CHEMISTRY
Spectrum

JEE ADVANCED
STEREOCHEMISTRY
AND NUCLEOPHILIC
SUBSTITUTION
REACTIONS
CHEMICAL KINETICS

JEE FOCUS
ELECTRICAL CONDUCTIVITY OF SOLUTIONS

Concept Map
THERMODYNAMICS

Master the NCERT
CHEMICAL BONDING

Exemplar Simplified
SOLID STATE

From the Editor's Desk
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Medi Centre
ELECTROCHEMISTRY

ASSERTION-REASON

DPP
Daily Practice Problem
AROMATICITY

SOLVED PAPERS 2015
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BOOKS WITH UNIQUE ASSEMBLAGE OF
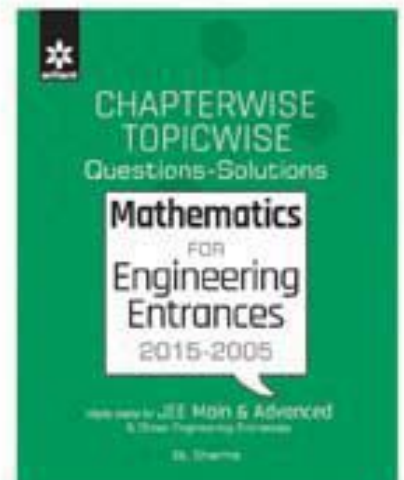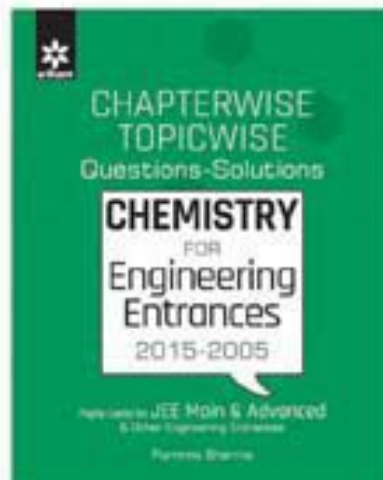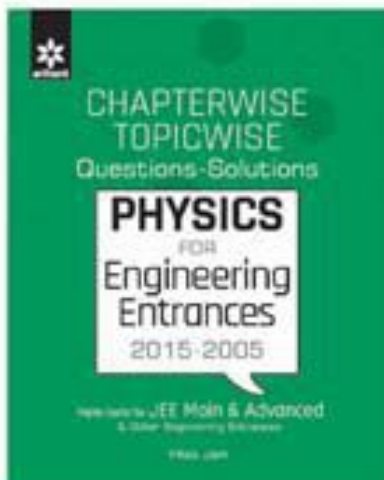# TOPICWISE PROBLEMS
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04

JEE FOCUS
ELECTRICAL CONDUCTIVITY OF SOLUTIONS

FROM THE EDITOR'S DESK

EQUILIBRIUM IN
STUDENT'S LIFE

FOR MANY STUDENTS, GOING TO SCHOOL/COACHINGS CAN BE THE MOST DIFFICULT PART OF THE DAY, NOT BECAUSE CLASSES ARE EXCRUCIATINGLY DIFFICULT BUT BECAUSE OF THE DEVELOPMENT OF DIFFERENT KIND OF PRESSURE IN THEIR ROUTINE WORK.

Schools and coachings are considered temples of learning, where the next generation is nurtured and nourished suitably to meet the demands of the society and the nation. A person spends 12-14 years of his life in school. These years see his/her transformation from a kid to an adolescent and afterwards to an adult. Within this span of a dozen or more years he/she learns about the world, the different forces that govern it, the different kinds of people and their languages, cultures etc. He/She is prepared to conquer the world with knowledge, courage and to innovate and lead. Student's today face unimaginable pressures, particularly from 3 different sources i.e., peer, parents and self. High scores in examinations are thus the obsessive concern of parents, teachers and school administrators. As an outcome, schools/coachings are being rated by the number of students they are able to send to higher educational institutions. It is within this social context that students are under tremendous pressure to become 'competitive' and academically successful.

FROM THE EDITOR'S DESK

Let us take these pressures one by one along with the ways to balance such pressures:

PEER PRESSURE

When students go to school, they move away from the comfort zone of their home and enter into a new world, where they try to adjust with others. They make new friends and bestow all their trust in them. Usually, their peer group becomes their identity and most of the times they even don't realise that their peer group begins to influence their actions just like a catalytic agent. It affects their emotions as well as their academic performance. The impact of peer group can be positive or negative. The positive peer pressure provides the sense of security and encourages to

- attend school with regularity,
- take part in school activities,
- set objectives to improve academic performance
- increase self-confidence,
- develop hobbies and opinion
- independent in making decisions

On the other hand negative impact of the peer group will tend to increase tendencies like:

- bunking classes,
- disobeying parents and teachers,
- getting away from home and loafing with friends
- making unreasonable demands
- bullying classmates and juniors
- incorporation of bad habits like smoking, drinking, stealing in extreme cases etc.,

Remember! The extent to which a peer group influences a student's life depends upon its age group and the kind of peers. Peer groups are highly influential during adolescence but the influence diminishes as the age progresses. Presence of toppers /good students has positive impact on all the peer group members and vice versa.

MANTRAS TO TACKLE PEER PRESSURE

It is really very difficult to deal with peer pressure. I always advice "Suno sabki, karo apne man ki" however in a more defined way you can rely on following facts to overcome such a pressure:

A. **Overpower the fear of losing friends** i.e., have a firm believe in the policy that nobody is indispensable in this world means make a firm policy for yourself "Tu nahin aur sahi, aur nahin aur sahi".

B. **Learn to say "NO"** The best example of this particular advice is Mr. Amitabh Bachchan who himself admitted the relevance of such a thought in some of his interviews where questions were asked regarding the initial failures of his firm ABCL corporation. Infact this particular mantra indirectly indicates our priorities. It is through that priority list only we can make a judgement for a Yes or no to a particular task.

Remember! While going for this mantra with a flat No may increase the level of difficulty for you, so manipulative skills are necessarily required for this mantra.

C. **Don't limit your friend circle.** This particular mantra works as a support system for first mantra.

PARENTAL PRESSURE

Most of the parents are ambitious about their child's performance. Their expectations sometimes become unrealistic resulting to additional pressure on the shoulders of child. They ignore the fact that this kind of attitude is responsible for the development of an adverse type of effect in the life of their children. Such a kind of pressure in excess creates havoc in their interpersonal relationships too.

MANTRAS TO TACKLE PARENTAL PRESSURE

Usually, it is seen that parents fail to make amendments in their attitude. However, following mantras may prove helpful in tackling parental pressures

- **Your reaction is important** i.e., you have to take the initiative and the responsibility to diffuse such kind of tension via pointing out for such a pressure.

Remember! This act must be in a very polite and informal way so that the ego of parents must also be satisfied.

- Try to express your love for your parents more frequently.
- Try to follow all the family rules. Help them in household work. This will convince your parents of your obedience.
- A very delicate factor in maintaining relationships is to remember that you may differ from your parent's point of view or you may not like their idea but it is not that you start disliking your parents.
- Be open with your parents. Don't try to hide things and don't tell lies.
- Don't over react to what they say. Don't be rude, harsh or loud with them.
- In case, there is a need for an mediator, you can take the help of one of your close relatives like your cousin or even a friend.

SELF-IMPOSED PRESSURE:

Most of the times the own ambitions of student are also responsible for the development of pressure. Most of the times these are connected with better results. This will directly affect the performance.

Remember! Self-imposed pressure is beneficial if you are going to face subjective type examination (Boards etc) however, it is hazardous for objective type examinations i.e., competitions. Hence, it is advisable. Always try to face a subjective examination with a tense mind set. Always try to face an objective examination with a cool mind set.

To my understanding the major cause of building anxiety or pressure is our unfounded fears and mismanaged priorities. When we feel too concerned about a thing, negative thoughts start creeping in our mind, resulting to such pressures. For such situations I always follow the lines of Helen Keller

"Keep Your face to the sunshine and you cannot see the shadow"

Rakhi Yadav

{ **JEE** Focus }

ELECTRICAL
CONDUCTIVITY
OF SOLUTIONS

Electrochemistry, the area of chemistry concerned with the interconversion of chemical and electrical energy, is enormously important in modern science and technology. It makes possible the manufacture of essential industrial chemicals and materials. For example, sodium hydroxide is used in the manufacture of paper, textiles, soaps and detergents, is produced by passing an electric current through the aqueous solution of sodium chloride. Many useful elements are obtained by the conduction of electricity through the electrolytic solution.

You have studied earlier that in metallic conductors resistance is the obstruction in the path of flow of electrons and conductance is inversely proportional to resistance or you can say that conductance is the ease of flow of electrons.

Conductivity is the measurement of conduction of electric current. In this article we shall explore about the study of conductivity of electrolytic solutions.

For this, first of all you should know what is electrolytic solution?

Electrolytic solutions are those solutions in which electrolytes are used as solutes, these solutions conduct electricity and undergo decomposition when current is passed through them, e.g. solution of acids, bases and salts in water.

On the basis of dissociation in aqueous solution or molten state electrolytes are classified as in the following chart.
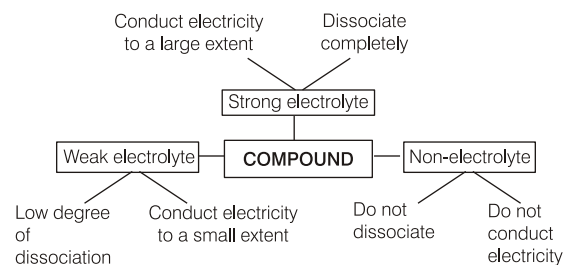
Factors Affecting Electrolytic Conductance

(a) **Solute-solvent interactions** These interactions operate between ions-furnished by solute and solvent molecules. Due to these interactions mobility of ions lowers down and conductance decreases. On dilution, these interactions become weaken due to which ionic mobility increases and here conductance of solution also increases.

(b) **Solute-solute interactions** These interactions operate between ions-furnished by solute. If these interactions are weaker, ions can move freely and so will be more conducting. On dilution, these weaker interactions disappear and ions move as independent species and conductivity reaches at its maximum value. If these interactions are stronger, ions could not move freely and so will be less conducting.

(c) **Solvent-solvent interactions** If these interactions are stronger, then viscosity of medium will be higher which results in less ionic mobility and so lower conductivity.

(d) **Temperature** On increasing the temperature, ions become more mobile as all type of interactions weaken and conductivity increases.

(e) **Concentration of an electrolyte** On increasing the concentration of an electrolyte, the number of ions in solution increases and hence, conductivity also increases.

Fact File of Electrochemistry

- SI unit of electric charge is coulomb (C).
- An electron or a single negative charged ion carries a charge of -1.6×10^{-19} C, a proton or a singly charged positive ion carries a charge of $+1.6 \times 10^{-19}$ C.
- The rate at which charge passes through a point is called the electric current (I). Current is measured in amperes (amps), A. 1A is the current when 1C of charge flows per second. $\quad 1\,A = 1\,Cs^{-1}$
- If there is a potential difference between two points in a circuit, electric current flows.
- The potential difference is the 'driving force' that pushes the electrons or ions around the circuit.
- Potential difference is measured in volts.
  Ohm's law The current flowing through a conductor is directly proportional to the potential difference across it. $\quad I \propto V$
 where, I = current in ampere, V = potential difference in volt $\quad$ or $\quad I = \dfrac{V}{R}$

  R = proportionality constant or resistance of conductor
- Resistance is the obstruction in the flow of current through a conductor and its unit is ohm (Ω).

Conductivity of Electrolytic Solutions

- In an electrolytic solution, the charge is carried out between the electrodes by dissolved ions. Just like metallic conductors, electrolytic solutions also obey ohm's law.

- The electrical conductivity of an electrolytic solution is measured by determining the resistance of the solution in a conductivity cell between two flat or cylindrical electrodes separated by a fixed distance.

Conductivity cell
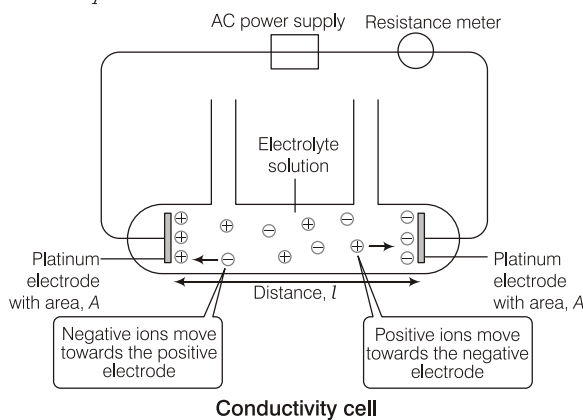
- Platinum electrode is used since, it is inert. A voltage is applied between the electrodes and the resistance R, is measured.
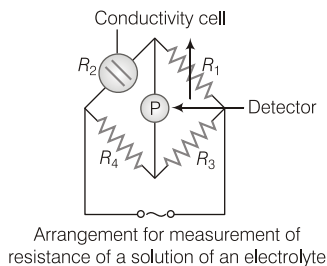- To prevent any chemical reaction due to electrolysis, alternating current is used.
  Resistance (R) $\propto$ distance between the electrodes (l)

  $$\propto \frac{l}{\text{area of cross - section of electrodes}} \quad \text{or} \quad R = \frac{l}{A}\rho$$

where, ρ = specific resistance or resistivity

ELECTRICAL CONDUCTIVITY OF SOLUTIONS

- If $l = 1\,cm$ and $A = 1\,cm^2$, then $R = \rho$
  Hence, specific resistance is the resistance of a conductor of 1 cm length and having a cross-sectional area of 1 cm^2.

- Unit of specific resistance is ohm-m.

- $\dfrac{l}{A}$ is known as cell constant and is expressed in cm^{-1}.

- Resistance of the electrolyte may be measured with the help of a conductivity cell in a wheat stone bridge.

Conductivity cell

R_2 R_1
P — Detector
R_4 R_3

Arrangement for measurement of resistance of a solution of an electrolyte

Types of Conductivity

Specific conductivity (κ)	Equivalent conductivity (Λ_{eq})	Molar conductivity (Λ_m)
Definition		
The conductance when conductor has unit length and unit cross-sectional area.	The conducting power of all the ions produced by dissolving 1g-equivalent of an electrolyte in the solution.	The conducting power of all the ions produced by dissolving 1 mole of an electrolyte in the solution.
Formula		
$\kappa = G \times \dfrac{l}{a}$	$\Lambda_{eq} = \dfrac{\kappa \times 1000}{N}$	$\Lambda_m = \dfrac{\kappa \times 1000}{M}$
$G =$ Conductance of solution	$N =$ Normality of solution	$M =$ Molarity of solution
Unit		
Siemens m^{-1} or Sm^{-1} or Scm^{-1}.	S cm^{2}eq^{-1} or Ω^{-1} cm^{2}eq^{-1} or Ω^{-1} m^2 eq^{-1}	S cm^2 mol^{-1} or Ω^{-1} cm^2 mol^{-1} or Ω^{-1} m^2 mol^{-1}.

Note Conductance and conductivity are additive properties, e.g. if an aqueous solution contains more than one electrolytes, the total conductance is given by

$$G_T = \sum_{i=1}^{n} G_i + G_{water}$$

where, $\sum\limits_{i=1}^{n} G_i$ is the total conductance of all the ions.

$G_{water} =$ Conductance for water

Electrical Conduction Involved in Heartbeats

- We generally think that heart is a mechanical device that circulates blood *via* regularly spaced muscular contraction.

- However, two scientists namely Luigi Galvani (1729-1787) and Alessandro Volta (1745-1827), discovered that contractions of heart are due to electrical phenomena. According to them pulses of electricity cause the heart to beat.

- The heart beats occur from a combination of electrochemistry and the properties of semipermeable membranes.

- Cell walls are membranes with variable permeability with respect to a number of important ions (Na^+, K^+ and Ca^{2+} etc).

- The concentrations of these ions are different for fluids inside the cells (the intracellular fluid or ICF) and outside the cells (the extracellular fluid or ECF).

- In cardiac muscle cells, e.g. the concentration of K^+ in the ICF and ECF are typically about 135 millimolar (mM) and 4 mM, respectively.

- For Na^+, however, the concentration difference between the ICF and ECF is opposite to that of K^+ ($[Na^+]_{ICF} = 10$ mM and $[Na^+]_{ECF} = 145$ mM.

- The cell membrane is initially permeable to K^+ ions but is much less to Na^+ and Ca^{2+}.

- The difference in concentration of K^+ ions between ICF and ECF generates a concentration cell.

- Inspite of same ions on both sides of the membranes, there is a potential difference between the two fluids which can be calculated by using Nernst equation with $E° = 0$ as

$$E = E° - \frac{2.303\,RT}{nF}\log\frac{[K^+]_{ICF}}{[K^+]_{ECF}};\ E = 0 - (61.5\,mV)\log\left(\frac{135\,mM}{4\,mM}\right)$$

$$= -94\,mV, (T = 37°C)$$

- The negative sign of the potential indicates that work is required to move K^+ into intracellular fluid.

- The cells of the heart that govern the rate of heart contraction are called pacemaker cells.

- The membranes of the cells, regulate the concentrations of ions in the ICF, allowing them to change in a systematic way, this concentration changes cause the emf to change in a cyclic fashion.

- The emf cycle determines the rate at which the heart beats. If the pacemakers cells malfunction because of disease or injury an artificial pacemaker can be surgically implanted.

- During the late 1800s scientists discovered that the electrical impulses that cause the contraction of heart muscle are strong enough to be detected. This observation formed the basis for *electrocardiography* noninvasive monitoring of the heart by using a complex arrangement of electrodes on the skin to measure the voltage changes during heart beats.

← 1 second →
emf
Time →

Electrocardiogram
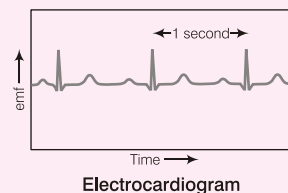
- Finally, although the heart's major function is the mechanical pumping of blood, but it is most easily monitored by using the electrical impulses generated by tiny voltaic cells.

Example 1 The correct order of equivalent conductance at infinite dilution of LiCl, NaCl and KCl is [IIT 2001, 1M]
(a) LiCl > NaCl > KCl
(b) KCl > NaCl > LiCl
(c) NaCl > KCl > LiCl
(d) LiCl > KCl > NaCl

Sol. **(b)** **Concept** The cations with smaller size become more hydrated in aqueous solution which results larger hydrated radius and smaller ionic speeds.

In the given problem anion is same. Hence, the ionic speed will be decided by the size of cations.

Smaller cation $\rightarrow$ larger hydrated radius $\rightarrow$ smaller ionic speed $\rightarrow$ smaller equivalent conductance.

$\therefore$ Correct order of equivalence conductance is
$$KCl > NaCl > LiCl$$

Relation between Molar and Equivalent Conductivities

As, $$\Lambda_{eq} = \kappa \times \frac{1000}{N} \qquad \ldots(i)$$

and $$\Lambda_m = \kappa \times \frac{1000}{M} \qquad \ldots(ii)$$

On dividing Eq. (i) by Eq. (ii), we get

$$\frac{\Lambda_{eq}}{\Lambda_m} = \frac{M}{N} = \frac{1}{\text{charge on anion or cation or valency factor}}$$

Hence, $\Lambda_m = \Lambda_{eq} \times$ valency factor

Example 2 Resistance of 0.2 M solution of an electrolyte is $50\,\Omega$. The specific conductance of the solution of same electrolyte is $1.4\ Sm^{-1}$ and resistance of same solution of the same electrolyte is $280\,\Omega$. The molar conductivity of 0.5 M solution of the electrolyte in $Sm^2\ mol^{-1}$ is [IIT 2014, Main]
(a) 5×10^{-4} (b) 5×10^{-3}
(c) 5×10^{3} (d) 5×10^{2}

Sol. **(a)** This problem can be solved by going through the following steps:

Step I Calculate the cell constant for the first solution.

$\because$ Specific conductance $(\kappa) = \dfrac{1}{R} \times \dfrac{l}{A}$

$$1.4\ Sm^{-1} = \frac{1}{50} \times \frac{l}{A}$$

or $$\frac{l}{A} = 70\ m^{-1}$$

Step II With the help of $\dfrac{l}{A}$ value calculate the specific conductance for second solution,

$$\kappa' = \frac{1}{280} \times 70 = \frac{1}{4}$$

Step III Finally, calculate the molar conductivity for second solution.

$$\Lambda_m = \frac{\kappa'}{1000 \times M}$$
$$= \frac{1/4}{1000 \times 0.5}$$
$$= \frac{1}{2000}$$
$$= 5 \times 10^{-4}\ Sm^2\ mol^{-1}$$

Effect of Different Parameters on Conductivity

(a) Effect of Nature of Electrolyte

Due to the difference in availability of ions present in electrolytes solution, conductivity affect by the nature of electrolytes.

Strong electrolytes $\xrightarrow[\text{completely}]{\text{Dissociate}}$ More ions in solutions

$\longrightarrow$ More conductivity

Weak electrolytes $\xrightarrow[\text{partially}]{\text{Dissociate}}$ Less ions in solutions

$\longrightarrow$ Less conductivity

(b) Effect of Dilution

The conductivity decreases on increase in concentration while equivalent conductivity and molar conductivity increases on increase in dilution due to decrease in number of ions per cm^3.

Note At infinite dilution, the conductivity of weak as well as strong electrolyte is same, i.e. equal to one, because weak electrolyte is also assumed to be completely ionised at infinite dilution but their variation is not same with increase in dilution.

(c) Effect of Temperature

On increase in temperature conductivity of an electrolytic solution also increases. It is due to the fact that on increasing the temperature of the solution, the kinetic energy of ions increases resulting increase in movement of ions.

For a small range of temperature, the temperature dependence of molar conductivity is given by the equation of the type.

$$\Lambda_t = \Lambda_{25}[1 + \beta(t - 2b)]$$

where, $\beta =$ constant

$\Lambda_t =$ conductivity at $t\,°C$

Molar conductivity in dilute solutions near room temperature changes by about 2% per degree change in temperature.
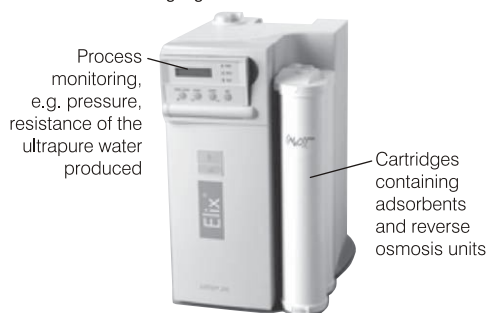
ELECTRICAL CONDUCTIVITY OF SOLUTIONS

Estimation of Purification of Water from Conductivity

Water is a very good solvent, infact most of the solutions are prepared from water. It contains several dissolved substances from the ground it passes through before collection. Tap water is filtered and disinfected to remove biological contaminants but it is far from pure. For example, many gases such as carbon dioxide, sulphur dioxide or oxides of nitrogen are absorbed from the atmosphere. These tend to decrease the pH of water.

Many of dissolved substances in water are ionic and change the conductivity of water.

The method for obtaining 'ultrapure' water in the laboratory is shown in the following figure.

Process monitoring, e.g. pressure, resistance of the ultrapure water produced

Cartridges containing adsorbents and reverse osmosis units

Tap water is passed through a series of cartridges. First, an active charcoal absorbent removes maximum dissolved organic matter, then a reverse osmosis module uses high pressure to force the water through the membrane which does not allow dissolved ions to pass. Finally, an ion-exchange resin replaces any remaining dissolved ions with H^+ ions.

In some methods, a high intensity ultraviolet lamp is used to irradiate the water for removing the final traces of organic matters.

As a check on the performance of the apparatus, the conductivity of the water is measured by using a conductivity meter incorporated into the apparatus.

The ultrapure water which we get is not so pure as it is a very good solvent, it dissolves components from the container in which it is stored - even glass to a very small extent.

Water rapidly absorbs carbon dioxide from the air and forms carbonic acid (H_2CO_3) which results pH of water to become 5.7 at room temperature.

Debye-Huckel-Onsager Equation

The variation of molar conductances for strong electrolyte, with concentration is given by Debye-Huckel-Onsager equation which is

$$\Lambda_m = \Lambda_m^\infty - b\sqrt{C}$$

where, $b = $ constant, $C = $ concentration,

$\Lambda_m^\infty = $ molar conductivity at infinite dilution

The value of b for a given solvent and temperature depends upon the type of electrode. The relation between molar conductivity (Λ_m) *versus* $\sqrt{C}$ is shown below.
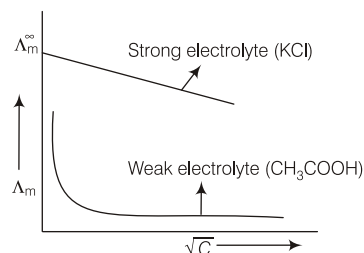
Clearly, for a strong electrolyte on extraplotation we can find the value of Λ_m^∞ at $C = 0$ but in case of weak electrolyte, we cannot find the value of Λ_m^∞.

For weak electrolytes, conductivity increases steeply but Λ^∞ cannot be obtained at $C = 0$ because at $C = 0$, conductivity of the solution is so low that it cannot be measured accurately.

Example 3 The equivalent conductances of NaCl at concentration C and at infinite dilution are Λ_C and Λ_∞, respectively. The correct relationship between Λ_C and Λ_∞ is given as (where, the constant B is positive) **[IIT 2014 Main]**

(a) $\Lambda_C = \Lambda_\infty + (b)C$
(b) $\Lambda_C = \Lambda_\infty - (b)C$
(c) $\Lambda_C = \Lambda_\infty - (b)\sqrt{C}$
(d) $\Lambda_C = \Lambda_\infty + (b)\sqrt{C}$

Sol. **(c)** According to Debye-Huckel-Onsager equation,

$$\Lambda_C = \Lambda_\infty - b\sqrt{C}$$

where, $\Lambda_C = $ limiting equivalent conductivity at concentration, C

$\Lambda_\infty = $ limiting equivalent conductivity at infinite dilution

$C = $ concentration of the solution, is so low that it cannot be measured accurately.

Kohlrausch Law

To overcome the problem of finding conductivity of weak electrolytes at infinite dilution Kohlrausch law was introduced. According to this law, the molar conductivity of an electrolyte at infinite dilution is the sum of molar conductivities of ions produced by the electrolyte at infinite dilution.

or $\qquad \Lambda_m^\infty = n^+ \Lambda_{cation}^\infty + n^- \Lambda_{anion}^\infty$

where, Λ_{cation}^∞ and Λ_{anion}^∞ are the molar conductivities of cation and anion at infinite dilution, n^+ and n^- are the number of cations and anions respectively.

Note The multiplication of number of ions with molar conductivity of a particular ion is called **molar ionic conductance** of that particular ion.

Applications of Kohlrausch Law

(a) **In the calculation of molar conductivities of weak electrolytes at infinite dilution**

Kohlrausch law provides an indirect method to calculate molar conductivities of weak electrolytes. e.g. calculation of molar conductance of CH_3COOH at infinite dilution.

$$\Lambda^{\infty}_{(CH_3COOH)} = \Lambda^{\infty}_{(CH_3COO^-)} + \Lambda^{\infty}_{(H^+)} \qquad \ldots(i)$$

Above equation may be obtained, if we know about molar conductivities of some strong electrolytes, i.e.

$$\Lambda^{\infty}_{(CH_3COO^-Na^+)} = \Lambda^{\infty}_{(CH_3COO^-)} + \Lambda^{\infty}_{(Na^+)} \qquad \ldots(ii)$$

$$\Lambda^{\infty}_{(HCl)} = \Lambda^{\infty}_{(H^+)} + \Lambda^{\infty}_{(Cl^-)} \qquad \ldots(iii)$$

$$\Lambda^{\infty}_{(NaCl)} = \Lambda^{\infty}_{(Na^+)} + \Lambda^{\infty}_{(Cl^-)} \qquad \ldots(iv)$$

Eq.(i) can be obtained by adding Eq. (ii) and Eq. (iii) and subtracting Eq. (iv) from them

$$\therefore \quad \Lambda^{\infty}_{(CH_3COOH)} = \Lambda^{\infty}_{(CH_3COONa)} + \Lambda^{\infty}_{(HCl)} - \Lambda^{\infty}_{(NaCl)}$$

(b) **In the calculation of degree of dissociation of weak electrolytes**

$$\alpha = \frac{\Lambda^C_m}{\Lambda^{\infty}_m}; \text{ where, } \alpha = \text{degree of dissociation}$$

Λ^C_m = molar conductance at any concentration
Λ^{∞}_m = molar conductance at infinite dilution

(c) **In the determination of ionisation constant for weak electrolytes**

(d) **In the determination of the solubility of a sparingly soluble salt**

(e) **In the calculation of ionic mobilities**

At infinite dilution under unit potential gradient the speed of an ion is termed as absolute ionic mobility.

Ionic mobility $\propto$ conductivity.

or $\qquad \Lambda^{\infty} \propto \mu^{\infty} \quad$ or $\quad \Lambda^{\infty} = F\mu^{\infty}$

PROBLEM SOLVING STRATEGY
ELECTRICAL CONDUCTIVITY OF SOLUTIONS

There are different types of problems asked in JEE from electrical conductivity of solutions.

Type 1 When length (l), area of cross section (a) of an electrolyte is given and asked to find out specific conductivity of solution, use the following formula,

$$\kappa \text{ (specific conductivity)} = G \times \frac{l}{a}$$

Type 2 When specific conductivity (κ) is given and asked to find out equivalent conductivity (Λ_{eq}) and molar conductivity (Λ_m) use the following formulae.

$$\Lambda_{eq} = \frac{\kappa \times 1000}{N}, \Lambda_m = \frac{\kappa \times 1000}{M}$$

where, M and N are molarity and normality respectively.

Type 3 When Λ_m and valency factor is given and asked to find Λ_{eq}, use the following formula

$$\Lambda_m = \Lambda_{eq} \times \text{valency factor}$$

Type 4 When molar conductivity at infinite dilution is given and asked to find it at certain concentration

$$\Lambda_m = \Lambda^{\infty}_m - b\sqrt{C}$$

Type 5 When molar conductivity of a weak electrolyte at certain concentration and at infinite dilution is given and asked to find out degree of dissociation of weak electrolyte use the following formula

$$\text{Degree of dissociation } (\alpha) = \frac{\Lambda^C_m}{\Lambda^{\infty}_m}$$

Type 6 When solubility and conductance are given and asked to find out conductivity use the following formula,

$$\text{Conductivity } (\kappa) = \text{solubility } (S) \times \text{conductance } (G)$$

Example 4 We have taken a saturated solution of AgBr, K_{sp} is 12×10^{-14}. If 10^{-7}M of $AgNO_3$ are added to 1L of this solution, find conductivity (specific conductance) of this solution in terms of $10^{-7} Sm^{-1}$ units. **[IIT 2006 Main]**

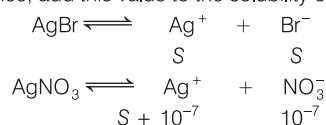Given, $\qquad \Lambda^{\infty}_{Ag^+} = 6 \times 10^{-3} Sm^2 mol^{-1}$

$$\Lambda^{\infty}_{Br^-} = 8 \times 10^{-3} Sm^2 mol^{-1}$$

$$\Lambda^{\infty}_{NO_3^-} = 7 \times 10^{-3} Sm^2 mol^{-1}$$

Sol. This problem may be solved by going through the following steps.

Step I Write down the equations of dissociation of AgBr and $AgNO_3$ along with their solubilities. Since, $AgNO_3$ is added to 1L of solution. Hence, add this value to the solubility of Ag^+.

$$\begin{array}{cccc} AgBr \rightleftharpoons & Ag^+ & + & Br^- \\ & S & & S \end{array}$$

$$\begin{array}{cccc} AgNO_3 \rightleftharpoons & Ag^+ & + & NO_3^- \\ & S + 10^{-7} & & 10^{-7} \end{array}$$

Step II Find the value of solubility with the help of K_{sp} value provided in the problem.

$$\because \qquad K_{sp} = S(S + 10^{-7})$$

or $\qquad 12 \times 10^{-14} = S(S + 10^{-7})$

or $\quad S^2 + S \times 10^{-7} - 12 \times 10^{-14} = 0$

On solving, $\qquad S = 3 \times 10^{-7}$M

Step III Since, conductivity = solubility $\times$ conductance

Calculate total specific conductance or conducivity of the solution as

$$\kappa = \kappa_{Br^-} + \kappa_{Ag^+} + \kappa_{NO_3^-}$$

$$= [\, 8 \times 10^{-3} \times 3 \times 10^{-7} + 6 \times 10^{-3} \times$$
$$\qquad 4 \times 10^{-7} + 7 \times 10^{-3} \times 10^{-7}]\, 1000$$

$$= 24 \times 10^{-7} + 24 \times 10^{-7} + 7 \times 10^{-7}$$

$$= 55 \times 10^{-7} Sm^{-1} \text{ or } 55 \text{ in terms of } 10^{-7} Sm^{-1}$$

Smart Practice

1. The saturated solution of $Co_2[Fe(CN)_6]$ has conductivity 2.0×10^{-6} Scm^{-1}. The conductivity of water used to prepare the solution is 8.0×10^{-7} Scm^{-1}. If the ionic molar conductivities of Co^{2+} and $[Fe(CN)_6]^{4-}$ are 80.0 and 440.0 $Scm^2 mol^{-1}$, respectively. Calculate the solubility product (K_{sp}) of $Co_2[Fe(CN)_6]$ assuming 100% ionisation of complex.

(a) $3.2 \times 10^{-17}M^3$
(b) $4.7 \times 10^{-16}M^3$
(c) $4.2 \times 10^{-17}M^3$
(d) $7.4 \times 10^{-17}M^3$

2. Equivalent conductivity of 0.10 N solution of CaI_2 is 100 $Scm^2 eq^{-1}$ at 298 K. If cell constant of the cell is 0.25 cm^{-1} , find out the value of current in ampere, when potential difference between electrode is 5 V.

(a) 0.3   (b) 0.2
(c) 0.1   (d) 0.4

3. If molar conductivity of acetic acid at infinite dilution is 390.7 and for 0.01M acetic acid is 3.9075 $cm^2 mol^{-1}$, calculate pH of the solution.

(a) 2   (b) 3
(c) 4   (d) 5

4. Consider the following molar conductivities at infinite dilution,

$\Lambda^{\infty}_{m[Ba(OH)_2]} = 457.6 \, \Omega^{-1} \, cm^2 \, mol^{-1}$
$\Lambda^{\infty}_{m(BaCl_2)} = 240.6 \, \Omega^{-1} \, cm^2 \, mol^{-1}$
$\Lambda^{\infty}_{m(NH_4Cl)} = 129.8 \, \Omega^{-1} \, cm^2 \, mol^{-1}$

Calculate Λ^{∞}_m for NH_4OH

(a) 238.3 S $cm^2 mol^{-1}$
(b) 189.4 S $cm^2 mol^{-1}$
(c) 294.7 S $cm^2 mol^{-1}$
(d) 500.7 S $cm^2 mol^{-1}$

5. The specific conductance of saturated solution of AgCl is found to be $1.86 \times 10^{-6} \, \Omega^{-1} \, cm^{-1}$ and that of water is $6 \times 10^{-8} \, \Omega^{-1} \, cm^{-1}$. The solubility of AgCl is (Given, $\Lambda^{\infty}_{AgCl} = 137.2 \, \Omega^{-1} cm^2 eq^{-1}$)

(a) 1.3×10^{-5} M
(b) 1.3×10^{-6} M
(c) 1.3×10^{-7} M
(d) 1.3×10^{-4} M

6. Resistance of a conductivity cell filled with a solution of an electrolyte of concentration 0.1 M is $100 \, \Omega$. The conductivity of this solution is $1.29 \, Sm^{-1}$. Resistance of the same cell when filled with 0.2M of the same solution is $520 \, \Omega$. The molar conductivity of 0.02 M solution of the electrolyte will be

(a) 124×10^{-4} $Sm^2 mol^{-1}$
(b) 1240×10^{-4} $Sm^2 mol^{-1}$
(c) 1.24×10^{-6} $Sm^2 mol^{-1}$
(d) 12.4×10^{-4} $Sm^2 mol^{-1}$

7. The specific conductivity of 0.02 M KCl solution at $25°C$ is $2.768 \times 10^{-3} \, \Omega^{-1} \, cm^{-1}$. The resistance of this solution at $25°C$ when measured with a particular cell was $250.2 \, \Omega$. The resistance of 0.01 M $CuSO_4$ solution at $25°C$ measured with the same cell was $8331 \, \Omega$. Calculate the molar conductivity of the copper sulphate solution.

(a) $7.479 \, \Omega^{-1} \, cm^2 \, mol^{-1}$
(b) $8.312 \, \Omega^{-1} \, cm^2 \, mol^{-1}$
(c) $9.382 \, \Omega^{-1} \, cm^2 \, mol^{-1}$
(d) $2.314 \, \Omega^{-1} \, cm^2 \, mol^{-1}$

8. Calculate the value of conductivity for a 0.001 M aqueous solution of NH_3.

$K_b = 1.6 \times 10^{-5}, \Lambda^{\infty} = 2.38 \times 10^{-2} \, \Omega^{-1} \, m^2 \, mol^{-1}$

(a) $9.228 \times 10^{-3} \, \Omega^{-1} \, cm^2 \, mol^{-1}$
(b) $2.772 \times 10^{-4} \, \Omega^{-1} \, cm^2 \, mol^{-1}$
(c) $8.729 \times 10^{-4} \, \Omega^{-1} \, cm^2 \, mol^{-1}$
(d) $2.998 \times 10^{-3} \, \Omega^{-1} \, cm^2 \, mol^{-1}$

9. Determine K_w at $25°$ C, if $\lambda^{\circ}_{(H^+)} = 3.4982 \times 10^{-2}$ $Sm^2 mol^{-1}$, $\lambda^{\circ}_{(OH^-)} = 1.98 \times 10^{-2}$ Sm^2 mol^{-1} and $\kappa = 5.7 \times 10^{-6} \, Sm^{-1}$ for H_2O.

(a) 1.086×10^{-14}
(b) 10^{-14}
(c) 1.086×10^{-13}
(d) 10^{-13}

10. A solution of 0.04 M solution of acetic acid at $25°$ C has $K_a = 1.8 \times 10^{-5}$ and Λ°_m $(CH_3COOH) = 390.5$ S $cm^2 mol^{-1}$. What is the resistance of the cell, if its cell constant is $0.206 \, cm^{-1}$?

