole of } H_2O}$

$= 0.0464$ mole of H

Step II *Find masses of* C, H *and* O *in the sample.*

Mass of C = $0.02324\text{ mole of C} \times \frac{12.01\text{ g of C}}{1\text{ mole of C}}$

$= 0.2791$ g of C

Mass of H = $0.0464\text{ mole of H} \times \frac{1.01\text{ g of H}}{1\text{ mole of H}}$

$= 0.0469$ g of H

Mass of O = 0.450 g – (0.2791 g + 0.0469 g)

$= 0.124$ g

Moles of O = $0.124\text{ g of O} \times \frac{1\text{ mole of O}}{16.00\text{ g of O}}$

$= 0.00775$ mole of O

Step III *Divide the moles of* C, H *and* O *by the smallest number of mole among them.*

$\underset{\frac{0.02324}{0.00775}}{C}\ \underset{\frac{0.0464}{0.00775}}{H}\ \underset{\frac{0.00775}{0.00775}}{O}$

$= C_3H_6O$

Hence, empirical formula of caproic acid is C_3H_6O.

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5. ***(a)*** Given, mass of hydrated compound = 1.023 g

Mass of anhydrous compound, $CuSO_4$ = 0.654 g

Mass of water = (1.023 – 0.654) g = 0.369 g

Molar mass of water = 18.02 g

Molar mass of $CuSO_4$ = 159.6 g

Number of moles present in 0.369 g of water = $\frac{0.369}{18.02}$

$= 0.02047 \simeq 0.0205$ mole of H_2O

Number of moles present in 0.654 g of $CuSO_4$ = $\frac{0.654}{159.6}$

$= 0.0040977 \simeq 0.00410$ mole of $CuSO_4$

For determining the value of x, take ratio of moles of the water to moles of $CuSO_4$

$$= \frac{0.0205 \text{ mol of } H_2O}{0.00410 \text{ mol of } CuSO_4} = \frac{5}{1}$$

The water to $CuSO_4$ ratio is 5 to 1, so the formula of the hydrated compound is $CuSO_4 . 5H_2O$. Its name is copper (II) sulphate pentahydrate.

6. ***(a)*** Number of moles of CO_2 isolated from the combustion.

$$= \frac{3.447 \text{ g}}{44.010 \text{ g mol}^{-1}} = 0.07832 \text{ mol of } CO_2$$

Number of moles of H_2O isolated from the combustion.

$$= \frac{1.647 \text{ g}}{18.015 \text{ g mol}^{-1}} = 0.09142 \text{ mol of } H_2O$$

For every mole of CO_2 isolated, 1 mole of C must have been present in the unknown compound.

∴ For 0.07832 mole of CO_2,

$= 1 \times 0.07832$ mol of C

= 0.07832 mol of C

For every mole of H_2O, 2 mole of H must have been present in the unknown compound.

∴ For 0.09142 mole of H_2O, mole of H present in the unknown compound

$= 2 \times 0.09142 = 0.1828$ mol of H

The original 1.125 g sample of compound therefore contained 0.07832 mole of C and 0.1828 mole of H.

To determine the empirical formula of the unknown compound, take the ratio of moles of H to moles of C

$$= \frac{0.1828 \text{ mole of H}}{0.07832 \text{ mole of C}} = \frac{2.335 \text{ mole of H}}{1.000 \text{ mole of C}}$$

Since, atoms combine to form molecules in whole number ratios, so, the transforming of this ratio $\left(\frac{2.335}{1}\right)$ to a whole number ratio by trial and error method.

Multiplying the numerator and denominator by 3 gives $\frac{7}{3}$, i.e. the empirical formula of the hydrocarbon is C_3H_7.

Comparing the experimental molar mass with the molar mass calculated from the empirical formula.

$$\frac{\text{Experimental molar mass}}{\text{Molar mass of } C_3H_7} = \frac{86.2 \text{ g / mol}}{43.1 \text{ g / mol}} = \frac{2}{1}$$

Hence, the molecular formula is twice the empirical formula. That is the molecular formula is $(C_3H_7)_2$ or C_6H_{14}.

7. ***(b)*** The balanced equation for the reaction of NaOH and $H_2C_2O_4$ is

$$H_2C_2O_4(aq) + 2NaOH(aq) \longrightarrow Na_2C_2O_4(aq) + 2H_2O(l)$$

Amount of NaOH = $C_{NaOH} \times V_{NaOH}$

$$= \frac{0.485 \text{ mole of NaOH}}{1 \text{ L}} \times 0.0344 \text{ L}$$

= 0.0167 mole of NaOH

The balanced equation for the reaction shows that 1 mole of oxalic acid requires 2 mole of sodium hydroxide.

0.0167 mole of NaOH requires

$$= \frac{1}{2} \times 0.0167 = 0.00836 \text{ mole of } H_2C_2O_4$$

The mass of oxalic acid which is found from the amount of the impure sample.

= mole of $H_2C_2O_4$ × molar mass of $H_2C_2O_4$

$= 0.00836 \times 90.04$

$= 0.753$ g of $H_2C_2O_4$

This mass of oxalic acid represents 72.8% of the total sample mass

$$= \left(\frac{0.753 \text{ g of } H_2C_2O_4}{1.034 \text{ g of sample}} \times 100\right)\%$$

$= 72.8\%$ of $H_2C_2O_4$

8. ***(b)*** Age of fossil bone can be calculated as

$$t_{age} = \frac{t_{1/2}}{0.693} \ln \frac{[C-14]_{living}}{[C-14]_{dead}}$$

$$t_{age} = \left\{\frac{5.73 \times 10^3}{0.693} \ln\left(\frac{100}{15}\right)\right\} \text{ yr}$$

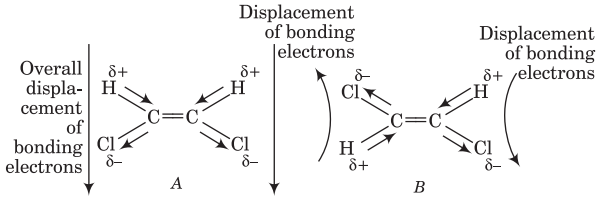
$t_{age} \approx 15688$ yr

9. ***(a)*** Here, the H and Cl-atoms are arranged around the C = C bonds with all bond angles 120° and all the atoms lie in a one plane.

The electronegativities of the atoms involved are in the order Cl(3.2) > C (2.5) > H (2.1). This means that the C—H and C—Cl bonds are polar with a net displacement of electron density away from the H-atoms and towards the Cl-atoms [$H^{\delta+} - C^{\delta-}$ and $C^{\delta+} - Cl^{\delta-}$].

In structure *A*, the Cl-atoms are located on one side of the molecule, so electrons in the H—C and C—Cl bonds are displaced towards the side of the molecule with Cl-atoms and away from the side with the H-atoms. Hence, molecule *A* is polar.

In structure *B*, the displacement of electron density toward the Cl-atom on one end of the molecule is counter balanced by an opposing displacement on the other end so, molecule *B* is not polar.