(a) $622.36 \, \Omega$
(b) $589.45 \, \Omega$
(c) $736.22 \, \Omega$
(d) $427.66 \, \Omega$

Answer *with* Explanations

1. **(a)** Molar conductivity of complex solution

$$\Lambda_m^{\circ} = 2\Lambda_{Co^{2+}}^{\circ} + \Lambda_{[Fe(CN)_6]^{4-}}^{\circ}$$

$$= 2 \times 80 + 440 = 600 \, S \, cm^2 \, mol^{-1}$$

Specific conductivity of complex

$$\kappa_{complex} = \kappa_{solution} - \kappa_{H_2O}$$

$$= 2 \times 10^{-6} - 8 \times 10^{-7}$$
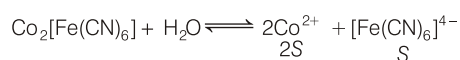
$$= 1.2 \times 10^{-6} \, S \, cm^{-1}$$

If S be the solubility of the complex, then

$$\Lambda_m^{\circ} = \frac{\kappa \times 1000}{S}$$

$$600 \, S \, cm^2 \, mol^{-1} = \frac{1.2 \times 10^{-6} Scm^{-1} \times 1000 cm^3}{S \, mol \, L^{-1}}$$

or $\quad \therefore \quad S = \frac{1.2 \times 10^{-6} \times 1000}{600}$

$$= 2 \times 10^{-6} \, mol/L$$

$$Co_2[Fe(CN)_6] + H_2O \rightleftharpoons 2Co^{2+} + [Fe(CN)_6]^{4-}$$
$$\qquad\qquad\qquad\qquad\qquad 2S \qquad\qquad S$$

$\therefore \qquad K_{sp} = [Co^{2+}][Fe(CN)_6]^{4-}$

$$= (2S)^2 \times S = 4S^3$$

$$= 4 \times (2 \times 10^{-6})^3$$

$$= 3.2 \times 10^{-17} \, M^3$$

2. **(b)** Given, $\Lambda_{eq} = 100 \, Scm^2 \, eq^{-1}$

Normality $(N) = 0.10$

Cell constant $= 0.25 \, cm^{-1}$

Now from, $\Lambda_{eq} = \dfrac{\kappa \times 1000}{N}, \kappa = \dfrac{\Lambda_{eq} \times N}{1000}$

or $\qquad \kappa = \dfrac{100 \times 0.1}{1000} = 0.01 \, Scm^{-1}$

Conductance $= \dfrac{\kappa}{\text{Cell constant}} = \dfrac{0.01}{0.25} = 0.04 \, \Omega^{-1}$ or S

Resistance $(R) = \dfrac{1}{G} = \dfrac{1}{0.04} = 25 \, \Omega$

$\therefore$ Current in ampere $= \dfrac{\text{Potential difference}}{\text{Resistance}}$

$$= \frac{5}{25} = 0.2 \, A$$

3. **(c)** Degree of dissociation is given as,

$$\alpha = \frac{\Lambda_m^C}{\Lambda_m^{\infty}} = \frac{3.907}{390.7} = 0.01$$

Given reaction,

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$
Initial conc. $\qquad C \qquad\qquad\quad 0 \qquad\quad 0$
Final conc. $\quad C(1-\alpha) \qquad\qquad C\alpha \qquad C\alpha$
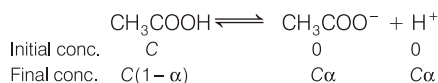
$\therefore \quad [H^+] = C\alpha = 0.01 \times 0.01$

$$= 10^{-4} \, M$$

or $\qquad pH = -\log 10^{-4}$

$$= 4$$

4. **(a)** This problem is based on Kohlrausch law,

$$\Lambda_{m[(Ba(OH)_2)]}^{\infty} = \Lambda_{Ba^{2+}}^{\infty} + 2\Lambda_{OH^-}^{\infty} = 457.6 \, Scm^2 \, mol^{-1}$$

$$\Lambda_{m(BaCl_2)}^{\infty} = \Lambda_{Ba^{2+}}^{\infty} + 2\Lambda_{Cl^-}^{\infty} = 240.6 \, S \, cm^2 \, mol^{-1}$$

$$\Lambda_{m(NH_4Cl)}^{\infty} = \Lambda_{NH_4^+}^{\infty} + \Lambda_{Cl^-}^{\infty} = 129.85 \, S \, cm^2 \, mol^{-1}$$

$$\Lambda_{m(NH_4OH)}^{\infty} = \Lambda_{m[NH_4Cl]}^{\infty} + \frac{1}{2}\Lambda_{m(Ba(OH)_2)}^{\infty} - \frac{1}{2}\Lambda_{m(BaCl_2)}^{\infty}$$

$$= 129.8 + \frac{1}{2}(457.6) - \frac{1}{2}(240.6)$$

$$= 238.3 \, S \, cm^2 \, mol^{-1}$$

5. **(a)** $\kappa_{AgCl} = \kappa_{AgCl} \, (\text{solution}) - \kappa_{H_2O}$

$$= 1.8 \times 10^{-6} - 6 \times 10^{-8}$$

$$= 1.8 \times 10^{-6} \, \Omega^{-1} \, cm^{-1}$$

$$\Lambda_{AgCl}^{\infty} = \kappa \times \frac{1000}{S}$$

$\therefore \qquad S = \kappa \times \dfrac{1000}{\Lambda_{AgCl}^{\infty}}$

$$= \frac{1.8 \times 10^{-6} \times 1000}{137.2}$$

$$= 1.31 \times 10^{-5} \, M$$

6. **(a)** $\kappa = \dfrac{1}{R} \times \dfrac{l}{a}$

$$1.29 = \frac{1}{100} \times \frac{l}{a}$$

or $\qquad \dfrac{l}{a} = 129 \, m^{-1} = \text{cell constant}$

$$\Lambda_m = \kappa \times \frac{1000}{M}$$

$$= \left(\frac{1}{R} \times \frac{l}{a}\right) \times \frac{1000}{M}$$

$$= \left(\frac{1}{520} \times 129\right) \times \frac{1000}{0.02} \times 10^{-6}$$

$$= 124 \times 10^{-4} \, Sm^2 \, mol^{-1}$$

7. **(b)** Cell constant $= \dfrac{\text{Specific conductivity of KCl}}{\text{Conductance of KCl}}$

$$= \frac{2.768 \times 10^{-3}}{\dfrac{1}{250.2}}$$

$$= 2.768 \times 10^{-3} \times 250.2$$

For 0.01 M $CuSO_4$ solution,

Specific conductivity = Cell constant $\times$ conductance

$$= 2.768 \times 10^{-3} \times 250.2 \times \frac{1}{8331}$$

Molar conductance = Specific conductivity $\times \dfrac{1000}{C}$

$$= \frac{2.768 \times 10^{-3} \times 250.2}{8331} \times \frac{1000}{1/100}$$

$$= 8.312 \, \Omega^{-1} \, cm^2 \, mol^{-1}$$

8. **(d)** $\because K_b = C\alpha^2$

$\therefore \qquad 1.6 \times 10^{-5} = 0.001 \times \alpha^2 \quad \text{or} \quad \alpha = 0.126$

Now, degree of dissociation $(\alpha) = \dfrac{\Lambda_m^C}{\Lambda_m^\infty}$

$$0.126 = \frac{\Lambda_m^C}{2.38 \times 10^{-2}}$$

or $\Lambda_m^C = 2.996 \times 10^{-3} \ \Omega^{-1} \ cm^2 \ mol^{-1}$

9. **(a)** Density of H_2O at $25°C = 1g/cm^3$

$$H_2O = \frac{1000}{18} mol/L = \frac{10^6}{18} mol/m^3$$

$$\Lambda_C = \frac{\kappa}{C} = \frac{5.7 \times 10^{-6} \ Sm^{-1}}{10^6 mol/m^3} \times 18$$

$$= 1.026 \times 10^{-10} \ Sm^2/mol.$$

$$\Lambda_{\infty(H_2O)} = \Lambda_{\infty(H^+)} + \Lambda_{\infty(OH^-)}$$

$$= (3.49 \times 10^{-2} + 1.98 \times 10^{-2}) Sm^2/mol$$

$$= 5.47 \times 10^{-2} \ Sm^2/mol$$

Degree of dissociation,

$$\alpha = \frac{\Lambda_C}{\Lambda_\infty} = \frac{1.026 \times 10^{-10} \ Sm^2/mol}{5.47 \times 10^{-2} \ Sm^2/mol} = 1.875 \times 10^{-9}$$

$$[H^+] = [OH^-] = C\alpha = \frac{1000}{18} \times 1.875 \times 10^{-9}$$

$$= 1.042 \times 10^{-7} \ mol/L$$

$$K_w = [H^+][OH^-] = (1.042 \times 10^{-7})^2$$

$$= 1.086 \times 10^{-14}$$

10. **(a)** Given, molarity of acetic acid solution = 0.04 M

$$K_a = 1.8 \times 10^{-5}$$

$$\Lambda_{m(AcOH)}^\circ = 390.5 \ S \ cm^2 \ mol^{-1}$$

Cell constant = $0.206 \ cm^{-1}$

By Ostwald's dilution law,

$$x = \sqrt{\frac{K_a}{C}}; \qquad (x = \text{degree of ionisation})$$

and, $\qquad x = \dfrac{\Lambda_m}{\Lambda_m^\circ} \implies \dfrac{\Lambda_m}{\Lambda_m^\infty} = \sqrt{\dfrac{K_a}{C}}$

$$\Lambda_m = \Lambda_m^\infty \sqrt{\frac{K_a}{C}} = 390.5 \sqrt{\frac{1.8 \times 10^{-5}}{0.04}}$$

$$= 8.25 \ S \ cm^2 \ mol^{-1}$$

Molar conductivity

$$\Lambda_m = \frac{\kappa \times 1000}{C} \implies \kappa = \frac{C \times \Lambda_m}{1000}$$

$$\implies \qquad = \frac{0.04 \times 8.28}{1000}$$

$$\kappa = 3.31 \times 10^{-4}$$

Specific conductivity, $\kappa = \text{Cell constant} \times \dfrac{1}{\text{Resistance}}$

$$\text{Resistance} = \frac{\text{Cell constant}}{\text{Conductivity}}$$
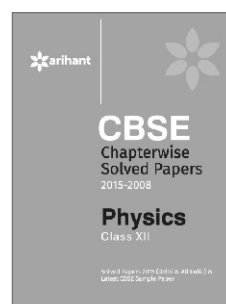
$$= \frac{0.206}{3.31 \times 10^{-4}} = 622.36\Omega$$
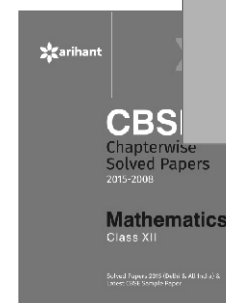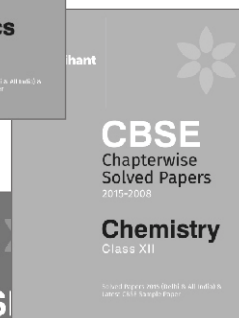
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CHEMICAL BONDING

for Class XI

1. Consider the following statements.

    I. The attractive force which holds various constituents together in different chemical species is called a chemical bond.

    II. Every system tends to be more stable and bonding is a synthetic way of lowering the energy of the system to attain stability.

    III. A group of atoms is found to exist together as one species having characteristic properties.

    Choose the correct option.

	I	II	III
(a)	True	False	True
(b)	False	True	True
(c)	True	True	True
(d)	False	False	False

2. Lewis pictured the …A… in terms of a …B… charged 'kernel' and the outer shell that could accommodate a maximum of …C… electrons. Here, A, B and C refer to

	A	B	C
(a)	atom	negatively	two
(b)	molecule	negatively	eighteen
(c)	ion	positively	thirty two
(d)	atom	positively	eight

3. Match the following Column I which represents atoms to the Column II representing their electronic configurations.

	Column I		Column II
A.	Na	p.	$[Ne]\ 3s^2\ 3p^5$
B.	Cl	q.	$[Ne]\ 3s^1$
C.	Ca	r.	$[He]\ 2s^2\ 2p^5$
D.	F	s.	$[Ar]\ 4s^2$

    Codes

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

4. According to Kossel and Lewis …A…, atoms can combine either by …B… of valence electrons from one atom to another or by …C… of valence electrons in order to have a/an …D… in their valence shell.

    Here A, B, C and D refer to

	A	B	C	D
(a)	electronic theory of chemical bonding	transfer	sharing	octet
(b)	electronic theory of chemical bonding	sharing	transfer	duplet
(c)	valence theory	transfer	sharing	octet
(d)	valence theory	sharing	transfer	duplet

5. Consider the following statements for covalent bond and choose the correct option given below for completing them.

   I. Each bond is formed as a result of …A… of an electron pair between the atoms.

    II. Each combining atom contributes at least …B… to the shared pair.

   III. The combining atoms attain the outer shell …C… configurations as a result of the sharing of electrons.

    IV. When two atoms share one electron pair they are said to be joined by a …D… .

	A	B	C	D
(a)	transfer	two electrons	noble gas	double covalent bonds
(b)	sharing	one electron	noble gas	single covalent bond
(c)	transfer	one electron	natural gas	single covalent bond
(d)	sharing	two electrons	natural gas	double covalent bonds

6. Which of the following Lewis dot structures are correct?

CHEMICAL BONDING

IV

VII
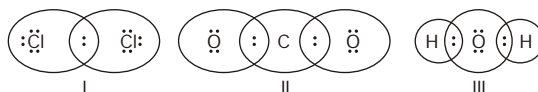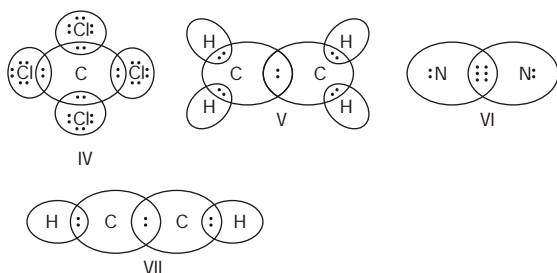
(a) I, II, III, IV and VII
(b) I, III, IV and VI
(c) All the above are correct
(d) All the above are incorrect

7. What is the formal charge on O-atom marked as 1?

(a) 0   (b) 2   (c) 1   (d) −1

8. Choose the correct drawback(s) of octet rule which are given below.
   I. Octet rule can not explain the formation of compounds like $XeF_2, KrF_2, XeOF_2$ etc.
   II. Octet rule does not account for the shape of molecules.
   III. Octet rule does not explain the relative stability of molecules.
   IV. Octet rule is totally silent about energy of a molecule.

   (a) I and II   (b) II and III
   (c) Only IV   (d) All of these

9. Match the Column I which represents bond parameter to the Column II representing their definition.

Column I	Column II
A. Bond length	p. The equilibrium distance between the nuclei of two bonded atoms in a molecule.
B. Covalent radius	q. The approximate radius of an atom's core which is in contact with the core of an adjacent atom in a bonded situation.
C. van der Waals' radius	r. The overall size of the atom which includes its valence shell in a non-bonded situation.

Codes
     A B C   A B C
(a) p r q   (b) r p q
(c) r q p   (d) p q r

10. According to the concept of resonance, whenever a …A…, cannot describe a molecule accurately, a number of structures with similar energy, …B… of nuclei, bonding and non-bonding pairs of electrons

are taken as the …C… of the hybrid which describes the molecule accurately.

Here, A, B and C refer to

	A	B	C
(a)	single Lewis structure	positions	canonical structures
(b)	Lewis dot structure	arrangements	hypothetical structures
(c)	single Lewis structure	arrangements	canonical structures
(d)	Lewis dot structure	positions	hypothetical structures

11. Which of the following option correctly represents resonance structure of CO_3^{2-} ion?
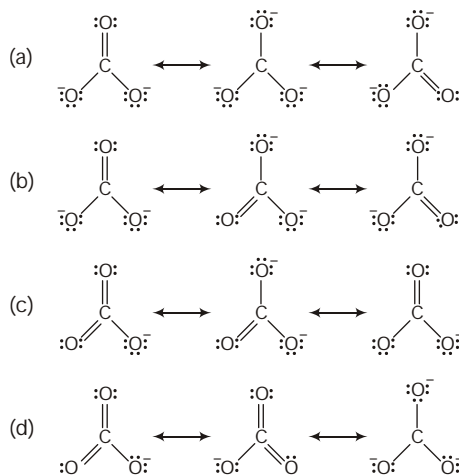
12. Consider the following statements about dipole moment.
   I. As a result of polarisation, the molecule possesses the dipole moment.
   II. Mathematically, dipole moment $(\mu) = $ charge $(Q) \times$ distance of separation (r).
   III. Dipole moment is usually expressed in Debye unit (D).
   $$1D = 3.33564 \times 10^{-28} \text{ Cm}$$
   IV. Dipole moment is a scalar quantity.

   Choose the correct statement(s).
   (a) III and IV   (b) Only I   (c) I and II   (d) Only II

13. Dipole moment of NH_3 is …A… than that of NF_3. This is because, in case of NH_3 the orbital dipole due to lone pair is in the …B… direction as the resultant dipole moment of the N—H bonds, whereas in NF_3 the orbital dipole is in the direction …C… to the resultant dipole moment of the three N—F bonds.
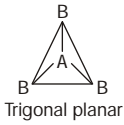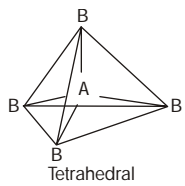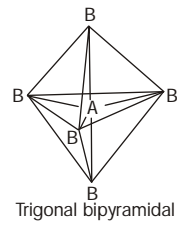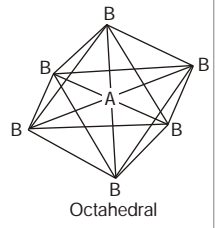
   Here A, B and C refer to

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	A	B	C
(a)	greater	same	opposite
(b)	smaller	same	opposite
(c)	greater	opposite	same
(d)	smaller	opposite	same

14. According to VSEPR theory, the repulsive interaction of electron pairs decrease in the order.

(a) Lone pair - lone pair < lone pair - bond pair < bond pair - bond pair

(b) Lone pair - lone pair > lone pair - bond pair > bond pair - bond pair

(c) Lone pair - lone pair = lone pair - bond pair > bond pair - bond pair

(d) Lone pair - lone pair > lone pair - bond pair = bond pair - bond pair

15. Match the following columns.
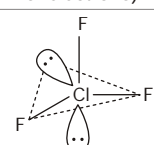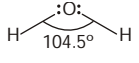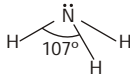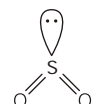
Column I (Molecular geometry)		Column II (Example)
A. Trigonal planar	p.	PCl_5
B. Tetrahedral	q.	BF_3
C. Trigonal bipyramidal	r.	SF_6
D. Octahedral	s.	NH_4^+

Codes

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

16. Match the following columns.

Column I (Number of bond pairs)		Column II (Arrangement of electrons)
A. 3	p.	(ClF$_5$ arrangement)
B. 4	q.	H_2O, $104.5°$
C. 2	r.	NH_3, $107°$
	s.	SO_2

Codes

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

17. Consider the following potential energy curve for the formation of H_2 molecule as a function of internuclear distance of the H-atoms.
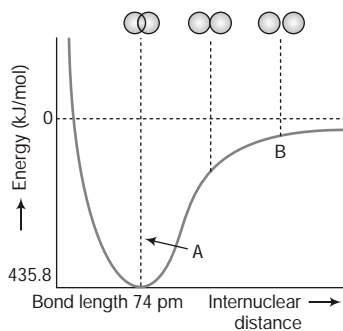
Identify A and B.

	A	B
(a)	Bond energy	Distance of separation
(b)	Bond energy	Repulsive force
(c)	Bond length	Distance of separation
(d)	Bond length	Repulsive force

18. In the formation of hydrogen molecule, there is a ...A... energy state, when two hydrogen atoms are so ...B... that their atomic orbitals undergo ...C... interpenetration. This partial merging of atomic orbitals is called ...D... of atomic orbitals.
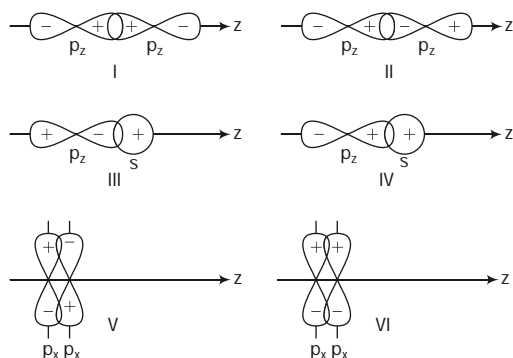
Here A, B, C and D refer to

	A	B	C	D
(a)	maximum	far	complete	overlapping
(b)	minimum	near	partial	overlapping
(c)	maximum	far	partial	mixing
(d)	minimum	near	complete	mixing

CHEMICAL BONDING

19. Identify the in phase and out of phase overlap from the following figures.

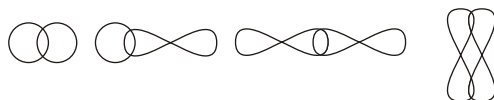|	In phase	Out of phase
(a)	II, III and V	I, II and III
(b)	I, III and IV	II, V and VI
(c)	I, II and III	IV, V and VI
(d)	I, IV and VI	II, III and V

20. Consider the types of overlapping given below, identify how many of these corresponds to σ-bonding?

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

21. In case of σ-bond, the overlapping of orbitals takes place to a …A… extent. Hence, it is …B… as compared to the π-bond, where the extent of overlapping occurs to a …C… extent.

Here, A, B and C refer to

	A	B	C
(a)	larger	stronger	smaller
(b)	larger	weaker	larger
(c)	smaller	stronger	larger
(d)	smaller	weaker	smaller

22. Which of the following conditions is incorrect for hybridisation?

(a) The orbitals present in the valence shell of the atom are hybridised

(b) The orbitals undergoing hybridisation should have different energies

(c) Promotion of electron is not essential condition prior to hybridisation

(d) It is not necessary that only half-filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridisation

23. Match the following columns.

Column I (Type of hybridisation)		Column II (Bond angle)	
A.	sp	p.	109.5°
B.	sp^2	q.	180°
C.	sp^3	r.	120°
D.	sp^3d	s.	120° and 90°

Codes

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

24. Match the following columns.

Column I (Shape of molecules/ions)		Column II (Examples)	
A.	Square planar	p.	SF_6
B.	Trigonal bipyramidal	q.	BrF_5
C.	Square pyramidal	r.	PF_5
D.	Octahedral	s.	$[Ni(CN)_4]^{2-}$

Codes

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

25. Consider the following statements about molecular orbital theory and identify the incorrect statement.

(a) The electrons in a molecule 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

(c) While an electron in an atomic orbital is influenced by one nucleus, in a molecular orbital it 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
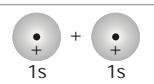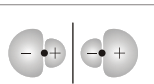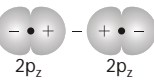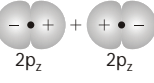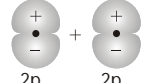
26. Consider the following energy diagram for molecular orbital theory and identify A and B.
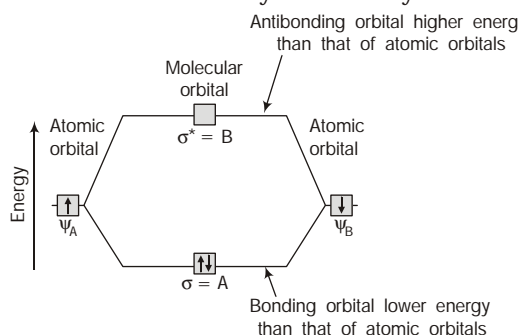
	A	B
(a)	$\psi_A + \psi_B$	$\psi_A - \psi_B$
(b)	$\psi_A - \psi_B$	$\psi_A + \psi_B$
(c)	$\psi_A - \psi_B$	$\psi_A - \psi_B$
(d)	$\psi_A + \psi_B$	$\psi_A + \psi_B$

{ MASTER THE NCERT }

27. Match the following columns.

Column I (Combination of atomic orbitals)		Column II (Molecular orbitals)
A.	1s + 1s	p.
B.	$2p_z - 2p_z$	q.
C.	$2p_z + 2p_z$	r.
D.	$2p_z + 2p_z$	s.

Codes

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

28. Consider the following statements about molecular orbital theory.

I. The increasing order of energies of various molecular orbitals for O_2 and F_2 is,

$$\sigma 1s < \overset{*}{\sigma} 1s < \sigma 2s < \overset{*}{\sigma} 2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y)$$

$$< (\overset{*}{\pi} 2p_x = \overset{*}{\pi} 2p_y) < \overset{*}{\sigma} 2p_z$$

II. The increasing order of energies of various molecular orbitals for Li_2, Be_2, B_2, C_2 and N_2 is

$$\sigma 1s < \overset{*}{\sigma} 1s < \sigma 2s < \overset{*}{\sigma} 2s < (\pi 2p_x = \pi 2p_y)$$

$$< \sigma 2p_z < (\overset{*}{\pi} 2p_x = \overset{*}{\pi} 2p_y) < \overset{*}{\sigma} 2p_z$$

III. Bond order is given as,

$$\text{Bond order} = \frac{1}{2}(N_a - N_b)$$

Choose the correct statement(s).

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

29. Match the following columns.

	Column I (Molecules)		Column II (Bond order)
A.	H_2	p.	0
B.	He_2	q.	1
C.	C_2	r.	2

Codes

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

30. Consider the following two types of molecules and identify the types of hydrogen bonding.
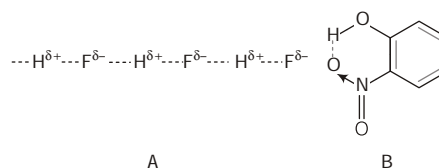
	A	B
(a)	Intramolecular	Intermolecular
(b)	Intermolecular	Intramolecular
(c)	Intermolecular	Intermolecular
(d)	Intramolecular	Intramolecular

Correct Answers along with NCERT Textbook Reference

1. (a) See page 96 Subunit-Introduction
2. (d) See page 97 Subunit-Kössel-Lewis approach to chemical bonding
3. (c) See page 97 Subunit-Kössel-Lewis approach to chemical bonding
4. (a) See page 98 Subunit-Octet rule
5. (b) See page 98 Subunit-Covalent bond
6. (b) See page 98 Subunit-Covalent bond
7. (c) See page 101 Subunit-Formal charge
8. (d) See page 102 Subunit-Limitations of the octet rule
9. (d) See page 103 Subunit-Bond parameters
10. (a) See page 105 Subunit-Resonance structure
11. (b) See page 106 Subunit-Resonance structure
12. (c) See page 107 Subunit-Polarity of bonds
13. (a) See page 108 Subunit-Polarity of bonds
14. (b) See page 109 Subunit-The valence shell electron pair repulsion theory
15. (b) See page 110 Subunit-The valence shell electron pair repulsion theory
16. (c) See page 112 Subunit-The valence shell electron pair repulsion theory

17. (a) See page 114 Subunit-Valence bond theory
18. (b) See page 114 Subunit-Orbital overlap concept
19. (d) See page 115 Subunit-Overlapping of atomic orbitals
20. (c) See page 116 Subunit-Types of overlapping and nature of covalent bonds
21. (a) See page 116 Subunit-Strength of sigma and pi-bonds
22. (b) See page 117 Subunit-Hybridisation
23. (c) See page 117 Subunit-Types of hybridisation
24. (a) See page 120 Subunit-Hybridisation of elements involving d-orbital
25. (d) See page 121 Subunit-Molecular orbital theory
26. (a) See page 122 Subunit-Formation of molecular orbitals, linear combination of atomic orbitals
27. (c) See page 124 Subunit-Energy level diagram for molecular orbitals
28. (a) See page 125 Subunit-Energy level diagram for molecualr orbitals, bond order
29. (b) See page 126 Subunit-Bonding in some homonuclear diatomic molecules
30. (b) See page 128 Subunit-Hydrogen bonding

SOLID STATE

One Option Correct Type

1. **Which of the following is not a characteristic of a crystalline solid?**
   (a) Definite and characteristic heat of fusion
   (b) Isotropic nature
   (c) A regular periodically repeated pattern of arrangement of constituent particles in the entire crystal
   (d) A true solid

2. **Which of the following is an amorphous solid?**
   (a) Graphite (C)
   (b) Quartz glass (SiO_2)
   (c) Chrome alum
   (d) Silicon carbide (SiC)

3. **Which of the following is true about the value of refractive index of quartz glass?**
   (a) Same in all directions
   (b) Different in different directions
   (c) Cannot be measured
   (d) Always zero

4. **The sharp melting point of crystalline solids is due to**
   (a) a regular arrangement of constituent particles observed over a short distance in the crystal lattice
   (b) a regular arrangement of constituent particles observed over a long distance in the crystal lattice
   (c) same arrangement of constituent particles in different directions
   (d) different arrangement of constituent particles in different directions

5. **Which of the following is a network solid?**
   (a) SO_2 (solid)
   (b) I_2
   (c) Diamond
   (d) H_2O (ice)

6. **Graphite is a good conductor of electricity due to the presence of**
   (a) lone pair of electrons
   (b) free valence electrons
   (c) cations
   (d) anions

7. **The total number of tetrahedral voids in the face-centred unit cell is**
   (a) 6
   (b) 8
   (c) 10
   (d) 12

8. **Which of the following statement is not true about the hexagonal close packing?**
   (a) The coordination number is 12
   (b) It has 74% packing efficiency
   (c) Tetrahedral voids of the second layer are covered by the spheres of the third layer
   (d) In this arrangement spheres of the fourth layer are exactly aligned with those of the first layer

9. **A ferromagnetic substance becomes a permanent magnet when it is placed in a magnetic field because**
   (a) all the domains get oriented in the direction of magnetic field
   (b) all the domains get oriented in the direction opposite to the direction of magnetic field
   (c) domains get oriented randomly
   (d) domains are not affected by magnetic field

More Than One Option Correct Type

10. **Which of the following features are not shown by quartz glass?**
    (a) This is a crystalline solid
    (b) Refractive index is same in all the directions
    (c) This has definite heat of fusion
    (d) This is also called super cooled liquid

11. **Which of the following defects decrease the density?**
    (a) Interstitial defect
    (b) Vacancy defect
    (c) Frenkel defect
    (d) Schottky defect

12. **Which of the following statements are true about semiconductors?**
    (a) Silicon doped with electron rich impurity is a p-type semiconductor
    (b) Silicon doped with an electron rich impurity is an n-type semiconductor
    (c) Delocalised electrons increase the conductivity of doped silicon
    (d) An electron vacancy increases the conductivity of n-type semiconductor

13. **Which of the following is not true about the voids formed in 3 dimensional hexagonal close packed structure?**
    (a) A tetrahedral void is formed when a sphere of the second layer is present above triangular void in the first layer
    (b) All the triangular voids are not covered by the spheres of the second layer
    (c) Tetrahedral voids are formed when the triangular voids in the second layer lie above the triangular voids in the first layer and the triangular shapes of these voids do not overlap
    (d) Octahedral voids are formed when the triangular voids in the second layer exactly overlap with similar voids in the first layer

{EXEMPLAR SIMPLIFIED}

Matching Type

14. Match the type of packing given in Column I with the items given in Column II.

	Column I		Column II
A.	Square close packing in two dimensions	p.	Triangular voids
B.	Hexagonal close packing in two dimensions	q.	Pattern of spheres is repeated in every fourth layer
C.	Hexagonal close packing in three dimensions	r.	Coordination number = 4
D.	Cubic close packing in three dimensions	s.	Pattern of sphere is repeated in alternate layers

15. Match the items given in Column I with the items given in Column II.

	Column I		Column II
A.	Mg in solid state	p.	p-type semiconductor
B.	$MgCl_2$ in molten state	q.	n-type semiconductor
C.	Silicon with phosphorus	r.	Electrolytic conductor
D.	Germanium with boron	s.	Electronic conductor

16. Match the type of unit cell given in Column I with the features given in Column II.

	Column I		Column II
A.	Primitive cubic unit cell	p.	Each of the three perpendicular edges compulsorily have the different edge length i.e. a ≠ b ≠ c.
B.	Body-centred cubic unit cell	q.	Number of atoms per unit cell is one.
C.	Face-centred cubic unit cell	r.	Each of the three perpendicular edges compulsorily have the same edge length, i.e. a = b = c.
D.	End centred orthorhombic unit cell	s.	In addition to the contribution from the corner atoms the number of atoms present in a unit cell is one.
		t.	In addition to the contribution from the corner atoms the number of atoms present in a unit cell is three.

17. Match the defects given in Column I with the statements in given Column II.

	Column I		Column II
A.	Simple vacancy defect	p.	Shown by non-ionic solids and increases density of the solid.
B.	Simple interstitial defect	q.	Shown by ionic solids and decreases density of the solid.

	Column I		Column II
C.	Frenkel defect	r.	Shown by non-ionic solids and density of the solid decreases.
D.	Schottky defect	s.	Shown by ionic solids and density of the solid remains the same

Short Answers Type

18. Why does white ZnO(s) becomes yellow upon heating?

19. In a compound, nitrogen atoms (N) makes cubic close-packed lattice and metal atoms (M) occupy one-third of the tetrahedral voids present. Determine the formula of the compound formed by M and N?

20. Explain why does conductivity of germanium crystals increase on doping with gallium?

21. Why does table salt, NaCl sometimes appear yellow in colour?

22. Inspite of long range order in the arrangement of particles, why are the crystals usually not perfect?

Assertion and Reason Type

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct answer out of the following choices.

- (a) Assertion and Reason both are correct statements and Reason is correct explanation for Assertion
- (b) Assertion and Reason both are correct statements but Reason is not correct explanation for Assertion
- (c) Assertion is correct statement but Reason is wrong statement
- (d) Assertion is wrong statement but Reason is correct statement

23. Assertion (A) Graphite is a good conductor of electricity however diamond belongs to the category of insulators.

Reason (R) Graphite is soft in nature on the other hand, diamond is very hard and brittle.

24. Assertion (A) Semiconductors are solids with conductivities in the intermediate range from $10^{-6} - 10^4$ ohm^{-1} m^{-1}.

Reason (R) Intermediate conductivity in semi-conductor is due to partially filled valence band.

25. Assertion (A) The packing efficiency is maximum for the fcc structures.

Reason (R) The coordination number is 12 in fcc structures.

Answer *with* **Explanations**

1. (b) Concept Isotropic and anisotropic properties are related to amorphous solid and crystalline solid respectively. These are shown as follows:

| Property	Types of solid	Physical properties
Isotropy	Amorphous solid	Same value
Anisotropy	Crystalline solid	Different values

Crystalline solid is anisotropic in nature as the solid shows different physical properties, e.g. electrical resistance, refractive index in different directions.

2. (b) Concept Quartz is a crystalline solid while quartz glass is an amorphous solid.
   Quartz glass (SiO_2) is an amorphous solid due to its short range order of constituent particles.

3. (a) Concept Quartz glass have short range order of constituents due to its amorphous nature.
   Value of refractive index is same in all directions, can be measured and not equal to zero always.

4. (b) Due to regular arrangement of constituent particles over a long distance in crystalline solids, these solids have sharp melting points.

5. (c) Thinking process A network solid (covalent network solid) is a chemical compound in which the atoms are bonded by covalent bonds in a continuous network extending throughout the material.
   Diamond is a giant molecule in which constituent atoms are held together by covalent bond. Hence, this is a network solid.

154 pm
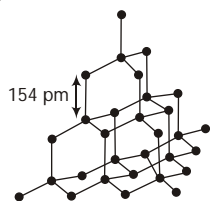
Network structure of diamond

6. (b) In graphite, each carbon is sp^2 hybridised having one free valence electron, i.e. electrons are delocalised or free to move around the hexagonal rings and which make graphite a good conductor of electricity.

340 pm

141.5 pm

sp^2 hybridised carbon
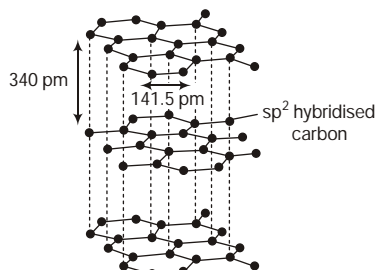
Structure of graphite

7. (b) Thinking process
   If number of atoms in fcc unit cell $= N$
   Number of tetrahedral voids $= 2\,N$
   Number of octahedral voids $= N$

∴ Number of tetrahedral voids
$$= 2 \times \text{number of octahedral voids}$$

Fcc unit cell contains 8 tetrahedral voids at centre of each 8 smaller cube of an unit cell as shown below.
Eight tetrahedral voids per fcc unit cell
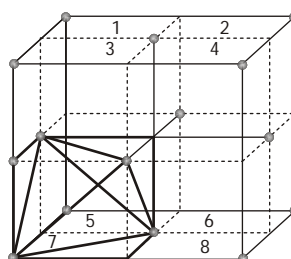
Tetrahedral void

Each cube represented by numeric 1, 2, 3, 4, 5, 6, 7, 8 contains one tetrahedral voids.
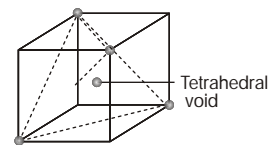
Each cube contains one tetrahedral void at its body centre as shown above

Number of atoms in fcc unit cell $= 4$
Number of octahedral voids $= 4$
Number of tetrahedral voids $= 8$

8. (d) Hexagonal close packing is shown in the following figure.

B
A
B
A
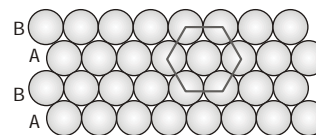
Option (a), (b) and (c) are correct but option (d) is incorrect as first layer is not exactly aligned with that of fourth layer.

9. (a) Concept Few substances such as Fe, Co, Ni, Gd and CrO_2 are attracted very strongly to a magnetic field. Such substances are known as ferromagnetic substances.
   When a ferromagnetic substance is placed in a magnetic field, it becomes a permanent magnet because all the domains get oriented in the direction of magnetic field even after removal of applied magnetic field.

10. (a,c) Quartz glass is an amorphous solid and it has following characteristics.
    • It has irregular shape due to short range order of constituent particles.
    • It is considered to be highly supercooled liquid of very high viscosity and hence also called pseudo solid.
    • It does not have definite heat of fusion.

11. (b,d) Vacancy and Schottky defect are the types of stoichiometric defect. Hence, these defects leads to decrease in density of crystal due to missing of ions.

12. (b,c) Silicon doped with an electron rich impurity such as P or As, which contains five electrons is a n-type semiconductor. Conductivity of n-type semiconductor is due to delocalisation of free valence electrons.

{EXEMPLAR SIMPLIFIED}

13. **(c, d)** *Thinking process* Tetrahedral holes are exactly above the triangular voids while octahedral holes are formed when triangular void of second layer is not exactly overlap with similar void in first layer.

Tetrahedral voids are formed when the triangular void in the second layer lie exactly above the triangular voids in the first layer and the triangular shape of these voids oppositely overlap.
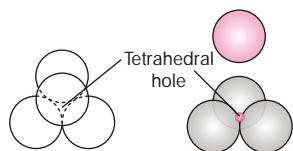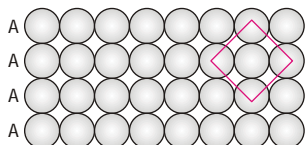
Tetrahedral hole

Octahedral voids are formed when triangular void of second layer is not exactly overlap with similar void in the first layer.

Octahedral hole
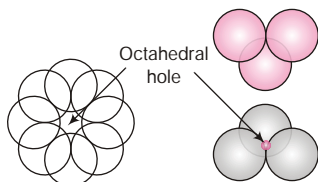
14. A → r ; B → p ; C → s ; D → q

   A. Square close packing in two dimensions is shown below,

   A
   A
   A
   A

   Clearly, each sphere has coordination number 4.

   B. Similarly, for hexagonal close packing in two dimensions,

   Triangular void (Surrounded by 3 spherical atom)

   B
   A
   B
   A
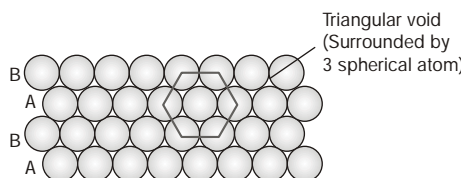
   C. For hexagonal close packing in three dimensions,

   A   B   A
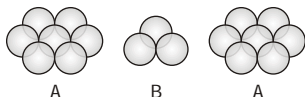
   Pattern of sphere is repeated in alternate layers. This pattern is also known as ABAB pattern.

   D. For cubic close packing in three dimensions.

   C
   B
   A
   C
   B
   A
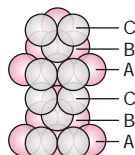
   Pattern of spheres is repeated in every fourth layer.

15. A → s ; B → r ; C → q ; D → p

   (a) Mg in solid state show electronic conductivity due to the presence of free electrons hence, they are known as electronic conductor.

   (b) $MgCl_2$ in molten state show electrolytic conductivity due to the presence of electrolytes in molten state.

   (c) Semiconductor obtained after doping of silicon with phosphorus contain one extra electron due to which it shows conductivity under the influence of electric field and it is known as n-type semiconductor.

   (d) Semiconductor obtained after doping of germanium with boron contain one hole due to which it shows conductivity under the influence of electric field and it is known as p-type semiconductor.

   Silicon atom   Mobile electron   Positive hole (no electron)

   Perfect crystal   n-type semiconductor   p-type semiconductor
      (a)   (b)   (c)
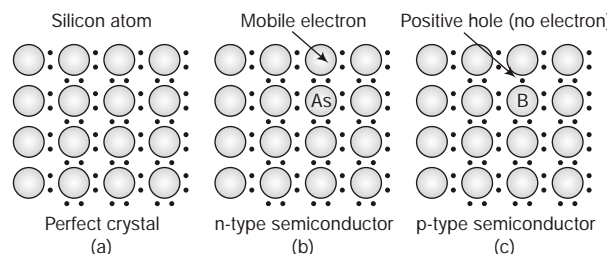
16. A → q, r ; B → r, s ; C → r, t ; D → p, s

   A. For primitive unit cell, a = b = c

   Total number of atoms per unit cell, = 1 / 8 × 8 = 1

   Here, 1/8 is due to contribution of each atom present at corner.

   B. For body-centred cubic unit cell, a = b = c

   This lattice contains atoms at corner as well as at body-centred. Contribution due to atoms at corner = 1 / 8 × 8 = 1, contribution due to atoms at body-centred = 1.

   C. For face-centred unit cell, a = b = c

   Total constituent ions per unit cell present at corners

   $$= \frac{1}{8} \times 8 = 1$$

   Total constituent ions per unit cell present at face centre

   $$= \frac{1}{2} \times 6 = 3$$

   D. For end-centred orthorhombic unit cell, a ≠ b ≠ c
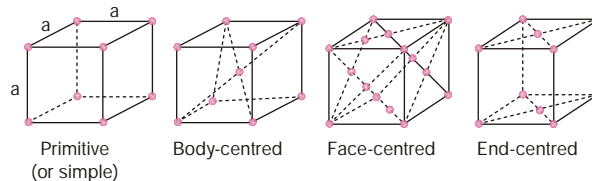
   Total contribution of atoms present at corner

   $$= \frac{1}{8} \times 8 = 1$$

   Total contribution of atoms present at end centre
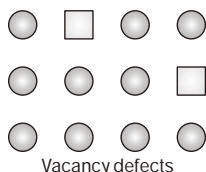
   $$= \frac{1}{2} \times 2 = 1$$

   Hence, other than corner it contain total one atom per unit cell.

   Primitive   Body-centred   Face-centred   End-centred
   (or simple)

17. $A \rightarrow r$; $B \rightarrow p$; $C \rightarrow s$; $D \rightarrow q$

A. When some of lattice sites are vacant in any non-ionic solid, the crystal is said to have vacancy defect and due to decrease in number of particles present in crystal lattice the density of crystal decreases.


Vacancy defects

B. Simple interstitial defect are shown by non-ionic solids in which some extra constituent particles are present in the interstitial site. Hence, density of solid increases.