A, polar displacement of bonding electrons to one side of the molecule

B, non-polar, no net displacement of bonding electrons to one side of the molecule

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10. ***(b)***

Initial condition	Final condition
$V_1 = 4.19 \times 10^3$ L	$V_2 = 2$ L
$p_1 = 754$ mm of Hg	$p_2 = 76.0$ mm of Hg
$T_1 = 22.5°C$ (295.7 K)	$T_2 = -33.0°C$ (240.2 K)

We can rearrange the general gas law to calculate the new volume V_2

$$V_2 = \left(\frac{T_2}{p_2}\right) \times \left(\frac{p_1 V_1}{T_1}\right) = V_1 \times \frac{p_1}{p_2} \times \frac{T_2}{T_1}$$

$$= 4.19 \times 10^3 \text{ L} \left(\frac{754 \text{ mm of Hg}}{76 \text{ mm of Hg}}\right)\left(\frac{240.2 \text{ K}}{295.7 \text{ K}}\right)$$

$$= 3.38 \times 10^4 \text{ L}$$

11. ***(a)*** m = mass of gas = 0.100 g,

p = 70.5 mm of Hg = 0.0928 atm

[$\because$ 1 atm = 760 mm of Hg]

V = 256 mL = 0.256 L, T = 22.3°C = 295.5 K

Density of gas (d) = $\frac{0.100 \text{ g}}{0.256 \text{ L}}$ = 0.391 g/L

$\because$ Molar mass, $M = \frac{dRT}{p}$

$$= \frac{0.391 \times 0.082057 \times 295.5}{0.0928}$$

$$= 102 \text{ g/mol}$$

$$\frac{\text{Experimental molar mass}}{\text{Mass of 1 mole } CHF_2}$$

$$= \frac{102}{51} = 2 \text{ formula units of } CHF_2 \text{ per mole}$$

Therefore, the formula of the compound is $C_2H_2F_4$.

12. ***(a)*** Amount of Li in mole

$$= \frac{0.125 \text{ g of Li}}{6.941 \text{ g mol}^{-1} \text{ of Li}} = 0.0180 \text{ mole of Li}$$

Amount of D_2O in mole

$$= 15 \text{ mL } D_2O \left(\frac{1.11 \text{ g of } D_2O}{1 \text{ mL of } D_2O}\right)\left(\frac{1 \text{ mole of } D_2O}{20.03 \text{ g of } D_2O}\right)$$

$$= 0.831 \text{ mole of } D_2O$$

For deciding the limiting reactant,

Ratio of moles of reactants available

$$= \frac{0.831 \text{ mole of } D_2O}{0.0180 \text{ mole of Li}} = \frac{46.2 \text{ mole of } D_2O}{1 \text{ mole of Li}}$$

The balance equation shows that the ratio should be 1 mole of D_2O to 1 mole of Li. From the calculated values, we see that D_2O is in large excess, so Li is the limiting reactant.

Quantity of D_2 produced

$$= 0.0180 \text{ mole Li} \left(\frac{1 \text{ mole } D_2 \text{ produced}}{2 \text{ mole Li}}\right)$$

$$= 0.009 \text{ mole } D_2 \text{ produced}$$

$$p = \frac{nRT}{V} = \frac{0.009 \times 0.082057 \times 295.2}{1.45}$$

$$= 0.150 \text{ atm}$$

13. ***(a)*** The half-life for the reaction is

$$t_{1/2} = 0.693/k$$

$$= \frac{0.693}{0.216 \text{ h}^{-1}} = 3.21 \text{ h}$$

Three half-life must involve before the fraction remaining to 0.126, so

Time required

$$= (3 \times 3.21) \text{ h}$$

$$= 9.63 \text{ h}$$

14. ***(b)*** A volume of 925 mL (or 9.25×10^2 cm^3) is equivalent to 886 g and this mass is in turn equivalent to 49.2 mole of water.

Amount of water in mole

$$= 925 \text{ mL}\left(\frac{0.958 \text{ g}}{1 \text{ mL}}\right)\left(\frac{1 \text{ mol}}{18.02 \text{ g}}\right)$$

$$= 49.2 \text{ mole of } H_2O$$

Therefore, the amount of energy required is

49.2 mole of H_2O (40.7 kJ mol^{-1})

$$= 2.00 \times 10^3 \text{ kJ}$$

15. ***(a)*** Electron mass = 9.109×10^{-31} kg

Electron speed = 40 per cent of light speed

$$= \frac{40 \times 2.998 \times 10^8}{100} \text{ ms}^{-1}$$

$$= 1.20 \times 10^8 \text{ ms}^{-1}$$

Substituting these values into de-Broglie's equation we have,

$$\lambda = \frac{h}{mv}$$

$$= \frac{6.626 \times 10^{-34} \text{ (kg m}^2/\text{s}^2)(\text{s})}{(9.109 \times 10^{-31} \text{ kg})(1.20 \times 10^8 \text{ m/s})}$$

$$= 6.07 \times 10^{-12} \text{ m}$$

In nanometers, the wavelength is

$$\lambda = (6.07 \times 10^{-22} \text{ m})\ (1.00 \times 10^9 \text{nm/ m})$$

$$= 6.07 \times 10^{-3} \text{ nm}$$

AMAZING REALITIES

The rarest naturally-occurring element in the Earth's crust is astatine. Named after the Greek word for unstable (astatos), Astatine is a naturally occurring semi-metal that results from the decay of uranium and thorium. In its most stable form, the element has a half-time of only 8.1 hours. The entire crust appears to contain about 28 g of the element. If scientists ever have to use it, they basically have to make it from scratch. Only 0.00000005 grams of astatine have been made so far.

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FUN ARCADE

Marie Curie

(07/11/1867-04/07/1934)

- Marie Sklodowska Curie (better known as Marie Curie), was born in Warsaw in modern day Poland on November 7, 1867.
- She was the first women to win Nobel Prize twice in Physics and Chemistry.
- She was the part of the Curie clan legacy of five Nobel Prizes.
- Her early researches, together with her husband (Pierre Curie) were often performed under difficult conditions.
- The laboratory arrangements were poor and both had to undertake much teaching to earn a livelihood.
- Marie Curie was fascinated with the work of Henri Becquerel, a French physicist, who discovered that uranium cast off rays, weaker rays than X-rays found by Wilhelm Conrad Roentgen.
- Marie Curie made history in 1903 when she became the first woman to receive the Nobel Prize in Physics. She won the prestigious honor alongwith her husband and Henri Becquerel, for their work on radioactivity. Curie received another great honor in 1911, winning her second Nobel Prize, in Chemistry. She received this award for her discovery of radium and Polonium, and became the first scientist to win Nobel Prize twice.
- She was died in 1934, at a sanatorium in Sancellemoz, France, due to aplastic anaemia. She was suffered from this disease because she brought on by exposure to radiation while carrying test-tubes of radium in her pockets during research, and in the course of her service in World War I mobile X-ray units that she had set-up.

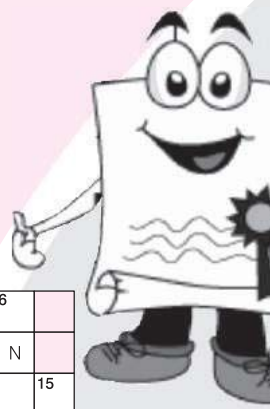
CROSSWORD

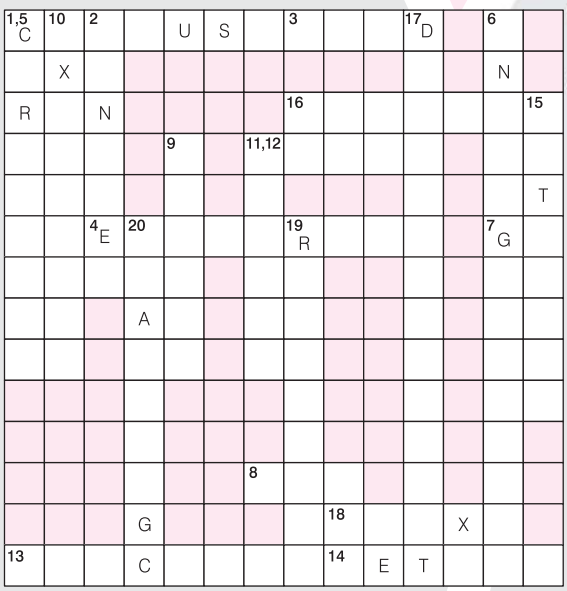
ACROSS

1. Burning something in air. (10)
3. An atom with an excess positive or negative electric charge. (3)
4. A tiny particle, much lighter than an atom, that carries a negative electric charge. (8)
8. Fossil fuel raw material used to make most plastics. (3)
11. Produce palatable food by application of heat. (4)
13. Where new chemical products formed from chemical reactants. (8)
14. A mixture of hydrocarbons used as a fuel in internal combustion engine. (6)
15. A substance that increases the rate of a chemical reaction but not used up itself. (8)
16. General name for a polymer like polythene, polypropylene nylon and polystyrene. (7)
18. A metal oxide obtained by heating an ore to high temperature. (4)

DOWN

2. A chemical building block used to form plastics. (7)
5. To react metal with the atmosphere and water. (9)
6. A negative ion that travels towards the positive anode. (5)
7. Fossil fuel used in jet air craft, also called kerosene. (8)
9. A fraction of crude oil that is used in buses and lorries as a fuel. (6)
10. Chemical reaction with oxygen. (9)
12. A positive ion that travels towards the negative cathode. (6)
17. A technique used to separate liquids with different boiling points. (12)
19. The preservation of integrity of the spatial arrangement of bonds to an asymmetric centre during a chemical reaction. (7)
20. A process by which soluble constituents of soil are removed by liquid. (8)





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PUZZLES TO PUZZLE YOU

1 A particular coal contains 2.5% sulphur by mass when this coal is burnt at a power plant, the sulphur is converted into sulphur dioxide gas, which is a pollutant. To reduce sulphur dioxide emission, calcium oxide (lime) is used. The sulphur dioxide reacts with calcium oxide to form solid calcium sulphate. If the coal is burned in a power plant that uses 2000 tons of coal per day, what mass of calcium oxide is required daily to eliminate the sulphur dioxide?

2 The mass percentage of chloride ion in a 25 mL sample of sea water was determined by titrating the sample with silver nitrate precipitating silver chloride. It took 42.58 mL of 0.2997 M silver nitrate solution to reach the equivalence point in the titration. What is the mass percentage of chloride ion in the sea water if its density is 1.025 g/mL?

3 An organic compound is analysed and found to contain 66.7% carbon, 11.2% hydrogen, and 22.1% oxygen by mass. The compound boils at 79.6°C. At 100°C and 0.970 atm, the vapour has a density of 2.28 g/L. The compound has a carbonyl group which cannot be oxidised to a carboxylic acid. Suggest a structure of the compound.

4 Cocaine is a weak organic base whose molecular formula is $C_{17}H_{21}NO_4$. An aqueous solution of cocaine was found to have pH of 8.53 and an osmotic pressure of 52.7 torr at 15°C. Calculate K_b for cocaine.

October 2016 issue Answers

(Crossword)

1, 12 N	O	R	M	13 A	L	I	T	Y											
I				C															
D				2 I	O	N	I	C				3 A	C	E	T	14 O	N	15 E	
4 O	R	E		D												X		L	
C							16 F		17 S					18 H		Y		U	
A				5, 19 N	I	T	R	O	L	I	U	M		A		G		E	
R				E			O		A					D		E		N	
B				S			T		G		20 C			R		N		T	
O				S			H				Y			O					
R				L		6 D	E	P	R	E	S	S	E	N	T				
A				E			R				T								
N			21 C		R'			S				E							
E			Y		S						7 I	N	V	A	R				
S			C								N						22 P		
	8 B	L	O	T	I	N				9 P	E	R	N	I	C	I	O	U	S
		O															I		
		T															S		
		10 R	E	A	C	T	O	R									E		
		O																	
		11 N	I	C	O	T	I	N	E										

Puzzles to Puzzle you

1. A = Blue; B = Red **2.** (i) 100 (ii) 997680 J mol^{-1}

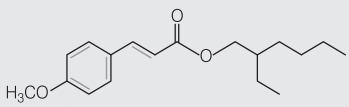
3. 3.310×10^8 yr

4. $C_3H_5(OH)_3 \xrightarrow[-3CH_3COOH]{3(CH_3(CO)_2O)} C_3H_5(OCOCH_3)_3$

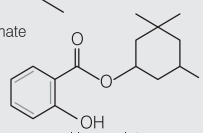
The acetyl derivative corresponds to $C_9H_{14}O_6$, the product actually obtained. As the organic compound contains three carbon atoms, so one —OH group is attached to each one of there, because more than one —OH at the same carbon atom makes the molecule unstable. So, the given compound is glycerol or 1, 2, 3 propanediol.

Chemical Connect : Ultraviolet Sunscreens and Sunblocks

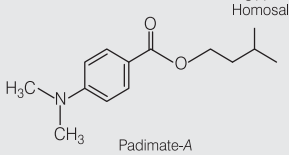
- You may have often seen some dark patches or felt burning or irritation in your skin while going out in the sun for a long time. These problems are seen specially in a particular portion of skin which directly come with contact to sun.
- Some people develop these problems during short exposure in sun.
- The main reason for these skin problems is Ultraviolet (UV) radiations.
- The UV radiation penetrating the earth's ozone layer, is arbitrarily divided into two regions namely UVB (290-320 nm) and UVA (320-400 nm)
- UVB, a more energetic form of radiation than UVA. It creates more radicals and hence does more oxidative damage.
- UVB radiation interacts directly with biomolecules of the skin and eyes, causing skin cancer, skin aging, eye damage leading to cataracts (clouding of lense in the eye leading decrease in vision). It delayed sunburn that appears 12-24 h after exposure.
- UVA radiation, by contrast, causes tanning. It also damages skin though much less efficiently than UVB.
- Staying out of the sun is one remedy but not a very practical one. There are many sun screen and sun block skin products available in the market now. These sun screens protect our skin from damage.
- Sun blocks are opaque substances such as zinc oxide titanium oxide, iron oxide, that protect by forming a shield on the skin. This shield reflects and scatters incident radiations. In essence sun blocks provide physical protection against sun exposure, including both visible and ultraviolet light. Sun screens are substance that chemically absorb ultraviolet light in the top layer of epidermis, protecting the underlying layers.
- These products are rated by skin protecting factor (SPF). SPF is the ratio of time required to get a sunburn with and without the protection applied. Thus, SPF-15 means, it takes 15 times as long to get a burn with the protection applied.
- Sun screens contain certain active ingredients that absorb UV radiations. And they do a pretty good, though not a perfect job. Some chemicals that block UVB don't absorb UVA, and some that block UVA let in UVB.
- There are three common esters used as UVB-screening agents, which are given below.



Octyl *p*-methoxycinnamate



Homosalate



Padimate-A

- What you want is a full-spectrum sun screen-one that contain ingredients that block both UVA and UVB. In general sun screens with a SPF of 15 or higher contain both UVA and UVB blocker while those with SPF below 15 contains UVB blockers only.

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GENERAL PRINCIPLES AND PROCESSES OF ISOLATION OF ELEMENTS

This section of magazine is aimed to increase the connectivity between reader and NCERT Textbook. Readers are advised to solve these questions with the help of references of NCERT books given at the end of the section.

1. Which of the following are the major steps to extract and isolate metals from their ores?
(a) Concentration of the ore
(b) Isolation of the metal from its concentrated ore
(c) Purification of the metal
(d) All of the above

2. Impure form of Al_2O_3 contain chromium (Cr) as impurity called
(a) sapphire *(b)* ruby *(c)* diamond *(d)* topaz

3. Match the following Columns.

Column I (Metal)	Column II (Ore)	Column III (Composition)
A. Aluminium	p. Malachite	I. Fe_3O_4
B. Iron	q. Bauxite	II. $CuCO_3 \cdot Cu(OH)_2$
C. Copper	r. Magnetite	III. $AlO_x(OH)_{3-2x}$ (where $0<x<1$)
D. Zinc	s. Calamine	IV. $ZnCO_3$

Codes

	A	B	C	D
(a)	q,III	r,I	p,II	s,IV
(b)	p,I	q,II	r,III	s,IV
(c)	s,IV	r,III	q,II	p,I
(d)	q,I	r,III	p,IV	s,II

4. Removal of unwanted materials from the ore is known as …*A*… dressing or benefaction. It involves several steps and selection of these steps depends upon the differences in …*B*… properties of the compound of the …*C*… present and that of the …*D*… .
Identify *A*, *B*, *C* and *D*.