Interstitial defects
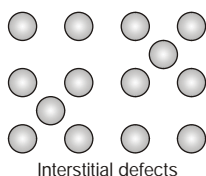
C. Frenkel defect is shown by ionic solids in which smaller ions get dislocated from its normal site to its interstitial site. Hence, there is no effect on density of crystal.

Frenkel defects
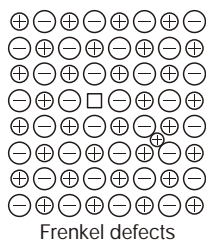
D. Schottky defect is shown by ionic solids in which equal number of cation and anion get missed from ionic solids and thus, density of solid decreases.

Schottky defects
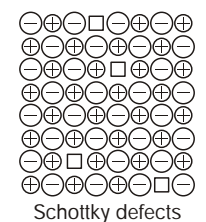
18. **Concept** F-centre impart colour to a crystal lattice.
On heating ZnO loses oxygen as follows

$$ZnO \xrightarrow{\text{Heat}} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$
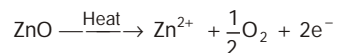
Zn^{2+} ions and electrons move to interstitial sites due to which F-centres are formed. These F-centres impart colour to ZnO(s).

19. **Concept** Number of tetrahedral voids
$= 2 \times$ number of octahedral voids
$= 2 \times$ number of lattice sites.

Let the number of N-atoms in ccp is x.
∴ Number of tetrahedral voids $= 2x$

∴ Number of M atoms $= \frac{1}{3} \times 2x$

$$\frac{\text{Number of N-atoms}}{\text{Number of M-atoms}} = \frac{3x}{2x} = \frac{3}{2}$$

So, the formula of the compound is M_2N_3.

20. **Concept** Conductivity increases due to deficiency of electrons (electron hole) which is full filled by neighbouring atoms.

On doping germanium with gallium some of the positions of lattice of germanium are occupied by gallium. Gallium atom has only three valence electrons. Therefore, fourth valency of nearby germanium atom is not satisfied and the place remains vacant.

This place is deficient of electrons and is therefore called electron hole or electron vacancy. Electron from neighbouring atom comes and fills the hole, thereby creating a hole in its original position.

Under the influence of electric field electrons move towards positively charged plates and conduct electricity. The holes appear to move towards negatively charged plates.

21. Yellow colour in NaCl is due to metal excess defect due to which unpaired electrons occupy anionic sites, known as F-centres. These electrons absorb energy from the visible region for the excitation which makes crystal appear yellow.

22. Crystals have long range repeated pattern of constituent particles but in the process of crystallisation some deviations from the ideal arrangement (i.e. defects) may be introduced, therefore, crystals are usually not perfect.

23. (b) Correct explanation is that graphite have layered structure with free delocalised valence electrons due to which it is a good conductor of electricity. On the other hand, diamond has tetrahedral arrangement with no unpaired electron. Therefore, diamond is hard and brittle, it also act as an insulator.

24. (c) **Concept**
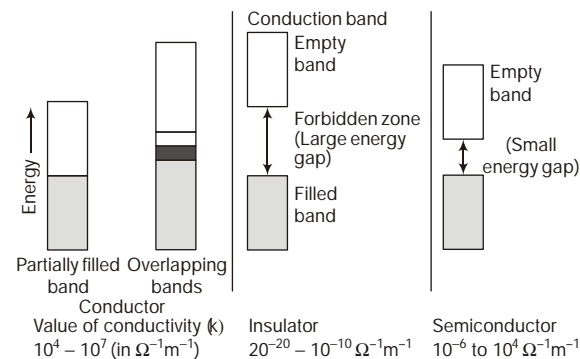
Semiconductors are solids with conductivities in the intermediate range. These conductivities varies from $10^{-6} - 10^4$ ohm^{-1} m^{-1}. Intermediate conductivity is due to small energy gap between valence band and conduction band.

25. (b) Correct (R) For fcc structure, the packing efficiency is maximum ($\cong 74\%$) because it consists of total four atoms per unit cell.
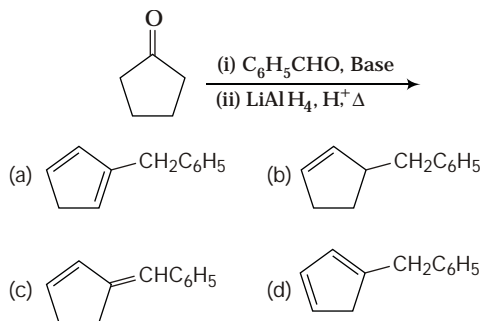
{EXAM DIARY}
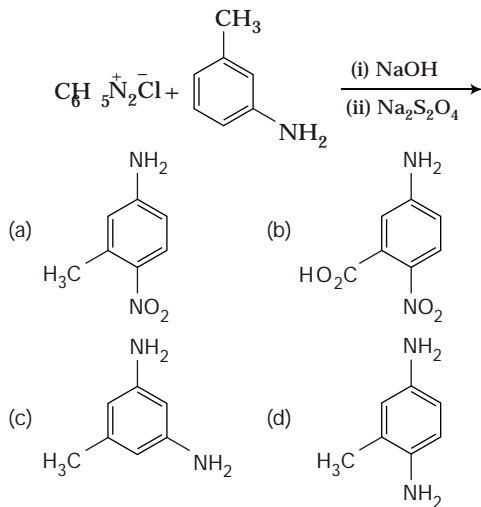
J&K
SOLVED
PAPER
2015

EXAM CRUX

- There are a total of 180 questions asked in J & K CET. Out of which 60 questions are asked from chemistry.
- Around 50% questions are asked from both class XI and class XII.
- This year most of the questions (around 30) were asked from the physical chemistry. There were 14 questions from organic chemistry 10 questions from inorganic chemistry and rest from miscellaneous interdisciplinary sections.
- Chapters from class XI which weighed heavy in this paper were Basic principles of organic chemistry (6Qs), Equilibrium (5Qs), Thermodynamics (5Qs), Bonding and Molecular Structure (4Qs).
- From class XII, the chapter given weightage were, Solutions, Coordination chemistry, Haloalkanes and Haloarenes and Organic compound containing oxygen, with each having a contribution of 3 questions.
- Difficulty Level On the basis of analysis done by the Arihant team around 40% questions were considered to be tough, around 30% moderate and 30% were easy. Overall, this year paper was a bit tougher in comparison to the previous year paper.

1. If a homogeneous colloid placed in dark is observed in the direction of light, it appears clear and if it is observed from a direction at right angles to the direction of light beam, it appears perfectly dark. This is known as
   (a) Brownian effect
   (b) Hardy Schulze effect
   (c) Einstein effect
   (d) Tyndall effect

2. When powdered plaster of Paris is mixed with correct amount of water, it sets into a solid mass of
   (a) $CaSO_4 \cdot 5H_2O$
   (b) $CaSO_4 \cdot 3H_2O$
   (c) $CaSO_4 \cdot 2H_2O$
   (d) $CaSO_4 \cdot 1/2H_2O$

3. pV value decreases with increase in p at constant temperature when
   (a) there is no attractive or repulsive forces between molecules
   (b) attractive and repulsive forces between molecules are equal
   (c) attractive forces between molecules are predominant
   (d) repulsive forces between molecules are predominant

4. For a reaction, $C(s) + CO_2(g) \longrightarrow 2CO(g)$ the partial pressure of CO_2 and CO are 4 and 8 atm, respectively. K_p for the reaction is
   (a) 0.5   (b) 2
   (c) 16   (d) 4

5. HA is a weak acid. At 25°C, the molar conductivity of 0.02 M HA is $150\ \Omega^{-1}\ cm^2\ mol^{-1}$. If its Λ_m^o is $300\ \Omega^{-1}cm^2\ mol^{-1}$, then equilibrium constant of HA dissociation is
   (a) 0.001
   (b) 0.005
   (c) 0.01
   (d) 0.02

6. The product of the following reaction is

7. Identify the major product for the reaction given below

$$CH_6H_5\overset{+}{N}_2\overset{-}{Cl} +$$

(with a benzene ring bearing CH_3 and NH_2 groups)

(i) NaOH
(ii) $Na_2S_2O_4$

(a) (structure with NH_2, H_3C, NO_2)

(b) (structure with NH_2, HO_2C, NO_2)

(c) (structure with NH_2, H_3C, NH_2)

(d) (structure with NH_2, H_3C, NH_2)

8. 30 mL of 0.02 M ammonium hydroxide is mixed with 15 mL of 0.02 M HCl. What will be the pH of the solution ($pK_b = 4.0$)?
(a) 4   (b) 8   (c) 4   (d) 10

9. In an acidified aqueous solution of Mn^{2+}, Ni^{2+}, Cu^{2+} and Hg^{2+} ions, H_2S gas was passed. Precipitates are
(a) MnS and CuS   (b) NiS and HgS
(c) MnS and NiS   (d) CuS and HgS

10. Shape of SF_4 is
(a) tetrahedral   (b) square planar
(c) trigonal pyramidal   (d) see-saw

11. The following tripeptide can be synthesised from the following amino acid,

(tripeptide structure)
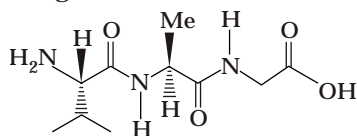
(a) Glycine, Leucine and Alanine
(b) Alanine, Isoleucine and Glycine
(c) Valine, Alanine and Glycine
(d) Alanine, Serine and Glycine

12. The species which cannot serve as an initiator for the free radical polymerisation, is

(a) (structure)
(b) (structure)
(c) H_3C—C(CN)(CH_3)—N=N—C(CN)(CH_3)—CH_3
(d) Ph—CH_2—CHO
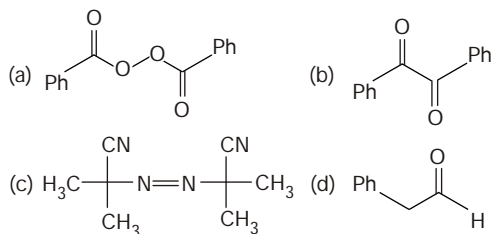
13. Nylon is a
(a) polyamide   (b) carbonate
(c) ester   (d) polycarboxylic acid

14. A gas at high temperature is cooled. The highest temperature at which liquefaction of gas first occurs is called
(a) Boyle temperature
(b) critical temperature
(c) boiling temperature
(d) freezing temperature

15. Buna-N synthetic rubber is obtained by the copolymerisation of
(a) $CH_2{=}CH{-}CH{=}CH_2$ and $H_5C_6{-}CH{=}CH_2$
(b) $CH_2{=}CH{-}CN$ and $H_2C{=}CH{-}CH{=}CH_2$
(c) $H_2C{=}CH{-}CN$ and $CH_2{=}CH{-}C(CH_3){=}CH_2$
(d) $H_2C{=}CH{-}C(Cl){=}CH_2$ and $H_2C{=}CH{-}CH{=}CH_2$

16. When the following amide is treated with Br_2/KOH, it gives

(amide structure)

(i) Br_2
(ii) KOH

(a) (structure with NH_2)
(b) (structure with OH)
(c) (structure with HN, O)
(d) (structure with N, H, O)
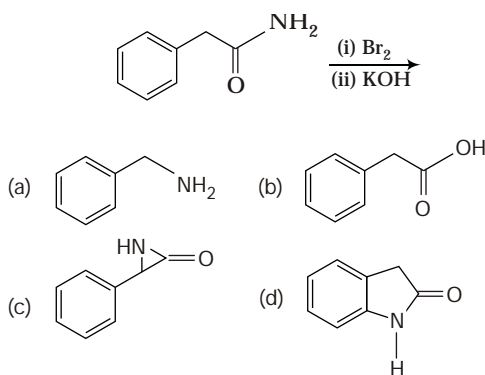
17. The IUPAC name of the coordination compound $[Co(H_2O)_2(NH_3)_4]Cl_3$ is
(a) tetraamminediaquacobalt (III) chloride
(b) cobalt (III) tetraamminediaqua chloride
(c) diaquatetraammine cobalt (III) chloride
(d) tetraamminediaquacobalt (II) chloride

18. Siderite is mainly ore of
(a) Zn   (b) Fe   (c) Cd   (d) Ru

19. Among P, S, Cl, F, the elements with most negative and least negative electron gain enthalpy respectively, are
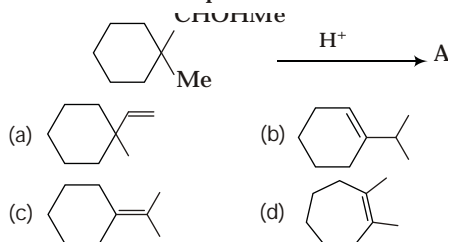(a) Cl, S   (b) F, S   (c) Cl, P   (d) F, P

20. For a reaction $2A \longrightarrow 3B$, if the rate of formation of B is x mol/L, the rate of consumption of A is
(a) x (b) $\dfrac{3x}{2}$
(c) $\dfrac{2x}{3}$ (d) $3x$

{EXAM DIARY}

21. The following alcohol after treatment with acid gives compound A. Ozonolysis of A gives nonane-2, 8-dione. The compound A is

$$\xrightarrow{H^+} A$$

(a)

(b)

(c)

(d)

22. In He_2, the electrons in bonding and antibonding orbitals are

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

23. 0.5 molal solution of a solute in benzene shows a depression in freezing point equal to 2 K. Molal depression constant for benzene is 5 K kg mol^{-1}. If the solute forms dimer in benzene, what is the % association?

(a) 40   (b) 50   (c) 60   (d) 80

24. The major product of the following transformation is

$$\xrightarrow{NaOMe/MeOH}$$

(a)

(b)

(c)

(d)
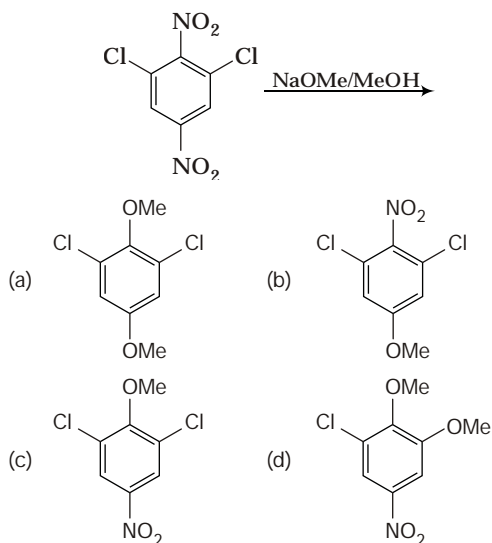
25. A highly stable conformation for the following compound is

(a)

(b)

(c)

(d)
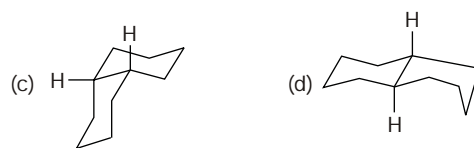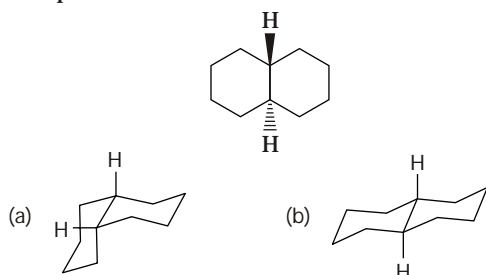
26. Molar enthalpy change for melting of ice is 6 kJ/mol. Then the internal energy change (in kJ/mol) when 1 mole of water is converted into ice at 1 atm at 0°C is

(a) RT/1000   (b) 6
(c) 6 − (RT / 1000)   (d) 6 + (RT / 1000)

27. Identify the correct product of the following reaction,

$$+ \ Me_2NH \longrightarrow$$

(a)

(b)

(c)

(d)
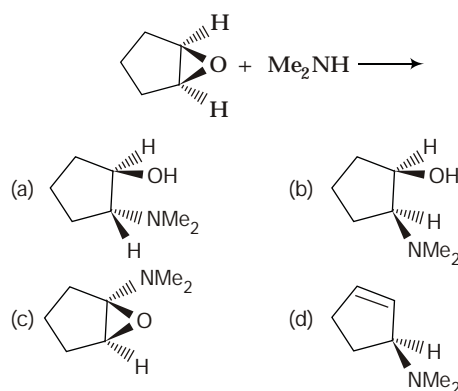
28. Among second period elements, the correct order for first ionisation enthalpy is

(a) Li < Be < B < C < N < O < F < Ne
(b) Li < B < Be < C < O < N < F < Ne
(c) Li > Be > B > C > N > O > F > Ne
(d) Li > B > C > Be > O > N > F > Ne

29. For the reaction,

$A(s) + 2B^+(aq) \longrightarrow A^{2+}(aq) + 2B(s)$; the E^o is 1.18 V.
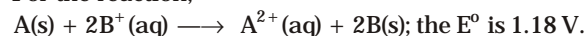
Then the equilibrium constant for the reaction is

(a) 10^{10} (b) 10^{20}
(c) 10^{40} (d) 10^{60}

30. Identify the correct statement about the following pairs of compounds.

A   B

C   D
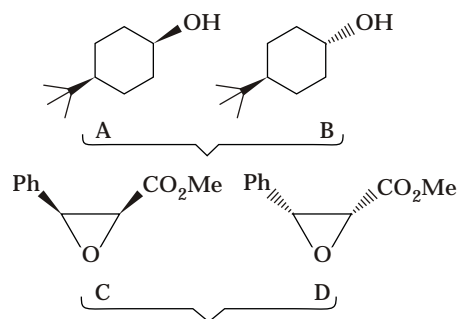
(a) A and B diastereomers ; C and D diastereomers
(b) A and B enantiomers ; C and D diastereomers
(c) A and B diastereomers ; C and D enantiomers
(d) A and B enantiomers ; C and D enantiomers

31. One of the following complexes shows geometrical isomerism. The complex is
(a) $PtCl_4$ (b) $Pt(NH_3)_2Cl_2$
(c) $Pt(NH_3)_3Cl$ (d) $Ni(NH_3)_3Cl$

32. The ionisation potential of hydrogen atom is 13.6 eV. The energy required to remove an electron from $n = 2$ state of hydrogen atom is
(a) 27.2 eV   (b) 13.6 eV
(c) 6.8 eV   (d) 3.4 eV

33. Among the following pair, which one has both variables as intensive variable?
(a) T, V   (b) m, p
(c) d, V   (d) p, T

34. Which one of the following will quickly react with $AgNO_3$?

(a)
(b)
(c)
(d)
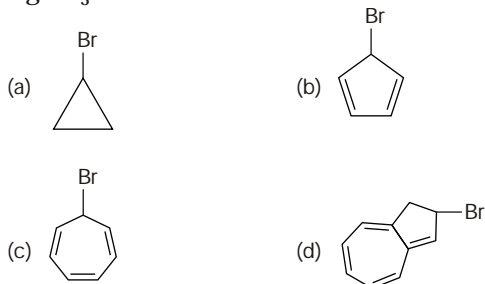
35. The number of tetrahedral and octahedral voids per unit cell of cubic closed packed structure is
(a) 4,8   (b) 4,4
(c) 8,4   (d) 8,8

36. In the following disaccharide,
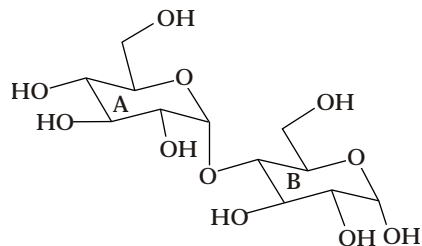
(a) Ring (A) is pyranone with α-glycosidic link
(b) Ring (A) is furanone with α-glycosidic link
(c) Ring (B) is pyranone with β-glycosidic link
(d) Ring (B) is furanone with α-glycosidic link

37. When a dilute solution of ammonia is saturated with H_2S it gives
(a) $(NH_4)_2S$ (b) NH_4HS
(c) $(NH_3)_2H_2S$ (d) $NH_3 \cdot H_2S$

38. If $E^o_{M^+/M} = -1.2$ V, $E^\circ_{X_2/X^-} = -1.1$ V and $E^\circ_{O_2/H_2O} = 1.23$V, then on electrolysis of aqueous solution of salt MX, the products obtained are
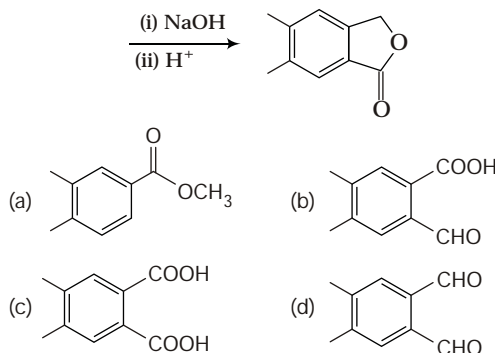(a) M, X_2 (b) H_2, X_2 (c) H_2, O_2 (d) M, O_2

39. For the process to occur under adiabatic condition, the correct condition is
(a) $\Delta T = 0$ (b) $\Delta U = 0$
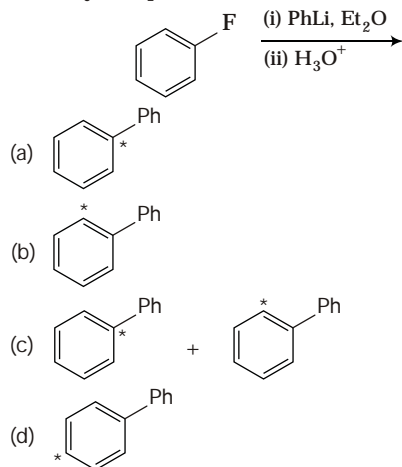(c) $\Delta p = 0$ (d) $\Delta q = 0$

40. Which of the element is available in carbonic anhydrase?
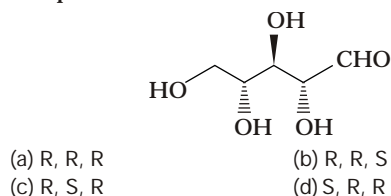(a) Pd   (b) Fe
(c) Zn   (d) Pt
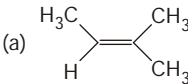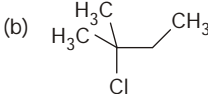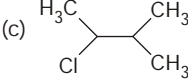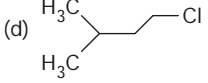
41. Identify reactant A for the following reaction,

(i) NaOH
(ii) H^+

(a)
(b)
(c)
(d)

42. Identify the product of the following reaction

(i) PhLi, Et_2O
(ii) H_3O^+

(a)
(b)
(c)   +
(d)

43. The absolute configuration of the following compound is

(a) R, R, R   (b) R, R, S
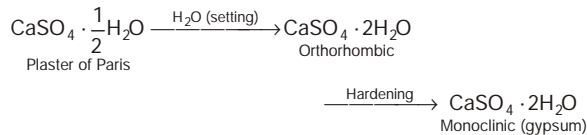(c) R, S, R   (d) S, R, R
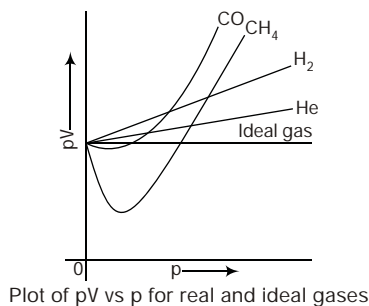
{EXAM DIARY}

44. The wrong statement among the following is
    (a) acid rain is mostly because of oxides of nitrogen and sulphur
    (b) greenhouse effect is responsible for global warming
    (c) ozone layer does not permit infrared radiation from the sun to reach earth
    (d) chlorofluorocarbons are responsible for ozone layer depletion

45. The vapour pressure of pure benzene at certain temperature is 1 bar. A non-volatile, non-electrolyte solid weighing 2 g when added to 39 g of benzene (molar mass 78g mol^{-1}) yields solution of vapour pressure of 0.8 bar. The molar mass of solid substance is
    (a) 32   (b) 16
    (c) 64   (d) 48

46. $HClO_4 \cdot 2H_2O$ after reaction with fuming sulphuric acid generates.
    (a) $ClO_2 + H_2SO_4$
    (b) $Cl_2O_7 + H_2SO_4$
    (c) $HClO_4 + H_2SO_4$
    (d) $Cl_2O_6 + H_2SO_4$

47. The compound formed upon combustion of potassium metal in excess air is
    (a) K_2O_2
    (b) KO_2
    (c) K_2O
    (d) KOH

48. Energy of activation of forward reaction for an endothermic process is 90 kJ. If enthalpy change for the reaction is 50 kJ then, activation energy for backward reaction will be
    (a) 40 kJ
    (b) 140 kJ
    (c) 90 kJ
    (d) 50 kJ

49. For ion O_2^-, the bond order is
    (a) 2   (b) 1.5   (c) 2.5   (d) 0

50. Extraction of mercury from cinnabar is achieved by
    (a) heating it in air
    (b) electrolytic reduction
    (c) roasting followed by reduction with carbon
    (d) roasting followed by reduction with another metal

51. The correct order of the ligands, OH^-, NO_3^-, PPh_3, pyridine, according to their increasing field strength is
    (a) $NO_3^- < OH^- <$ pyridine $< PPh_3$
    (b) $OH^- < NO_3^- < PPh_3 <$ pyridine
    (c) $OH^- < NO_3^- <$ pyridine $< PPh_3$
    (d) $NO_3^- < OH^- < PPh_3 <$ pyridine

52. When $(CH_3)_3CCH_2Cl$ is heated at 300°C, it gives
    (a) [structure: H_3C, CH_3, H, CH_3 alkene]
    (b) [structure: H_3C, H_3C, CH_3, Cl]
    (c) [structure: H_3C, CH_3, Cl, CH_3]
    (d) [structure: H_3C, H_3C, Cl]

53. If the density of methanol is $0.8\ \text{kg L}^{-1}$, what is its volume needed for making 4L of its 0.25M solution?
    (a) 4 mL   (b) 8 mL
    (c) 40 mL   (d) 80 mL

54. The number of Na atom in 46 g Na (Atomic weight of Na $= 23$) is
    (a) 6.023×10^{23} (b) 2
    (c) 1   (d) 12.046×10^{23}

55. If the solubility of a sparingly soluble salt AX_2 is S mol/L, the solubility product is
    (a) $4S^3$ (b) $8S^3$
    (c) $4S^2$ (d) S^2

56. Which one of the following does not have sp^3 hybridisation?
    (a) CH_4 (b) XeF_4
    (c) H_2O (d) NH_3

57. Milk is an example of
    (a) emulsion   (b) sol
    (c) gel   (d) foam

58. $\dfrac{K_p}{K_C}$ for the reaction,
    $A(g) + 2B_2(g) \longrightarrow AB_2(g)$ is
    (a) RT   (b) $(RT)^2$
    (c) $\dfrac{1}{RT}$ (d) $\dfrac{1}{(RT)^2}$

59. 1 mole of an ideal gas expands isothermally and reversibly from 2 L to 20 L at 300 K. If the final pressure of the gas is 1 bar, the work done by the gas is
    (a) $-300\ R\ \ln 10$
    (b) $300\ R\ \ln 10$
    (c) 18
    (d) -18

60. A unit cell with edge length $a \neq b \neq c$ and axial angles $\alpha = \beta = \gamma = 90°$ is called
    (a) cubic
    (b) tetragonal
    (c) orthorhombic
    (d) hexagonal

Answer *with* Explanations

1. (d) The colloidal system show following optical property. When light falls on sol particle, it absorbs the light and scatter it. This scattering of light is called Tyndall effect. The illuminated path of light passing through the colloids is called Tyndall cone.

2. (c) When powdered plaster of Paris mixed with water it takes up the water of crystallisation and forms a plastic mass that gets converted into hard solid (gypsum) within 5 to 15 min.

$$CaSO_4 \cdot \frac{1}{2}H_2O \xrightarrow{H_2O \text{ (setting)}} \underset{\text{Orthorhombic}}{CaSO_4 \cdot 2H_2O}$$
$$\underset{\text{Plaster of Paris}}{}$$

$$\xrightarrow{\text{Hardening}} \underset{\text{Monoclinic (gypsum)}}{CaSO_4 \cdot 2H_2O}$$

3. (c)

Plot of pV vs p for real and ideal gases

It can be seen easily that at constant temperature, pV vs p plot for real gases is not a straight line. There is a significant deviation from ideal behaviour. Two types of curves are seen. In the curves for dihydrogen and helium, as the pressure increases the value of pV also increases.

The second type of plot is seen in the case of other gases like carbon monoxide and methane. In these plots, first there is a negative deviation from ideal behaviour, then pV value decreases with increase in pressure and reaches to a minimum value characteristic of gas. In second case, attractive forces between molecules are predominant. Compressibility factor (Z) is less than one.

4. (c) $C(s) + CO_2(g) \longrightarrow 2CO(g)$

Applying the law of mass action

$$K_p = \frac{(p_{CO})^2}{(p_C)(p_{CO_2})}$$

Given, $\quad p_{CO} = 8 \text{ atm}$
$$p_{CO_2} = 4 \text{ atm}$$
and for solid $C(s)$
$$p_C = 1$$

$$\therefore \qquad K_p = \frac{(8)^2}{1 \times 4}$$

$$\Rightarrow \qquad K_p = \frac{64}{4} = 16$$

5. (c) Given, molar conductivity $(\Lambda_m) = 300 \, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$

Limiting molar conductivity $(\Lambda_m^\circ) = 150 \, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
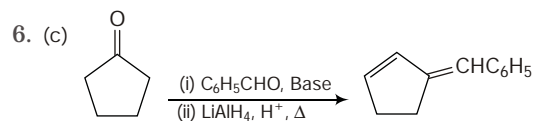
Concentration $(C) = 0.02 \text{ M}$

$\therefore$ Degree of dissociation $(\alpha) = \dfrac{\Lambda_m}{\Lambda_m^\circ}, \quad \alpha = \dfrac{150}{300} = 0.5$

Now, by using following reaction, we can determine the value of its dissociation constant
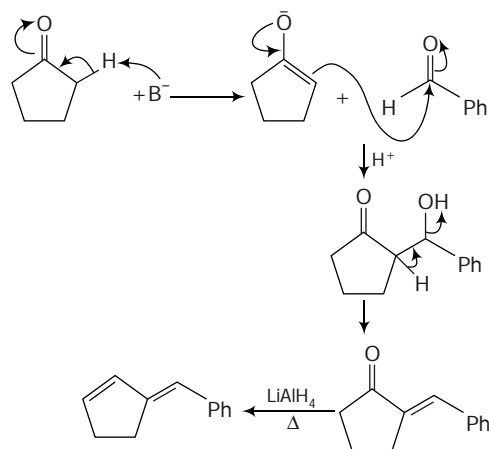
$$K_a = \frac{C\alpha^2}{(1-\alpha)}$$

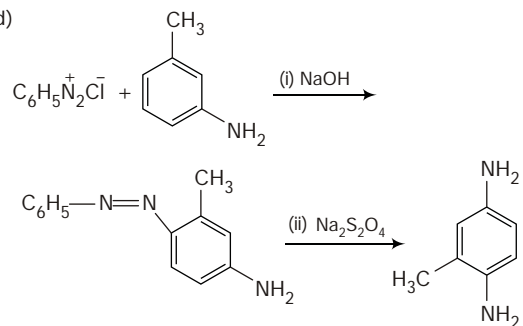$$K_a = \frac{0.02 \times (0.5)^2}{(1-0.5)}$$
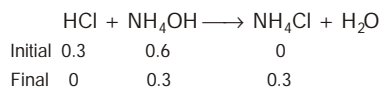
$$= \frac{0.02 \times 0.5 \times 0.5}{0.5} = 0.01$$

6. (c)

Mechanism

7. (d)

8. (d) 30 mL of 0.02 M NH_4OH + 15 mL of 0.02 M HCl

Number of millimoles of $NH_4OH = 30 \times 0.02$
$$= 0.6 \text{ mol}$$

Number of millimoles of HCl = $15 \times 0.02 = 0.3 \text{ mol}$
In an acid-base reaction, salt will always form but we have to check what is left or consumed.

$HCl + NH_4OH \longrightarrow NH_4Cl + H_2O$

Initial 0.3   0.6   0

Final   0   0.3   0.3

Basic buffer will form as weak base NH_4OH is left in the solution

$[NH_4Cl] = \dfrac{0.3}{\text{Total volume}} = \dfrac{0.3}{45}$

$[NH_4OH] = \dfrac{0.3}{\text{Total volume}} = \dfrac{0.3}{45}$

Applying $pOH = pK_b + \log \dfrac{[Salt]}{[Base]}$

$pOH = 4 + \log \dfrac{\dfrac{0.3}{45}}{\dfrac{0.3}{45}}$

$pOH = 4 + \log 1$ $[\because \log 1 = 0]$

$pOH = 4$

$\because \qquad pH = 14 - pOH$

$\therefore \qquad pH = 14 - 4$

$\qquad pH = 10$

9. (d) The black precipitates of CuS and HgS will be formed.

$Cu^{2+} + H_2S \longrightarrow CuS \text{ (black)} \downarrow + H_2 \uparrow$

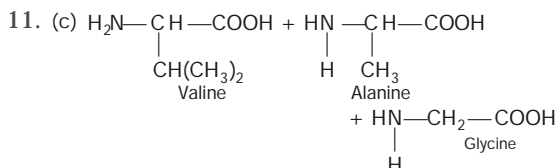$Hg^{2+} + H_2S \longrightarrow HgS \text{ (black)} \downarrow + H_2 \uparrow$

10. (d) In this molecule, S is the central atom with six valence electrons. Out of which four are involved in bonding with four F-atoms and the remaining two behave as a lone pair (lp). The possible arrangement of these pairs are as follows,

(i)   (ii) See-saw (more stable)
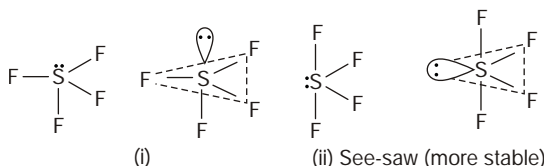
Shape of sulphur tetrafluoride (SF_4) molecule

In structure (i) the lp occupy axial position so there are three lp-bp repulsion at 90°. In structure (ii), the lp occupy an equatorial position and hence, there are two lp-bp repulsions. Hence, arrangement (ii) is more stable. The shape shown in structure (ii) is a distorted tetrahedron, a folded square or a see-saw.

11. (c) $H_2N{-}CH{-}COOH + HN{-}CH{-}COOH$

CH(CH$_3$)$_2$ H   CH$_3$

Valine   Alanine

$+ HN{-}CH_2{-}COOH$

H

Glycine
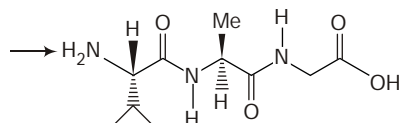
12. (d) A variety of unsaturated compounds such as alkenes, alkadienes and their derivatives readily undergo polymerisation in the presence of radical initiator (radical generating catalyst) such as dioxygen, benzoyl peroxide, acetyl peroxide, tert-butyl peroxide etc. As PhCH$_2$CHO does not have peroxide linkage

and it does not serve as radical initiator. On the other hand, in (b), due to presence of two $\,>\!C\!=\!O$ groups (−I-effect) C—C bond get weaker and easily broken into radical and serve as initiator.
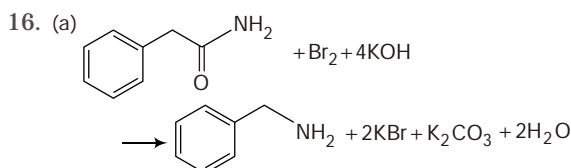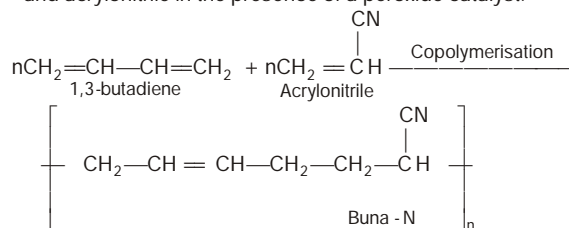
13. (a) The polymers possessing amide linkages are important examples of synthetic fibres and are termed as nylons.

Amide linkage

Nylon
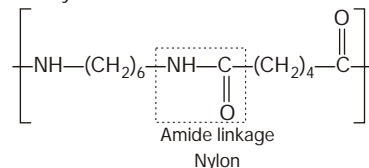
14. (b) The highest particular temperature at which a gas liquefied or above which it cannot be liquefied however high pressure may be applied on the gas is called the critical temperature (T_C). $T_C = \dfrac{8a}{27\,Rb}$

15. (b) Buna-N is obtained by copolymerisation of 1, 3-butadiene and acrylonitrile in the presence of a peroxide catalyst.

$nCH_2{=}CH{-}CH{=}CH_2 + nCH_2{=}CH$ $\xrightarrow{\text{Copolymerisation}}$

1,3-butadiene   Acrylonitrile

Buna - N

16. (a)

$+Br_2+4KOH$

$\longrightarrow$ $NH_2 + 2KBr + K_2CO_3 + 2H_2O$

This reaction is also termed as Hofmann's bromamide reaction which gives primary amine one carbon less than that of parent amide.

17. (a) $[Co(H_2O)_2(NH_3)_4]Cl_3$

IUPAC name is, tetraamminediaquacobalt (III) chloride

18. (b) Siderite ($FeCO_3$) is mainly ore of iron (Fe).

19. (c) Generally, electron gain enthalpy increases as we move from left to right in a period and decreases as we go down the group. But electron affinities of second period elements (F, N) are less negative as compared to corresponding third period element. This is because of the small atomic size of second period elements and presence of d-orbitals. Hence, the correct order of electron affinities is P < S < F < Cl

 Least negative (EA)   Most negative (EA)

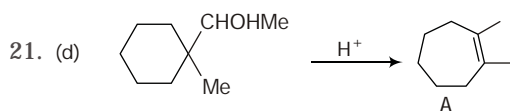20. (c) For reaction, $2A \longrightarrow 3B$

$\therefore \qquad -\dfrac{1}{2}\dfrac{d[A]}{dt} = \dfrac{1}{3}\dfrac{d[B]}{dt}$

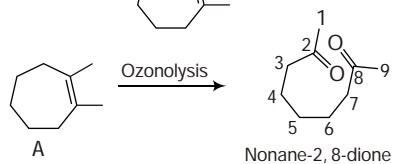Given, $\dfrac{d[B]}{dt} = x \text{ mol/L}$

$\therefore \qquad \dfrac{d[A]}{dt} = -\dfrac{2}{3}\dfrac{d[B]}{dt} = -\dfrac{2}{3}x$

Hence, rate of consumption of A $= \left[\dfrac{d[A]}{dt}\right] = \dfrac{2}{3}x$

21. (d)

CHOHMe / Me (cyclohexane) $\xrightarrow{H^+}$ A

The structure of A is (methyl-cycloheptene) .

A $\xrightarrow{\text{Ozonolysis}}$ Nonane-2, 8-dione

(numbering 1,2(O),3,4,5,6,7,8(O),9)

22. (a) Number of electrons in $He_2 = 4$

MO configuration of $He_2 = \sigma 1s^2, \sigma^* 1s^2$

Here, N_b (bonding electrons) = 2

N_a (antibonding electrons) = 2

23. (a) Given, molality of solution, m = 0.5 m

$$\Delta T_f = 2 \text{ K}$$
$$K_f = 5 \text{ K kg mol}^{-1}$$

% of association, $\alpha = ?$

Step I Calculation of van't Hoff factor (i)

$$\Delta T_f = iK_f M, \quad i = \frac{\Delta T_f}{K_f M}$$

$$i = \frac{2K}{5 \text{ K kg mol}^{-1} \times 0.5 \text{ m}}, \quad i = \frac{4}{5}$$
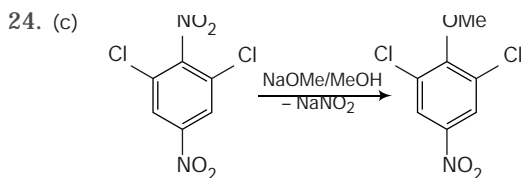
Step II Calculation of % association of acid (α).
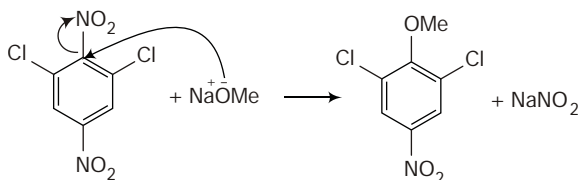
As solute form dimer in benzene,

i.e. $2A \rightleftharpoons A_2$

Therefore, value of x = 2

$$\alpha = \frac{i-1}{1/x - 1}, \quad \alpha = \frac{4/5 - 1}{1/2 - 1} = 0.4$$

$\therefore$ % of $\alpha = 0.4 \times 100 = 40\%$

24. (c)

(2,6-dichloro-1-nitro... benzene with NO_2, Cl, Cl, NO_2) $\xrightarrow[-\ NaNO_2]{\text{NaOMe/MeOH}}$ (OMe, Cl, Cl, NO_2 product)

Mechanism

(mechanism structures) + $Na\overset{+}{\overset{-}{O}}Me$ $\longrightarrow$ (product) + $NaNO_2$

—NO_2 group which is present at ortho position to chloro group will be easily removed as compare to nitro group present at meta position.

This is due to steric inhibition of resonance effect, in which —NO_2 group between two —Cl group lie above the plane and does not take part in resonance so C — N bond becomes weak and easily broken by nucleophile.

25. (b)

(decalin conformation with H e / H e) 1, 2 e/e = trans
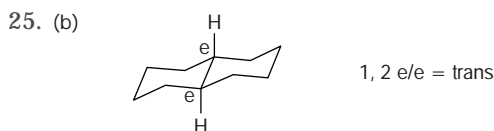
It is highly stable conformation because rings fused at equatorial positions which can not flip.

26. (b) Given, $\Delta H = 6 \text{ kJ/mol}$
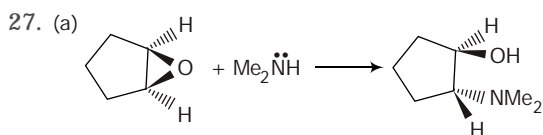
$$\Delta U = ?$$

$$H_2O(l) \rightleftharpoons Ice(s)$$

$\because$ $\Delta H = \Delta U + \Delta n_g RT$

Here, $\Delta n_g = 0$

$\therefore$ $\Delta H = \Delta U$

$\Rightarrow$ $\Delta U = 6 \text{ kJ/mol}$

27. (a)

(epoxide) + $Me_2\ddot{N}H$ $\longrightarrow$ (amino alcohol product with OH, NMe₂)

Mechanism

(mechanism structures) + $Me_2\ddot{N}H$ $\longrightarrow$ (intermediate with $\overset{+}{N}$—H, Me Me)

$\downarrow H^+ \text{transfer}$

(product with OH, NMe₂, H)
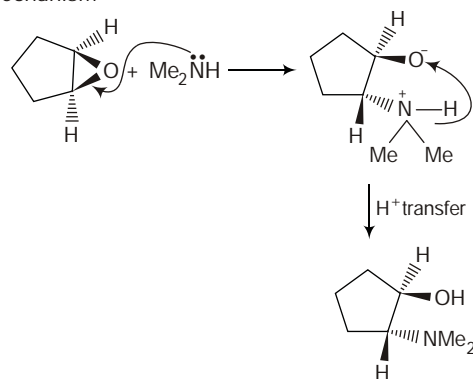
28. (b) The first ionisation energy (IE) increases in a period. Thus, the first IE of the elements of second period should be as follows:

$$Li < Be < B < C < N < O < F < Ne$$

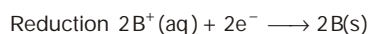But in practice, the elements do not follow the above order.

The first IE of these element is

$$Li < B < Be < C < O < N < F < Ne$$

The lower IE of B than that of Be is because in B ($1s^2 2s^2 2p^1$), electron is to be removed from 2p which is easy while in Be ($1s^2, 2s^2$), electron is to be removed from 2s which is difficult. The IE of O is lower than that of N because of the half-filled 2p orbitals in N ($1s^2, 2s^2, 2p^3$).

29. (c) $A(s) + 2B^+(aq) \longrightarrow A^{2+}(aq) + 2B(s)$

Oxidation $A(s) \longrightarrow A^{2+}(aq) + 2e^-$

Reduction $2B^+(aq) + 2e^- \longrightarrow 2B(s)$

Here, $n = 2$

$$E° = 1.18 \text{ V}$$

$$K_{eq} = ?$$

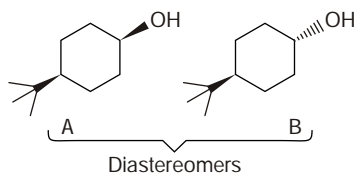$\because$ $\log K_{eq} = \frac{nE° F}{RT}$ $\left[\frac{F}{RT} = \frac{1}{0.059}\right]$

{ **EXAM** DIARY }

$\therefore$ $\log K_{eq} = \dfrac{2 \times 1.18 \times 1}{0.059}$

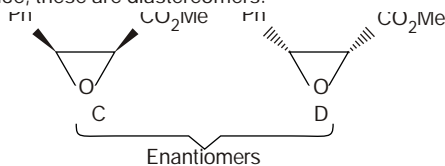$\therefore$ $\log K_{eq} = 40$

or $K_{eq} = 10^{40}$

30. (c)

Diastereomers

Because A and B are not the mirror images of each other. Hence, these are diastereomers.

Enantiomers

Both C and D are the mirror images of each other hence, are enantiomers.

31. (b) Heteroleptic complexes with coordination numbers 4 and 6 show this type of isomerism. It arises due to the difference in the geometrical arrangement of the ligands around the central metal ion.

When same ligands occupies the adjacent position in the polyhedra are known as cis-isomers, whereas when same ligands occupy the opposite position in the polyhedra are known as trans-isomers.


cis-isomer   trans-isomer

(Geometrical isomers of $[Pt(NH_3)_2Cl_2]$)
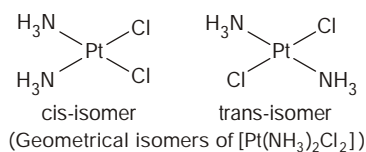
32. (d) Energy of electron in nth orbit of H-atom is given by

$$E_n = -\dfrac{13.6}{n^2} \text{ eV/atom}$$

For n = 2, $E_2 = -\dfrac{13.6}{(2)^2} \text{eV} = -3.4 \text{ eV}$

33. (d) The properties which do not depend upon the quantity or size of matter are called intensive properties, e.g. pressure, temperature, density, concentration, surface tension, viscosity, refractive index etc.

34. (c)

will react quickly with $AgNO_3$.
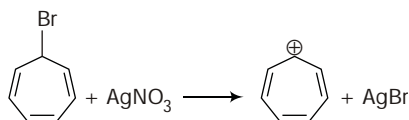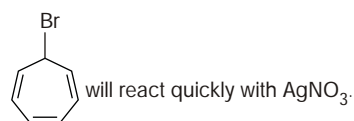
As it forms carbocation which is resonance stabilised and also aromatic in nature.

35. (c) In ccp or fcc structure

Number of lattice points (Z) = 4

$\because$ Number of octahedral voids = Number of lattice points
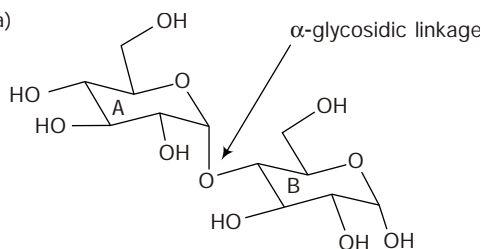
$\therefore$ Number of octahedral voids = 4

and number of tetrahedral voids

      = 2 × number of octahedral voids

$\therefore$ Number of tetrahedral voids
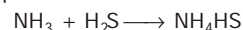
      = 2 × 4 = 8

36. (a)

The ring A is pyranone. In α-type glycosidic linkage, the hydroxyl group (OH) nearer the oxygen atom of ring is written on lower side, whereas in β-type it is written on upper side.

37. (b) Ammonium hydrogen sulphide (NH_4HS) is produced when a dilute aqueous ammonium solution is saturated with hydrogen sulphide.

$$NH_3 + H_2S \longrightarrow NH_4HS$$

38. (b) Given,

$$E^\circ_{M^+/M} = -1.2 \text{ V}$$
$$E^\circ_{X_2/X^-} = -1.1 \text{ V}$$
$$E^\circ_{O_2/H_2O} = 1.23 \text{ V}$$

On electrolysis of aqueous solution of salt MX, the products obtained depend on the given E° values, i.e. cathodic reaction will be one with higher E°_{red} value. Anodic reaction will be one with higher E°_{oxi} value or lower E°_{red} value. Hence, the products are H_2 and X_2.

39. (d) In adiabatic process, the system does not exchange heat with its surroundings, i.e. no heat can flow in or out of the system. In this process, the wall separating the system and the surroundings is called the adiabatic wall.
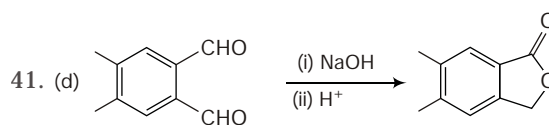
For an adiabatic process, dq = 0

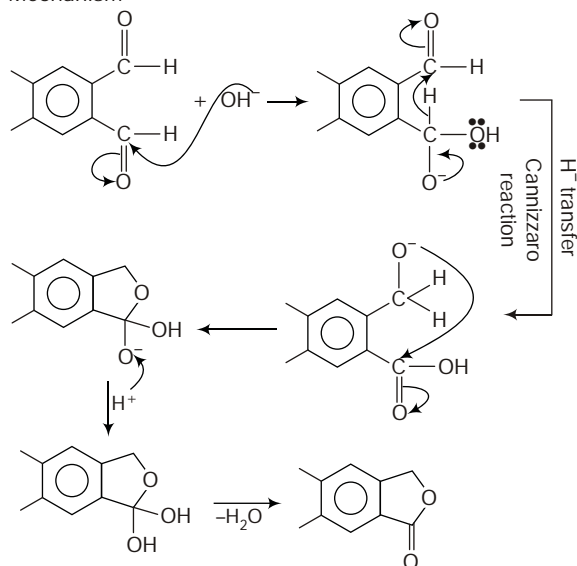**40.** (c) Carbonic anhydrase catalysed the following conversion,

$$CO_2 + H_2O \longrightarrow H_2CO_3$$
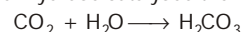
Structure of carbonic anhydrase is given below:
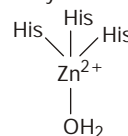
The available element in carbonic anhydrase is zinc.

41. (d)

Mechanism

42. (c) This reaction occur through benzyne mechanism.

43. (a)

As H is above the plane (Anti-clockwise)

As H is above the (Anti-clockwise)
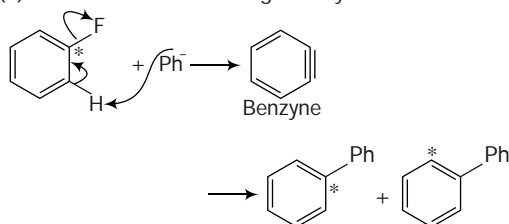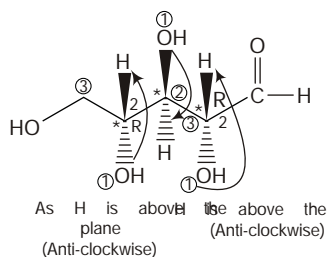
Hence, the absolute configuration of the given compound is R, R, R.

44. (c) Ozone is formed in the upper atmosphere from oxygen by the action of ultraviolet rays. Ozone can absorb UV light to reform oxygen. Thus, ozone layer acts as a screen and prevent the harmful UV radiations from reaching the surface of earth. Ozone layer permits IR, visible and X-rays or γ-rays from Sun to reach Earth.

45. (b) **Step I** Calculation of number of moles

$$p_{Solution} = p_{benzene} \times \chi_{benzene}$$
$$P_{solution} = 0.8 \text{ bar}$$
$$p_{C_6H_6} = 1 \text{ bar}$$
$$\chi_{C_6H_6} = \frac{p_{solution}}{p_{C_6H_6}} = \frac{0.8 \text{ bar}}{1 \text{ bar}}$$
$$\chi_{C_6H_6} = 0.8$$

$$\chi_{C_6H_6} = \frac{\text{Moles of C}_6\text{H}_6}{\text{Moles of C}_6\text{H}_6 + \text{moles of solute}}$$
$$\chi_{C_6H_6} = \frac{(39/78)\text{gmol}^{-1}}{(39/78)\text{gmol}^{-1} + n_{solute}}$$
$$0.8 = \frac{0.5}{0.5 + n_{solute}}$$
$$0.4 + 0.8\,n \text{ solute} = 0.5$$
$$0.8\,n \text{ solute} = 0.5 - 0.4$$
$$n \text{ solute} = 0.1 / 0.8$$
$$n \text{ solute} = \frac{1}{8} \text{ mol}$$

Step II Calculation of molecular mass of solute

$$\text{Molecular mass} = \frac{\text{Mass of solute}}{\text{Number of moles of solute}}$$
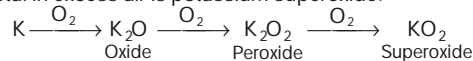$$\text{Molecular mass} = \frac{2 \text{ g}}{(1/8) \text{ mol}}$$
$$= 16 \text{ g mol}^{-1}$$

46. (c) $HClO_4 \cdot 2H_2O + 2H_2S_2O_7 \longrightarrow HClO_4 + 2H_2SO_4$ (Fuming)

$HClO_4$ corresponding to $HClO_4 \cdot 2H_2O$ distilled at low pressure in the presence of fuming sulphuric acid avoiding all contact with oxidisable substances to obtain the anhydrous acid.

47. (b) The compound formed upon combustion of potassium metal in excess air is potassium superoxide.

$$K \xrightarrow{O_2} \underset{\text{Oxide}}{K_2O} \xrightarrow{O_2} \underset{\text{Peroxide}}{K_2O_2} \xrightarrow{O_2} \underset{\text{Superoxide}}{KO_2}$$

48. (a) Given, $E_f = 90 \text{ kJ}$

$$E_b = ?$$
$$\Delta H = 50 \text{ kJ}$$
$$\Delta H = E_f - E_b$$
$$50 = 90 - E_b$$
$$E_b = (90 - 50) \text{ k J}$$
$$E_b = 40 \text{ kJ}$$

49. (b) Number of electrons in $O_2^- = 8 + 8 + 1 = 17$

MO configuration of $O_2^- = \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2 p_z^2, \pi 2 p_x^2$

$$\approx \pi 2 p_y^2, \overset{*}{\pi} 2 p_x^2 \approx \overset{*}{\pi} 2 p_y^1$$

Here, N_b (bonding electrons) = 10

N_a (antibonding electrons) = 7

$\because$ Bond order $= \dfrac{N_b - N_a}{2}$

$\therefore$ Bond order $= \dfrac{10 - 7}{2} = 1.5$

50. (a) Mercury can be obtained from cinnabar HgS by heating the cinnabar ore in the presence of air and condensing the mercury vapour formed. Due to its relatively low boiling point, mercury can be easily purified by vacuum distillation.
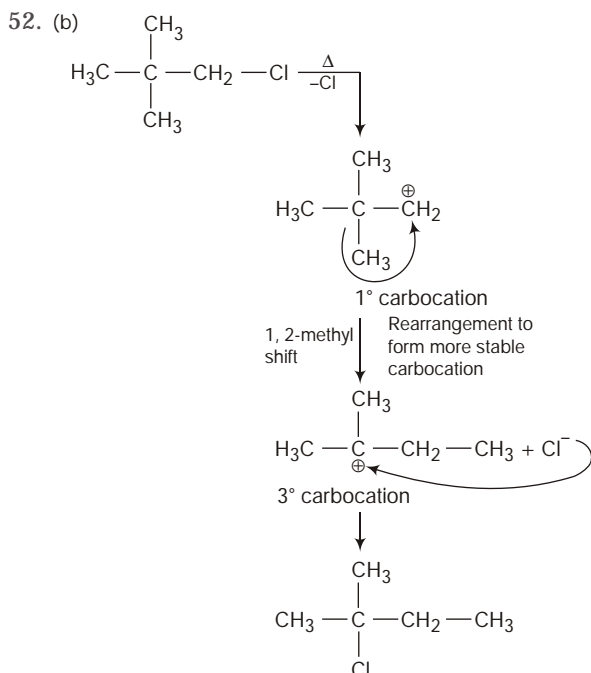
$$HgS + O_2 \longrightarrow Hg + SO_2 \uparrow$$
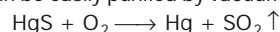
51. (a) Increasing order of crystal field splitting power is as follows:

$$NO_3^- < OH^- < \text{pyridine} < PPh_3$$
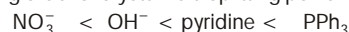
Weak field ligand   Strong field ligand

{**EXAM** DIARY}

52. (b)

$$H_3C - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_2 - Cl \xrightarrow[-Cl]{\Delta}$$

$$H_3C - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - \overset{\oplus}{CH_2}$$

1° carbocation

1, 2-methyl shift | Rearrangement to form more stable carbocation

$$H_3C - \underset{\underset{\oplus}{}}{\overset{\overset{CH_3}{|}}{C}} - CH_2 - CH_3 + Cl^-$$

3° carbocation

$$CH_3 - \underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_2 - CH_3$$

53. (c) Given, density of $CH_3OH = 0.8 \, kg \, L^{-1}$

Molarity = 0.25 M
Volume of 0.25 M = 4 L
Volume needed = ?
First of all we find mass of methanol (i.e. given mass)

$$Molarity = \frac{Number \ of \ moles}{Volume \ of \ solution \ (L)}$$

$$Molarity = \frac{Given \ mass}{Molar \ mass} \times \frac{1}{Volume \ of \ solution \ (L)}$$

Molar mass of $CH_3OH = 12 + 3 + 16 + 1 = 32 \, g \, mol^{-1}$

$$\therefore \ 0.25 \, mol \, L^{-1} = \frac{Given \ mass}{32 \, g \, mol^{-1}} \times \frac{1}{4 \, L}$$

$\therefore$ Given mass = 32 g or 0.032 kg

Again $\because \qquad density = \frac{given \ mass \ (kg)}{volume \ (mL)}$

$$\therefore \qquad 0.8 \, kg \ L^{-1} = \frac{0.032 \, kg}{V \ (mL)}$$

or $\quad 0.8 \times 1000 \, kg \, mL^{-1} = \frac{0.032 \, kg}{V(mL)}$

$$\therefore \qquad V(mL) = \frac{0.032 \, kg}{0.8 \, kg \, L^{-1}} \times 1000$$

$$V(mL) = 40$$

54. (d) $\because$ 23 g of Na contains = 6.023×10^{23} atoms

$$\therefore \quad 1 \ g \ of \ Na \ contains = \frac{6.023 \times 10^{23}}{23} \ atoms$$

$$\therefore \quad 46 \ g \ of \ Na \ contains = \frac{6.023 \times 10^{23}}{23} \times 46 \ atoms$$

$$= 12.046 \times 10^{23} \ atoms$$

55. (a) $AX_2 \rightleftharpoons \underset{S}{A^{2+}} + \underset{2S}{2 \, X^-}$

$$K_{sp} = [A^{2+}][X^-]^2$$
$$K_{sp} = (S)(2S)^2$$
$$K_{sp} = (S)(4S^2)$$
$$K_{sp} = 4S^3$$

56. (b) (a) $CH_4 \longrightarrow$ = 4σ bond ⇒ sp³ hybridisation

(b) $XeF_4 \longrightarrow$ = 4σ bond + 2 lone pairs ⇒ sp³d² hybridisation

(c) $H_2O \longrightarrow$ = 2σ bond + 2 lone pairs ⇒ sp³ hybridisation

(d) $NH_3 \longrightarrow$ = 3σ bond + 1 lone pair ⇒ sp³ hybridisation
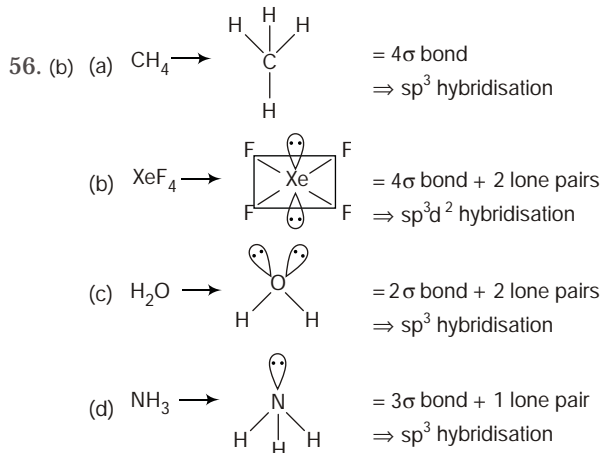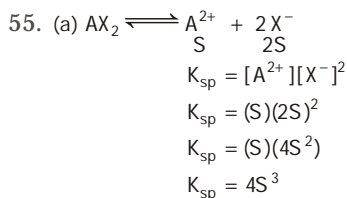
57. (a) Milk is an example of emulsion. These are formed when both the dispersed phase and dispersion medium are liquids in a colloidal system. If a mixture of two immiscible or partially miscible liquids is shaken, cause dispersion of one liquid on the other is obtained, which is known as emulsion. They also show Brownian movement and Tyndall effect. They can be broken into their constituent liquids by freezing, heating and centrifuging etc.

58. (d) $A(g) + 2B(g) \longrightarrow AB_2(g)$
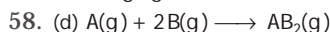
$$K_p = K_C(RT)^{\Delta n_g}$$

Δn_g = change in number of moles
= moles of gaseous product – moles of reactants
= 1 – 3 = – 2

$$\therefore \qquad K_p = K_C(RT)^{-2} \quad \Rightarrow \quad \frac{K_p}{K_C} = \frac{1}{(RT)^2}$$

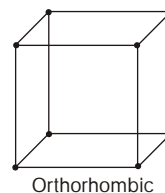**59.** (a) Given, $V_1 = 2 \, L$, $V_2 = 20 \, L$, $T = 300 \, K$, $p_2 = 1 \, bar$

Work done for ideal gas expands isothermally and reversibly

$$\Rightarrow \qquad W = -RT \ln \frac{V_2}{V_1}$$

$$\Rightarrow \qquad W = -R \times 300 \ln \frac{20}{2}$$

$$\Rightarrow \qquad W = -300R \ln 10$$

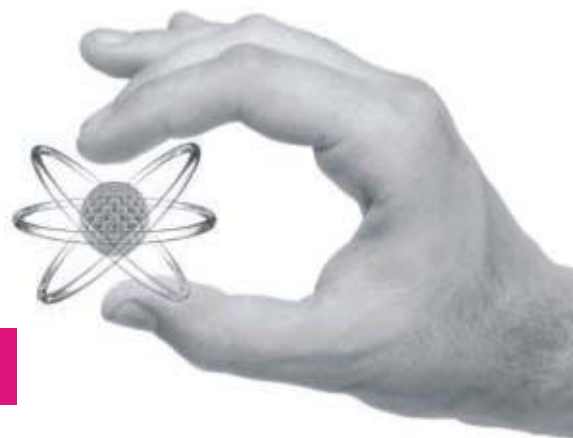**60.** (c) A unit cell with edge length $a \neq b \neq c$ and axial angles $\alpha = \beta = \gamma = 90°$ is called orthorhombic, e.g. rhombic sulphur, KNO_3 and $BaSO_4$.

Orthorhombic

{JEE ADVANCED CORNER}

Rakhi Yadav

STEREOCHEMISTRY
—— OF NUCLEOPHILIC ——
# SUBSTITUTION REACTIONS : Part I

Stereochemistry is an important part to understand the mechanism of chemical reactions. In this article, we shall study about a particular class of reactions named as **nucleophilic substitution reactions.** To understand stereochemistry of these reactions, we need to know about some stereochemical principle and notations.

Some Stereochemical Principles and Notations

Optical Activity and Chirality

Any compound that rotates the plane of polarised light (the light waves in which vibrations occur in a single plane) is said to be optically active.
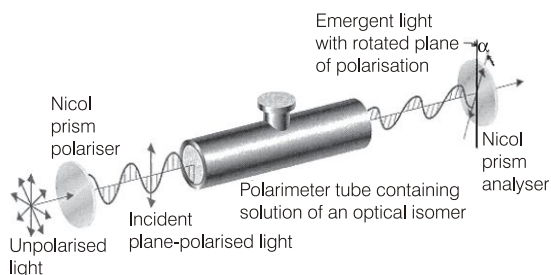
- The compound that does not rotate the plane of polarised light is known as optically inactive.
- The property of non-superimposability of a molecule on its mirror image is known as chirality.
- The molecule that is not superimposable on its mirror image is known as **chiral** and that is superimposable on its mirror image is known as **achiral.**

- Two structures of a molecule that are not identical but mirror images of each other are called **enantiomers.** Here *A* and *B* are enantiomers.
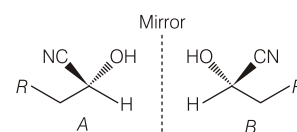

- Enantiomers possess identical physical and chemical properties except the following two aspects:
  (i) Enantiomers rotate the plane of polarised light in opposite directions in equal amounts, the isomer which rotates the plane of polarised light to the left, i.e. anti-clockwise direction, is called **laevorotatory** and negative (–) sign is placed before the degree of rotation. The isomer that rotates the plane of polarised light to the right, i.e. clockwise direction, is called **dextrorotatory** and positive (+) sign is placed before the degree of rotation.
  (ii) Enantiomers have identical properties in symmetrical environment while these may have different properties in unsymmetrical environment. They react at different rates with other chiral compounds. This is the reason that many compounds are biologically active while their enantiomers are not.
- The criteria of a molecule to be optically active is chirality, i.e. non-superimposability on its mirror image.

Molecular Asymmetry

In a molecule, if a carbon atom is attached by four different substituents, such carbon is called asymmetric carbon or stereocentre and the molecule is referred as asymmetric molecule. The asymmetry of the molecule is responsible for the optical activity of such organic compounds.
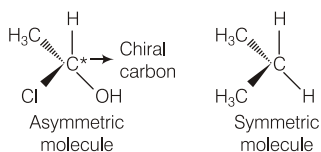
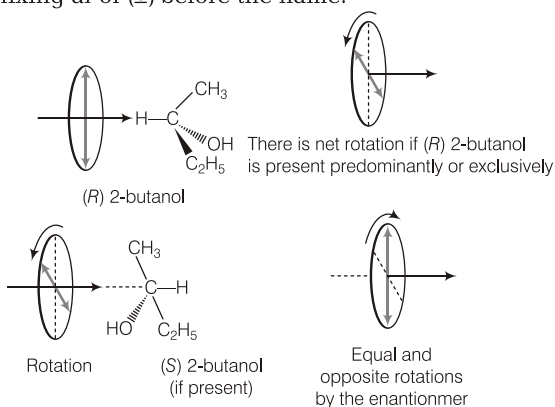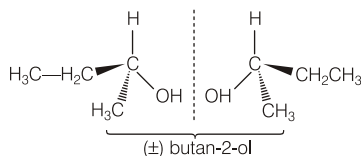- It there is one chiral atom present in a molecule, the molecule must be optically active

e.g. $Br-CH_2-CH_2-\overset{*}{C}H-CH_2-CH_2-Br$
$\hspace{5cm}|$
$\hspace{5cm}CH_3$
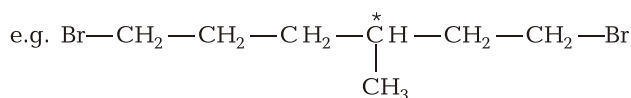
- Optical activity has been observed in cases, where one group is hydrogen and other is deuterium.

e.g. $CH_3-CH_2-CH_2-\overset{\overset{H}{|}}{\underset{\underset{D}{|}}{C}}-OH$
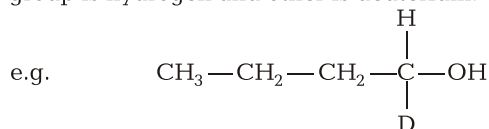
- The amount of rotation is greatly dependent on the nature of four groups attached to chiral carbon atom. In general, amount of rotation increases with increase in difference in polarisabilities among the groups.

Racemic Mixtures

Mixtures of equal amounts of enantiomers are optically inactive since the equal and opposite rotations cancel each other. These type of mixtures are called **racemic mixtures** or **racemates**. A racemic mixture is denoted by prefixing *dl* or (±) before the name.

There is net rotation if (*R*) 2-butanol is present predominantly or exclusively

Equal and opposite rotations by the enantiomer

Retention

It is a process in which the relative configuration or absolute configuration of an asymmetric centre is retained during a chemical reaction, i.e. attacking species occupies the same site as that of leaving species. e.g.
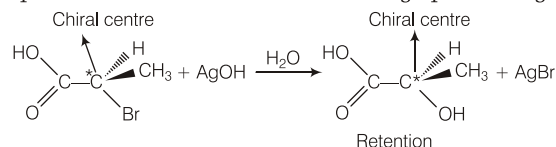
Inversion

It is a process in which the relative configuration or absolute configuration of an asymmetric centre is inverted during a chemical reaction, i.e. attacking species occupies the opposite site as that of leaving group.
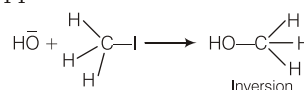
Specific Rotation $[\alpha]$

The number of degrees that the plane of polarisation is rotated as the plane polarised light passes through a solution of an enantiomer depends upon the number of chiral molecules that it encounters, length of the tube and the concentration of the enantiomer.

On standard basis, chemists calculate a quantity called the specific rotation $[\alpha]$ as,

$$[\alpha] = \frac{\alpha}{Cl}$$

where, $[\alpha]$ = specific rotation

α = observed rotation

C = concentration of solution in g/mL

l = length of tube in decimeters (1 dm = 10 cm)

- The specific rotation also depends upon the temperature and wavelength of the light employed. It is denoted as $[\alpha]_D^{25}$

where, D = line of a sodium lamp (λ = 589.6 nm)

$25 = 25°C$ temperature

Problem based on specific rotation

Example 1 The optical rotation of an optically active compound is +20°. The length of tube is 10 cm and the density of solution is 0.4 g mL^{-1}. The specific rotation of the compound is

(a) + 60°   (b) + 70°   (c) + 50°   (d) + 40°

Sol. **(c)** Observed rotation α = + 20°

Length of tube = 10 cm = 1 dm

Concentration of solution = 0.4 g mL^{-1}

∴ Specific rotation $[\alpha] = \dfrac{\alpha}{Cl} = \dfrac{+20°}{1 \times 0.4} = + 50°$

JEE ADVANCED CORNER

The Biological Significance of Chirality

- The human body is structurally chiral with the heart lying to the left of centre and the liver to the right. Helical seashells are chiral and most are spiral, such as a right handed screw.
- Many plants show chirality in the way they wind around supporting structures. Honeysuckle winds as a left-handed way.
- DNA is a chiral molecule. The double helical form of DNA turns in a right-handed way.
- Indeed, all but one of the 20 amino acids that make up naturally occurring proteins are chiral and all of these are classified as being left-handed.
- The molecules of natural sugars are almost all classified as being right handed.
- Most pharmaceutical drugs are chiral. Usually only one mirror image form of a drug provides the desired effect. The other mirror image form is often inactive or less active. In some cases, the other mirror image form of a drug actually has many side effects or toxicity.
- Our senses of taste and smell depend on chirality, one mirror image form of a chiral molecule may have a certain odour or taste while its mirror image have completely different odour and taste.
- The food we eat is largely made of molecules of one mirror image form. If we have to eat that was somehow made of molecules with unnatural mirror image for we would likely starve because the enzymes in our bodies are chiral and preferentially react with natural image form of their substrates.

Nomenclature of Enantiomers
(The Cahn-Ingold-Prelog System)

If we take two enantiomers and name these according to the IUPAC system of nomenclature, both enantiomers will have the same name.

Cahn, Ingold and Prelog introduced a system of nomenclature, that when added to IUPAC system, solves the naming problem of enantiomers. This system is known as **R, S-system** or **Cahn-Ingol-dPrelog system** (CIP Rule) in which the four groups on an asymmetric carbon are ranked according to a set of sequence rules.

These sequence rules are as follow :

- Substituents are listed in the order of decreasing atomic number of the atom directly attached to the asymmetric carbon atom, e.g.
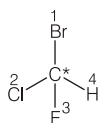
Priority order : Br > Cl > F > H

- After giving the priority follow these rules for R and S nomenclature.
- Rotate the molecule so that the group with lowest priority (4) is detected away from us or below the plane.
- If the other groups (1, 2 and 3) are oriented in clockwise, the molecule is designated as R and if anti-clockwise, then S.

Since, arrows are clockwise. Hence, configuration of molecule is R and it is named as (R) -2-butanol.

- If fourth group is above the plane or towards the viewer, then after finding the configuration of molecule revert this configuration, e.g. therefore, configuration of the above molecules is S.

Clockwise, i.e. R ——revert it——> S

- When a priority cannot be assigned on the basis of the atomic number of the atoms that are directly attached to the stereogenic carbon, then the next set of atoms in the unassigned groups is examined. This process is continued until a decision can be made. e.g.

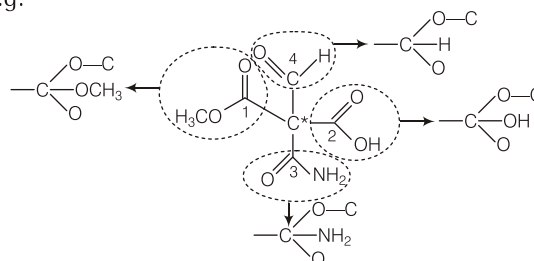- In case of isotope, the isotope having higher mass will have preference first.
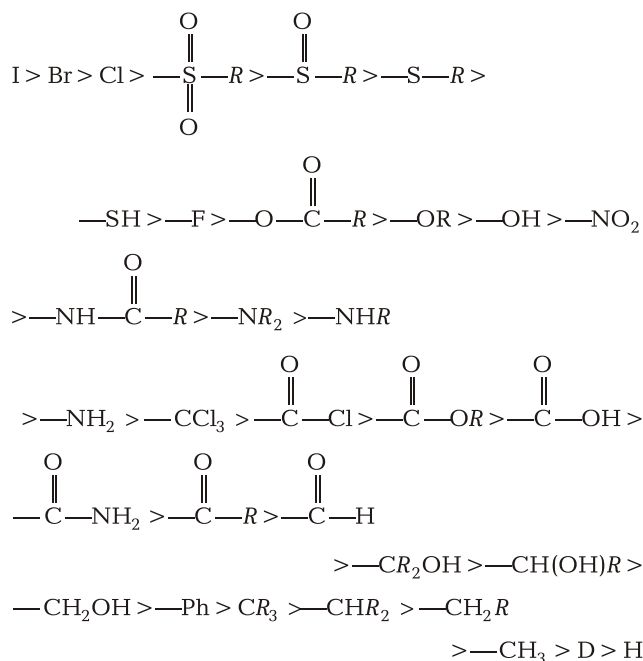e.g.
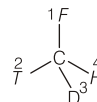
Priority order: $F > T > D > H$

- If there is a double and triple bond are present in a molecule, the double bond becomes duplicated and triple bond becomes triplicated as shown below.
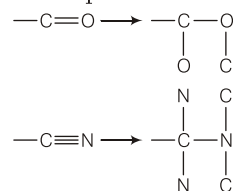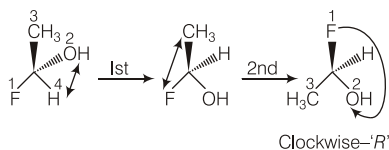
e.g.

Generalised Priority Order

$$I > Br > Cl > -\overset{\overset{O}{\|}}{\underset{\overset{\|}{O}}{S}}-R > -\overset{\overset{O}{\|}}{S}-R > -S-R >$$

$$-SH > -F > -O-\overset{\overset{O}{\|}}{C}-R > -OR > -OH > -NO_2$$

$$> -NH-\overset{\overset{O}{\|}}{C}-R > -NR_2 > -NHR$$

$$> -NH_2 > -CCl_3 > -\overset{\overset{O}{\|}}{C}-Cl > -\overset{\overset{O}{\|}}{C}-OR > -\overset{\overset{O}{\|}}{C}-OH >$$

$$-\overset{\overset{O}{\|}}{C}-NH_2 > -\overset{\overset{O}{\|}}{C}-R > -\overset{\overset{O}{\|}}{C}-H$$

$$> -CR_2OH > -CH(OH)R >$$

$$-CH_2OH > -Ph > CR_3 > -CHR_2 > -CH_2R$$

$$> -CH_3 > D > H$$

If fourth group (less priority group) is on the plane, then do double interchange as follow :


Clockwise–'R'

Fischer Projection

- It is the representation of tetrahedral carbon atoms as a two-dimensional structure on paper.
- To construct a Fischer projection, the molecule is first arranged with the horizontal bonds to its chiral centre projecting above the plane of the page and the vertical bonds projecting behind the page.
- Prior group is placed at the top of the main chain of the molecule vertically. e.g.

Projected form
(Fischer projection)
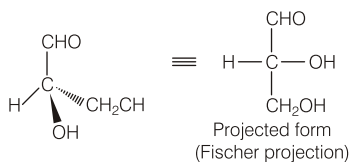
## Assignment of *R*, *S*-Configuration in Fischer Projection

- If the lowest priority substituent on asymmetric carbon occupies vertically upward or downward position in Fischer projection, the configuration obtained is equal to the actual configuration of the molecule, e.g.

Anti-clockwise   Clockwise
S   *R*
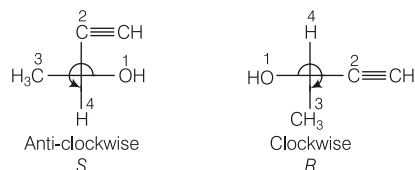
- If lowest priority substituent on asymmetric carbon occupies either of horizontal position change the configuration from *R* to *S* or *S* to *R*. e.g.

Clockwise   Anti-clockwise
R   *S*
Hence, configuration   Hence, configuration
is *S*   is *R*
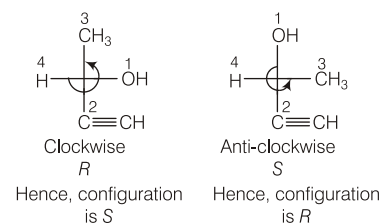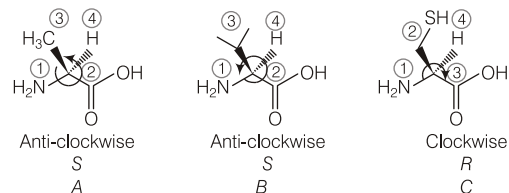
- For more than one chiral atom in a molecule, assign their configuration one by one as follow.

(2*S*, 3*S*)
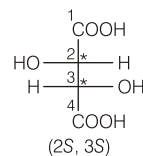
Problems related to (*R*) and (*S*) nomenclature

Example 2 Assign (*R*) and (*S*) designation to each of the following compounds.

Sol.

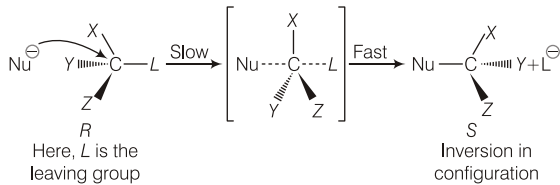Anti-clockwise   Anti-clockwise   Clockwise
S   *S*   *R*
A   *B*   *C*
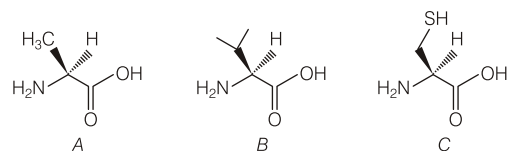
Stereochemistry Involved in Mechanism of S_N1, S_N2, and S_Ni Reactions

Mechanism for S_N2 reaction

Here, L is the leaving group

Inversion in configuration

If configuration of reactant is R then configuration of product must be S or vice-versa.

Mechanism for S_N1 reaction

Inversion in configuration (50%) 'R'

Retention in configuration (50%) 'S'

Racemic mixture
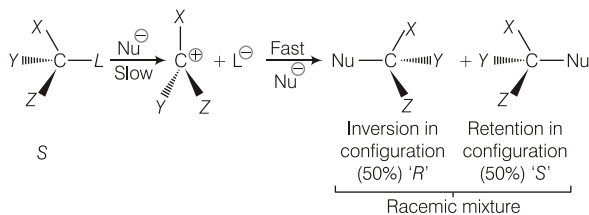
Mechanism for S_Ni reaction

Retention in configuration
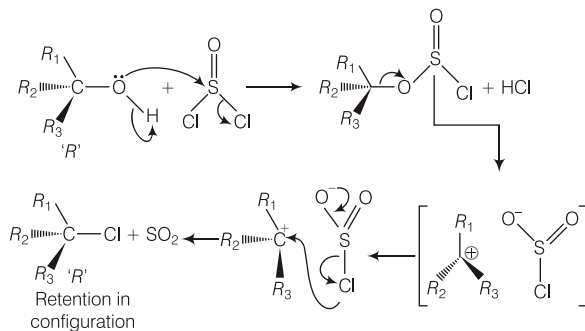
Example 3 Draw the stereochemical structure of product in the following reaction.

Sol. (a)

$\bar{O}H$ nucleophile attacks from the back side of the leaving group, i.e. Br^-.

Smart Practice

Single Option Correct Type Questions

1. Find the absolute configuration of the following compounds.

             A   B
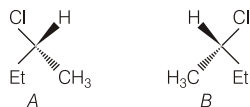
  (a) R and R *(b)* R and S
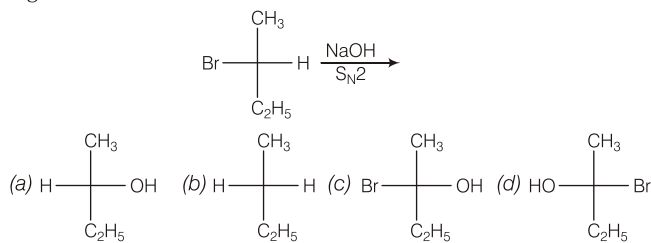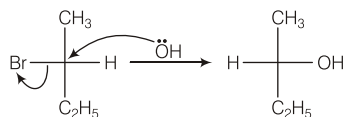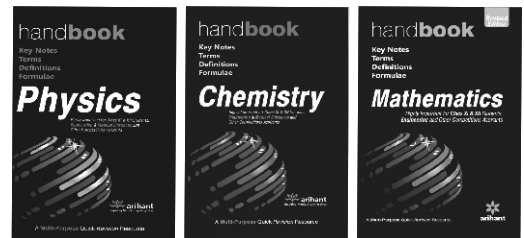
  (c) S and S *(d)* S and R

2. Which of the following pairs represents pair of enantiomers?
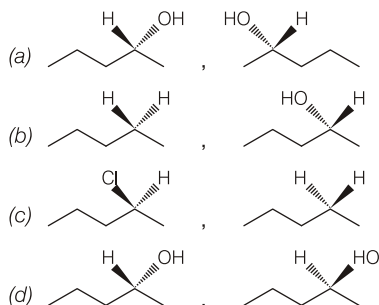
3. Which of the mechanism gives racemic mixture after the attack of nucleophile on the asymmetric centre?