A	B	C	D
(a) Filtration	physical	non-metal	ore
(b) Concentration	chemical	non-metal	gangue
(c) Concentration	physical	metal	gangue
(d) Filtration	chemical	metal	ore

5. Froth floatation method is used for removing gangue from sulphide ores. In this process, a suspension of the powdered ore is made with water. To it pine oil and aniline are added to the suspension, which act respectively as,
(a) Collectors and froth stabilisers
(b) Froth stabilisers and collectors
(c) Collectors and depressants
(d) Froth stabilisers and depressants

6. To separate two sulphide ores, we adjust the proportion of oil to water or by using depressants. For example in case of ore containing ZnS and PbS we use
(a) Na_2S
(b) NaCN
(c) Xanthates
(d) fatty acids

7. Which of the following reactions is not involved in the process of leaching of alumina from bauxite.
(a) $Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \longrightarrow 2Na[Al(OH)_4](aq)$
(b) $2Na[Al(OH)_4](aq) + CO_2 \longrightarrow Al_2O_3 \cdot xH_2O(s) + 2NaHCO_3(aq)$
(c) $Al_2O_3 \cdot xH_2O(s) \xrightarrow{1470K} Al_2O_3(s) + xH_2O(g)$
(d) $2Al(s) + 12CN^-(aq) + 3H_2O + O_2(g) \longrightarrow 4[Al(CN)_3]^-(aq) + 4OH^-(aq)$

8. The sulphide ores of copper are heated in reverberatory furnace. If the ore contains iron, it is mixed with a compound (*Z*) before heating, so that iron oxide slages of the compound (*Z*) is
(a) $FeSiO_3$
(b) Cu_2S
(c) SiO_2
(d) Mixture of SiO_2 and $FeSiO_3$

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9. Some basic concepts of thermodynamics help us in understanding the theory of metallurgical transformations. Gibbs energy is the most significant term, which can be described by the equation.
(a) $\Delta G = \Delta H - T\Delta S$
(b) $\Delta G^\circ = -RT \ln K$
(c) Both (a) and (b)
(d) None of the above

10. The reducing agent forms its oxide when the metal oxide is reduced. The role of reducing agent is
(a) to provide ΔG° negative and large enough
(b) to provide ΔS° negative and large enough
(c) to provide ΔH° positive and large enough
(d) to provide K (Equilibrium constant) negative and large enough

11. Although thermodynamically, feasible magnesium can reduce alumina (Al_2O_3), but in practice, Mg is not used for reduction of alumina because
(a) reaction is exothermic in nature
(b) process require so, high temperature that it becomes uneconomical
(c) the free energy of the reaction is positive
(d) process requires very low temperature, which is not possible to achieve

12. In blast furnace, ...*A*... of iron oxides takes place in different temperature ranges. Hot air is blown from the ...*B*... of the furnace and ...*C*... is burnt to give temperature upto about ...*D*... in the lower portion itself.

Indentity *A*, *B*, *C* and *D*.

	A	B	C	D
(a)	Oxidation	top	metal	1100 K
(b)	Reduction	top	metal	1100 K
(c)	Oxidation	bottom	coke	2200 K
(d)	Reduction	bottom	coke	2200 K

13. During extraction of iron from Fe_3O_4, in a blast furnace, select the incorrect reaction
(a) $FeO(s) + CO \longrightarrow Fe + CO_2$
(b) $Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$
(c) $3Fe + 4CO_2 \longrightarrow Fe_3O_4 + 4CO$
(d) $Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2$

14. Carbon content in cast iron is
(a) more than pig-iron *(b)* less than pig-iron
(c) free from carbon *(d)* about 10%

15. Which of the following process is used for extraction of copper oxide from its sulphide ore?
(a) Roasting *(b)* Calcination
(c) Both (a) and (b) *(d)* None of these

16. Which of the following reaction is not a part of extraction of copper from its sulphide ores?
(a) $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$
(b) $2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$
(c) $4Cu + O_2 \longrightarrow 2Cu_2O$
(d) All are correct

17. The reaction $Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$; ($\Delta G^\circ = -421$kJ), is thermodynamically feasible but does not take place at room temperature because
(a) requirement of activation energy, is achieved above the room temperature
(b) free energy for the reaction is zero at room temperature
(c) ΔH and ΔS at room temperature is equal to zero
(d) All are correct

18. During electrolysis for extraction of metals, flux is added
(a) for making the molten mass more conducting
(b) to act as reducing agent
(c) to act as oxidising agent
(d) to act as electrode for the proper collection of metal

19. For metallurgy of aluminium by Hall-Heroult process, which of the following statements is incorrect ?
(a) Na_3AlF_6 is used to lower the melting point of mixture
(b) CO and CO_2 are produced at anode
(c) 0.5 kg of carbon-anode is burnt away for the production of each kilogram of aluminium
(d) Electrolysis of molten mass is carried out in an electrolytic cell using iron electrodes

20. Copper low grade ores and scraps are leached out by using
(a) acids like HCl *(b)* bacteria
(c) Both (a) and (b) *(d)* None of these

21. To extract chlorine gas by electrolysis of brine is based on
(a) reduction of chlorine, present in brine
(b) oxidation of chlorine, present in brine
(c) we will not get chlorine by electrolysis of brine
(d) reduction of oxygen, present in solution

22. In early days extraction of gold and silver involves leaching the metal with
(a) CO_2 *(b)* H_2O *(c)* CN^- *(d)* All of these

23. For obtaining metals of high purity, distillation is used for
(a) high boiling metals
(b) low boiling metals
(c) metals present in crystalline form
(d) metal and impurity have same boiling point

24. Liquation method to get pure metal is used to purify the metals
(a) Having low melting point
(b) Having high melting point
(c) Which are non-conductor of heat
(d) Which are non-conductor of electricity

25. In electrolytic refining method, the impure metal is made to act as anode. A strip of same metal in pure form is used as cathode. They are put in a suitable electrolytic both containing soluble of the same salt. Identify the incorrect statement.

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(a) The more basic metal remains in the solution and less basic ones go to the anode mud
(b) The reactions occurs at anode and cathode can be expressed as
Anode $M \longrightarrow M^{n+} + ne^-$
Cathode $M^{n+} + ne^- \longrightarrow M$
(c) A strip of pure metal is used as cathode
(d) Reduction occurs at anode electrode

26. Copper is refined using electrolytic method, identify the correct statement about this process.
(a) Impurities from the blister copper deposit as anode mud
(b) Anodes are of impure copper and pure copper strips are taken as cathode
(c) Commonly, electrolyte is an acidified solution of copper sulphate
(d) All of the above

27. The method useful for producing semiconductors and other metals of very high purity, e.g. germanium, silicon, etc. by moving a circular heater around the impure metal is called
(a) van Arkel method
(b) Mond's process
(c) Zone refining
(d) Vapour phase refining

28. Some metals are converted into volatile compounds and collected elsewhere. It is then decomposed to give pure metal. The basic requirement for such a purification is/are
(a) the metal should form a volatile compound with an available reagent
(b) the volatile compound should be easily decomposable, so that the recovery is easy
(c) Both (a) and (b)
(d) All are incorrect

29. Mond's process and van Arkel method for refining are respectively related with the metals
(a) nickel and zirconium
(b) zirconium and nickel
(c) titanium and iodine
(d) titanium and nickel

30. Identify the correct statement.
(a) Aluminium is used for extraction of chromium and manganese.
(b) Copper is used to make alloys like brass, bronze and coinage alloys
(c) Zinc dust is used as a reducing agent in the manufacture of dye-stuffs, paints etc.
(d) All of the above