  (a) $S_N 2$ *(b)* $S_N 1$ *(c)* $S_N i$ *(d)* None of these

4. A tube of length 20 cm containing 0.5 g/cc of an optically active compound. If observed optical rotation is $+10°$, find the value of specific rotation.

  (a) $+10°$ *(b)* $+20°$ *(c)* $+30°$ *(d)* $+40°$

5. Identify the pair of enantiomers from the following:

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

  (c) I and III   *(d)* None of these

More Than One Correct Type Questions

6. Which of the following compounds are optically active?

  (a) $CH_3CHCClCH_3$ *(b)* $CH_3CH_2CH(CH_3)COOH$

  (c) $CH_3CH_2CH(NH_2)CH_3$ *(d)* $CH_2(OH)CH_2(OH)$

7. Which of the following has R configuration?
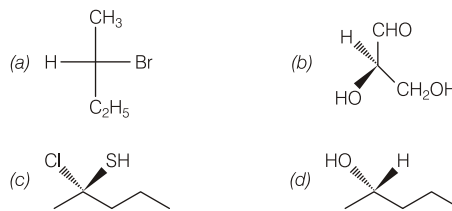
Passage Based Type

For a $S_N 2$ reaction,

Substrate + Nucleophile $\rightarrow$ Products

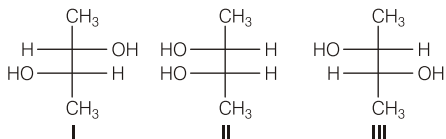Rate $\propto$ [Substrate] [Nucleophile]

The reaction is favoured by strong nucleophile and in the presence of polar aprotic solvent, optically active halides given Walden inversion by $S_N 2$ mechanism.

8. Which of the following will give $S_N 2$ reaction?

  (a) MeBr   *(b)*

  (c) Ph   Br   *(d)* All of these

9. Which of the following will give Walden inversion?

  (a) Ph   Br   *(b)* C_4H_9—CH—Br

  (c)   Br   *(d)* All of these

Integer Type Question

10. How many of the following compounds are optically active?

  Heptan-4-ol,   3-aminohexane,

  2-chloropentane,   Butan-2-ol

Answers

1. (b)   **2.** (a)   **3.** (b)   **4.** (a)   **5.** (c)   **6.** (b,c)   **7.** (b,c)   **8.** (d)   **9.** (b)   **10.** (3)

BASIC TERMS USED IN THERMODYNAMICS

System Specific portion of matter which is under thermodynamic studies.

Surroundings Besides the system, the rest of the universe that can interact with the system.

Boundary The real or imaginary surfaces or lines separating two or more systems or a system from its surroundings.

TYPES OF SYSTEM

(i) **Open system** can exchange both matter and energy to its surrounding.

(ii) **Closed system** can exchange energy but does not exchange matter to its surroundings.

(iii) **Isolated system** neither energy nor matter can be exchange to the surroundings.

(iv) **Homogeneous system** consists only one phase.

(v) **Heterogeneous system** consists more than one phase.

THERMODYNAMIC PROPERTIES (MACROSCOPIC PROPERTIES)

Intensive properties do not depend upon the quantity of matter in the system, e.g. pressure, temperature, density, concentration, surface tension, viscosity, refractive index etc.

Extensive properties depend upon the quantity of matter in the system, e.g. volume, number of moles, enthalpy, entropy, mass, work etc.

State variables measurable properties which define a particular state of a system, e.g. temperature, pressure, volume etc.

State functions properties whose values depend only upon the initial and final state of the system not the path by which these state has been attained, e.g. enthalpy, entropy, internal energy etc.

Path functions properties whose values depend upon the path followed to attain a state, e.g. work, heat etc.

TYPES OF THERMODYNAMIC PROCESSES

Isothermal process in which temperature remains fixed.

**Adiabatic process** in which exchange of heat does not occur between the system and the surroundings.

Isobaric process in which change of state is brought about at constant pressure.

Isochoric process in which volume remains constant.

Cyclic process in which a system undergoes a number of different states and finally returns to its initial state.

Reversible process which occurs infinitesimally slowly and whose direction at any point can be reversed by infinitesimal change in the state of the system.

Irreversible process which cannot be reversed by small change in variables and goes from initial to final state in a simple step in finite time.
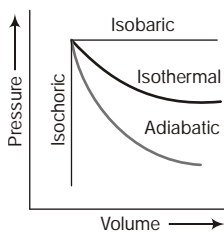
WORK (W)

It is a mode of energy transfer to or from a system with reference to the surroundings.

Work associated with change in volume of a system against external pressure is called mechanical work.

$$W = -p\Delta V$$

$$W_{expansion} = -ve \qquad (\Delta V = positive)$$

$$W_{contraction} = +ve \qquad (\Delta V = negative)$$

HEAT (q)

The quantity of energy, which flows between system and surroundings on account of temperature difference.

It is a path function $q = mc\Delta T$

where, m = mass of substance, c = specific heat

ΔT = temperature difference

SIGN CONVENTION OF '*W*' AND '*q*'

W	q
Work done on the system = +ve	Heat taken by the system = +ve
Work done by the system = −ve	Heat given out by the system = −ve

INTERNAL ENERGY (U)

It is the sum of all forms of kinetic and potential energies of all nanoscale particles (atoms, molecules, ions) in the system.

$$U_{total} = U_{translational} + U_{rotational} + U_{vibrational} + U_{bonding} + U_{electronic} + \ldots$$

For a chemical reaction change in internal energy $(\Delta U) = U_{products} - U_{reactants}$

ENTHALPY(H)

It is the total heat content of a system at constant pressure.

Mathematically, $H = U + pV$

Change in enthalpy, $\Delta H = H_{final\ state} - H_{initial\ state}$

THERMODYNAMIC LAWS

ZEROTH LAW OF THERMODYNAMICS

If two objects A and B are in thermal equilibrium with a third object C then objects A and B are also in thermal equilibrium with each other.

FIRST LAW OF THERMODYNAMICS

Energy can neither be created nor destroyed however, it can be transformed from one form to another. Mathematically, $\Delta U = q + W$

SECOND LAW OF THERMODYNAMICS

Entropy of universe always tends to increase during any spontaneous process.

THIRD LAW OF THERMODYNAMICS

The entropy of a perfectly crystalline solid is zero at absolute zero temperature (0 K).

ENTHALPY CHANGE

$\Delta H = \Delta U + \Delta(pV); \quad \Delta H = \Delta U + p\Delta V + V\Delta p$

From first law of thermodynamics, $\Delta U = q - p\Delta V$

At constant pressure, $\Delta H = q_p$

At constant volume, $\Delta U = q_V$

Relationship between ΔH and ΔU

$$\Delta H = \Delta U + p\Delta V$$

For a chemical reaction, $\Delta H = \Delta U + \Delta n_g(RT)$

Δn_g = Number of moles of gaseous products− number of moles of gaseous reactants

If $\quad \Delta n_g = 0, \Delta H = \Delta U$

$\quad \Delta n_g = -ve, \Delta H < \Delta U$

$\quad \Delta n_g = +ve, \Delta H > \Delta U$

HEAT CAPACITY (C)

The quantity of heat required to raise the temperature of a system by one degree.

Heat capacity $(C) = \dfrac{dq}{dT}$

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THERMODYNAMICS

Chemical reactions involve transfer of energy. Fuels like methane, cooking gas or coal burns in air and the energy of products is less than the energy of reactants. The left over energy shows up in anything that is in contact with the reactants and products. Consequently, it is very important to understand how energy and chemical reactions are related to each other. This requires knowledge of thermodynamics, the science of heat or any other form of energy, work and transformations of one to the other due to physical or chemical transformations.

At constant pressure, heat capacity $(C_p) = \left(\dfrac{\partial q}{\partial T}\right)_p = \left(\dfrac{\partial H}{\partial T}\right)_p$

At constant volume, heat capacity $(C_V) = \left(\dfrac{\partial q}{\partial T}\right)_V = \left(\dfrac{\partial U}{\partial T}\right)_V$

SPECIFIC HEAT CAPACITY(C)

The quantity of heat required to raise the temperature of one unit mass of a system by one degree, $C = \dfrac{q}{m \times \Delta T}$

MOLAR HEAT CAPACITY (C_m)

The quantity of heat required to raise the temperature of one mole of a system by one degree, $C_m = \dfrac{q}{n \times \Delta T}$

(n = number of moles of gas)

Relationship between C_p and C_V

For n moles of an ideal gas, $C_p - C_V = nR$

For 1 mole, $C_p - C_V = R$

C_p is always greater than C_V, as at constant pressure, gas expands while at constant volume, gas is not allowed to expand. Hence, at constant pressure, more heat is required to raise the temperature of a gas by 1°C.

$$\dfrac{C_p}{C_V} = \gamma,$$

Here, γ = atomicity

Note For monoatomic, diatomic and triatomic gases, γ has values 1.67, 1.40 and 1.33 respectively.

ENTHALPY CHANGE OF A REACTION ($\Delta_r H$)

$\Delta_r H$ = Sum of enthalpies of products − sum of enthalpies of reactants

$$\Delta_r H = \sum_i x_i H_P - \sum_j y_j H_R$$

where, x_i and y_j = stoichiometric coefficients of products and reactants respectively in a balanced equation.

H_P = Enthalpy of formation of products

H_R = Enthalpy of formation of reactants

STANDARD ENTHALPY OF REACTION ($\Delta_r H°$)

The enthalpy change when the reaction is carried out at standard conditions, i.e. at 1 atm pressure and 298 K.

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DYNAMICS

APPLICATIONS
- In the determination of feasibility of physical or chemical change.
- In the determination of yields of products for a particular reaction.
- Various laws like law of mass action, phase rule, Raoult's law, van't Hoff law, laws of thermochemistry etc., are in accordance with laws of thermodynamics.
- In the prediction of energy change during a reaction.

LIMITATIONS
- The laws of thermodynamics are applicable to macroscopic system only.
- The rate of reaction cannot be evolved through thermodynamics.
- It is not helpful in evolving the mechanism of process and is concerned only with the initial and final states of a system.

ENTHALPY CHANGE DURING PHASE TRANSFORMATION
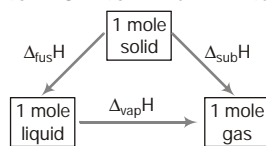
where,
$\Delta_{fus}H$ = Enthalpy of sublimation
$\Delta_{vap}H$ = Enthalpy of vaporisation
$\Delta_{sub}H$ = Enthalpy of sublimation
$\Delta_{sub}H = \Delta_{fus}H + \Delta_{vap}H$

TYPES OF ENTHALPIES OF REACTION

ENTHALPY OF FORMATION ($\Delta_f H$)
The enthalpy change when one mole of a compound is formed from its elements in their most stable state of aggregation.
e.g. $C(graphite) + 2H_2(g) \longrightarrow CH_4(g); \Delta_f H = -74.8 kJ$

ENTHALPY OF COMBUSTION ($\Delta_c H$)
The amount of heat evolved or absorbed when one mole of the substance is completely burnt in oxygen or air.
e.g. $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l); \Delta_c H = -192$ kcal
Heat of combustion is measured in kcal / g or kJ / g, it is called the calorific value.

ENTHALPY OF ATOMISATION ($\Delta_a H$)
The enthalpy change when one mole of the substance broken into isolated atoms in the gas phase. e.g. $CH_4(g) \longrightarrow C(g) + 4H(g)$;

ENTHALPY OF NEUTRALISATION ($\Delta_n H$)
The enthalpy change when one equivalent of an acid is neutralised by one equivalent of a base.
e.g. $HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O; \Delta_n H = -13.7 kcal$

LATTICE ENTHALPY ($\Delta_U H$)
The enthalpy change when one mole of a crystal is completely separated into isolated particles in the gaseous phase.
e.g. $NaCl(s) \longrightarrow Na^+(g) + Cl^-(g)$;

$$\Delta_U H = 786 kJ mol^{-1}$$

ENTHALPY OF HYDRATION ($\Delta_{hyd}H$)
The enthalpy change when one mole of the ions in gaseous phase is hydrated.
e.g. $CuSO_4(s) + 5H_2O(l) \longrightarrow CuSO_4 \cdot 5H_2O(s); \Delta_{hyd}H = 78.22 kJ$

ENTHALPY OF SOLUTION ($\Delta_{sol}H$)
The enthalpy change when one mole of solute is dissolved completely in excess of solvent.
e.g. $NH_4Cl(s) + H_2O(l) \longrightarrow NH_4Cl(aq)$;
$$\Delta_{sol}H = 3.90 kcal$$
$\Delta_{sol}H$ = Hydration enthalpy – Lattice enthalpy

ENTHALPY OF DILUTION ($\Delta_{dil}H$)
The enthalpy change when the solution containing one mole of a substance is dilute from one concentration to another.
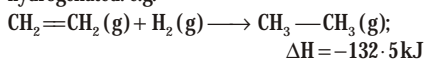e.g $KCl(200H_2O) \longrightarrow KCl(300H_2O); \Delta_{dil}H = x kJ$

ENTHALPY OF IONISATION ($\Delta_{ion}H$)
The enthalpy change when one mole of a weak electrolyte is completely ionised into its constituents. e.g.
$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

ENTHALPY OF HYDROGENATION (ΔH)
The enthalpy change when one mole of an unsaturated organic compound is completely hydrogenated. e.g.
$CH_2{=}CH_2(g) + H_2(g) \longrightarrow CH_3{-}CH_3(g)$;
$$\Delta H = -132.5 kJ$$

ENTHALPY OF TRANSITION ($\Delta_t H$)
The enthalpy change when one mole of a substance changes from its one allotropic form to another.
e.g. $S_{(rhombic)} \longrightarrow S_{(monoclinic)}; \Delta_t H = -13.14 KJ$

BOND ENERGY(BE)
When a bond is formed between two atoms in gaseous state to form a molecule.

BOND DISSOCIATION ENERGY
The amount of energy required to dissociate a bond of a particular type present in one molecule.
$\Delta_r H$ = Sum of BE of reactants – Sum of BE of products

HESS'S LAW
Enthalpy change in a particular reaction is always constant and is independent of the path in which reaction takes place.
$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

ENTROPY(S)
The property of a system which measures the degree of randomness in a system. Entropy is a state function.

$\Delta S = S_{final} - S_{initial}$
Unit of entropy = Joule/kelvin-mol
Order of entropy, gas > liquid > solid
For a reversible change at constant pressure.
$$\Delta S = \frac{q_{rev}}{T} = S_{final} - S_{initial}$$
If $\Delta S > 0$, heat is absorbed; $\Delta S < 0$, heat is evolved.

ENTROPY CHANGE DURING PHASE TRANSITION
$$\Delta S_{melting} = \frac{\Delta H_{fusion}}{T_m}; T_m = melting point$$
$$\Delta S_{vaporisation} = \frac{\Delta H_{vaporisation}}{T_b}$$
$$\Delta S_{sublimation} = \frac{\Delta H_{sublimation}}{T_{sub}}$$

Entropy at equilibrium At equilibrium, value of entropy is maximum while change in entropy is equal to zero.

GIBBS FREE ENERGY (G) OR FREE ENERGY
The maximum amount of energy available to a system, during a process, that can be converted into useful work. $G = H - TS$
Change in Gibbs free energy, $\Delta G = \Delta H - T\Delta S$. This equation is called Gibbs Helmholtz equation.
The standard free energy change ($\Delta G°$) is related to equilibrium constant K as $\Delta G° = -2.303 RT \log K$
The free energy change (ΔG) is related to the electrical work done in the cell as $\Delta G = -nFE_{cell}$
In standard state, $\Delta G° = -nFE°$
Efficiency of a fuel cell
$$= \frac{Total\ useful\ work}{Total\ heat\ given} \times 100 = \frac{\Delta G}{\Delta H} \times 100$$

SPONTANEOUS AND NON-SPONTANEOUS PROCESSES
A physical or chemical change that occurs on its own, i.e. without outside help is called spontaneous process. Rest of the other processes which require a continuous supply of energy from outside the system are called non-spontaneous.
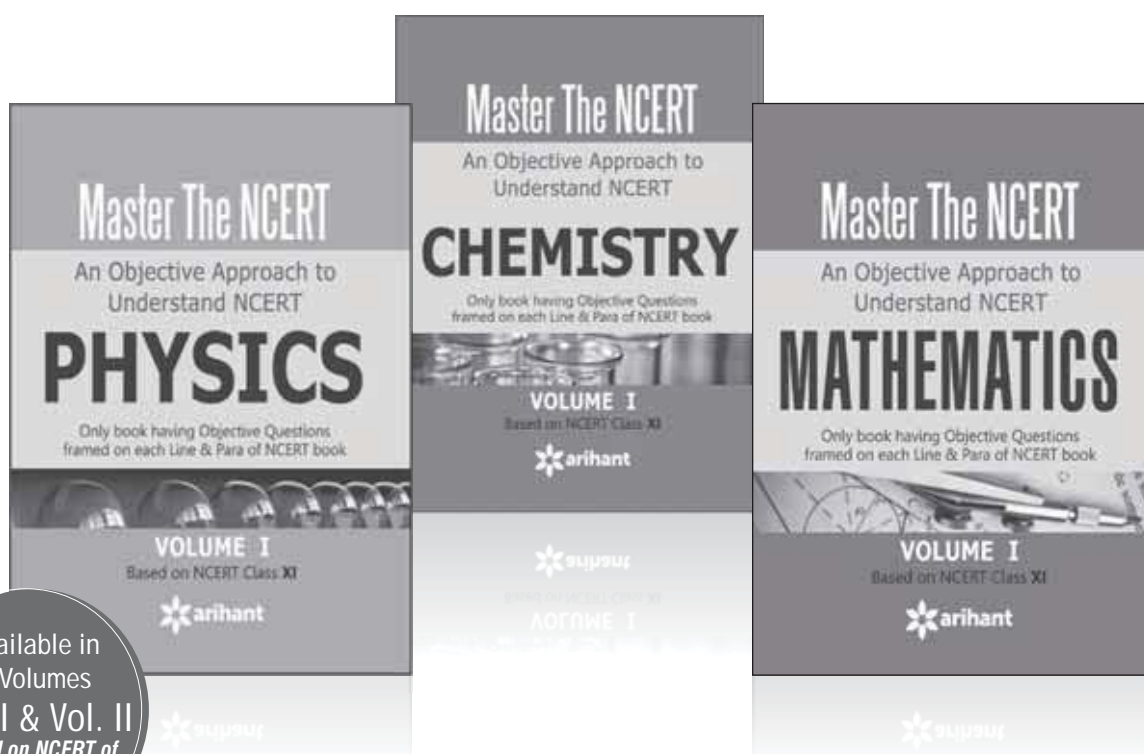
Criteria for spontaneity

ΔS	ΔH	ΔG	Process
+	–	–ve at all temperatures	Spontaneous at all temperatures
–	–	–ve at low temperature but +ve at high temperature	Spontaneous at low temperature but non-spontaneous at high temperature
+	+	+ve at low temperature and –ve at high temperature	Spontaneous at high temperature
+	+	+ve at all temperatures	Non-spontaneous at all temperatures

FORMULAE FOR CALCULATION OF W, q, ΔU AND ΔH FOR DIFFERENT PROCESSES

Process	W	q	ΔU	ΔH
Reversible Isothermal Expansion	$-nRT \ln(V_2/V_1)$	$nRT \ln(V_2/V_1)$	0	0
Compression	$nRT \ln(V_2/V_1)$	$-nRT \ln(V_2/V_1)$	0	0
Irreversible isothermal Expansion	$-p_2(V_2-V_1)$	$p_2(V_2-V_1)$	0	0
Compression	$p_2(V_2-V_1)$	$-p_2(V_2-V_1)$	0	0
Reversible adiabatic Expansion Compression	$\frac{1}{\gamma-1}(p_2V_2 - p_1V_1)$	0	$[nC_v(T_2-T_1)]$	$[nC_p(T_2-T_1)]$
Irreversible adiabatic Expansion compression	$-p_{ext}R\left(\frac{p_1T_2 - p_2T_1}{p_1p_2}\right)$	0	$[nC_v(T_2-T_1)]$	$[nC_p(T_2-T_1)]$

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50 Best Questions on Electrochemistry
for Medical Entrances

1. On passing 0.6F of electricity through NaCl, the amount of Cl deposited on cathode is
   (a) 35 g   (b) 18 g   (c) 21 g   (d) 142 g

2. Which of the following statement is false?
   (a) The conductance of $1\ cm^3$ (or 1 $unit^3$) of a solution is called specific conductance
   (b) Specific conductance increases while molar conductivity decreases on progressive dilution
   (c) The limiting equivalent conductivity of weak electrolyte cannot be determine exactly by extrapolation of the plot of Λ_{eq} against $\sqrt{C}$
   (d) None of the above

3. Match the following columns.

Column I	Column II
A. $Pt \mid Fe^{3+} \mid Fe^{2+}$	p. Metal-metal ion half-cell
B. $Pt \mid H_2 \mid H^+$	q. Gas-gas ion half-cell
C. $Pt \mid Hg \mid Hg_2^{2+}$	r. Oxidation-reduction half-cell
D. $Pb \mid PbSO_4 \mid SO_4^{2-}$	s. Metal sparingly soluble salt half-cell

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

4. Two students use the same stock solution of $ZnSO_4$ and a solution of copper sulphate. The emf of one cell is 0.03 V higher than the other. The concentration of copper sulphate in the cell with higher emf value of 0.5 M. Find out the concentration of $CuSO_4$ in the other cell. (2.303 RT/F= 0.06)
   (a) 0.01   (b) 0.09   (c) 0.05   (d) 0.02

5. A 1.0 M solution of Cd^{2+} is added to excess iron and the system is allowed to reach equilibrium. What is the concentration of Cd^{2+}?
   $$Cd^{2+}(aq) + Fe(s) \longrightarrow Cd(s) + Fe^{2+}(aq); E° = 0.037$$
   (a) 0.195   (b) 0.097   (c) 0.053   (d) 0.145

6. A current of 96.5 A is passed for 18 min between nickel electrodes in 500 mL solution of 2M $Ni(NO_3)_2$. The molarity of solution after electrolysis would be
   (a) 0.46 M   (b) 0.92 M
   (c) 0.625 M   (d) 1.25 M

7. Calculate the emf of the following cell at 298 K, Sn/Sn^{2+} (aq) (0.1M) $\|$ Ag^+ (aq) (0.01 M)/Ag.
   Given, $E°_{Sn^{2+}/Sn} = -0.14\ V$; $E°_{Ag^+/Ag} = 0.8 V$.
   $[R = 8.31\ JK^{-1}\ mol^{-1}, F = 96500\ C]$
   (a) 0.76 V   (b) 0.91 V   (c) 1.07 V   (d) None of these

8. Consider the following statement(s).
   I. Weak electrolytes like acetic acid have lower degree of dissociation at higher concentrations.
   II. In weak electrolytes electrical conductivity is low.
   III. In metallic conduction, the conductivity of metals is generally low.
   IV. Non-electrolytes are covalent compounds such as glucose.
   Identify the false statement(s) and choose the correct option.
   (a) Only I   (b) I, II and III   (c) Only IV   (d) Only III

9. Electrode potential for Mg electrode varies according to the equation,
   $$E_{Mg^{2+}/Mg} = E°_{Mg^{2+}/Mg} - \frac{0.059}{2}\log\left[\frac{1}{[Mg^{2+}]}\right]$$
   The graph of $E_{Mg^{2+}/Mg}$ versus $\log[Mg^{2+}]$ is

10. In the electrolysis of acidulated water, it is desired to obtain 1.12 cc of hydrogen per second under STP condition. The current to be passed is
    (a) 9.65 A   (b) 19.3 A   (c) 0.965 A   (d) 1.93 A

11. Match the following columns.

Column I	Column II
A. Dilute solution of HCl	p. O_2 evolved at anode
B. Dilute solution of NaCl	q. H_2 evolved at cathode
C. Conc. solution of NaCl	r. Cl_2 evolved at anode
D. Fairly concentrate solution of $AgNO_3$	s. Ag deposition at cathode

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

12. The conductance of a salt solution (AB) measured by two parallel electrodes of area $100\ cm^2$ separated by 10 cm was found to be $0.0001\Omega^{-1}$. If volume enclosed between two electrodes contains 0.1 mole of salt, what is the molar conductivity ($S\ cm^2\ mol^{-1}$) of salt at same concentration?
(a) 10   (b) 0.1
(c) 1   (d) None of these

13. $HNO_3\ (aq)$ is titrated with NaOH (aq) conductometrically, graphical representation of the titration as
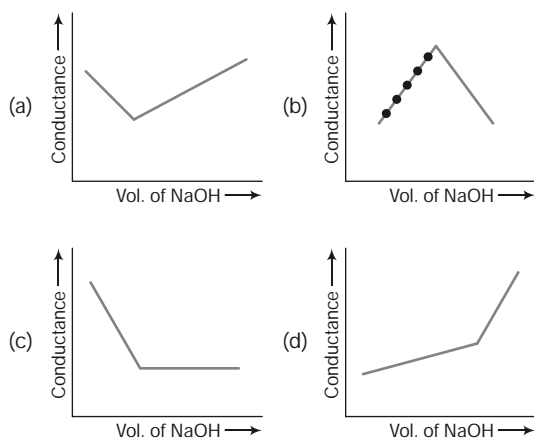
14. A solution containing H^+ and D^+ ions is in equilibrium with a mixture of H_2 and D_2 gases at 25°C. If the partial pressures of both gases is 1.0 atm, find the ratio of $[D^+]/[H^+]$.
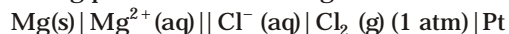[Given : $E^\circ_{D^+/D_2} = 0.003\ V$]
(a) 1.13   (b) 1.26
(c) 0.11   (d) 1.0

15. Calculate the potential of a half-cell having reaction
$$Ag_2S(s) + 2e^- \rightleftharpoons 2Ag(s) + S^{2-}\ (aq)$$
in a solution buffered at pH = 3 and which is also saturated with 0.1 M $H_2S\ (aq)$; $[K_{sp}\ (Ag_2S) = 10^{-49}$, $K_{a_1} \cdot K_{a_2} = 10^{-21}]$
(a) 1.18 V   (b) 0.17
(c) – 0.19 V   (d) None of these

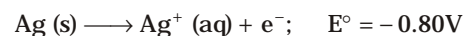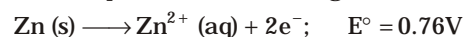16. Which is the correct Nernst equation for reaction taking place in the following cell?
$$Mg(s)\,|\,Mg^{2+}(aq)\,||\,Cl^-\ (aq)\,|\,Cl_2\ (g)\ (1\ atm)\,|\,Pt$$

(a) $E_{cell} = E^\circ_{cell} - \dfrac{0.0591}{n} \times \log \dfrac{[Cl^-]^2}{[Mg^{2+}]}$

(b) $E_{cell} = E^\circ_{cell} - \dfrac{0.0591}{n} \times \log \dfrac{[Mg^{2+}]}{[Cl^-]}$

(c) $E_{cell} = E^\circ_{cell} - \dfrac{0.0591}{n} \times \log [Mg^{2+}][Cl^-]^2$

(d) $E_{cell} = E^\circ_{cell} - \dfrac{0.0591}{n} \times \log \dfrac{[Mg^{2+}]}{[Cl^-]^2}$

17. Which of the following statement is true?
(a) 1 Coulomb electricity deposits 1 g-equivalent of a substance
(b) Conductivity decreases with the decrease in concentration of both the weak and strong electrolytes
(c) $\Delta S = nFT \left(\dfrac{dE}{dT}\right)_p$
(d) Electrode potential is an extensive property

18. Standard oxidation potential of Zn and Ag at 20°C are
$$Zn\ (s) \longrightarrow Zn^{2+}\ (aq) + 2e^-; \qquad E^\circ = 0.76V$$
$$Ag\ (s) \longrightarrow Ag^+\ (aq) + e^-; \qquad E^\circ = -0.80V$$
Which of the following reaction actually takes place?
(a) $Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$
(b) $Zn^{2+}(aq) + 2Ag(s) \longrightarrow 2Ag^+(aq) + Zn(s)$
(c) $Zn(s) + Ag(s) \longrightarrow Zn^{2+}(aq) + 2Ag^+(aq)$
(d) $Zn^{2+}(aq) + Ag(aq) \longrightarrow Zn(s) + Ag(s)$

19. The resistance of 0.1 N solution of formic acid is $200\ \Omega$ and cell constant is $2.0\ cm^{-1}$. The equivalent conductivity (in $S\ cm^2\ eq^{-1}$) of 0.1 N formic acid is
(a) 100   (b) 10
(c) 1   (d) None of these

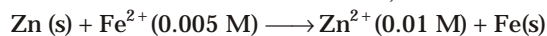20. Which of the following statement is false?
(a) Potential difference is the difference between the electrode potentials of two electrodes under any condition
(b) It is not responsible for the flow of steady current in the circuit
(c) emf is the maximum voltage obtainable from the cell
(d) emf is measured by a simple voltmeter

21. The standard emf of a galvanic cell involving cell reaction with n = 2 was found to be 0.295 V at 25°C. The equilibrium constant of the reaction would be
(a) 2×10^{11} (b) 4×10^{12}
(c) 1×10^2 (d) 1×10^{10}
(e) 3×10^{10}

22. Calculate the emf for the reaction,
$$Zn\ (s) + Fe^{2+}\ (0.005\ M) \longrightarrow Zn^{2+}\ (0.01\ M) + Fe(s)$$
$[E^\circ_{Zn/Zn^{+2}} = 0.76V; E^\circ_{Fe^{+2}/Fe} = -0.44V]$
(a) 0.10111 V   (b) 0.02 V
(c) 0.0089 V   (d) 0.0086 V
(e) 0.3111 V

23. Match the cell with the chemical constituents used.

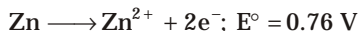| Column I		Column II
A.	Dry cell	p.	Mercuric oxide
B.	Ruben-Mallory cell	q.	Zinc chloride
C.	Ni-cadmium cell	r.	Potassium hydroxide
D.	$H_2 - O_2$ fuel cell	s.	Ammonium chloride

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

24. Calculate the K_{sp} for AgBr, if the conductivity κ of a saturated solution of AgBr at 298 K is 8.5×10^{-7} S cm^{-1}. If $\lambda^\circ_{Ag^+}$ and $\lambda^\circ_{Br^-}$ are 62 and 78 S cm^2 mol^{-1}, respectively.
   (a) 4.0×10^{10} mol^{2}L^{-2}
   (b) 3.6×10^{-11} mol^{2}L^{-2}
   (c) 2.7×10^2 mol^{2}L^{-2}
   (d) 1×10^{22} mol^{2}L^{-2}
   (e) 6.1×10^{-11} mol^{2}L^{-2}

25. The zinc/silver oxide cell is used in electric watches
$$Zn \longrightarrow Zn^{2+} + 2e^-; \ E^\circ = 0.76 \ V$$
$$Ag_2O + H_2O + 2e^- \longrightarrow 2Ag + 2OH^-; \ E^\circ = -0.344 \ V$$
   Find ΔG° in joules
   (a) 2.13×10^2
   (b) $- 2.13 \times 10^5$
   (c) 2.13×10^5
   (d) $- 2.13 \times 10^3$
   (e) None of these

26. Find the equilibrium constant for the reaction, $Zn + Cd^{2+} \rightleftharpoons Zn^{2+} + Cd$, if $E^\circ_{Cd^{2+}/Cd} = -0.403$ V and $E^\circ_{Zn^{2+}/Zn} = -0.763$ V.
   (a) 2.57×10^2 (b) 2×10^2 (c) 7×10^{11} (d) 5.2×10^{11}
   (e) 1.52×10^{12}

27. The molar conductivities of NaOH, NaCl and BaCl$_2$ at infinite dilution are 2.481×10^{-2} Sm^2 mol^{-1}, 1.265×10^{-2} Sm^2 mol^{-1} and 2.800×10^{-2} Sm^2 mol^{-1}, respectively. Calculate $\Lambda^\circ_m [Ba(OH)_2]$
   (a) 2×10^{-11} S m^2 mol^{-1}
   (b) 5.232×10^{-2} S m^2 mol^{-1}
   (c) 4.267×10^{-2} S m^2 mol^{-1}
   (d) 9×10^{-2} S m^2 mol^{-1}
   (e) 6.023×10^2 S m^2 mol^{-1}

28. If 0.05 M solution of M$^+$ is replaced by 0.0025 M solution of M$^+$, then the magnitude of the cell potential would be [Given, $E_{cell}(0.05M) = 0.07V$]
   (a) 35 mV (b) 80 mV (c) 140 mV (d) 700 mV
   (e) 1 mV

29. Consider the following statement.
   I. Copper sulphate solution can be kept in a zinc vessel.
   II. Copper liberates hydrogen from a dilute solution of hydrochloric acid.
   III. Kohlrausch law states that the molar conductivity of a strong electrolyte at infinite dilution is the sum of molar conductivities of its ions.

IV. Copper metal gets readily corroded in an acidic aqueous solution.
   Identify the true statement?
   (a) Only I
   (b) Both I and II
   (c) Only IV
   (d) None of these
   (e) Only III

30. For the half-cell,

$+ 2H^\oplus + 2e^-; E^\circ = 1.30 \ V$
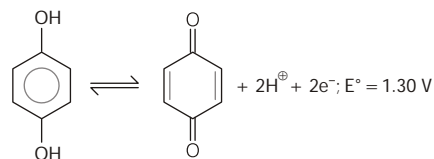
   At pH = 2, the electrode potential is
   (a) 1.36 V
   (b) 2.04 V
   (c) 1.42 V
   (d) 1.30 V
   (e) 1.20 V

31. Match the following columns.

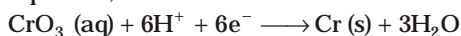| Column I		Column II	
A.	Concentration of copper sulphate solution is doubled	p.	Decreases with dilution
B.	Specific conductance	q.	emf of the cell increases
C.	Aluminium	r.	Most active
D.	Concentration of both the copper sulphate and zinc sulphate solution are doubled	s.	No effect on emf

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

32. Match the following columns.

Column I		Column II	
A.	Gibbs energy change	p.	$G^* = l/A$
B.	Molar conductivity	q.	$\Lambda^\circ_m = V_+ \lambda^\circ_+ + V_- \lambda^\circ_-$
C.	Kohlrausch law	r.	$-\Delta G = nFE_{cell}$
D.	Cell constant	s.	$\Lambda_m = \dfrac{\kappa}{C}$

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

33. Chromium metal can be plated out from an acidic solution containing CrO_3 according to the following equation,
$$CrO_3 \ (aq) + 6H^+ + 6e^- \longrightarrow Cr \ (s) + 3H_2O$$
   How long will it take to plate out 1.5 g of Cr by using 12.5 A current?
   (a) 2.1 s
   (b) 1336.15 s
   (c) 125.5 s
   (d) 1072.62 s
   (e) Zero

34. In the cell reaction,
Inert electrodes
At anode $\quad$ $2H_2O\ (l) \longrightarrow O_2\ (g) + 4H^+\ (aq) + 4e^-$
At cathode $Ag^+\ (aq) + e^- \longrightarrow Ag(s)$
A current of 1.50 A was passed through an electrolytic cell containing $AgNO_3$ solution with inert electrodes. The weight of Ag deposited was 1.50 g. How long did the current flow?
(a) 1336 s $\qquad$ (b) 893.52 s
(c) 993 s $\qquad$ (d) 1656.9 s
(e) 0.1332 s

35. For the equilibrium reaction,
$Fe(s) + Cd^{2+}(aq) \rightleftharpoons Fe^{2+}(aq) + Cd(s)$
What will be the equilibrium constant?
[Given, $E^\circ_{Cd^{2+}/Cd} = -0.40\ V,\ E^\circ_{Fe^{2+}/Fe} = -0.44\ V$]
(a) 10 $\qquad$ (b) 11.23 $\qquad$ (c) 17.11 $\qquad$ (d) 22.57
(e) Zero

36. For the reaction, $3Sn^{4+} + 2Cr \longrightarrow 3Sn^{2+} + 2Cr^{3+}$
The value of equilibrium constant is
[Given, $E^\circ = 0.885\ V$]
(a) 1×10^{10} $\qquad$ (b) 2×10^{-11}
(c) 1×10^{90} $\qquad$ (d) 0.2

37. Conductivity of 0.00241 M acetic acid is $7.896 \times 10^{-5}\ Scm^{-1}$. If Λ°_m for acetic acid is 390.5 S $cm^2\ mol^{-1}$, calculate its dissociation constant?
(a) 2.85×10^{-11} $\qquad$ (b) 1.86×10^{-4}
(c) 1×10^{-11} $\qquad$ (d) 2×10^{-20}

38. What would be the ionic strength (μ) of the 0.1 M solution of KCl?
(a) 0.1 $\qquad$ (b) 0.6 $\qquad$ (c) 0.3 $\qquad$ (d) zero

39. The emf diagram for some ions is given as
$FeO_4^{2-} \xrightarrow{E^\circ = +2.20\ V} Fe^{3+} \xrightarrow{E^\circ = +0.77\ V} Fe^{2+} \xrightarrow{E^\circ = -0.445\ V} Fe^0$
The value of $E^\circ_{FeO_4^{2-}/Fe^{2+}}$ is

(a) 2 V $\qquad$ (b) 3 V $\qquad$ (c) 4 V $\qquad$ (d) 1.84 V
(e) 2.18 V

40. A zinc rod is dipped in 0.1 M solution of $ZnSO_4$. The salt is 95% dissociated at this dilution at 298K. Calculate the electrode potential
[Given, $E^\circ_{Zn^{2+}/Zn} = -0.76\ V$]

(a) + 0.7902 V $\qquad$ (b) − 0.7902 V
(c) − 0.0295 V $\qquad$ (d) + 0.7625 V

41. Consider the following redox reaction occurring in acidic medium

$BrO_3^- \xrightarrow{E^\circ = 1.5\ V} BrO^- \xrightarrow{E^\circ = 1.6\ V} Br_2$
$\xrightarrow{E^\circ = ?\ V}$

The unknown standard reduction potential is
(a) −1.6 V $\qquad$ (b) 1.6 V
(c) −1.52 V $\qquad$ (d) 1.52 V

42. The weight of silver (atomic weight $=108$) displaced by a quantity of electricity which displaces 5600 mL of O_2 at STP will be
(a) 5.4 g $\qquad$ (b) 10.8 g $\qquad$ (c) 54.0 g $\qquad$ (d) 108.0 g

43. Standard electrode potential for Sn^{4+}/Sn^{2+} couple is $+0.15$ V and that for the Cr^{3+}/Cr couple is $-0.74V$. These two couples in their standard state are connected to make a cell. The cell potential will be
(a) +1.83 V $\qquad$ (b) + 1.19 V $\qquad$ (c) + 0.89 V $\qquad$ (d) + 0.18 V

44. The reduction potential at pH $=14$ for the Cu^{2+}/Cu couples is
$E^\circ_{Cu^{2+}/Cu} = 0.34\ V; K_{sp}\ [Cu(OH)_2] = 1 \times 10^{-19}$
(a) 0.34 V $\qquad$ (b) − 0.34 V $\qquad$ (c) 0.22 V $\qquad$ (d) − 0.22 V

45. On the basis of information available from the reaction,
$\frac{4}{3}Al + O_2 \longrightarrow \frac{2}{3}Al_2O_3;\ \Delta G = -827\ kJ\ mol^{-1}$ of O_2,
the minimum emf required to carry out an electrolysis of Al_2O_3 is (F $= 96500\ C\ mol^{-1}$)
(a) 6.42 V $\qquad$ (b) 8.56 V
(c) 2.14 V $\qquad$ (d) 4.28 V

46. The molar conductances of NaCl, HCl and CH_3COONa at infinite dilution are 126.45, 426.16 and 91 ohm^{-1} cm^2 mol^{-1} respectively. The molar conductance of CH_3COOH at infinite solution is
(a) 201.28 ohm^{-1} cm^2 mol^{-1} $\quad$ (b) 390.71 ohm^{-1} cm^2 mol^{-1}
(c) 698.28 ohm^{-1} cm^2 mol^{-1} $\quad$ (d) 540.48 ohm^{-1} cm^2 mol^{-1}

47. Given, $\quad Pb^{2+}/Pb = -0.126\ V;\quad Zn^{2+}/Zn = -0.763\ V$
Find the emf of the following cell,
$Zn/Zn^{2+}(0.1\ M)\ |\ |Pb^{2+}(1M)/Pb$
(a) − 0.637 $\qquad$ (b) + 0.66 $\qquad$ (c) > 0.637 $\qquad$ (d) + 0.889

48. When 0.1 mole of MnO_4^{2-} is oxidised the quantity of the electricity required to completely oxidise MnO_4^{2-} to MnO_4^- is
(a) 96500 C $\qquad$ (b) 2×96500 C
(c) 9650 C $\qquad$ (d) 96.50 C

49. The rusting of iron takes place as follows
$2H^+ + 2e^- + 1/2\ O_2 \longrightarrow H_2O\ (l);\qquad E^\circ = +1.23\ V$
$Fe^{2+} + 2e^- \longrightarrow Fe\ (s);\qquad E^\circ = -0.44\ V$
Calculate ΔG° for the net process.
(a) − 161 kJ mol^{-1} $\qquad$ (b) − 322 kJ mol^{-1}
(c) −152 kJ mol^{-1} $\qquad$ (d) − 76 kJ mol^{-1}

50. Al_2O_3 is reduced by electrolysis at low potentials and high current. If 4.0×10^4 A of current is passed through molten Al_2O_3 for 6 h, what mass of aluminium is produced?
[Assume 100% current efficiency, at. wt. of Al $= 27$]
(a) 9.0×10^3 g $\qquad$ (b) 8.1×10^4 g
(c) 2.4×10^3 g $\qquad$ (d) 1.3×10^4 g

Answer *with* Explanations

1. (c) Equivalent of Cl deposited
$$= \text{Number of Faraday passed} = 0.6$$
Weight of Cl $= 0.6 \times$ equivalent weight
$$= 0.6 \times 35.5 = 21.30 \approx 21\,g$$

2. (b) Specific conductance decreases while molar conductivity increases on progressive dilution.

3. (b) $A \rightarrow r; B \rightarrow q; C \rightarrow p; D \rightarrow s$

4. (c) The cell is represented as,
$Zn(s)/Zn^{2+}(aq) \| Cu^{2+} (aq)| Cu(s)$
$[Cu^{2+}]$ in the second cell $= 0.5$
$[Cu^{2+}]$ in the first cell may be calculated, as follows;
According to Nernst equation,

$$E_1 = E^{\circ}_{cell} - \frac{2.303\,RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]_1} \qquad \ldots(i)$$

$$E_2 = E^{\circ}_{cell} - \frac{2.303RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]_2} \qquad \ldots(ii)$$

$$(E_2 - E_1) = \frac{2.303\,RT}{2F}\left(\log \frac{[Zn^{2+}]}{[Cu^{2+}]_1} - \log \frac{[Zn^{2+}]}{[Cu^{2+}]_2}\right)$$

$$E_2 - E_1 = \frac{2.303\,RT}{2F} \log \frac{[Cu^{2+}]_2}{[Cu^{2+}]_1} \qquad \ldots(iii)$$

Given that, $E_2 - E_1 = 0.03\,V; 2.303\,RT/F = 0.06$
Substituting the value in Eq. (iii),

$$0.03 = \frac{0.06}{2} \log \frac{[Cu^{2+}]_2}{[Cu^{2+}]_1};$$

$$\log \frac{[Cu^{2+}]_2}{[Cu^{2+}]_1} = \frac{0.03 \times 2}{0.06} = 1$$

$$\log \frac{[0.5]}{[Cu^{2+}]_1} = 1 \quad \text{or} \quad \frac{0.5}{[Cu^{2+}]_1} = 10$$

$$\therefore \qquad [Cu^{2+}]_1 = \frac{0.5}{10} = 0.05\,M$$

5. (c) $\qquad Cd^{2+}(aq) + Fe(s) \rightleftharpoons Cd(s) + Fe^{2+}(aq)$

Initially	1 M	excess	0	0
At equilibrium	$1-x$	–	–	x

$$E^{\circ} = \frac{0.0591}{2} \log \left(\frac{Fe^{2+}}{Cd^{2+}} \right)$$

$$0.037 = \frac{0.0591}{2} \log \left(\frac{x}{1-x} \right)$$

$$x = [Fe^{2+}] \Rightarrow 0.947\,M$$

$$\therefore \quad [Cd^{2+}] = 1 - x = 1 - 0.947 = 0.053\,M$$

6. (b) Number of moles of $Ni(NO_3)_2$ in 500mL of

$$\text{2M } Ni(NO_3)_2 = \frac{2}{1000/500} = 1\,mol$$

Charge deposited $= 96.5 \times 18 \times 60 = 104220$ coulomb
Reaction of electrolysis is, $Ni^{2+} + 2e^- \longrightarrow Ni$
$\because 2 \times 96500\,C$ deposit 1 mole of $Ni(NO_3)_2$
$\therefore 104220\,C$ will deposit $= \dfrac{104220}{2 \times 96500} = 0.54\,mol$
So, moles of $Ni(NO_3)_2$ left in solution

$$= 1.0 - 0.54 = 0.46\,mol$$
Thus, molarity of $Ni(NO_3)_2$ solution
$$= 2 \times 0.46 = 0.92\,mol / L = 0.92\,M$$

7. (b) For given cell,
$$Sn + 2Ag^+ \longrightarrow Sn^{2+} + 2Ag$$
$$E^{\circ}_{cell} = E^{\circ}_{Ag^+/Ag} - E^{\circ}_{Sn^{2+}/Sn} = 0.8\,V - (-0.14\,V)$$
$$= 0.94\,V$$
Using Nernst equation,

$$E_{cell} = E^{\circ}_{cell} - \frac{2.303\,RT}{nF} \log \frac{[Sn^{2+}]}{[Ag^+]^2}$$
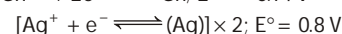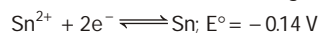
$Sn^{2+} + 2e^- \rightleftharpoons Sn; E^{\circ} = -0.14\,V$
$[Ag^+ + e^- \rightleftharpoons (Ag)] \times 2; E^{\circ} = 0.8\,V$
Here, $n = 2$
Substituting the values, we get

$$E^{\circ}_{cell} = 0.94\,V - \frac{2.303 \times 8.314\,JK^{-1}mol^{-1} \times 298\,K}{2 \times 96500\,C\,mol^{-1}} \cdot \log \left[\frac{0.1}{0.01} \right]$$

$$= 0.94\,V - 0.0295 = 0.91\,V$$

8. (d) Metallic conductors have generally high conductivity of metals.

9. (b) We know that, $E = E^{\circ} + \dfrac{0.059}{2} \log [Mg^{2+}]$
Thus, E vs log $[Mg^{2+}]$ is linear
with positive slope and intercept $= E^{\circ}$

10. (a) Number of moles of $H_2 = \dfrac{1.12}{22400}$
$\therefore$ Number of equivalents of hydrogen
$$= \frac{1.12 \times 2}{22400} = 10^{-4}$$
Number of Faradays required $= 10^{-4}$
$\therefore$ Current to be passed in 1s
$$= 96500 \times 10^{-4} = 9.65\,A$$

11. (a) $A \rightarrow p,q; B \rightarrow p,q; C \rightarrow q, r; D \rightarrow p,s$

12. (b) $G^* = \dfrac{l}{a} = \dfrac{10}{100} = 0.1\,cm^{-1}$
$$G = 0.0001\,S$$
$$V = 100 \times 10 = 1000\,cm^3 = 1\,L$$
$$\kappa = GG^* = 0.1 \times 0.0001 = 10^{-5}$$
$$\Lambda_m = \frac{\kappa \times 1000}{M}$$
$$= \frac{(0.1 \times 0.0001) \times 1000}{0.1} = 0.1\,S\,cm^2\,mol^{-1}$$

13. (a) Molar conductivity of H^+ and $\bar{O}H$ ions are very high as compare to other ions.
Initially conductance of solution sharply decreases due to consumption of free H^+ then increases due to the formation of salt (NaCN) and after complete neutralisation further sharply increases due to the presence of $\bar{O}H$.

14. (b) $E^{\circ}_{cell} = \dfrac{0.0591}{2} \log K_{eq}$

$$0.003 = \frac{0.0591}{2} \log \frac{[D^+]^2}{[H^+]^2} \Rightarrow \frac{[D^+]}{[H^+]} = 1.126$$

ELECTROCHEMISTRY

15. (c) $H_2S \rightleftharpoons 2H^+ + S^{2-}$

$$K_{a_1} \cdot K_{a_2} = \frac{[H^+]^2 [S^{2-}]}{[H_2S]}$$

$$= 10^{-21} \times 0.1 \qquad \ldots(i)$$

$\because \qquad pH = 3 \Rightarrow -\log[H^+] = 3$

or $\qquad [H^+] = 10^{-3}$

$\therefore \qquad K_{a_1} \cdot K_{a_2} = [H^+]^2[S^{2-}]$

$$= [10^{-3}]^2 [S^{2-}] \qquad \ldots(ii)$$

On equating Eqs. (i) and (ii), we get

$$[S^{-2}] = 10^{-16}$$

$$E_{S^{-2}|Ag_2S|Ag} = E^\circ_{Ag^+/Ag} - \frac{0.06}{2} \log \frac{[S^{2-}]}{K_{sp}}$$

$$= 0.80 - \frac{0.06}{2} \log \frac{10^{-16}}{10^{-49}}$$

$$= 0.80 - \frac{0.06}{2} \times 33 = -0.19 \text{ V}$$

16. (c) $Mg(s)|Mg^{2+}(aq)||Cl^-(aq)|Cl_2(g)(1 atm)|Pt$

Oxidation $\qquad Mg \longrightarrow Mg^{2+} + 2e^-$

Reduction $\qquad \dfrac{Cl_2 + 2e^- \longrightarrow 2Cl^-}{Mg + Cl_2 \longrightarrow Mg^{2+} + 2Cl^-}$
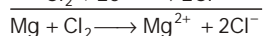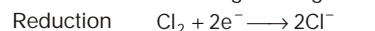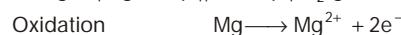
Nernst equation, $E_{cell} = E^\circ_{cell} - \dfrac{0.0591}{n} \log [Cl^-]^2 [Mg^{2+}]$

17. (b) Since, the number of ions per unit volume decreases on dilution, Hence, conductivity also decreases.
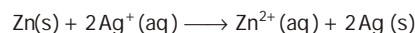
18. (a) Given potentials are oxidation potentials.

$\therefore$ The reduction potential will be

$$E^\circ_{Zn/Zn^{2+}} = -0.76 \text{ V and } E^\circ_{Ag/Ag^+} = 0.80 \text{ V}$$

Reduction potential of Ag is more than Zn, hence, Ag will get reduced and Zn will oxidise.

Half cell reaction, $(Ag^+ + e^- \longrightarrow Ag) \times 2$ (reduction)

$\qquad\qquad\qquad Zn \longrightarrow Zn^{2+} + 2e$ (oxidation)
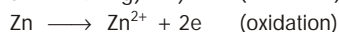
Hence, the reaction

$$Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$$

19. (a) $\kappa = G \cdot G^* \Rightarrow \dfrac{1}{200} \times 2 \Rightarrow 0.01$

$$\Lambda_{eq} = \frac{\kappa}{N} \times 1000 \Rightarrow \Lambda_{eq} = \frac{0.01}{0.1} \times 1000 = 100 \text{ S cm}^2\text{eq}^{-1}$$

20. (d) emf is not measured by a voltmeter, it is measured by potentiometric method only, so that the emf sent by the potentiometric source is equal and opposite to that of the cell and there is no net current flowing in the circuit. It cannot be measured by voltmeter which draws current.

21. (d) $E^\circ = \dfrac{0.0592}{2} \log K_{eq}$; $0.295 = \dfrac{0.0592}{2} \log K_{eq}$
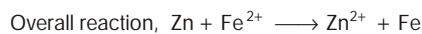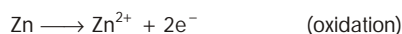
$$\log K_{eq} = \frac{0.295 \times 2}{0.0592} = 9.96$$

$$\log K_{eq} \approx 1.0$$

$$K_{eq} = \text{antilog} [1.0] = 1 \times 10^{10}$$

22. (e) Cell representation,

$$Zn/Zn^{2+}(0.01M)||Fe^{2+}(0.005M)Fe$$

Half-cell reaction,

$$Zn \longrightarrow Zn^{2+} + 2e^- \qquad \text{(oxidation)}$$

$$Fe^{2+} + 2e^- \longrightarrow Fe \qquad \text{(reduction)}$$

Overall reaction, $Zn + Fe^{2+} \longrightarrow Zn^{2+} + Fe$

E°_{cell} is given by

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = -0.44 + 0.76 = 0.32 \text{ V}$$

From the Nernst equation,

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Fe^{2+}]}$$

$$= 0.32 - 0.0295 \log \left(\frac{0.01}{0.005}\right)$$

$$= 0.32 - 0.0295 \log 2$$

$$= 0.32 - 0.0295 \times 0.3010$$

$$= 0.32 - 0.0089 = 0.3111 \text{ V}$$

23. (e) $A \rightarrow q,s; B \rightarrow p,r; C \rightarrow r; D \rightarrow r$

24. (b) $\Lambda^\circ_{m(AgBr)} = \lambda^\circ_{Ag^+} + \lambda^\circ_{Br^-}$
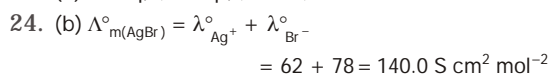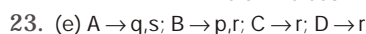
$$= 62 + 78 = 140.0 \text{ S cm}^2 \text{ mol}^{-2}$$

$\therefore \qquad \Lambda^\circ_{m(AgBr)} = \Lambda_{m(AgBr)} = \dfrac{\kappa \times 1000}{S}$

$$140.0 \text{ S cm}^2 \text{ mol}^{-1} = \frac{8.5 \times 10^{-7} \times 10^3}{S}$$

$\therefore \qquad S = (8.5 \times 10^{-7} \times 10^3)/140.0$

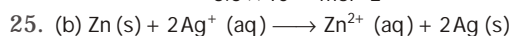$$= 0.06 \times 10^{-4} \text{ mol L}^{-1}$$

$$(\because 1 \text{ mole of AgBr} = 188 \text{ g AgBr})$$

$$= 0.06 \times 10^{-4} \times 188 \text{ g } L^{-1}$$

$$= 1.128 \times 10^{-3} \text{ g L}^{-1}$$

$\therefore K_{sp}$ of AgBr $= (S \text{ mole } /L)^2 = (0.06 \times 10^{-4})^2$
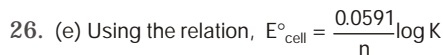
$$= 3.6 \times 10^{-11} \text{ mol}^2 L^{-2}$$

25. (b) $Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = E^\circ_{Zn^{2+}/Zn} - E^\circ_{Ag^+/Ag}$$

$$= 0.76 - (-0.344) = 1.104 \text{ V}$$

$$n = 2 \text{ mol}, F = 96500 \text{ C mol}^{-1}$$

$$\Delta G^\circ = -nFE^\circ_{cell} = -2 \times 96500 \times 1.104$$

$$= -213072 \text{ J} = -2.13 \times 10^5 \text{ J}$$

26. (e) Using the relation, $E^\circ_{cell} = \dfrac{0.0591}{n} \log K$

Given that, $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$$= -0.403 - (-0.763) = 0.36 \text{ V}$$

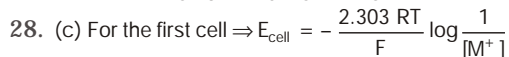$\Rightarrow \qquad 0.36 \text{ V} = \dfrac{0.0591}{2} \log K$

$$\log K = 12.1827$$

$$K = \text{antilog} (12.1827) = 1.52 \times 10^{12}$$

27. (b) Using Kohlrausch's law,

$\Lambda^\circ_m [Ba(OH)_2] = \Lambda^\circ_m (BaCl_2) + 2\Lambda^\circ_m (NaOH) - 2\Lambda^\circ_m (NaCl)$

$$= 2.800 \times 10^{-2} + 2 (2.481 \times 10^{-2}) - 2 (1.265 \times 10^{-2})$$

$$= 5.232 \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}$$

28. (c) For the first cell $\Rightarrow E_{cell} = -\dfrac{2.303 \text{ RT}}{F} \log \dfrac{1}{[M^+]}$

$$-\frac{2.303 \text{ RT}}{F} (1.301) = 0.07$$

$$-\frac{2.303 \text{ RT}}{F} = 0.0538$$

For new cell, $E_{cell} = -\dfrac{2.303 \text{ RT}}{F} \log \dfrac{1}{0.0025}$

$$= 0.0538 \log 400 = 0.0538 \times 2.6021$$

$$= 0.140 \text{ V} = 140 \text{ mV}$$

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29. (e) Kohlrausch law states that the molar conductivity of an electrolyte at infinite dilution is the sum of the ionic conductivity of the cations and anions each multiplied with the number of ions present in one formula unit of the electrolyte Mathematically, Λ°_m for $A_x B_y = x\,\lambda^\circ_{A^{y+}} + y\,\lambda^\circ_{B^{x-}}$

where, Λ°_m = limiting molar conductivity of the electrolyte.

30. (c) In this electrode,

[A] = [B] in quinhydrone electrode

Hence, $Q = [H^+]^2$
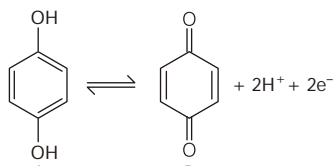
$$E = E^\circ - \frac{0.0591}{2}\log [H^+]^2$$

$$= E^\circ - 0.0591\log [H^+] = E^\circ + 0.0591\,pH$$

$$= 1.30 + 0.059 \times 2 = 1.42\ V$$

31. (b) AP. Concentration of copper sulphate solution is doubled when emf of the cell increases.

BP. Specific conductance decreases with dilution.

Cr. Aluminium is the most active metal.

Ds. When concentration of both copper sulphate and zinc sulphate solutions are doubled, there is no effect on emf.

32. (b) Gibbs energy charge $\Rightarrow -\Delta G = nFE_{cell}$

Molar conductivity $\Rightarrow \Lambda_m = \dfrac{\kappa}{C}$

Kohlrausch law $\Rightarrow \Lambda^\circ_m = V_+\lambda^\circ_+ + V_-\lambda^\circ_-$

Cell constant $\Rightarrow G^* = \dfrac{l}{A}$

33. (b) Given,

$$w_{Cr} = 1.5\ g$$
$$i = 12.5\ A$$
$$t = ?\ E_{Cr} = 52/6 \qquad [E = \text{equivalent mass}]$$

According to Faraday's law,

$$\therefore \qquad w = \frac{i\cdot E\cdot t}{96500}$$

$$1.5 = \frac{12.5 \times 52 \times t}{6 \times 96500}$$

$$t = 1336.15\ s$$

34. (b) $Ag^+ + e^- \longrightarrow Ag$

Quantity of charge required to deposit 108 g of silver = 96500 C

∴ Quantity of charge required to deposit 1.50 g of silver

$$= \frac{96500}{108} \times 1.50 = 1340.28\ C$$

$$t = \frac{Q}{I}$$

∴ Time taken $= \dfrac{1340.28}{1.50} = 893.52\ s$

35. (d) $Fe(s) + Cd^{2+}(aq) \rightleftharpoons Fe^{2+}(aq) + Cd(s)$

$$\log K_{eq} = \frac{nE^\circ_{cell}}{0.059}$$

Here, n = 2

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$
$$= E^\circ_{Cd^{2+}/Cd} - E^\circ_{Fe^{2+}/Fe}$$
$$= -0.40 - (-0.44)$$
$$= -0.40 + 0.44$$
$$= 0.04\ V$$

$$\log K_{eq} = \frac{2 \times 0.04}{0.059} = \frac{0.08}{0.059}$$

$$\log K_{eq} = 1.3536$$

$$K_{eq} = \text{antilog } 1.3536 = 22.57$$

36. (c) $E^\circ_{cell} = \dfrac{0.059}{n}\log K_{eq}$, n = 6

$$0.885 = \frac{0.059}{6}\log K_{eq}$$

$$\log K_{eq} = \frac{6 \times 0.885}{0.059} = 90$$

$$K_{eq} = \text{antilog } 90 = 1 \times 10^{90}$$

37. (b) C = 0.00241 M, $\kappa = 7.896 \times 10^{-5}$ S cm^{-1},

$$\Lambda^\circ_m = 390.5\ S\ cm^2\ mol^{-1}$$

$$\Lambda_m = \frac{\kappa \times 1000}{C}$$
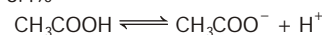
Substituting the values, we get

$$\Lambda_m = \frac{7.896 \times 10^{-5}\ S\ cm^{-1} \times 1000\ cm^3\ L^{-1}}{0.00241\ mol\ L^{-1}}$$

$$= 32.76\ S\ cm^2\ mol^{-1}$$

$$\alpha = \frac{\Lambda^c_m}{\Lambda^\circ_m} = \frac{32.76}{390.5} = 0.084$$

$$\alpha = 8.4\%$$

	$CH_3COOH \rightleftharpoons$	CH_3COO^-	$+ H^+$
Initial conc.	C	0	0
Concentration at equilibrium	C (1 − α)	Cα	Cα

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{C\alpha\cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

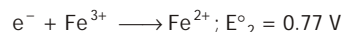$$K_a = \frac{0.0241\,(0.084)^2}{(1-0.084)}$$

$$= 1.86 \times 10^{-4}$$

38. (a) μ (KCl)

$$= \frac{1}{2}\Sigma C_i Z_i^2 = \frac{1}{2}(C_1 Z_1^2 + C_2 Z_2^2)$$
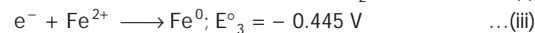
$$= \frac{1}{2}[0.1\,(1)^2 + 0.1\,(-1)^2] = 0.1$$

39. (d) $3e^- + Fe^{6+} \longrightarrow Fe^{3+}$; $E^\circ_1 = 2.20$ V

$$\therefore \qquad -\Delta G^\circ_1 = 3 \times 2.20\ F \quad \dots(i)$$

$e^- + Fe^{3+} \longrightarrow Fe^{2+}$; $E^\circ_2 = 0.77$ V

$$\therefore \qquad -\Delta G^\circ_2 = 1 \times 0.77\ F \quad \dots(ii)$$

$e^- + Fe^{2+} \longrightarrow Fe^0$; $E^\circ_3 = -0.445$ V $\quad\dots(iii)$

$$\therefore \qquad -\Delta G^\circ_3 = -0.445 \times 1F$$

By addition of Eqs. (i) and (ii), we get

$Fe^{6+} + 4e^- \longrightarrow Fe^{2+}$; $-\Delta G^\circ = 6.60 + 0.77$ F
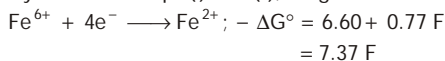
$$= 7.37\ F$$

or $\qquad nE^\circ F = 7.37\ F$

$$E^\circ = +\frac{7.37}{4} = 1.84\ V$$

40. (b) Electrode reduction written as reduction reaction
$$Zn^+(aq) + 2e^- \longrightarrow Zn(s)$$
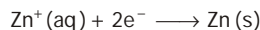
Using Nernst equation,

$$E_{Zn^{2+}/Zn} = E°_{Zn^{2+}/Zn^-} - \frac{0.0591}{2}\log\frac{1}{[Zn^{2+}]}$$

0.1 M $ZnSO_4$ solution is 95% dissociated
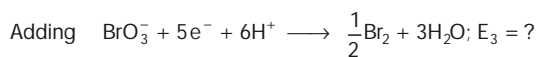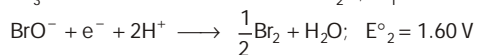
i.e. $$[Zn^{2+}] = \frac{95}{100} \times 0.1 = 0.095\ M$$
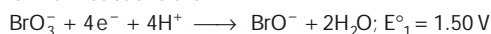
$$E_{Zn^{2+}/Zn} = -0.76 - \frac{0.0591}{2}\log\frac{1}{[0.095]}$$

$$= -0.76 + 0.02955\log(0.095)$$
$$= -0.76 - 0.02955 \times 1.0223$$
$$= -0.7902\ V$$

41. (d) The given half-reactions are

$$BrO_3^- + 4e^- + 4H^+ \longrightarrow BrO^- + 2H_2O;\ E°_1 = 1.50\ V$$
$$BrO^- + e^- + 2H^+ \longrightarrow \frac{1}{2}Br_2 + H_2O;\ E°_2 = 1.60\ V$$

Adding $BrO_3^- + 5e^- + 6H^+ \longrightarrow \frac{1}{2}Br_2 + 3H_2O;\ E_3 = ?$

$$\Delta G°_1 = -nE°_1\ F = -6F$$
$$\Delta G°_2 = -nE°_2\ F = -1.6\ F$$
$$\therefore \quad \Delta G°_3 = -7.6\ F = -5E°_3 F$$
$$\therefore \quad E°_3 = \frac{7.6}{5} = 1.52\ V$$

42. (d) At STP, 22, 400 mL of O_2 = 32 g of O_2 (1 mole of O_2)

$\therefore$ 5600 mL of O_2 = 8 g of O_2 at STP

$\therefore$ Weight of O_2 displaced (w_{O_2}) in gram = 8 g

Equivalent weight of silver (Ag) = $\frac{108}{1}$ = 108

Equivalent weight of O_2 $(E_{O_2})= \dfrac{\frac{1}{2} \times 32}{2} = 8$

$\therefore \quad \dfrac{w_{Ag}}{w_{O_2}} = \dfrac{E_{Ag}}{E_{O_2}}$ (Faraday's second law of electrolysis)

$\therefore \quad w_{Ag} = \dfrac{108}{8} \times 8 = 108\ g$

43. (c) The electrode with higher reduction potential in cathode
So, $Sn^{4+}|Sn^{2+}$ is cathode and $Cr^{3+}|Cr$ is anode

$$E_{cell} = E°_{cathode} - E°_{anode}$$
$$= +0.15 - (-0.74)$$
$$= +0.15 + 0.74$$
$$= +0.89\ V$$

44. (d) Given, pH = 14

$$pOH = 0 \quad \text{and} \quad [OH^-] = 1M$$
$$[Cu^{2+}][OH^-]^2 = K_{sp} = 1.0 \times 10^{-19}$$
$$\therefore \quad [Cu^{2+}] = 1.0 \times 10^{-19}M$$

For the half-reaction

$$Cu^{2+} + 2e^- \longrightarrow Cu$$
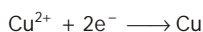
$$E_{Cu^{2+}/Cu} = E°_{Cu^{2+}/Cu} - \frac{0.0591}{2}\log\frac{1}{[Cu^{2+}]}$$

$$= 0.34 - \frac{0.0591}{2}\log 10^{19}$$
$$= -0.22\ V$$

45. (c) $\dfrac{4}{3}Al + O_2 \longrightarrow \dfrac{2}{3}Al_2O_3;\ \Delta G = -827\ kJmol^{-1}$
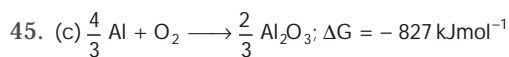
$\because \quad \Delta G = -nE°F$ (Value of n = 4)

$$-827 \times 10^3\ J = -4 \times E° \times 96500$$
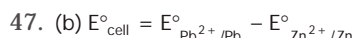$$E° = \frac{827 \times 10^3}{4 \times 96500}$$
$$E° = 2.14$$

46. (b) $\Lambda°_m\ (CH_3COOH)$

$$= \Lambda°_{(CH_3COONa)} + \Lambda°_{(HCl)} - \Lambda°_{(NaCl)}$$
$$= 91 + 426.16 - 126.45$$
$$= 390.71\ \Omega^{-1}\ cm^2\ mol^{-1}$$

47. (b) $E°_{cell} = E°_{Pb^{2+}/Pb} - E°_{Zn^{2+}/Zn}$

$$= -0.126 - (-0.763)$$
$$= +0.637\ V$$

$$E_{cell} = E°_{cell} - \frac{0.0591}{n}\log\frac{[Zn^{2+}]}{[Pb^{2+}]}$$

$$= 0.637 - \frac{0.0591}{2}\log 0.1$$
$$= 0.637 + 0.02955$$
$$= 0.667\ V$$

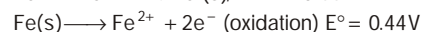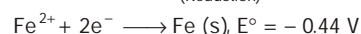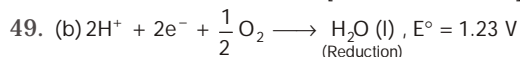**48.** (c) $\overset{+6}{Mn}O_4^{2-} \longrightarrow \overset{+7}{Mn}O_4^- + e^-$
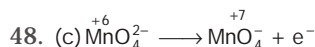
The above oxidation reaction involves one mole of electron.

$\because$ 1 mole of MnO_4^{2-} is completely oxidised to 1 mole of MnO_4^- using 1 F of electricity [By definition of Faraday]

$\therefore$ 0.1 mole of MnO_4^- is completely oxidised to 0.1 mole of MnO_4^- using 0.1 F of electricity.

i.e. 9650 C [1 F = 96500 C/mole]

49. (b) $2H^+ + 2e^- + \dfrac{1}{2}O_2 \longrightarrow H_2O\ (l)$, $E° = 1.23\ V$ (Reduction)

$$Fe^{2+} + 2e^- \longrightarrow Fe\ (s),\ E° = -0.44\ V$$
$$Fe(s) \longrightarrow Fe^{2+} + 2e^-\ (oxidation)\ E° = 0.44V$$

$\because$ During rusting, metal iron oxidises to iron oxide

$$n = 2$$
$$\therefore \quad E° = E°_{red} + E°_{oxid}$$
$$= 1.23 + (+0.44)$$
$$= +1.67\ V$$
$$\Delta G° = -nFE°$$
$$= -2 \times 96500 \times 1.67$$
$$= -322\ kJ\ mol^{-1}$$

50. (b) Reaction is $Al^{3+} + 3e^- \longrightarrow Al$

$$\therefore \quad E_{Al} = \frac{\text{Atomic weight}}{3} = \frac{27}{3} = 9$$

Now, $w = \dfrac{E \cdot i \cdot t}{96500} = \dfrac{9 \times 4 \times 10^4 \times 6 \times 60 \times 60}{96500}$

$$= 8.05 \times 10^4$$
$$\simeq 8.1 \times 10^4\ g$$

PERSONALITIES SPECTRUM

"Personalities column is an effort to introduce great scientists, whose contribution in Chemistry is unforgettable. In this issue, we will introduce Fritz Haber and Svante August Arrhenius".

FRITZ HABER
(1868-1934)

Fritz Haber was a German physical chemist and winner of the 1918 Nobel Prize for Chemistry for his successful work on nitrogen fixation. The Haber-Bosch process combined nitrogen and hydrogen to form ammonia in industrial quantities for the production of fertilizer and amunitions. Haber is also well known for his supervision on the German poison gas program during World War I.

LIFE HISTORY

Fritz Haber was born on December 9, 1868 in Breslau, Prussia as the son of Siegfried Haber, a merchant. He studied chemistry at the University of Heidelberg under Bunsen, at the University of Berlin under A.W. Hofmann and at the Technical School at Charlottenburg under Liebermann.

In 1896 Haber completed his thesis on experimental studies of the decomposition and combustion of hydrocarbons and in 1906 he was appointed as Professor of physical and electrochemistry and Director of the Institute established at Karlsruhe to study these subjects.

In 1911 he succeeded Engler as Director of the Institute for physical and electrochemistry at Berlin-Dahlem, where he remained until, 1933. He died of a massive heart attack in January, 1934 in Basel, Switz, while in route to Palestine to join directorship at the Daniel Sieff Research Institute, founded at Rehovot.

CONTRIBUTION TO CHEMISTRY
- During his time at University of Karlsruhe. Haber and his assistant Robert Le Rossignol invented the Haber-Bosch process which is the catalytic formation of ammonia from hydrogen and atmospheric nitrogen under conditions of high temperature and pressure.
- This led to the production of nitrogen-based products such as fertilizer and chemical feedstocks which was previously dependent on limited natural deposits. Haber was awarded the 1918 Nobel Prize in Chemistry for this work.
- Haber played a major role in the development of chemical warfare in World War.
- In his studies of the effects of poison gas, Haber noted that exposure to a low concentration of a poisonous gas for a long time often had the same effect (death) as exposure to a high concentration for a short time.
- He formulated a simple mathematical relationship between the gas concentration and the necessary exposure time. This relationship became ventually Haber's rule.

SVANTE AUGUST ARRHENIUS
(1859-1927)

"We must not waste what we have, but must have as much as possible for coming generations".

Svante August Arrhenius a founding father of physical chemistry, was trained in both chemistry and physics. He is known for his theory of electrolytic dissociation and his model of the greenhouse effect. In 1903, he was awarded the Nobel Prize for Chemistry.

LIFE HISTORY

Svante August Arrhenius was born on February 19, 1859 in Vik Sweden. He attended Cathedral school in Uppsala and then entered Uppsala University, from where he received a bachelor's degree (1878) and a doctorate degree (1884).

He was given the honorary title of docent at Uppsala University in 1884 and awarded a travel stipend by the Royal Swedish Academy of Sciences in 1886. Arrhenius's later years were darkened by World War I, which dealt a blow to his internationalist outlook and cut him off from many of his friends. He suffered a stroke in 1924 and from which he never fully recovered. He died at Stockholm on October 2, 1927 and is buried at Uppsala.

CONTRIBUTION TO CHEMISTRY
- Arrhenius's main contribution to physical chemistry was his theory (1887) that electrolytes can be separated or dissociated into electrically charged particles or ions, even when there is no current flowing through the solution.
- According to Arrhenius, acids were substances that contained hydrogen and yielded hydrogen ions in aqueous solution; bases contained the hydroxyl group and yielded hydroxide ions in aqueous solution.
- Arrhenius estimated the effect of the burning of fossil fuels as a source of atmospheric CO_2. He predicted that a doubling concentration of CO_2 due to fossil fuel burning alone would take 500 years and would lead to temperature increase of 3 to 4 °C (about 5 to 7 °F). Arrhenius was probably the first to have provided a model for the effect of industrial activity on global warming.
- Arrhenius was a member of the Nobel Committee for Physics of the Royal Swedish Academy of Sciences from 1901 to 1927 and he had a decisive influence on awarding Nobel Prizes in physics and chemistry.
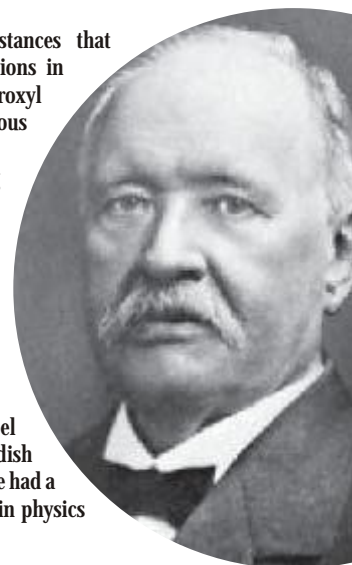
CONCEPT
Misconcept

General perception On addition of salt to blanching water, vegetables cook faster

Reality *Addition of salt will cause the boiling point to rise by only very small extent which may be consider negligible.*

Explanation Although this is technically true. Adding salt or any non-volatile solute to water will raise the temperature (boiling point) of water. This is a colligative property. Hot water will cook food faster. But if we add typically small amount of salt say 20 g into 5 L of water, will cause the water's boiling point to rise by only seven hundredths of one degree Fahrenheit. Hence, for increasing the boiling point of blanching water we need to add a lot of salt.

General perception All ionic solids are water soluble at 25°C

Reality *Compounds containing carbonates (CO_3^{2-}), phosphates (PO_4^{3-}), chromates (CrO_4^{2-}), sulphides (S^{2-}) etc., are insoluble in water at 25°C.*

Explanation Most of the ionic solids are water soluble but several exception are also known. In such cases enthalpy of solvation is less than the lattice enthalpy of ionic solids, e.g. $BaSO_4$, $CaSO_4$ etc.

General perception Thermal pollution is the increase in temperature of environment

Reality *It is deficiency of dissolved oxygen in water.*

Explanation Aquatic animals use dissolved oxygen in water for their respiration. As the temperature is increased the dissolved air escapes out and makes water unfit for survival of aquatic animals. It is called thermal pollution.

General perception Osmosis and diffusion processes are same

Reality *These are entirely two different processes.*

Explanation Diffusion involves movement of solute particles. When a solute is dissolved in solvent, solute particles moves from higher concentration region to lower concentration region till the concentration of solute becomes uniform throughout the solution, this process is known as diffusion. Osmosis is the net flow of solvent molecules from dilute solution to concentrated solution, when the two are separate through semipermeable membrane.

General perception Gases at higher temperature are more soluble in liquids

Reality *At higher temperature, gases are less soluble in liquids.*

Explanation At higher temperature, gas molecules have higher kinetic energy and due to it their escaping tendency becomes more than that of at lower temperature.

General perception Molecular mass of a volatile solute can be determined by the elevation of boiling point

*Reality* *Molecular mass of a non-volatile solute is determined by the elevation of boiling point.*

Explanation This method is suitable only for non-volatile electrolytes. When a solution of volatile substance is heated, the solute vaporises off.

General perception Boiling point, freezing point and vapour pressure are colligative properties

Reality *Elevation of boiling point, depression of freezing point, relative lowering of vapour pressure and osmotic pressure are colligative properties.*

Explanation Colligative properties are those properties which depend upon the number of solute particles in the solution. Boiling point, freezing point and vapour pressure are those properties which does not depend upon the number of solute particles rather these depend upon the magnitude of intermolecular forces between solvent particles.

Master Resource

B O O K S F O R

JEE MAIN
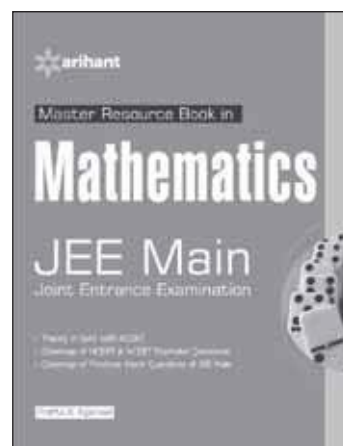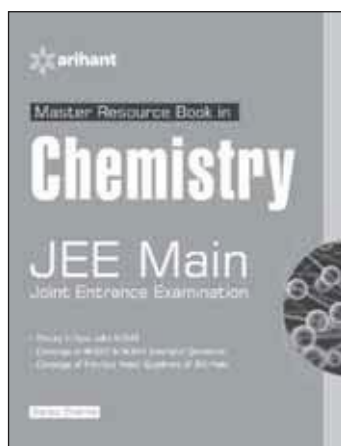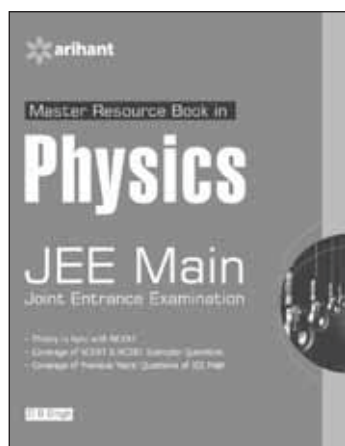
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arihant

Sanjay Sharma

REACTION MECHANISMS
A MATHEMATICAL APPROACH

In the last issue, we gathered a brief idea about the importance and requirements of organic reaction mechanisms. Hope you have understood the importance of structure for such mechanisms and how to use the structural aspect for your benefit. From this issue onwards, we will focus on this structural aspect only, i.e. how to get the visibility of the accurate electronic picture of an organic compound. As I wrote in previous issue also, two factors play major role in the visualisation of the exact electronic picture of a compound, i.e.

(a) IUPAC nomenclature

(b) Electron displacement effects

IUPAC nomenclature gives us the outline idea about the structure of a compound, i.e. through this we can get the idea about the groups (functional or alkyl or others) alongwith their position within the organic compound. I consider this nomenclature as the alphabets of organic chemistry.

RULES FOR WRITING IUPAC NAMES

Rules to select the longest chain
The longest possible chain can be selected in accordance with following rules:

- Normally the chain with maximum number of C-atoms will be the longest possible chain.
- In case of two or more chains with same number of C-atoms, select the chain with maximum number of side chains as the longest possible chain.
- If a double bond/triple bond/functional group is present in the molecule, then it must be included in the longest possible chain.
- Avoid the longest chain rule even if the chain containing multiple bonds or functional group falls smaller than other chains (the rule of exception).

So, the longest possible chain can be defined as "the chain containing the principal functional group + secondary functional group + multiple bonds as many as possible".

Rules for numbering the C-atoms of longest chain
In numbering a chain, following rules are considered:

- Numbering can be done from either of its ends for a symmetrical compound.
- If single branch (side chain) is present in the compound then numbering must be done in such a manner so that the side chain acquires the least possible number.
- If more than one side chains are present in the compound and if
    (i) All the chains are of same length, then numbering must be done in accordance with lowest sum rule, i.e. numbering should be done in such a way that the sum of numbers of side chains will be the least.
    (ii) In case of branches of different length, the numbering must be done in accordance with "lowest set of locants rule". (The word, "locant" is used by IUPAC for those C-atoms in a chain which bear a branch or a multiple bond or a functional group). According to this rule "while comparing two or more different sets of locants containing the same number of terms, then that set of locants is lowest which when compared term by term has the lowest term at the first point of difference.
    (iii) The side chains of different length are present at same distance from the ends, then the chain with least number of carbon atoms must get the least possible number.
- If multiple bond* is present alongwith the side chain, numbering must be done in such a manner that multiple bond will get the lowest possible number.
- If double bond and triple bond both are present in the compound then double bond must be preferred.

Remember here, the comparison can be made only when the bonds are present on the same footings only, i.e. situated at equal distance from the ends.