Correct Answers along with NCERT Textbook Reference

1.	***(d)*** Page No. 147	Introduction
2.	***(b)*** Page No. 148-(6.1)	Occurrence of metals
3.	***(a)*** Page No. 148-(6.1)	Occurrence of metals
4.	***(c)*** Page No. 148-(6.2)	Concentration of ore
5.	***(a)*** Page No. 149-(6.2.3)	Froth floatation method
6.	***(b)*** Page No. 149-(6.2.3)	Froth floatation method
7.	***(d)*** Page No. 150-(6.2.4)	Leaching
8.	***(c)*** Page No. 151-(6.3)	Extraction of crude metal from concentrated ore
9.	***(c)*** Page No. 151-(6.4)	Thermodynamic principles of metallurgy
10.	***(a)*** Page No. 153-(6.4)	Thermodynamic principles of metallurgy
11.	***(b)*** Page No. 154-(Ex. 6.2)	Thermodynamic principles of metallurgy
12.	***(d)*** Page No. 155-(6.4.1)	Applications (a) Extraction of iron from its oxides
13.	***(c)*** Page No. 155-156 (6.4.1)	Applications (a) Extraction of iron from its oxides
14.	***(b)*** Page No. 156-(6.4.1)	Applications, (a) Extraction of iron from its oxides
15.	***(a)*** Page No. 156-(6.2.1)	Applications, (b) Extraction of copper from cuprous oxide
16.	***(c)*** Page No. 156-157 (6.4.1)	Applications, (b) Extraction of copper from cuprous oxide
17.	***(a)*** Page No. 157-(6.4.1)	(Intex Questions-6.3)
18.	***(a)*** Page No. 157-(6.5)	Electrochemical principles of metallurgy
19.	***(d)*** Page No. 158-(6.5)	Electrochemical principles of metallurgy (Aluminium)
20.	***(c)*** Page No. 158-(6.5)	Electrochemical principles of metallurgy (copper from low grade ores and scraps)
21.	***(b)*** Page No. 158-(6.6)	Oxidation-Reduction
22.	***(c)*** Page No. 159-(6.6)	Oxidation-Reduction
23.	***(b)*** Page No. 159-(6.7)	Refining (distillation)
24.	***(a)*** Page No. 159-(6.7)	Refining (Liquation)
25.	***(d)*** Page No. 159-(6.7)	Refining (Electrolytic refining)
26.	***(d)*** Page No. 159-(6.7)	Refining (Electrolytic refining)
27.	***(c)*** Page No. 160-(6.7)	Refining (Zone-Refining)
28.	***(c)*** Page No. 160-(6.7)	Refining (vapour phase refining)
29.	***(a)*** Page No. 160-(6.7)	Refining (Mond's process and van Arkel method)
30.	***(d)*** Page No. 162-(6.8)	Uses of aluminium, copper, zine and iron

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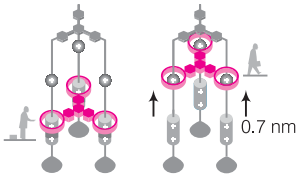
Continued from Page 02

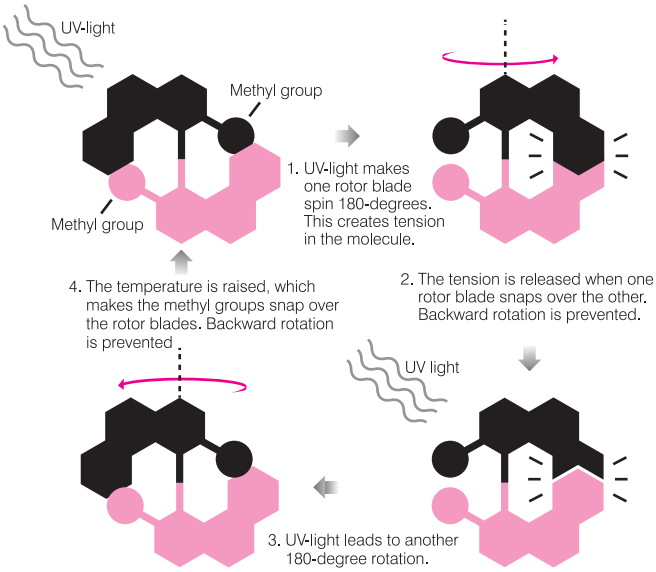
the ring so that it remained on the molecular axle. He had thus, with a high yield, created a rotaxane: a ring-shaped molecule that is mechanically attached to an axle.



Since 1994, Stoddart's research group has used various rotaxanes to construct numerous molecular machines, including a lift (2004,), which can raise itself 0.7 nanometres above a surface, and an artificial muscle (2005), where rotaxanes bend a very thin gold lamina.

BEN FERINGA BUILDS THE FIRST MOLECULAR MOTORS

Ben Feringa produced the first molecular motor *via* using a number of clever tricks to get it to spin in one and the same direction. Normally, molecules' movements are governed by chance. On average, a spinning molecule moves as many times to the right as to the left. But Ben Feringa designed a molecule that was mechanically constructed to spin in a particular direction as shown below –



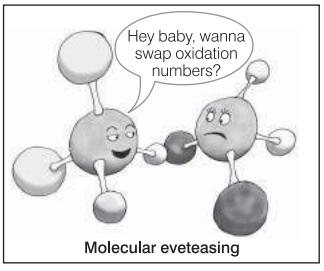
The molecule was composed of something that can be likened to two small rotor blades, two flat chemical structures that were joined with a double bond between two carbon atoms. A methyl group was attached to each rotor blade. These, and the parts of the rotor blade, worked like ratchets that forced the molecule to keep rotating in the same direction.

When the molecule was exposed to a pulse of ultraviolet light, one rotor blade jumped 180 degrees around the central double bond. Then the ratchet moved into position. With the next light pulse, the rotor blade jumped another 180 degrees. And so it continued, round and round in the same direction.

TOWARDS A NEW AND VIBRANT CHEMISTRY

An important part of the development that has resulted in the Nobel Prize in Chemistry 2016 is that researchers have driven molecular systems away from what is called equilibrium. All chemical systems strive for equilibrium – a lower energy state – but this is somewhat of a stalemate. We can take life as an example.

When we eat, the body's molecules extract the energy from the food and push our molecular systems away from equilibrium, to higher energy levels. The biomolecules then use the energy to drive the chemical reactions necessary for the body to work. If the body was in chemical equilibrium, we'd be dead. Just like the molecules of life, Sauvage's, Stoddart's and Feringa's artificial molecular sytems perform a controlled task. Chemistry has thus taken the first steps into a new world.



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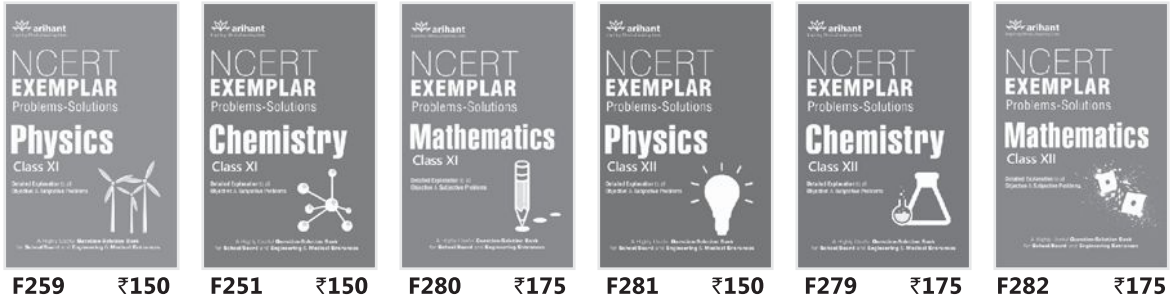

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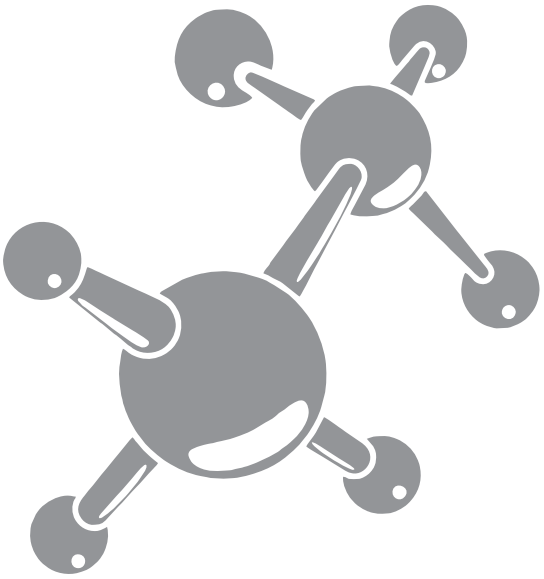
FOR CLASS XI



Topicwise Collection of best Subjective Problems

Very Short Answer Type [1 Mark]

1. Name the element of group-13 which exists as liquid over a wide range of temperature and used for measuring high temperature.
2. Why Pb^{4+} acts as an oxidising agent?
3. Write the bond order for CO_2 and CO_3^{2-}.
4. Name the element of group-13 which is not likely to act as central atom in MF_6.
5. Between Al and Ga, which element has higher first ionisation energy?
6. Write the name of the anhydride of H_2CO_3.

Very Short Answer Type [2 Marks]

7. Write two differences between allotropes and iso-structural species.
8. Will, boric-acid is a protic-acid in aqueous solution? If not, explain its acidic nature in short.
9. Write reactions to establish that aluminium is amphoteric in nature.
10. Between BBr_3 and BF_3, which one is more stronger Lewis acid and why?
11. What is inorganic benzene, draw its structure and write one reaction of its preparation.
12. Why diamond and graphite show different hybridisation for carbon in there structures.
13. Write reaction(s) for preparation of
    (i) water gas
    (ii) producer gas

Short Answer Type [3 Marks]

14. Why boron show anomalous behaviour with respect to other members of the same group?
15. Explain structure of di-borane?
16. What are electron deficient compounds? Are BCl_3 and $SiCl_4$ are electron deficient species? Explain. [NCERT Text Book]
17. Between BF_3 and $SiCl_4$, which one is not hydrolysed by water? Also explain the reason.
18. BF_3 can form $H_3N \longrightarrow BF_3$ but CCl_4 does not form any such coordinate compound with NH_3. Explain the reason.
19. Draw resonating structures of CO_3^{2-} and HCO_3^-. [NCERT Text Book]
20. Which is more basic, $N(SiH_3)_3$ or $N(CH_3)_3$, give reason in support of your answer.
21. Is CO_2 and SiO_2 are iso-structural, if not explain why?
22. (i) Can aluminium container be used to carry HNO_3 (conc.)?
    (ii) What happen when aluminium is treated with con $\cdot HNO_3$?
23. A compound (A) of boron reacts with NMe_3 to give an adduct (B), which on hydrolysis gives a compound (C) and hydrogen gas, compound (C) is an acid.
    Identify the compounds (A), (B), (C). Give the reactions involved. [NCERT Exemplar] [HOTS]
24. Is B—F bond length in BF_3 and BF_4^- are different, if so, suggest the reason?

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25. Account for the following, [NCERT Exemplar]
(i) CO is more harmful than CO_2.
(ii) Carbon show more catenation than other members of group-14?
(iii) PbO_2 is a stronger oxidising agent than SnO_2.

Value Based Type [4 Marks]

26. Rakhi and her father went to a shop to purchase a battery for their invertor. The shopkeeper showed them two types of batteries, one with cadmium plates and other with lead plates.

The battery with lead plates was cheaper than the cadmium plated battery. Rakhi's father wanted to purchase lead battery as it was cheaper. But Rakhi, as a student of chemistry, was against to her father's decision and suggested him to buy cadmium battery.

After reading the above passage answer the following questions.
(a) Why, Rakhi suggested to her father to buy the expensive cadmium plate battery. Give two reasons?
(b) What are the values associated with her in above decision?

Long Answer Type [5 Marks]

27. What are silicones? How are they prepared? Write its properties and uses.

28. Account for the following,
(i) CO_2 is a gas while SiO_2 is a solid. (1½)
(ii) Graphite is used as Lubricant. (1)
(iii) CO is more stable than SiO. (1½)
(iv) CO_2 is responsible for global warming. (1)
[NCERT Exemplar] [HOTS]

29. Write balanced equation for
(i) $BF_3 + LiH \longrightarrow$ (ii) $B_2H_6 + H_2O \longrightarrow$
(iii) $NaH + B_2H_6 \longrightarrow$ (iv) $H_3BO_3 \xrightarrow{\Delta}$
(v) $B_2H_6 + 2NH_3 \longrightarrow$ [NCERT Text Book]

30. (i) Aluminium trifluoride is insoluble in HF but dissolved on addition of NaF.
Aluminium trifluoride precipitates out from the resulting solution when gaseous BF_3 is bubbled through. Given reasons. (3)
(ii) Why, +1 oxidation state for group-13 elements becomes more and more stable as we move down the group? (1)
(iii) Why boron does not exist as B^{3+} ion? (1)
[NCERT Text Book] [HOTS]

Solutions

1. Gallium (Ga) is the element exists as liquid over a wide range of temperature and is used for measuring high temperature.

2. Due to inert pair effect, Pb^{2+} is more stable than Pb^{4+}, thus Pb^{4+} will easily reduced to Pb^{2+} and act as an oxidising agent.

3. $\because$ Bond order (B.O) $= \dfrac{\text{Total number of bonds}}{\text{Number of sigma}(\sigma)\text{ bonds}}$

Thus, B.O for $CO_3^{2-} = \dfrac{4}{3} = 1.33$

B.O for $CO_2 = \dfrac{4}{2} = 2.00$

4. Among group-13 elements, boron cannot act as central atom in MF_6, as it cannot expand its octet due to absence of *d*-orbitals.

5. Gallium (Ga) has higher first ionisation energy because of smaller size as compared to Al which is due to poor screening by inner *d*-orbitals.

6. Carbon dioxide (CO_2) is anhydride of H_2CO_3, as

$$H_2CO_3 \xrightarrow[-H_2O]{} CO_2$$

7. **Allotropes** Any element which exist in two or more than two structures having different physical but same chemical properties are called allotropes. e.g. carbon has many allotropes like diamond, graphite etc.

Iso-structural Species having same number of lone pair of electrons and same hybridisation of central atom show similar structures are called *iso*-structurals most of their physical and chemical properties are different.
e.g. (i) H_3O^+ and NH_3 (ii) NH_4^+ and CH_4

8. No, boric acid is not a 'protic acid' as it will not provide protons (H^+ ions) in aqueous solution. The protons produced in the aqueous solution are due to acceptance of OH^- ion of water by the boric acid.

$$B(OH)_3 + H_2O \longrightarrow [B(OH)_4]^- + H^+$$

9. Aluminium is amphoteric in nature as it reacts with acids and bases both, e.g.

(i) $2Al + \underset{\text{(Acid)}}{6HCl}\ (aq) \longrightarrow 2Al^{3+}(aq) + 6Cl^-(aq) + 3H_2(aq)$

(ii) $2Al + \underset{\text{(Base)}}{2NaOH}\ (aq) + 6H_2O \longrightarrow \underset{\text{Sodium tetrahydroxoaluminate (III)}}{2Na^+[Al(OH)_4]^-}\ (aq) + 3H_2(g)$

10. BBr_3 is more stronger acid as compared to BF_3 due to the following reasons.
(i) In BF_3, due to availability of vacant orbital of boron and small size of F-atoms having 3 lone pair of electrons, F-atom may easily form the coordinate bond (called back bonding). As a result of the back donation of electrons from fluorine to boron, the electron deficiency of boron atom gets compensated and therefore, the Lewis acid character of BF_3 decreases.
(ii) In BBr_3, bromine being of larger size, its lone pair of electrons are far away from B-atoms thus are not capable to form effective back-bond with B-atom.
Hence, BBr_3 is more stronger acid as compared to BF_3.