- If any other functional group is present in the compound (other than multiple bond) then numbering must be done in such a manner that the functional group will get the lowest possible number.
- If more than one functional groups are present in the compound then the group which comes first in the following preferential order will be considered as principal functional group and rest of the functional groups are considered as substituent groups or branch.

Radicals > Anions > Cations > Zwitter ionic compounds > Acids > Anhydrides > Esters > Acid halides > Anides > Hydrazide > Imides > Nitriles > Aldehydes > Ketones > Alcohols and phenols > Hydroperoxides > Amines > Imines > Hydrazines. Ethers > Peroxides > Alkene > Alkyne > Halo, nitroso, nitro, alkoxy > Oxiranes (Cyclic ethers)

If you have grip over the above written rules, try to name following compounds :

1.

2. CH_2CN
   |
   CHCN
   |
   CH_2COOH

3. (cyclobutane) CHO
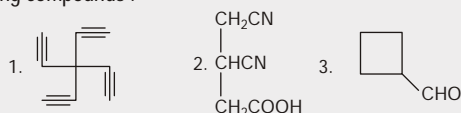
As IUPAC nomenclature is rule based hence, it requires more of practice than anything else. This is the reason why we will be concentrating more on the second aspect written above, i.e. electronic displacement effects. The very first effect in this category in inductive effect. But before going in detail about this effect, first let us understand how this effect will help us in our learning of organic reaction mechanism. We know all organic compounds contain C and H mainly with O, X, N, P like elements. It is also very clear to us that presence of organic compounds in such a huge quantity is due to the unique catenation power of carbon. Beside we can also draw a few more conclusion from the lines written above, i.e.

- The bonds present in all organic compounds are same naturewise means all of them are covalent bonds.

- The covalent bonds between C-atoms and C + H are of non-polar type.

- The covalent bonds which carbon forms with atoms other then C and H (O, X, N, P, S etc) are of polar type.

In simpler words, we can say that organic compounds contain 2 types of covalent bonds namely polar and non-polar. To my understanding inductive effect helps in the study of the effect of polar covalent bonds on non-polar ones within an organic molecule. This can be justified from the definition of inductive effect which states as "polarity produced in a molecule due to the presence of a polar bond".

Thus, a molecule with polar bond can be visualised as :

$$\delta\delta\delta\delta+ \quad \delta\delta\delta+ \quad \delta\delta+ \quad \delta+ \quad \delta-$$
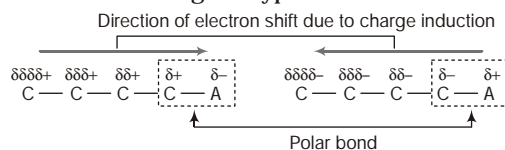$$C - C - C - C - X$$
Polar bond
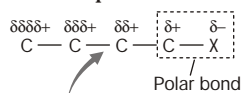
Look at the C-chain of the molecule the partial positive charge of it induced in the C-chain through the C-atom of polar bond

This induction of polarity in an otherwise non polar bond is inductive effect. This effect is transmitted through σ (sigma) bonds only and have the tendency to decrease with increase in distance from the source, i.e. the polar bond.

Inductive Effect at a Glance

- Related to permanent induction of charge from a polar bond (source) towards non-polar bonds.
- Operates through σ-bonds only thus a feature of saturated (σ-chain containing) compounds only.
- Induction of charge is always unidirectional.
- The electrons involved never leave their original atomic orbitals.
- The magnitude of induced charge decreases with increase in distance from the polar bond. Its magnitude is so less after two C-atoms that we consider it negligible beyond that.
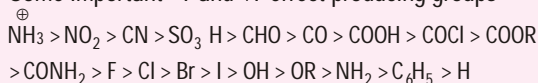
The possibility of induction of charge from the polar bond source can be of following two types:

Direction of electron shift due to charge induction

$$\delta\delta\delta\delta+ \quad \delta\delta\delta+ \quad \delta\delta+ \quad \delta+ \quad \delta-$$
$$C - C - C - C - A$$

$$\delta\delta\delta\delta- \quad \delta\delta\delta- \quad \delta\delta- \quad \delta- \quad \delta+$$
$$C - C - C - C - A$$

Polar bond

	Case I	Case II
1.	Positive charge is induced in the carbon chain due to shifting of electrons of non-polar bonds towards the polar bond.	Negative charge is induced in the C-chain due to shifting of electron of non-polar bond away from the polar bond.
2.	Thus, group A is called electron attracting and effect shown by this group is called –I-effect.	Thus, group A is called electron releasing and effect shown by this group is called +I-effect.

Conclusion Remember! whenever a polar bond is present in the molecule, it affects the complete structure (σ skeleton of the molecule which in turn affects the reactivity of mole).

Some important –I-and +I-effect producing groups

$$\overset{\oplus}{NH_3} > NO_2 > CN > SO_3H > CHO > CO > COOH > COCl > COOR$$
$$> CONH_2 > F > Cl > Br > I > OH > OR > NH_2 > C_6H_5 > H$$

→

–I power of groups in decreasing order with respect to the reference H

ter. alkyl > sec. alkyl > p-alkyl > CH_3 > H

→

Note Among the p-alkyl groups, +I power ∝ number of C-atoms in the chain

The inductive effect proved helpful in
1. Checking the stability of reaction intermediates.
2. In comparing the strength of acids and bases.

Hope by now you must be having a good idea of the impact of the presence of a polar bond over the electronic distribution within the sigma (σ) skeleton of an organic molecule. We will take the application part, i.e. how this electronic distribution affects reaction mechanisms or how to tackle the problems of inductive effect which you usually seen in examination papers alongwith the answers of my questions on IUPAC in the next issue.

BIHAR CECE
2015 SECOND STAGE
SOLUTIONS

1. (c) Both Ca and CaH_2 gives hydrogen gas on hydrolysis.

$$CaH_2(s) + 2H_2O\,(l) \longrightarrow Ca(OH)_2(aq) + 2H_2(g)$$
$$Ca(s) + 2H_2O\,(l) \longrightarrow Ca(OH)_2(aq) + H_2(g)$$

2. (c) Volume strength of $H_2O_2 = 11.2 \times M = 11.2 \times \dfrac{N}{2}$

Given, normality $(N) = 1.5$

∴ Volume strength $= 11.2 \times \dfrac{1.5}{2} = 8.4\text{ L}$

3. (c) The size of Mg^{2+} is minimum among Na^+, Ca^{2+}, K^+ and Mg^{2+} and size of Cl^- is more than F^-. Hence, ratio of the sizes of cation to anion is smallest in $MgCl_2$.

4. (b) $\underset{X}{CaCO_3\,(s)} \longrightarrow \underset{\text{Residue}}{CaO} + CO_2(g)$

$\underset{\text{Residue}}{CaO} + H_2O\,(l) \longrightarrow \underset{Y}{Ca(OH)_2(aq)}$

$\underset{Y}{Ca(OH)_2\,(aq)} + \underset{\text{Excess}}{CO_2(g)} \longrightarrow Ca(HCO_3)(aq)$

$2Ca(HCO_3)_2(aq) \longrightarrow \underset{X}{CaCO_3}\downarrow + CO_2 + H_2O(l)$

5. (b) Oxides of metals are basic in nature. Magnesium shows more metallic character than zinc and aluminium while nitrogen is a non-metal hence, shows least metallic character. Hence, MgO is most basic oxide among ZnO, MgO, Al_2O_3 and N_2O_5.

6. (b) $Al_2O_3(s) + 3C(s) + 3Cl_2(g) \longrightarrow 2AlCl_3(g) + 3CO(g)$

7. (a) NCl_5 does not form because nitrogen atom does not have empty d-orbitals to extend its octet.

8. (d) $NH_2-NH_2 + H_2O_2 \xrightarrow{Ca^{2+}} N_2 + 2H_2O$

9. (b) The colour of liquid O_2 is pale blue and it is strongly paramagnetic in nature.

10. (b)

In H_3PO_3, there are two hydrogen available to be furnished as proton (H^+). Hence, basicity of H_3PO_3 is 2.

11. (b) $CrO_3 + 2\overset{-}{O}H \longrightarrow CrO_4^{2-} + H_2O$

12. (a) Sc^{3+} is colourless in its aqueous solution because it does not have any unpaired electron in its outermost orbital or it has noble gas electronic configuration.

Electronic configuration of Sc^{3+} is

$Sc^{3+}(18e^-) = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6 = [Ne]$

13. (c) Let oxidation number of $Ni = x$

∴ For $[Ni(C_2O_4)_3]^{4-}$

$x + (-2) \times 3 = -4$ or $x - 6 = -4$ or $x = +2$

14. (c) A compound should contain at least one chiral carbon atom to be optically active. There is one chiral carbon atom present in 2-chlorobutane. Hence, it is optically active.

$$CH_3-\overset{*}{C}H-CH_2-CH_3$$
with Cl attached to the starred carbon

15. (b) Sodium fusion test is used in the analysis of elements like halogens, nitrogen and sulphur in a sample.

In this test the sample is strongly heated with clean sodium metal.

For nitrogen atom,

Organic compound $+ Na + N \longrightarrow NaCN$

16. (d) Boron nitride (BN) is known as inorganic graphite. It is most stable in crystalline hexagonal form. It is named as inorganic graphite because it has layered structure similar to graphite.

17. (a) $\underset{\text{Glass}}{SiO_2(s)} + 4HF(aq) \longrightarrow SiF_4(g) + 2H_2O(l)$

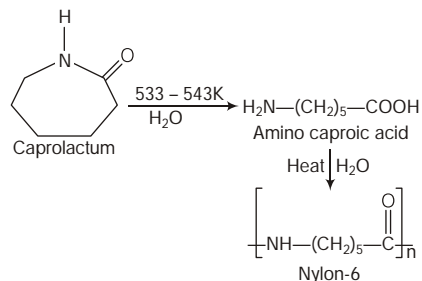**18.** (a)

∴ Number of chiral C = 5

{ EXAM DIARY }

19. (c) Nitro group present in o-nitrophenol is a strong deactivating group. It attracts the lone pairs of oxygen towards itself by resonance. Hence, O—H bond in alcoholic group become weak and H^+ can be easily taken out, thus, acidity increases.
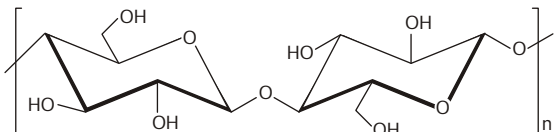
20. (a) $CH \equiv CH + NaNH_2 \longrightarrow CH \equiv CNa + NH_3$

21. (c) $RCl + AlCl_3 \longrightarrow \underset{\text{Electrophile}}{R^+} + AlCl_4^-$

22. (c)

$$\underset{\text{Caprolactum}}{\text{(structure of caprolactam)}} \xrightarrow[H_2O]{533 - 543K} \underset{\text{Amino caproic acid}}{H_2N—(CH_2)_5—COOH}$$

Heat $\downarrow H_2O$

$$\underset{\text{Nylon-6}}{\left[-NH—(CH_2)_5—\overset{O}{\overset{\|}{C}}\right]_n}$$

23. (a) Cellulose is a polysaccharide consisting a linear chain of several hundred to many thousands of $\beta(1-4)$ linked D-glucose units.

While wool, silk and nylon polymers have amide group (—CO—NH—) which provides hydrogen bonding between polyamide chains.

24. (c) Buna-S, is a synthetic rubber, in which S stands for styrene.

25. (c) $\overset{1}{C}H_3—\overset{2}{C}\equiv\overset{3}{C}—\overset{4}{C}H_2—\overset{5}{C}H_3$

Pent-3-yne is an incorrect name because numbering of carbon atoms should start from the side by which triple bonded carbon atom gets minimum number.

Hence, correct name is pent-2-yne.

26. (c) $CH\equiv CH + AsCl_3 \longrightarrow$

27. (b) $CH\equiv CH \xrightarrow[Hg^{2+}]{CH_3COOH} CH_3—\overset{O}{\overset{\|}{C}}—O—CH\equiv CH_2$

$\downarrow CH_3COOH$

$CH_3—CH\,(OOCCH_3)_2$

28. (a) $(C_2H_5)_4Pb$ is an example of negative catalyst which is used to stop the reaction.

29. (a) Fischer-Tropsch method is a set of chemical reactions which change a mixture of carbon monoxide gas and hydrogen gas into liquid hydrocarbons. Mn metal is taken as a part of catalyst in this method.

30. (a) The octane number is based on an arbitrary scale with zero assigned to n-heptane and 100 to 2, 2, 4-trimethylpentane.

31. (c) Organometallic compounds are the compounds which contain at least one bond between carbon atom of an organic compound and a metal. In CH_3ONa and C_2H_5SNa, Na metal is

bonded to oxygen and sulphur respectively while in CH_3MgI, magnesium metal is bonded to carbon atom and iodine. Hence, CH_3MgI is an organo metallic compound.

32. (b) $CCl_2\equiv CHCl$
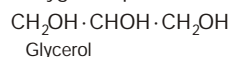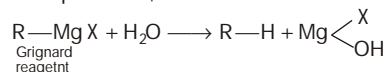
1, 1, 2-trichloroethene

33. (d) Here, X is $AgNO_3$

34. (d) $CH_3CH_2COOAg + Br_2 \longrightarrow CH_3CH_2Br + CO_2\uparrow + AgBr$

35. (b) Glycerol is hygroscopic, sweet in taste and non-poisonous.

$$\underset{\text{Glycerol}}{CH_2OH \cdot CHOH \cdot CH_2OH}$$

36. (a) Due to basic nature, Grignard reagent readily reacts with water and takes proton as,

$$\underset{\substack{\text{Grignard}\\\text{reagetnt}}}{R—Mg\,X} + H_2O \longrightarrow R—H + Mg\underset{OH}{\overset{X}{<}}$$
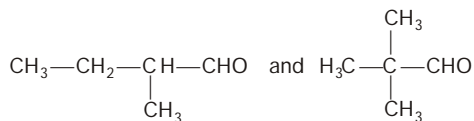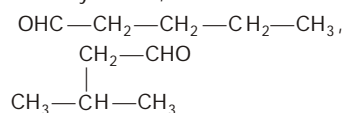
Ether $(C_2H_5OC_2H_5)$ is used as solvent during reactions with Grignard reagent.
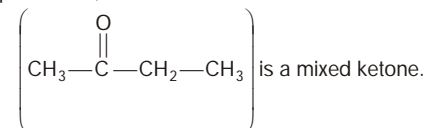
37. (b) KI is added to ether to test its purity.

38. (c)

39. (a) $Zn/Hg + HCl$ convert a ketone into acid not alcohol.

40. (d) Isomeric aldehydes are,

$$OHC—CH_2—CH_2—CH_2—CH_3,$$
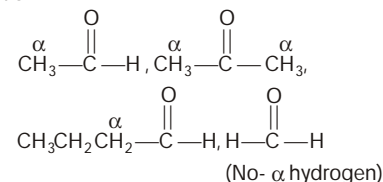
$$\underset{CH_3—CH—CH_3}{\overset{CH_2—CHO}{|}}$$

$$CH_3—CH_2—\underset{CH_3}{\overset{|}{C}H}—CHO \quad \text{and} \quad H_3C—\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}—CHO$$

41. (b) Mixed ketones are the compounds which have two different alkyl groups. Hence, butan-2-one

$$\left(\underset{}{CH_3—\overset{O}{\overset{\|}{C}}—CH_2—CH_3}\right) \text{ is a mixed ketone.}$$

42. (b) Ketones do not react with Fehling's solution.

43. (a) For aldol condensation a compound must have at least one α-hydrogen. Hence, formaldehyde (HCHO) does not give aldol condensation.
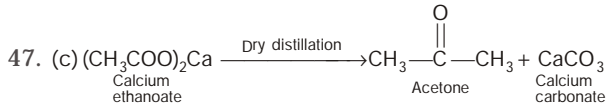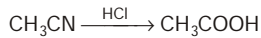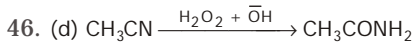
$$\overset{\alpha}{CH_3}—\overset{O}{\overset{\|}{C}}—H, \overset{\alpha}{CH_3}—\overset{O}{\overset{\|}{C}}—\overset{\alpha}{CH_3},$$

$$\overset{}{CH_3CH_2}\overset{\alpha}{CH_2}—\overset{O}{\overset{\|}{C}}—H, H—\overset{O}{\overset{\|}{C}}—H$$

(No- α hydrogen)

44. (b) Acrolein $\left(\overset{O}{\overset{\|}{\underset{H_2C}{\diagup}\diagdown H}}\right)$ is the simplest unsaturated aldehyde.

45. (d) $FeSO_4 + H_2O_2$ is called Fenton's reagent. It is used to oxidise contaminants or waste water.

46. (d) $CH_3CN \xrightarrow{H_2O_2 + \overline{O}H} CH_3CONH_2$

   $CH_3CN \xrightarrow{HCl} CH_3COOH$

47. (c) $(CH_3COO)_2Ca \xrightarrow{Dry\ distillation} CH_3-\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}-CH_3 + CaCO_3$
   Calcium   Acetone   Calcium
   ethanoate   carbonate

48. (a) Reactions involved in electrolysis of concentrated aqueous solution of CH_3COOK, is

   $2R-\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}-O^- \xrightarrow[-2CO_2]{-2e^-} R-R$

49. (c) $CO + NaOH \xrightarrow[10\ atm]{210\ ^{\circ}C} HCOONa$
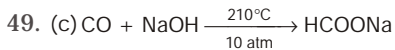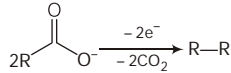
50. (c) Calcium oxalate $\left(\begin{array}{c} COO \\ | \\ COO \end{array} \hspace{-4pt} \rangle Ca \right)$ is insoluble in acetic acid.

51. (d) Alkaline hydrolysis of an ester is called saponification.

   Triglyceride
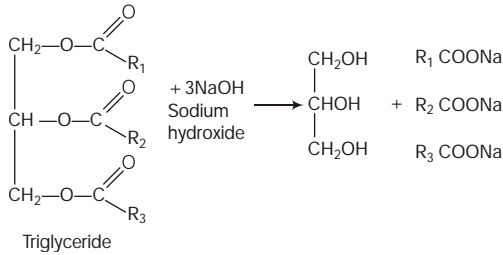
52. (b) Biuret ($NH_2CONHCONH_2$) is the result of condensation of two molecules of urea and it is a impurity in urea-based fertilisers.

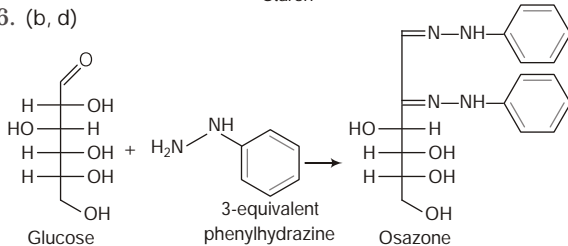53. (b) Glucose is known as grape-sugar because it is found in wine grapes.

54. (c) Number of chiral carbon in glucose = 4

   ∴ Number of stereoisomers of glucose = $4^2 - 1 = 15$

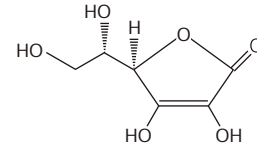55. (a) In starch, monosaccharides are bonded by glycosidic linkage.

   Starch

56. (b, d)

   Glucose   3-equivalent   Osazone
              phenylhydrazine
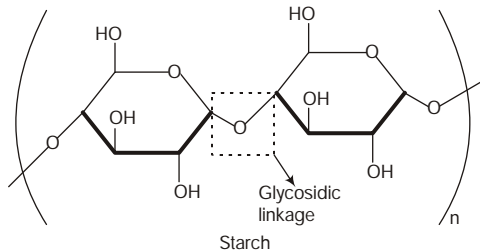
   Glucose reacts with bromine water ($Br_2 + H_2O$) and produces gluconic acid.

57. (b) Glucose is an aldohexose with an aldehyde group at one end.
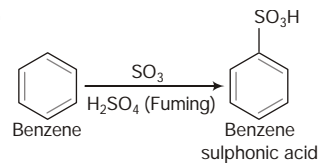
58. (b) Formula of vitamin C is,
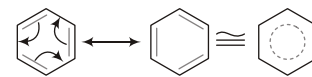

59. (a) Vitamin D is a water insoluble vitamin.

60. (a) Nyctalopia (night blindness) happens due to deficiency of vitamin A.

61. (b) Mostly vitamin B_{12} (cyanocobalamin), is available from animal products. Hence, this vitamin is less available to vegetarians.

62. (b)

   Benzene   Benzene
              sulphonic acid

63. (c)

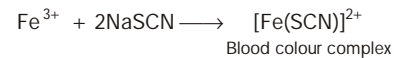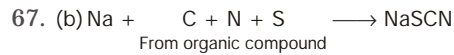   Here, 6 electrons are delocalised.

64. (a) Cyanide group decreases the electron density at meta-position due to its electron withdrawing nature. Hence, it is a meta-directing group in benzene during substitution reactions.

65. (a) % of oxygen = $100 - (40 + 6.66) = 53.34\%$.

Elements	Molecular mass of atoms	% of elements	Ratio (% / Molecular Mass)	Minimum ratio
C	12	40	3.33	1
H	1	6.66	6.66	2
O	16	53.34	3.33	1

   ∴ Empirical formula of compound = CH_2O

66. (d) Paper chromatography has liquid, liquid mobile and stationary phases.

67. (b) $Na + \underset{\text{From organic compound}}{C + N + S} \longrightarrow NaSCN$

   $Fe^{3+} + 2NaSCN \longrightarrow \underset{\text{Blood colour complex}}{[Fe(SCN)]^{2+}}$

68. (a) Concentrations of both reactants should be same for getting

   $k = \dfrac{1}{t} \cdot \dfrac{x}{a(a-x)}$ for second order reaction.

   If concentration of two reactants is different,

   $k = \dfrac{1}{b-a} \ln \dfrac{(b-x)a}{(a-x)b}$

69. (a) Concentration of succinic acid in water layer

   $= (1.843/100)\ g/mL$

   Concentration of succinic acid in ether layer = $\dfrac{0.127}{50}\ g/mL$

$\therefore$ Distribution coefficient $= \dfrac{\text{Concentration in water layer}}{\text{Concentration in ether layer}}$

$= \dfrac{1.843}{100} \times \dfrac{50}{0.127} = 7.25$

70. (b) If van't Hoff factor in a reaction is less than 1 then association takes place.

71. (c) In water, $\qquad [H^+] = [\bar{O}H] = 10^{-7}$

$[H^+][\bar{O}H] = 10^{-14}$

or, $\qquad \log[H^+][\bar{O}H] = \log 10^{-14}$

or, $\quad \log[H^+] + \log[\bar{O}H] = -14 \quad [\because \log[AB] = \log A + \log B]$

or, $\; -\log[H^+] - \log[\bar{O}H] = 14$

or, $\qquad\qquad pH + pOH = 14 \quad \left[\begin{array}{l}\because -\log[H^+] = pH, \\ -\log[\bar{O}H] = pOH\end{array}\right]$

72. (a) Complementary base pairs in DNA are A and T , G and C.
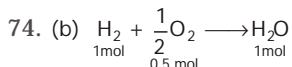A stands for adenine, T stands for thymine.
G stands for guanine and C stands for cytosine

73. (b) At constant temperature,

$\Delta S = \dfrac{\Delta H}{T}$

or, $\qquad T = \dfrac{\Delta H}{\Delta S} = \dfrac{30.58 \text{ kJ}}{66.1 \text{ JK}^{-1}} = \dfrac{30.58 \times 1000 \text{ J}}{66.1 \text{ JK}^{-1}}$

or $\qquad T = 462.6 \text{ K}$

74. (b) $\underset{1\text{mol}}{H_2} + \underset{0.5 \text{ mol}}{\frac{1}{2}O_2} \longrightarrow \underset{1\text{mol}}{H_2O}$

Given, number of moles of hydrogen $= \dfrac{10}{2} = 5$ mol

Number of moles of oxygen $= \dfrac{64}{32} = 2$ mol

From, the reaction it is clear that number of moles of oxygen required is less than half of the number of moles of hydrogen.
$\therefore$ For 5 moles of H_2, number of moles of O_2 needed = 2.5 mol
But the number of moles of O_2 we have = 2
Hence, oxygen is a limiting reagent.
$\therefore$ Number of moles of water formed will be decided by oxygen.
$\therefore$ 0.5 mole of oxygen formed $H_2O = 1$ mol
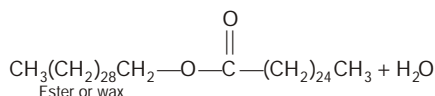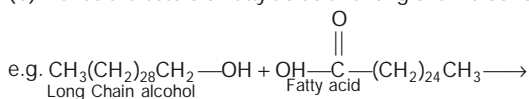$\therefore$ 2 moles of oxygen will formed $H_2O = \dfrac{1}{0.5} \times 2 = 4$ mol

75. (a) Value of 1/n is between 0 and 1.

76. (c) Dettol is a mixture of chloroxylenol and terpineol.

77. (a) Human body can not produce vitamins. It gets these vitamins from outer sources.

78. (b) Diphenylhydramine is an antihistamines. It is used to relieve symptoms of allergy, common cold and heavy fever.

79. (b) Waxes are esters of fatty acids and long chain alcohols.

e.g. $\underset{\text{Long Chain alcohol}}{CH_3(CH_2)_{28}CH_2} {-\!\!-}OH + OH{-\!\!-}\overset{\displaystyle O}{\overset{\displaystyle \|}{\underset{\text{Fatty acid}}{C}}}{-\!\!-}(CH_2)_{24}CH_3 \longrightarrow$

$\underset{\text{Ester or wax}}{CH_3(CH_2)_{28}CH_2{-\!\!-}O{-\!\!-}\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}{-\!\!-}(CH_2)_{24}CH_3} + H_2O$

80. (c) Number of electrons

$N_2 = 7 + 7 = 14$

$CO = 6 + 8 = 14$

$CN^- = 6 + 7 + 1 = 14$

81. (a)

Compound	Number of ions after dissociation
$K_4[Fe(CN)_6]$	$4K^+ + [Fe(CN)_6]^{4-} = 5$
$[Co(NH_3)_6]\,Cl_3$	$[Co(NH_3)_6]^{3+} + 3Cl^- = 4$
$[Cu(NH_3)_4]\,Cl_2$	$[Cu(NH_3)_4]^{2+} + 2Cl^- = 3$
$[Ni(CO)_4]$	0

Since, $K_4[Fe(CN)_6]$ dissociates into maximum number of ions. Hence, it will show maximum ionic conductivity.

82. (a) $[Cr(CO)_6] = Cr^0 = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^1$

3d $\boxed{1}\boxed{1}\boxed{1}\boxed{1}\boxed{1}$ 4s $\boxed{1}$
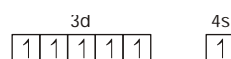
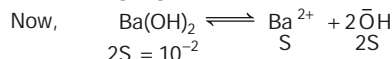Due to the presence of six unpaired electrons, $[Cr(CO)_6]$ is paramagnetic.

83. (b) In ClO_2, the central atom Cl is sp^2 hybridised with O—Cl—O angle of 118°, the molecule is paramagnetic due to the presence of one electron in a p-orbital of chlorine atom.

84. (d) $pH = 12, pOH = 14 - pH = 14 - 12 = 2$

$pOH = -\log[\bar{O}H] \Rightarrow 2 = -\log[\bar{O}H]$

or $\qquad [\bar{O}H] = 10^{-2}$ M

Now, $\qquad Ba(OH)_2 \underset{S}{\overset{}{\rightleftharpoons}} \underset{S}{Ba^{2+}} + \underset{2S}{2\bar{O}H}$

$2S = 10^{-2}$

$\therefore \qquad S = 0.5 \times 10^{-2}$

$\therefore \qquad K_{sp} = S(2S)^2 = (0.5 \times 10^{-2})(10^{-2})^2$

$K_{sp} = 0.5 \times 10^{-7} \text{ M}^3$

85. (c) Reverse osmosis (RO) is a water purifying technology in which semipermeable membrane is used to remove solution particle from sea water.

86. (b) Given, $\qquad Fe^{2+} + 2e^- \longrightarrow Fe, E° = -0.44 \qquad$ …(i)

$Fe^{3+} + e^- \longrightarrow Fe^{2+}, E° = 0.77 \qquad$ …(ii)

If Fe^{2+}, Fe^{3+} and Fe blocks are kept together, reaction (ii) is favourable in forward direction while reaction (i) is favourable in backward direction due to their positive and negative values of electrode potentials respectively. Hence, it will lead to decrease in conentration of Fe^{3+}.

87. (d) Since, SCN is a bidentate ligand. Hence, $[Cr(SCN)_2(NH_3)_4]^+$ will have highest number of isomers because extra linkage isomers are also included.

88. (b) $3A \longrightarrow 2B$

Rate of reaction is,

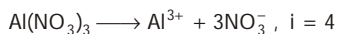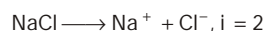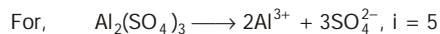$-\dfrac{1}{3}\dfrac{d[A]}{dt} = \dfrac{1}{2}\dfrac{d[B]}{dt}$

$\therefore \qquad \dfrac{d[B]}{dt} = -\dfrac{2}{3}\dfrac{d[A]}{dt}$

89. (b) SO_3^{2-} has $p\pi - d\pi$ bond because S has empty d-orbitals while oxygen has electron containing p-orbitals.
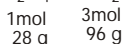
90. (a) Bauxite has SiO_2 impurity.

91. (c) For ideal mixing, volume of solution remains constant and there is no loss of energy. Hence, enthalpy also remains constant.

92. (a) van't Hoff factor (i) for $K_4[Fe(CN)_6]$ = 5

For, $Al_2(SO_4)_3 \longrightarrow 2Al^{3+} + 3SO_4^{2-}$, i = 5

$NaCl \longrightarrow Na^+ + Cl^-$, i = 2

$Al(NO_3)_3 \longrightarrow Al^{3+} + 3NO_3^-$, i = 4

$Na_2SO_4 \longrightarrow 2Na^+ + SO_4^{2-}$, i = 3

93. (c) $\underset{\underset{28\,g}{1mol}}{C_2H_4} + \underset{\underset{96\,g}{3mol}}{3O_2} \longrightarrow 2CO_2 + 2H_2O$

28 g ethylene needed O_2 for complete combustion = 96 g

$\dfrac{28}{1000}$ kg ethylene needed O_2 for complete combustion
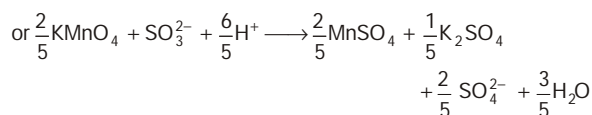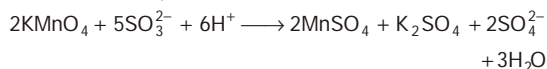
$$= \frac{96}{1000}\,kg$$

∴ 1 kg ethylene needed O_2 for complete combustion

$$= \frac{96}{1000} \times \frac{1000}{28} = \frac{96}{28}\,kg$$

or 2.8 kg needed O_2 for complete combustion = $\dfrac{96}{28} \times 2.8$

$$= 9.6\,kg$$

94. (b) In acidic medium,

$$2KMnO_4 + 5SO_3^{2-} + 6H^+ \longrightarrow 2MnSO_4 + K_2SO_4 + 2SO_4^{2-} + 3H_2O$$

or $\dfrac{2}{5}KMnO_4 + SO_3^{2-} + \dfrac{6}{5}H^+ \longrightarrow \dfrac{2}{5}MnSO_4 + \dfrac{1}{5}K_2SO_4$

$$+ \frac{2}{5}\,SO_4^{2-} + \frac{3}{5}H_2O$$

∴ Number of moles of $KMnO_4$ needed to react with 1 mole of SO_3^{2-} in acidic solution is $\dfrac{2}{5}$.
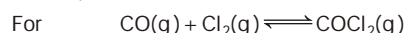
95. (a) $H\!-\!C \equiv C\!-\!H$
Acetylene

It has 1σ and 2π bonds between C-atoms.

96. (c) At CMC, surfactant molecules associate.

97. (c) ∵ $K_p = K_C(RT)^{\Delta n_g}$

For $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$

Δn_g = Number of moles of gaseous products
– Number of moles of gaseous reactants.

$$= 1 - 2 = -1$$

∴ $K_p = K_C(RT)^{-1}$

or $\dfrac{K_p}{K_C} = \dfrac{1}{RT}$

98. (a) Conjugate base of $OH^- = O^{2-}$ (Conjugate base has one proton less than the corresponding base).

99. (b) To get precipitate of CaF_2 ionic product should be higher than the solubility product.

100. (b) $Na_2CO_3 \cdot 10H_2O$ is washing soda.
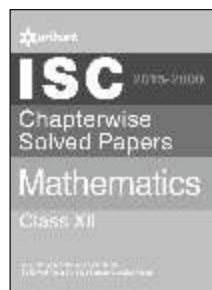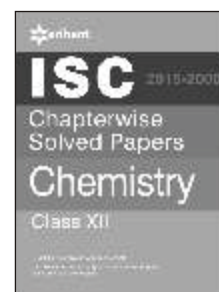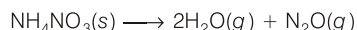
CHEMISTRY
SPECTRUM
for You

01 Dear sir, I heard a lot about laughing gas. Please explain me, how it is prepared and how does this simple gaseous compound make us laugh? [Nupur Gupta, Pune]

➥ Laughing gas (N_2O) is a colourless gas with a little sweet odour and taste.

(i) **Preparation of N_2O** (Nitrous oxide)

N_2O gas is present in the trace amounts of earth's atmosphere as a result of high temperature reactions between nitrogen and oxygen.

Industrially, the gas is prepared by gently heating of ammonium nitrate.

$$NH_4NO_3(s) \longrightarrow 2H_2O(g) + N_2O(g)$$

(ii) To have a better understanding of the mechanism of effects of nitrous oxide you would need to have some basic concepts of neuroscience. Apart from chemistry, after inhaling nitrous oxide gas it mixes into the blood through the lungs and reaches to the mesolimbic region of our brain, which is responsible for our emotional behaviour. It enters into the synapses of neurons and attach with neural receptors (like acetylcholine receptor or N-methyl-D-aspartate receptor) blocking the neural signal transmission, which is necessary alertness and for muscles being active.

This results in mind signaling for induced dopamine release and activating dopaminergic neurons. Release of dopamine is responsible for elated mood and euphoric feeling.

02 Dear sir, I always remain in confusion while writing primary and secondary valencies in coordination compounds. Explain me this in an easy way with some examples. [Vandana Verma, Meerut]

➥ Primary and secondary valencies in a coordination compound explained by Werner. He proposed a theory called Werner's coordination theory, which explained properties of complexes.

The main postulates of this theory are:

• Metals possess two types of valencies.

(i) Primary valency (ii) Secondary valency

• **Primary valency** (linkages) are ionisable and are exhibited by a metal in the formation of its simple salts such as $CoCl_3$, $CuSO_4$ and $AgCl$. In these salts primary valencies of Co, Cu and Ag are 3, 2 and 1 respectively.

Now a days, primary valency is referred as the oxidation state of the metal ion.

• **Secondary valencies** (linkages) are non-ionisable and are exhibited by a metal in the formation of its complex ions such as $[Co(NH_3)_6]^{3+}$, $[Cu(NH_3)_4]^{2+}$ and $[Ag(NH_3)_2]^{+}$. In these complexes, the secondary valencies of Co^{3+}, Cu^{2+} and Ag^+ are 6, 4 and 2 respectively.

The secondary valency is also referred as the coordination number of metal cation.

• Primary valencies are satisfied by negative ions while, secondary valencies can be satisfied, by neutral molecules or negative ions or in some cases positive ions (ligands) also. This happens in case of mixed complexes.

• Every metal atom or ion has a fixed number of secondary linkages. In other words, the coordination number of metal atom is fixed. Thus, the coordination number gives the total number of neutral molecules of negative or positive groups which may be directly linked to the metal cation in the formation of its complexes.

• Every metal has a tendency to satisfy both its primary as well as secondary valencies.

The ligands satisfying secondary valencies are always directed towards fixed positions in space about the central metal atom or ion. Thus, the coordination compounds have a definite geometry.

Some coordination compounds are summarised in the following table.

Werner complex	Modern notation	Ionisation	Secondary valency satisfied by	Primary valency satisfied by
$CoCl_3 \cdot 6NH_3$	$[Co(NH_3)_6]Cl_3$	$[Co(NH_3)_6]^{3+} + 3Cl^-$	$6\,NH_3$	$3Cl^-$
$CoCl_3 \cdot 5NH_3$	$[Co(NH_3)_5Cl]Cl_2$	$[Co(NH_3)_5]^{2+} + 2Cl^-$	$5\,NH_3$ and $1Cl^-$	$3Cl^-$ including $1Cl^-$ with dual nature
$CoCl_3 \cdot 4NH_3$	$[Co(NH_3)_4Cl_2]\,Cl$	$[Co(NH_3)_4Cl_2]^+ + Cl^-$	$4\,NH_3$ and $2Cl^-$	$3Cl^-$ including $2Cl^-$ with dual nature
$CoCl_3 \cdot 3NH_3$	$[Co(NH_3)_3Cl_3]$	$[Co(NH_3)_3\,Cl_3]$	$3\,NH_3$ and $3Cl^-$	$3Cl^-$ all with dual nature

[03]

Dear sir, please explain me what is tautomerism and why tautomerism occur in many compounds?

[Abhishek, Delhi]

➥ Tautomerism is a special type of functional isomerism. ''When the molecules have same molecular formulae, but different structural formulae due to wandering nature of hydrogen atom in between two polyvalent atoms, the isomers are called tautomers and this phenomena is known as tautomerism.''

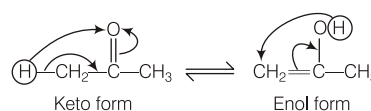Many compounds show tautomerism. These compounds have some structural requirements for tautomerism as explain below:

(i) The compound must have at least one highly electronegative atom (e.g. F, O and N) bonded with a multiple bond.

(ii) Compound should have at least one acidic hydrogen present on α-carbon atom of the molecule.
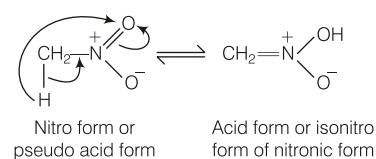
e.g.
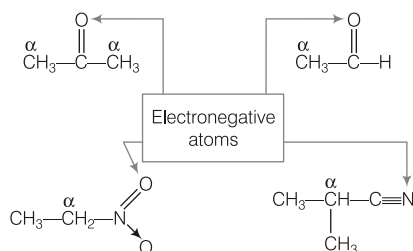
The basic cause of tautomerism is the migration of acidic hydrogen from carbon to multiple bonded electronegative atom.

e.g. In acetone, tautomerism will be seen as

Keto form   Enol form

Similary, nitroalkanes containing α-hydrogen show tautomerism as :

Nitro form or pseudo acid form   Acid form or isonitro form of nitronic form

These examples of tautomerism comes under TRIAD system as these involve three molecules in tautomeric system, i.e.

 3 atoms involved in tautomerism

The other system of tautomers in tautomerism is DYAD system which involves only two atoms along with acidic hydrogen, i.e.

$H\!-\!C\!\equiv\!N$ $H\!-\!N\!\rightleftharpoons\!C$
Hydrocyanic acid   Isohydrocyanic acid
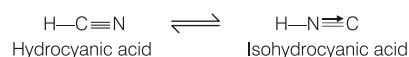
Note Silver nitrate or silver nitrite is the only compound in which tautomerism is shown of migration of the silver ion instead of hydrogen ion.

1,2-tautomerism
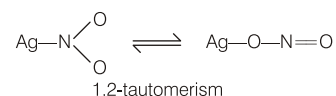
DPP
THE MOST SUCCESSFUL WAY OF
JEE PREPARATION

{**JEE Advanced** Practice} **Sahana Ansari**

Single Integer Type Questions on

CHEMICAL KINETICS

A collection of chapterwise best questions of their types

1. In case of a first order reaction, the time taken for completion of 99.9% reaction is A times the time required for half change of the reaction. Find the value of A – 2.

2. For an elementary reaction $2A + B \longrightarrow 3C$, the rate of appearance of C at time t is 1.3×10^{-4} $molL^{-1}s^{-1}$. Calculate the rate of reaction at this time (in the unit of 10^{-5} $molL^{-1}s^{-1}$).

3. The time required for 10% completion of a first order reaction at 298K is equal to that of required for its 25% completion at 308K. If the value of A is $4 \times 10^{10}s^{-1}$, calculate k at 318 K (in the unit of $10^{-2}s^{-1}$).

4. The rate constants of a reaction at 700K and 760 K are $0.011 Ms^{-1}$ and $0.105\ Ms^{-1}$ respectively. Calculate the value of Arrhenius parameter, the approximate value must be multiple of $10^{10} M^{-1}s^{-1}$.

5. Consider a reversible reaction, $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} P$

   which is of first order in both the directions. A concentration vs time curve for A and P are as follows:

   If all the information is provided at 25°C, determine the time in minute at which 25% of A would be exhausted.

6. The gas phase decomposition of dimethyl ether follows first order kinetics,
   $$CH_3OCH_3(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$$
   The reaction is carried out in a constant volume container at 500°C and has a half-life of 14.5 min. Initially only dimethyl ether is present at a pressure of 0.40 atm. What is the total pressure of the system after 12 min? Assume ideal gas behaviour.