To be Continued at Page 77

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SURFACE CHEMISTRY

FOR CLASS XII

Topicwise Collection of Best Subjective Problems

Very Short Answer Type Questions [1 Mark]

1. During adsorption, what is the value of ΔH at equilibrium?
2. What do you mean by term 'sorption'?
3. Write one example of adsorption.
4. What happens when a Lyophilic sol is added to a lyophobic sol?
5. Why do we add alum to purify water? [NCERT Exemplar]
6. What is the difference between electro-osmosis and electrophoresis.

Very Short Type Questions [2 Marks]

7. Write any four differences between physical and chemical adsorption. [Delhi 2011]
8. Define the following :
   (i) Peptisation (ii) Reversible sols
9. The critical temperature for CO_2, SO_2 and H_2 are respectively 304, 630 and 33 K. Which gas will adsorb least on a definite amount of charcoal. Also give the reason.
10. Write the expression for Freundlich adsorption isotherm; when
    (i) $\frac{1}{n} = 0$ (ii) $n = 1$
11. (i) What happens to chalk-stick, when dipped in ink?
    (ii) Give name of one Emulsifying agent.
12. (i) A colloidal solution is made as follows :
    $$\underset{\text{(From KI)}}{AgI + I^-} \longrightarrow \underset{\text{(Sol)}}{AgI : I^-};$$
    To coagulate the sol ($AgI : I^-$): which ion be the most suitable ion among $Ca^{2+}, SO_4^{2-}, PO_4^{3-}, Al^{3+}$.
    (ii) What is colloidion? [NCERT Exemplar]
13. (i) What are shape selective catalyst?
    (ii) Write one example of reaction in which homogeneous catalyst is used.

Short Answer Type Questions [3 Marks]

14. (i) What is desorption? What is its role in process of catalysis.
    (ii) What are zeolites? Give one example.
    (iii) Write the names of catalyst and promoter used in Haber's process. [NCERT in text]
15. Write short notes on
    (i) Tyndall effect
    (ii) Brownian movement
16. What are enzyme catalysis, write mechanism of enzyme catalysis? Give one example of biochemical catalysis.
17. What is effect of pressure and temperature on the adsorption of gases on solids? [NCERT]
18. What do you mean by term 'CMC', why detergents with low 'CMC' are more economical to use?
19. Explain adsorption theorem of heterogeneous catalyst.
20. Write the difference between dialysis and electrodialysis.
21. Explain the observations given below.
    (i) When an electrolyte NaCl is added to hydrated ferric oxide solution.
    (ii) When a beam of light is passed through a colloidal solution.
    (iii) When electric current is passed through a colloidal solution. [NCERT, All India 2008]

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22. Explain the following terms with suitable example :
(i) Alcosol (ii) Aerosol
(iii) Hydrosol [NCERT]

23. Write short notes on
(i) Multimolecular colloids
(ii) Macromolecular colloids
(iii) Associated colloids

24. What are the factors which influence the adsorption of the gas on a solid? [NCERT]

25. Write short notes on
(i) Hardy-Schulze rule
(ii) Helmholtz electrical double layer theory
(iii) Electrical precipitation of smoke

Value Based Type Questions [4 Marks]

26. A doctor gave a bottle of powdered medicine to the patient. He gave him instruction to add boiled water (after cooling) upto the shown mark and shake it well before the use. On the basis of said activity answer the following:
(i) Why doctor gives the medicine to the patient in powdered form?
(ii) Why doctor advised to shake the bottle well, before the use?
(iii) What is the particle range of solution obtained after shaking?
(iv) What are the values associated with doctor's suggestion?

Long Answer Type Questions [5 Marks]

27. (i) What are micelles? Write cleansing action of soaps.
(ii) What is Kraft-temperature?

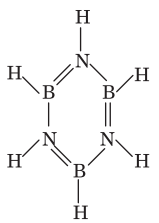
28. (i) Explain, how adsorption is useful in each of the following cases: [Delhi 2011]
(a) Production of vacuum
(b) Heterogeneous catalysis
(c) Froth floating process

29. Explain the following:
(i) Powdered substances are more effective adsorbent than their crystalline forms. [NCERT]
(ii) Chemical adsorption shows higher negative enthalpy of adsorption.
(iii) Out of NH_3 and N_2, which gas adsorbed more readily and why?
(iv) Role of activated charcoal in gas masks.
(v) Ester hydrolysis is slow in the begining and becomes faster after sometimes. [NCERT]

30. (i) What do you mean by activity and selectivity of the catalyst? [NCERT]
(ii) Write two applications of adsorption.
(iii) What do you understand by activation of adsorbent? How is it achieved? [NCERT]
(iv) Write a method for protection of colloids.
(v) Why colour of sky is blue?

Continued from Page 75

11. $B_3N_3H_6$ is known as inorganic benzene.
It is also called borazole. Its structure is as follows



or $(B_3N_3H_6)$

Preparation

$$6NH_3 + 3B_2H_6 \xrightarrow{450K} 3[BH_2(NH_3)_2]^+[BH_4]^- \xrightarrow{\Delta} 2B_3N_3H_6 + 12H_2$$

12. In structure of diamond, all the four valence electrons of C-atom are covalently bonded with its neighbouring C-atoms, forming four sigma (σ) bonds.
Thus, has sp^3-hybridisation.

On the other hand one of the valence electron of C-atom in graphite remain unbounded and is free to move in the plane of sheet of C-atoms. Thus, only 3-electrons of C-atoms are covalently bonded with three neighbouring. C-atoms forming three sigma bonds, hence in graphite C-atoms show sp^2-hybridisation.

13. Reaction for preparation of
(i) **Water gas**

$$CH_4(g) + H_2O(g) \xrightarrow[\Delta]{} \underbrace{CO(g) + 3H_2(g)}_{\text{(Water gas)}}$$

Mixture of CO and H_2 is called water gas also known as 'syn-gas'.

(ii) **Producer gas**

$$2C(s) + O_2(g) + 4N_2(g) \xrightarrow{\Delta} \underbrace{2CO(g) + 4N_2(g)}_{\text{(Producer gas)}}$$

Mixture of CO and N_2 is called producer gas.

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Solutions

1. ∵ At equilibrium,

$$\Delta G = 0$$

$$\therefore \quad \Delta H = T\Delta S$$

2. Occurrence of absorption and adsorption both simultaneously on same surface is called sorption.

3. Adsorption of water vapours over silica gel is an example of adsorption.

4. Lyophilic sol will protect the lyophobic sol by making a coating (layer) of lyophilic sol over lyophobic sol.

5. Alum coagulates with impurities, which when settled down, give pure water after filteration.

6. Electro-osmosis refers as movement of dispersion medium in an electric field. Electrophoresis refers as movement of colloidal particles under the applied electric field.

7. Difference between physical and chemical adsorptions are as follows :

S. No.	Physical adsorption	Chemical adsorption
1.	It arises because of van der Waals' forces.	It is caused by chemical bond formation.
2.	It is non-specific in nature.	It is highly specific in nature.
3.	It is reversible in nature.	It is irreversible in nature.
4.	It depends on the nature of gas. More easily liquefiable gases are adsorbed readily.	It also depends on the nature of gas. Gases which can react with the adsorbent show chemisorption.
5.	Enthalpy of adsorption is low (20-40 kJ mol^{-1})	Enthalpy of adsorption is high (80-240 kJ mol^{-1}).

8. (i) **Peptisation** The process of conversion of a fresh precipitate into sol by shaking it with dispersion medium in the presence of electrolyte, is called peptisation.

(ii) **Reversible sols** Lyophilic colloids are also known as reversible sols. These sols are directly formed by mixing substances like gum, gelatin, starch. etc. with a suitable liquid. These sols are stable and can not be easily coagulated.

9. (i) More be the critical temperature (T_C) more will be the possibility to liquify a gas and more easily it get adsorbed.

(ii) Adsorption $\propto$ size

$\propto$ mass

Thus, $H_2(g)$ due to least value of T_C, mass and size, will adsorb least on a definite amount of charcoal.

10. **Freundlich Adsorption Isotherm**

Freundlich gave the relationship between x/m and p at a particular temperature.

$$\frac{x}{m} = K \cdot p^{1/n} \qquad (n > 1)$$

where, m = mass of adsorbent, x = mass of the gas adsorbed on mass (m) of adsorbent, p = pressure,

K, n = constants; n = integer

- When $\frac{1}{n} = 0$, $\frac{x}{m}$ = constant, the adsorption is independent of pressure.
- When $\frac{1}{n} = 1, \frac{x}{m} = Kp$; i.e. $\frac{x}{m} \propto p$, the adsorption varies directly with pressure.

11. (i) When a chalk-stick is dipped into the ink, coloured part of the ink is adsorbed on the chalk surface and solvent is absorbed by the chalk.

(ii) Casein in milk, acts as an emulsifying agent.

12. (i) Since, AgI : I^- is a negative sol, thus will be coagulated by positive electrolyte.
More be the charge over positive electrolyte, more suitable be the ion, i.e requires less in quantity.
As, $Al^{3+}$is a positive ion with 3 units of charge. Hence, is most suitable to coagulate for the given sol.

(ii) The usual collodion is a 4% solution of nitrocellulose in a mixture of alcohol and ether.

13. (i) When a catalytic reaction depends upon the porous structure of catalyst, size of the reactant and the product molecules, the reaction is known as **shape-selective catalysis**.

(ii) Example of a reaction in which homogeneous catalyst is used

Inversion of sugar

$$\underset{\text{(Sugarcane)}}{C_{12}H_{22}O_{11}} + H_2O(l) \xrightarrow{H_2SO_4(l)} \underset{\text{(Glucose)}}{C_6H_{12}O_6\,(aq)} + \underset{\text{(Fructose)}}{C_6H_{12}O_6\,(aq)}$$

AMAZING REALITIES

A rubber tire is technically one single, giant, polymerised molecule. Some molecules can be very big, but most are still microscopic. Not the vulcanised tire, though it's all one, big, freakin' molecule! Basically, the vulcanised tire is all made of large polymers chains that have been crosslinked together with covalent bonds.

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1. In cities, near water bodies, winter time temperatures are higher within a few hundred meters of the water front than a few kilometers away from the water, unless the water freezes, why?

2. Why is hydrogen never the central atom in a molecule or ion?

3. Mercury is a highly toxic metal. Although it is a liquid at room temperature, it has a high vapour pressure and a low enthalpy of vaporisation (294 J/g). What quantity of heat energy is required to vapourise 0.500 mL of mercury at 357°C, its normal boiling point? (Density of Hg(/) is 13.6 g mL^{-1})

4. If the mouth of a glass-stoppered bottle containing sodium hydroxide is not routinely cleaned, a white solid compound formed from the top of the bottle to the neck, making it difficult to open the bottle. What is the name of this solid compound?

5. Methanol is toxic for human but not for horses, rats and some other animals, why?

Fill in the Blanks

6. When lead ions and chromate ions, come together in an aqueous solution, the brilliant ..... precipitate of lead chromate is formed.

7. Usually, we fill our automobile tires with compressed air because it is cheap. But race cars, jet aircraft and some heavy trucks use .....

8. When a cucumber is soaked in a concentrated salt solution, water flows from the plant cells into salt solution by .....

9. The addition of aqueous ammonia to aqueous Cu^{2+} ions forms the intense deep blue coloured ..... complex ion.

10. When liquid bromine is poured onto small pieces of aluminium, nothing appears to happen at first. Eventually the mixture becomes hot and a violent ..... reaction occurs.

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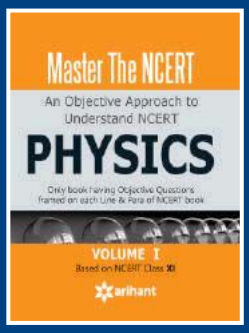

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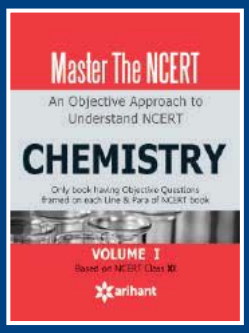

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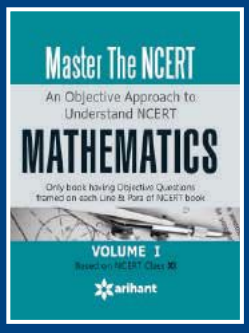

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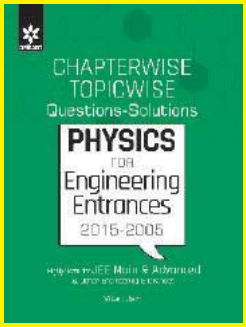

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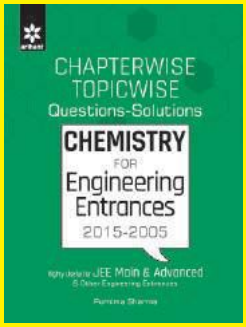

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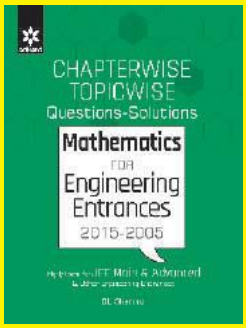

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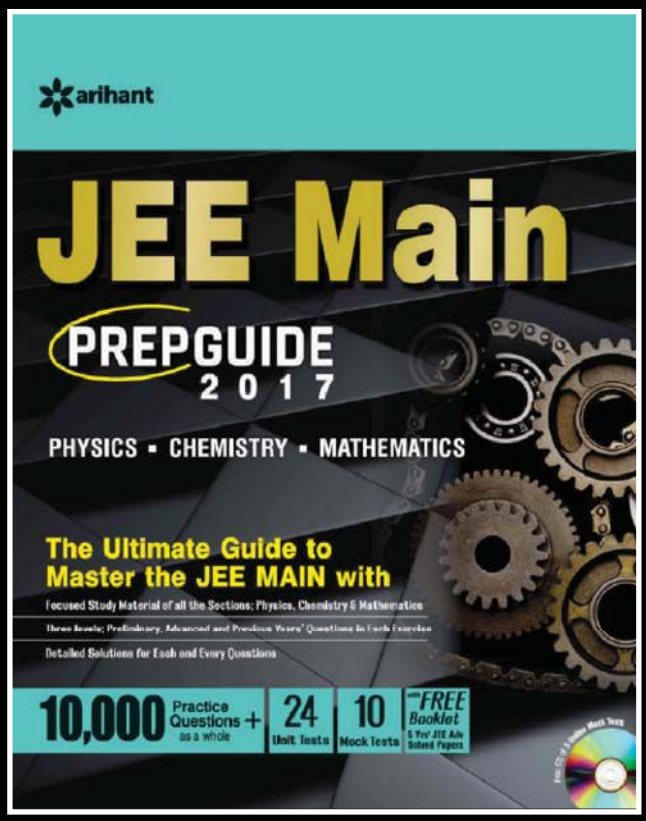

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