7. Nitrogen pentoxide decomposed according to equation,
   $$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$
   This first order reaction was allowed to proceed at 40°C and the data below was collected.

$[N_2O_5]$ (M)	Time (min)
0.400	0.00
0.289	20.0
0.209	40.0
0.157	60.0
0.109	80.0

   Calculate the rate constant in the unit of $10^{-2} min^{-1}$.

8. The rate of a gaseous reaction becomes half, when volume of the vessel is doubled. What is the order of the reaction?

9. For the chemical reaction,
   $$I^- + OCl^- \xrightarrow{\bar{O}H} Cl^- + OI^-$$
   $$Rate = \frac{k[OCl^-][I^-]}{[OH^-]}$$
   If molecularity with respect to $\bar{O}H$ is x, find x + 3.

10. Consider a reaction, $aG + bH \longrightarrow Products$. When concentrations of both the reactants G and H are doubled, the rate increases by eight times. However, when concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is

11. The following mechanism has been proposed for the reaction of NO with Br_2 to form NOBr,
    $$NO(g) + Br_2(g) \overset{Fast}{\rightleftharpoons} NOBr_2(g)$$
    $$NOBr_2(g) + NO(g) \xrightarrow{Slow} 2NOBr(g)$$
    If the second step is the rate determining step, the order of the reaction with respect to NO(g) is

**12.** In the following first order competing reactions,

$$A + reagent \longrightarrow Product$$
$$B + reagent \longrightarrow Product$$
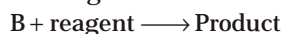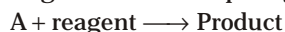
if only 50% of B and 94% of A has been reacted, the ratio of $\dfrac{k_1}{k_2}$ is

13. The hydrolysis of methyl acetate in alkaline solution

$$CH_3COOCH_3 + \bar{O}H \longrightarrow CH_3COO^- + CH_3OH$$

followed, Rate = $k[CH_3COOCH_3][\bar{O}H]$ with k equal to $0.145 \, L \, mol^{-1} \, s^{-1}$ at 25°C. A reaction mixture was prepared to have initial concentration of methyl acetate and $\bar{O}H$ of 0.045 M each. How long would it take for 5% methyl acetate to be hydrolysed at 298 K? The value should be in second.

14. Ethylene is produced by the reaction $C_4H_8 \longrightarrow 2C_2H_4$, the rate constant is $2.48 \times 10^{-4} \, s^{-1}$. Find molar ratio of ethylene to cyclobutane after 27.25 min (Given, antilog (0.176) = 1.5).

15. For the reaction $A(g) \longrightarrow B(g)$, graph drawn between log (rate) versus log [A] is given below.
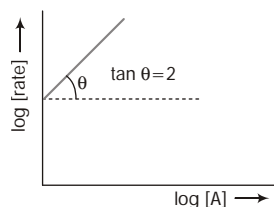
Find the order of reaction.

16. A reaction was found to be second order with respect to the concentration of carbon monoxide. If the concentration of carbon monoxide is doubled, when everything else kept as same, the rate of reaction will become ....

17. What is the rate and order of reaction? Mechanism of the reaction is

$$2NO + H_2 \xrightarrow{\text{(Slow reaction)}} N_2 + H_2O_2$$

$$H_2O_2 + H_2 \xrightarrow{\text{(Fast reaction)}} 2H_2O$$
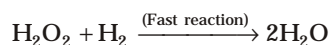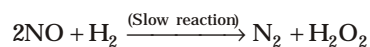
18. The half-life of first order reaction is 1.26×10^{14} s. Calculate the average life of the reactant in the units of $(10^6 \, yr)$.

19. For the reaction $2 \, NOCl(g) \longrightarrow 2NO(g) + Cl_2(g)$, find the order of the reaction if equimolar mixture of NO and Cl_2 gases at 0.15 atm was half changed to 175 s and when at 0.35 atm, was half changed in 75 s.

20. Pseudo first order rate for the reaction $A + B \longrightarrow P$, when studied in 0.1 M of B is given by $-\dfrac{d[A]}{dt} = -k[A]$, where $k = 1.85 \times 10^4 \, s^{-1}$. Calculate the value of second order rate constant in terms of $10^5 \, L \, mol^{-1} \, s^{-1}$.

21. The rate constant for a reaction of zero order in A is $0.0030 \, mol \, L^{-1} s^{-1}$. How long will it take for the initial concentration of A to fall from 0.10 M to 0.075 M.

22. Show by using rate laws how much the rate of reaction, $2 \, NH_3 \longrightarrow N_2 + 3H_2$ will change if the volume of the reaction vessel is diminished to 1/3rd of its initial volume?

23. 4 g H_2 gas and 256 g HI gas are present in 2L flask. What is the active mass of HI?

24. For a first order reaction, calculate the ratio between the time taken to complete 3/4th of the reaction and time taken to complete half of the reaction.

25. If one starts with 1 curie (Ci) of radioactive substance ($t_{1/2}$ = 15 h), the activity left after a period of two weeks will be about 0.02 x μCi. Find the value of x.

26. A second order reaction requires 70 min to change the concentration of reactants from 0.08 M to 0.01 M. The time required to become 0.04 M is 2x min. Find the value of x in minute.

27. Following is the graph between log t_{50} and log a (where, a is initial concentration) for a given reaction at 27°C. If order of reaction is n. Find the value of n + 3.
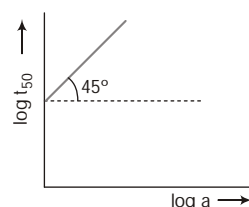
28. The rate constant, activation energy and Arrhenius parameter of a chemical reaction are $3 \times 10^{-4} \, s^{-1}$, 104.4 kJ/mol and $6 \times 10^{14} \, s^{-1}$, respectively. Calculate the value of rate constant in the unit of $10^{14} \, s^{-1}$.

29. For a reaction, $A \longrightarrow B$, $E_a = 10$ kJ/mol and $\Delta H = 5$ kJ/mol. Thus, potential energy profile of this reaction is

Reaction progress
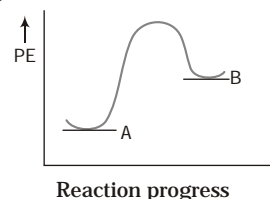
Calculate the energy of activation of $B \longrightarrow A$.

{JEE Advanced Practice}

30. A radioactive substance decays 20% in 10 min. If at the start there are 5×10^{20} atoms present, after what time will the number of atoms be reduced to 10^{18} atoms (correct to the nearest integer).

31. $C_6H_5N_2Cl + H_2O \xrightarrow{\Delta} C_6H_5OH + N_2 + HCl$
This reaction is pseudo unimolecular with respect to $C_6H_5N_2Cl$. 50 mL of 1M benzene diazonium chloride A is taken. After 1h, 1.226 L of N_2 gas at 1 atm and 300 K is obtained. Calculate rate constant in the unit of 10^{-2} min^{-1}.

32. H_2O and oxygen atoms react in upper atmospheric level bimolecularly to form two OH radicals having heat of reaction 72 kJ at 400K and energy of activation being 77 kJ/mol. Find E_a for bimolecular combination of two OH radicals to form H_2O and O-atom.

33. Trans-1,2-dideuterocyclopropane (A) undergoes a first order decomposition. The observed rate constant at a certain temperature measured in terms of disappearance of A was 1.52×10^{-4} s^{-1}. Analysis of products showed that the reaction followed two parallel paths, one leading to dideuteropropane (B) and the other to cis-1,2 -dideuterocyclopropane (C). B found to constitute 11.2% of the reaction products, independent of extent of reaction. What is the value of rate constant for formation of C?

34. A certain radioisotope $_ZX^A$ (half-life = 10 days) decays to give $_{Z-2}Y^{A-4}$. If 1g atom of X is kept in a sealed vessel and volume of helium accumulated at STP in 20 days is 1.7×10^x. Find the value of x.

35. The activation energy for the reaction, $2 AB \longrightarrow A_2(g) + B_2(g)$ is 159.7 kJ/mol at 500K. Calculate the fraction of molecules of reactants (in the units of 10^{-17}) having energy equal to or greater than activation energy .
[Given, 2.3×8.314 JK^{-1} mol$^{-1} \times 500$ K = 9561.1J/mol]

36. An optically active drug has one chiral center and only dextrorotatory isomer is effective. Moreover, it becomes ineffective when its optical activity is reduced to 35% of original. It was found that mutarotation of this drug was first order reaction with a rate constant of 10^{-8} s^{-1}. Find the expiration time of the drug in years (correct to the nearest integer).

37. The oxidation of iodide ion by perdisulphate ion is given below.
$$I^- + S_2O_8^{2-} \rightarrow I_3^- + SO_4^{2-}$$
If the rate of disappearance of $S_2O_8^{2-}$ ions is 1.5×10^{-3} M s^{-1}. Find the average rate of formation of SO_4^{2-} ions in the unit of 10^{-3} M s^{-1}.

38. A gaseous reaction,
$$A_2(g) \longrightarrow B(g) + \frac{1}{2}C(g)$$
shows increase in pressure from 100 mm to 120 mm in 5 min. What is the rate of disappearance of A_2?

39. The half-life period of a radioactive element is 40 days. If 32 g of this element is stored for 160 days, calculate the weight of the element that would remain in gram.

40. At 380°C, the half-life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ/mol. Calculate the time required for 75% decomposition at 450°C in terms of 10^3 s.

41. The rate expression for the reaction, $NH_4CNO \rightleftharpoons NH_2CONH_2$ can be derived from the mechanism.

  I. $NH_4CNO \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NH_4NCO$ (fast)

  II. $NH_4NCO \underset{k_4}{\overset{k_3}{\rightleftharpoons}} NH_3 + HNCO$ (fast)

  III. $NH_3 + HNCO \xrightarrow{k} NH_2CONH_2$ (slow)

  Find the order of reaction with respect to urea.

42. Two first order reactions having same reactant concentrations proceed at 25°C at the same rate. The temperature coefficient of the rate of the first reaction is 2 and that of second reaction is 3. Find the ratio of the rates of these reactions at 75°C.

43. Hydrogenation of vegetable ghee at 25°C reduces the pressure of H_2 from 2 atm to 1.2 atm in 50 min. Calculate the rate of reaction in terms of change of molarity per second (in the unit of 10^{-5}).

44. A drop of solution (volume 0.05 mL) contains 3×10^{-6} mole of H$^+$. If the rate constant of disappearance of H$^+$ is 1×10^7 mol L^{-1} s^{-1}. How long would it take for H$^+$ in drop to disappear (in the unit of 10^{-9} s)?

45. For the reaction A + B $\longrightarrow$ C,

S. No.	[A]	[B]	$\dfrac{-d[A]}{dt}$
1.	1 M	1 M	0.25 M min^{-1}
2.	2 M	1 M	0.50 M min^{-1}
3.	1M	2 M	0.25 M min^{-1}

Find the order of reaction with respect to A.

Answer *with* Explanations

1. (8) When 99.9% reaction is completed,

$$[R] = [R]_0 - \frac{99.9}{100}[R]_0 = 0.001 \ [R]_0$$

$$t_{(99.9\%)} = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$

$$= \frac{2.303}{k} \log \frac{[R]_0}{0.001 \, [R]_0}$$

$$= \frac{2.303}{k} \log 10^3 = \frac{2.303 \times 3}{k} \qquad \ldots(i)$$

When half of the reaction is completed

$$[R] = [R]_0 - 0.5[R]_0$$

$$= 0.5[R]_0$$

$$t_{1/2} = \frac{2.303}{k} \log \frac{[R]_0}{0.5[R]_0}$$

$$= \frac{2.303}{k} \log 2$$

$$= \frac{2.303 \times 0.3010}{k} \qquad \ldots(ii)$$

Dividing Eq. (i) by Eq. (ii), we get

$$\frac{t_{(99.9\%)}}{t_{1/2}} = \frac{3}{0.3010}$$

$$= 10 \text{ times}$$

∴ A = 10 and A − 2 = 8

2. (4) For the reaction,

$$2A + B \longrightarrow 3C$$

$$\text{Rate} = -\frac{1}{2} \cdot \frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{1}{3}\frac{d[C]}{dt}$$

$$\text{Rate of reaction} = \frac{1}{3}\frac{d[C]}{dt} = \frac{1}{3} \times 1.30 \times 10^{-4}$$

$$= 4.33 \times 10^{-5} \text{mol L}^{-1}\text{s}^{-1}$$

$$\approx 4 \times 10^{-5} \text{mol L}^{-1}\text{s}^{-1}$$

3. (1) For 10% completion of the reaction,

$$k(298\,K) = \frac{2.303}{t} \log \frac{100}{90}$$

For 25% completion of reaction,

$$k(308K) = \frac{2.303}{t} \log \frac{100}{75}$$

$$\frac{k(308\ K)}{k(298\ K)} = \frac{\frac{2.303}{t} \log \frac{100}{75}}{\frac{2.303}{t} \log \frac{100}{90}}$$

$$= \frac{0.1249}{0.0458} = 2.73$$

Now, $\log \dfrac{k(308\ K)}{k(298\ K)} = \dfrac{E_a}{2.303\ R}\left[\dfrac{T_2 - T_1}{T_1 T_2}\right]$

$$\log 2.73 = \frac{E_a}{2.303 \times 8.314} \times \left(\frac{308 - 298}{308 \times 298}\right)$$

$$0.436 = \frac{E_a}{2.303 \times 8.314} \times \frac{10}{308 \times 298}$$

∴ $E_a = \dfrac{0.436 \times 2.303 \times 8.314 \times 308 \times 298}{10}$

$$= 76623 \text{ J mol}^{-1} = 76.623 \text{ kJ mol}^{-1}$$

Now, $\qquad \log k = \log A - \dfrac{E_a}{2.303 \, RT}$

$$= \log(4 \times 10^{10}) - \frac{76623}{2.303 \times 8.314 \times 318}$$

$$= 10.6020 - 12.5843$$

$$\log k\,(318) = -1.9823$$

$$k\,(318) = 1.042 \times 10^{-2}\text{s}^{-1} \approx 1\text{s}^{-1}$$

4. (3) $\log \dfrac{k_2}{k_1} = \dfrac{E_a}{2.303\ R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]$

$$k_1 = 0.011 \text{ Ms}^{-1}, T_1 = 700\text{K}$$

$$k_2 = 0.105 \text{ Ms}^{-1}, T_2 = 760\text{K}$$

$$R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$$

∴ $\qquad \log \dfrac{0.105}{0.011} = \dfrac{E_a}{2.303 \times 8.314}\left[\dfrac{1}{700} - \dfrac{1}{760}\right]$

$$\log 9.545 = \frac{E_a}{2.303 \times 8.314}\left[\frac{760 - 700}{700 \times 760}\right]$$

$$0.9798 = \frac{E_a \times 60}{2.303 \times 8.314 \times 700 \times 760}$$

∴ $\qquad E_a = \dfrac{0.9798 \times 2.303 \times 8.314 \times 700 \times 760}{60}$

$$= 166.342 \times 10^3 \text{ J mol}^{-1} = 166.342 \text{ kJ mol}^{-1}$$

Now, $\qquad \log k = \log A - \dfrac{E_a}{2.303 \, RT}$

or, $\qquad \log A = \log k + \dfrac{E_a}{2.303 \, RT}$

$$\log A = \log 0.011 + \frac{166.34 \times 10^3}{2.303 \times 8.314 \times 700}$$

$$= -1.9586 + 12.411 = 10.452$$

$$A = 2.831 \times 10^{10} \text{M}^{-1}\text{s}^{-1} \qquad [2.8 \approx 3]$$

5. (7) From graph, $\qquad k = k_1 / k_2$

For a reversible reaction,

Rate of forward reaction = rate of backward reaction

$$k_1 [A] = k_2 [P]$$

$$\frac{k_1}{k_2} = \frac{0.1}{0.2} = 0.5$$

i.e. $\qquad k_2 = 2 k_1$

Also if x is the instantaneous concentration of product at time t and a is the initial concentration of A, then

$$\frac{dx}{dt} = k_1(a - x) - k_2 x$$

$$= k_1(a - x) - 2k_1 x$$

$$= k_1(a - 3x)$$

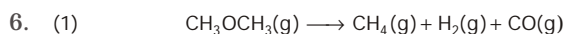$$\Rightarrow \qquad \int_0^x \frac{dx}{(a - 3x)} = k_1 \int_0^t dt$$

$$\left[-\frac{1}{3}\ln(a - 3x)\right]_0^x = k_1[t]_0^t \quad \left(\because \int \frac{1}{(a - nx)}dx = -\frac{1}{n}\ln(a - nx) + C\right)$$

$$\Rightarrow \qquad k_1 t = \frac{1}{3}\ln \frac{a}{(a - 3x)} = \frac{1}{3}\ln 4 \qquad \left[\because x = \frac{a}{4}\right]$$

$$\Rightarrow \qquad t = \frac{2\ln 2}{3k_1} = \frac{2 \times 0.693}{3 \times 7 \times 10^{-2}} = 6.6\text{min}$$

$$= 7 \text{ min}$$

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6. (1) $\qquad CH_3OCH_3(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$

Initial p $\qquad$ 0.40 atm $\qquad$ 0 $\qquad$ 0 $\qquad$ 0

Final p after 12 min $\quad (0.40-p)$ $\qquad$ p $\qquad$ p $\qquad$ p

For a first order reaction,

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x} \qquad \text{...(i)}$$

For ideal gas behaviour,

Number of moles $\propto$ pressure (at constant V and T)

$\therefore \qquad a \propto 0.40,$

$$(a-x) \propto (0.40-p)$$

$$k = \frac{0.693}{t_{1/2}}$$

$$\frac{0.693}{14.5} = \frac{2.303}{12} \log_{10} \frac{0.40}{(0.40-p)} \qquad \text{[From Eq. (i)]}$$

$\therefore \qquad p = 0.175 \text{ atm}$

$\therefore$ Pressure of ether decomposed $= 0.175$

Total pressure $\qquad 0.40 - p + p + p + p$

$$= 0.40 + 2p = 0.40 + 2 \times 0.175$$

$$= 0.75 \text{ atm} \approx 1 \text{ atm}$$

7. (2) Since, it is a first order reaction,

$$\therefore \qquad k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

k can be calculated as

At $t = 20$ min, $\quad k = \frac{2.303}{20} \log \frac{0.400}{0.289} = \frac{2.303}{20} \times 0.141$

$$= 0.016 \text{ min}^{-1}$$

At $t = 40$ min, $\quad k = \frac{2.303}{40} \log \frac{0.400}{0.209} = \frac{2.303}{40} \times 0.282$

$$= 0.016 \text{ min}^{-1}$$

At $t = 60$ min, $\quad k = \frac{2.303}{60} \log \frac{0.400}{0.151} = \frac{2.303}{60} \times 0.423$

$$= 0.016 \text{ min}^{-1}$$

At $t = 80$ min, $\quad k = \frac{2.303}{80} \log \frac{0.400}{0.109} = \frac{2.303}{80} \times 0.565$

$$= 0.016 \text{ min}^{-1}$$

The average value of rate constant,

$$k = 0.016 \text{ min}^{-1}$$

or $\qquad = 1.6 \times 10^{-2} \text{ min}^{-1}$

$$\approx 2 \times 10^{-2} \text{ min}^{-1}$$

8. (1) For the gaseous reaction,

$$A \longrightarrow \text{Products}$$

Let, the order of reaction is n,

$$\text{rate} = k[A]^n$$

$$r = k(a-x)^n \qquad \text{...(i)}$$

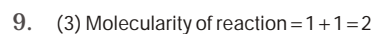When volume of vessel becomes double, molar concentration becomes half. Since, rate becomes half therefore,

$$\frac{r}{2} = k\left[\frac{a-x}{2}\right]^n \qquad \text{...(ii)}$$

Dividing Eq. (i) by Eq. (ii), we get

$$2 = 2^n$$

$$n = 1$$

$\therefore$ Order $= 1$

9. (3) Molecularity of reaction $= 1 + 1 = 2$ $\qquad [I^-, OCl^-]$

Molecularity wrt $[OH^-] = 0$

$\therefore \qquad x = 0$

Hence, $\qquad x + 3 = 3$

10. (3) Given reaction is,

$$aG + bH \longrightarrow \text{Products}$$

Rate of the reaction is given as,

$$r = k[G]^a [H]^b \qquad \text{...(i)}$$

Case I When concentrations of [G] and [H] double, rate becomes eight times i.e.

$$8r = k[2G]^a [2H]^b$$

or $\qquad 8r = 2^{a+b} k[G]^a [H]^b \qquad \text{...(ii)}$

Case II When concentration of [H] keeps constant and concentration of [G] doubles, rate becomes doubled i.e.

$$2r = k[2G]^a [H]^b$$

or $\qquad 2r = 2^a k[G]^a [H]^b \qquad \text{...(iii)}$

On dividing Eq. (i) from Eq. (iii), we get

$$\frac{1}{2} = \frac{1}{2a} \Rightarrow a = 1$$

Now, on dividing Eq. (ii) by Eq. (i), we get

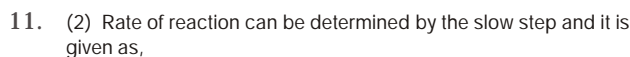$$8 = 2^{a+b} \Rightarrow 2^3 = 2^{a+b}$$

$$a + b = 3$$

or $\qquad b = 2 \qquad [\because a = 1]$

$\because \qquad \text{Rate} \propto [G]^a [H]^b$

$\therefore \qquad a = 1, b = 2$

Overall order $= 1 + 2 = 3$

11. (2) Rate of reaction can be determined by the slow step and it is given as,

$$r = k'[NOBr_2] [NO] \qquad \text{...(i)}$$

Equilibrium constant for slow step is,

$$k_c = \frac{[NOBr_2]}{[NO] [Br_2]} \qquad \text{...(ii)}$$

From Eqs. (i) and (ii), we get

$$r = k' k_c [NO] [Br_2] [NO]$$

$$= k''[NO]^2 [Br_2]$$

i.e. order with respect to NO is 2.

12. (4) $k_2 = \frac{2.303}{t_2} \log \frac{100}{50}$ for 50% B reacted
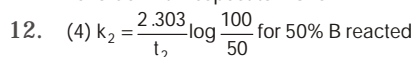
$$k_1 = \frac{2.303}{t_1} \log \frac{100}{6} \text{ for 94\% A reacted.}$$

$$\therefore \qquad \frac{k_2}{k_1} = \frac{t_1}{t_2} \times \frac{0.3010}{1.2218}$$

At $t_2 = t_1$ because 50% B and 94% A has been reacted.

$$\therefore \qquad \frac{k_2}{k_1} = \frac{0.3010}{1.2218} = 0.246 \approx 0.25 \text{ and } \frac{k_1}{k_2} \approx 4$$

13. (8) 5% of 0.045 M $= 0.00225$ M

We know that, Rate, $\dfrac{\Delta x}{\Delta t} = k [CH_3COOCH_3] [\overline{O}H]$

$$\therefore \qquad \Delta t = \frac{\Delta x}{k[CH_3COOCH_3] [\overline{O}H]}$$

$$= \frac{0.00225}{0.145 \times 0.045 \times 0.045} \approx 8 \text{ s}$$

14. (1)
$$C_4H_8 \longrightarrow 2C_2H_4$$

Initial moles $\quad\quad a \quad\quad\quad 0$

Moles after time t $\quad a - x \quad\quad 2x$

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

or
$$\frac{kt}{2.303} = \log \frac{a}{a-x}$$

$$\frac{2.48 \times 10^{-4} \times 27.25 \times 60}{2.303} = \log \frac{a}{a-x}$$

or
$$0.176 = \log \frac{a}{a-x}$$

$\Rightarrow \quad$ antilog $(0.176) = \dfrac{a}{a-x}$

or,
$$\frac{a}{a-x} = 1.5 \Rightarrow x = \frac{a}{3}$$

Molar ratio of ethylene to cyclobutane is
$$\frac{2x}{a-x} = \frac{2a}{3} / \frac{2a}{3} = 1$$

15. (2) Order of the reaction,
$$r = k[A]^n$$
$$\log r = \log k + n \log A$$
Comparing the equation with $y = mx + C$

Here,
$$y = \log[r]$$
$$x = \log[A]$$
$$C = \log k$$
$$m = n = \tan\theta = 2$$
$$\tan\theta = n = 2$$
$\therefore \quad\quad\quad$ Order $= 2$

16. (4) $\quad r_1 = k[CO]^2$; $\quad r_2 = k[2\,CO]^2$

$\therefore \quad\quad\quad \dfrac{r_2}{r_1} = 4$

17. (3) We know that, slowest step is the rate determining step.
Hence, the rate of the reaction $= k[NO]^2[H_2]^1$

$\therefore$ Order of reaction $= 2 + 1 = 3$

18. (6) The average life $(\lambda) = \dfrac{1}{k} = \dfrac{t_{1/2}}{0.693} = \dfrac{1.26 \times 10^{14}}{0.693} = 1.81 \times 10^{14}$ s

$$\lambda(\text{yrs}) = \frac{1.81 \times 10^{14}}{60 \times 60 \times 24 \times 365} = 5.76 \times 10^6 \text{ yrs}$$

$$\approx 6 \,(\times 10^6 \text{ yrs})$$

19. (2) $\dfrac{t_2}{t_1} = \left(\dfrac{a_1}{a_2}\right)^{n-1} \Rightarrow \dfrac{75}{175} = \left(\dfrac{0.15}{0.35}\right)^{n-1} \Rightarrow (0.428)^1 = (0.428)^{n-1}$

$$n - 1 = 1 \Rightarrow n = 2$$

20. (2) For $A + B \longrightarrow P$,

$$-\frac{d[A]}{dt} = k[A] = 1.85 \times 10^4 [A] \quad\quad \text{...(i) [for pseudo order]}$$

$$\frac{-d[A]}{dt} = k'[A][B] = k'[A][0.1] \quad\quad \text{...(ii) [for second order]}$$

Dividing Eq. (i) by Eq. (ii), we get

$$1 = \frac{1.85 \times 10^4}{k'[0.1]} \Rightarrow k' = 1.85 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$$

$$\approx 2 \,(\times 10^5 \text{ L mol}^{-1} \text{ s}^{-1})$$

21. (8) For a zero order reaction,
$$k = 0.0030 \text{ mol L}^{-1}\text{s}^{-1}$$
$$[A]_0 = 0.10 \text{ M}$$
$$[A] = 0.075 \text{ M}$$
$$k_0 = \frac{[A]_0 - [A]}{t}$$
$$t = \frac{[A]_0 - [A]}{k}$$
$$t = \frac{0.10 - 0.075}{0.0030} = 8.335 \simeq 8 \text{ s}$$

22. (9) $\quad 2\,NH_3 \longrightarrow N_2 + 3\,H_2$
$$r_1 = k[NH_3]^2$$

When the volume is reduced to one-third of initial value, the concentration becomes three times.
$$r_2 = k[3\,NH_3]^2$$
$$\frac{r_2}{r_1} = 9 \Rightarrow r_2 = 9r_1$$

23. (1) Mass of HI $= 256$ g

Molar mass of HI $= 128$ g

Volume of flask $= 2$ L

Active mass of HI $= \dfrac{256}{128 \times 2} = 1 \text{ mol/L}$

24. (2)
$$t_{1/2} = \frac{0.69}{k}$$
$$t_{3/4} = \frac{2.303}{k}\log\frac{a}{a - \frac{3a}{4}} = \frac{2.303}{k}\log 4$$
$$= \frac{2.303}{k} \times 2 \times 0.3010 = \frac{0.69 \times 2}{k}$$
$$\frac{t_{3/4}}{t_{1/2}} = \frac{0.69 \times 2}{k} \times \frac{k}{0.69} = 2$$

25. (9)
$$k = \frac{0.693}{15 \text{ h}} = 0.0462 \text{ h}^{-1}$$
$$k = \frac{2.3}{14 \times 24 \text{ h}} \log \frac{C_0}{C_t}$$
$$0.0462 \text{ h}^{-1} = \frac{2.3}{14 \times 24 \text{ h}} \log \frac{1}{C_t}$$
$\therefore \quad\quad C_t = 1.82 \times 10^{-7} \text{ Ci} \approx 0.18\,\mu \text{ Ci}$
$$0.18\,\mu\text{Ci} = 0.02 \text{ x}\,\mu\text{Ci}$$
$\therefore \quad\quad\quad x = 9$

26. (5) For second order reaction,
$$a = [R]_{\text{initial}} = 0.08 \text{ M}, [R]_{\text{final}} = (a - x) = 0.01 \text{ M}$$
$$x = 0.08 - 0.01 = 0.07 \text{ M}$$
$$k_2 = \frac{1}{t} \cdot \frac{x}{a(a-x)} = \frac{1}{70 \text{ min}} \times \frac{0.07 \text{ M}}{0.08 \text{ M} \times 0.01 \text{ M}} \quad \text{...(i)}$$

Now, time required to become concentration $= 0.04$ M, i.e.
$$x = 0.04 \text{ M}$$
$$k_2 = \frac{1}{t} \times \frac{0.04 \text{ M}}{0.08 \text{ M} \times (0.08 - 0.04)\text{ M}} \quad \text{...(ii)}$$

From Eq. (i) and (ii), we get
$$\frac{0.07}{70 \times 0.08 \times 0.01} = \frac{0.04}{t \times 0.08 \times 0.04}$$
$$t = 10 \text{ min} = 2x$$
$\therefore \quad\quad\quad x = 5 \text{ min}$

27. (3) $\quad\quad\quad t_{1/2} \propto \left(\dfrac{1}{a}\right)^{n-1}; \, t_{1/2} = k\,(a)^{1-n}$

$\quad\quad\quad\quad\quad \log \, t_{1/2} = \log \, k + (1-n)\log \, a \quad\quad [y = c + mx]$

$\quad\quad\quad\quad\quad\quad\quad slope = (1-n) = \tan 45° = 1$

$\therefore \quad\quad\quad\quad\quad\quad (1-n) = 1 \Rightarrow n = 0$

$\therefore \quad\quad\quad\quad\quad\quad n + 3 = 0 + 3 = 3$

28. (6) Given, $k = 3 \times 10^{-4} \, s^{-1}$, $A = 6 \times 10^{14} \, s^{-1}$

$\quad\quad\quad\quad\quad\quad E_a = 104.4 \, kJ/mol$

Arrhenius equation is $k = Ae^{-E_a/RT}$

as $\quad\quad\quad\quad\quad\quad T \to \infty$

$\quad\quad\quad\quad\quad\quad\quad k = Ae^{-E_a/RT}$

or $\quad\quad\quad\quad\quad\quad k = Ae° \quad\quad\quad \left[\because \dfrac{-Ea}{R \times \infty} = 0\right]$

or $\quad\quad\quad\quad\quad\quad k = A$

$\therefore \quad\quad\quad\quad\quad\quad k = 6 \times 10^{14} \, s^{-1}$ when $T \to \infty$

29. (5) $E_a = 10 \, kJ/mol$ for $A \to B$

and $\Delta H = 5 \, kJ/mol$ for $A \to B$
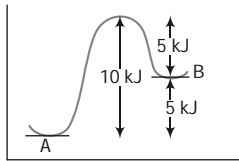
then, $E_a = 5 \, kJ/mol$ for $B \to A$

30. (5) Radioactive substance decays 20% in 10 min.

Hence, rate constant of first order disintegration is

$$k = \dfrac{2.303}{10} \log \left(\dfrac{100}{80}\right) = 0.0223 \, min^{-1}$$

Initially, there are 5×10^{20} atoms, which reduces to 10^{18} atoms after time t min.

$$t = \dfrac{2.303}{k} \log \dfrac{N_0}{N}$$

$$= \dfrac{2.303}{0.0223} \log \dfrac{5 \times 10^{20}}{10^{18}} = 278.7 \, min = 4.65 \, h \approx 5 \, h$$

31. (9) $\quad\quad\quad\quad A + H_2O \longrightarrow C_6H_5OH + N_2 + HCl$

At start $(t = 0)$ $\quad$ a $\quad\quad\quad\quad\quad\quad\quad$ 0

At time t $\quad\quad$ $(a - x)$ $\quad\quad\quad\quad\quad\quad$ x

N_2 gas is due to reaction of A with H_2O

N_2 gas formed at anytime $t = x$

50 mL of 1 M of $A = 0.05 \, mol$ of $A = a$

1.226 L of N_2 gas at 1 atm and at 300 K

$\quad\quad\quad\quad\quad = 0.0498 \, mol = x \quad\quad\quad \left[n = \dfrac{pV}{RT}\right]$

$$k = \dfrac{2.303}{t} \log \dfrac{a}{(a-x)}$$

$$= \dfrac{2.303}{60 \, min} \log \dfrac{0.05}{0.05 - 0.0498} = 9.2 \times 10^{-2} min^{-1}$$

32. (5) $H_2O + O \underset{}{\overset{E_a = 77 \, kJ}{\rightleftharpoons}} 2\,\overline{O}H; \, \Delta H = 72 \, kJ$

$\quad\quad\quad\quad 2\,\overline{O}H \longrightarrow H_2O + O; \, \Delta H = -72 \, kJ$
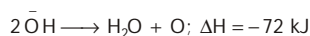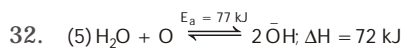
$\quad\quad\quad\quad\quad E_a(f) - E_a(b) = \Delta H$

$\quad\quad\quad\quad\quad\quad E_a(f) - 77 = -72$

$\quad\quad\quad\quad\quad\quad\quad\quad E_a(f) = 5 \, kJ$

33. (1) $\quad\quad\quad\quad\quad\quad A \longrightarrow B \quad\quad\quad\quad\quad$ (11.2%)

$\quad\quad\quad\quad\quad\quad\quad\quad A \longrightarrow C \quad\quad\quad\quad\quad$ (88.8%)
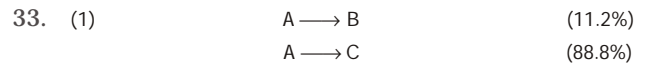
In case of parallel path reaction,

$k_B = k_A \times$ fractional yield of B

$k_C = k_A \times$ fractional yield of C

$\quad\quad\quad\quad\quad = 1.52 \times 10^{-4} \times 0.888$

$\quad\quad\quad\quad\quad = 1.35 \times 10^4 \, s^{-1}$

$\quad\quad\quad\quad\quad \approx 1(\times 10^{-4} \, s^{-1})$

34. (1) $\quad\quad\quad\quad _zX^A \quad \to \quad _{z-2}X^{A-4} + \, _2He^4$

Initial amount $\quad\quad$ 1 $\quad\quad\quad\quad$ 0 $\quad\quad\quad$ 0

Final amount $\quad\quad$ $1-x$ $\quad\quad\quad$ x $\quad\quad\quad$ x

$\quad\quad\quad n =$ number of half-lives $= \dfrac{20}{10} = 2$

Moles of X left $= \left(\dfrac{1}{2}\right)^n \times a_0$

$\quad\quad\quad\quad = \left(\dfrac{1}{2}\right)^2 \times 1 = \dfrac{1}{4} \, mol = (1-x) \, mol$

Moles of helium formed $= 1 - \dfrac{1}{4} = \dfrac{3}{4} \, mol = x \, mol$

$\quad\quad\quad\quad = \dfrac{3}{4} \times 22.4 \, L = 16.8 \, L$

$\quad\quad\quad\quad \approx 17 \, L$ or $1.7 \times 10^1 \, L$

$\therefore \quad\quad\quad\quad\quad x = 1$

35. (2) Fraction of molecules having energy equal to or greater than activation energy is

$$x = \dfrac{n}{N} = e^{-E_a/RT}$$

$\therefore \quad\quad\quad\quad\quad x = e^{-E_a/RT}$

$$\ln x = -\dfrac{E_a}{RT}$$

$\Rightarrow \quad\quad\quad 2.3 \log x = \dfrac{-E_a}{RT}$

$$\log x = -\dfrac{159.7 \times 10^3 \, J \, mol^{-1}}{2.3 \times 8.314 \, J \, K^{-1} \, mol^{-1} \times 500 \, K}$$

$$= \dfrac{159.7 \times 10^3 \, Jmol^{-1}}{9561.1 \, Jmol^{-1}}$$

$$= -16.7$$

$\therefore \quad\quad\quad\quad x = $ antilog (-16.7)

$\quad\quad\quad\quad = $ antilog $(-16 - 0.7 + 1 - 1)$

$\quad\quad\quad\quad = $ antilog $(\overline{17}.3)$

$\quad\quad\quad\quad = 2 \times 10^{-17}$

36. (1) The optical activity remained = 35%

So, 65% optical activity has been lost. It means 35% of dextrorotatory isomer has been converted to laevorotatory isomer. Applying integrated rate law for first order reaction,

$$2.303 \log \dfrac{100}{65} = 1 \times 10^{-18} \times t$$
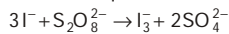
$$t = 4.31 \times 10^7 \, s$$

$$= 1.37 \, yr$$

$$\approx 1 \, yr$$

CHEMICAL KINETICS

{**JEE Advanced** Practice}

37. (3) The balanced equation is

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

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

$$-\frac{d[S_2O_8^{2-}]}{dt} = 1.5 \times 10^{-3} M\,s^{-1} \qquad \text{(Given)}$$

$$\therefore \qquad \frac{d[SO_4^{2-}]}{dt} = 2 \times 1.5 \times 10^{-3} = 3 \times 10^{-3} M\,s^{-1}$$

38. (8)

$$A_2(g) \longrightarrow B(g) + \frac{1}{2}C(g)$$

At initial   p   0   0

At equilibrium $p-x$ x   x/2

Total pressure $= p - x + x + \frac{x}{2} = p + \frac{x}{2}$

Initial pressure (p) = 100 mm

Final pressure = total pressure = 120 mm

$$\therefore \qquad p + \frac{x}{2} = 120$$

$$100 + \frac{x}{2} = 120 \Rightarrow x = 40\,mm$$

$$\therefore \qquad -\frac{d[A_2]}{dt} = \frac{40}{5} = 8\,mm\,min^{-1}$$

39. (2) Amount remaining after n half-lives

$$= \frac{N_0}{2^n}$$

where, N_0 = initial amount

$$= \frac{32}{(2)^4} = 2g \quad [n = \text{number of half-lives} = \frac{160}{40} = 4]$$

40. (1) Rate constant for first order reaction at 380°C

$$k_1 = \frac{0.693}{t_{1/2}} = \frac{0.693}{360} = 1.925 \times 10^{-3} s^{-1}$$

Rate constant at 450°C

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$= \frac{200 \times 10^3}{2.303 \times 8.314}\left[\frac{1}{653} - \frac{1}{723}\right]$$

$$= 1.548$$

$$\frac{k_2}{k_1} = \text{antilog}(1.548) = 35.32$$

$$k_2 = 35.32 \times k_1 = 35.32 \times 1.925 \times 10^{-3}$$

$$= 0.068$$

Time required for 75% decomposition of H_2O_2

$$t_2 = \frac{2.303}{k_2}\log\frac{[R_0]}{[R]}$$

$$= \frac{2.303}{0.068}\log\,4 = \frac{2.303 \times 2 \times 0.3010}{0.068}$$

$$= 20.39\,min \times 60\,s/min = 1223.3\,s$$

$$= 1.223 \times 10^3\,s$$

41. (1) The rate of formation of urea is given by Eq. (iii)

$$\frac{d[urea]}{dt} = k\,[NH_3][HNCO] \qquad \dots(i)$$

Using Eq. (ii), we have

$$\frac{[NH_3][HNCO]}{[NH_4NCO]} = \frac{k_3}{k_4} = k_{34} \qquad \dots(ii)$$

and by Eq. (i) $\qquad \frac{[NH_4NCO]}{[NH_4CNO]} = \frac{k_1}{k_2} = k_{12} \qquad \dots(iii)$

$\therefore$ By Eqs. (ii) and (iii),

$$[NH_3][HNCO] = k_{34} \cdot k_{12}\,[NH_4CNO] \qquad \dots(iv)$$

$\therefore$ By Eqs. (i) and (iv),

$$\frac{d[urea]}{dt} = k \cdot k_{34} \cdot k_{12}\,[NH_4CNO]$$

$$\frac{d[urea]}{dt} = k'\,[NH_4CNO]$$

Hence, order of reaction with respect to urea is one.

42. (8) For first order reaction, $r_1 = k[C]^1$

$$\therefore \frac{R_1}{R_2} = \frac{k_1}{k_2} = \text{temperature coefficient}$$

Let $\qquad \frac{R_{35}}{R_{25}} = \frac{k_{35}}{k_{25}} = a \qquad \dots(i)$

$$\frac{R_{45}}{R_{35}} = \frac{k_{45}}{k_{35}} = a \qquad \dots(ii)$$

On multiplying Eqs. (i) and (ii), we get

$$\therefore \qquad \frac{R_{45}}{R_{25}} = a^2$$

Similarly, $\qquad \frac{R_{75}}{R_{25}} = a'^5$

For I reaction, $(R_{75})_I = 2^5(R_{25})_I$

For II reaction $(R_{75})_{II} = 3^5(R_{25})_{II}$

$$\therefore \qquad \frac{(R_{75})_{II}}{(R_{75})_I} = \frac{3^5}{2^5} = 7.95 \approx 8$$

43. (1) Change in molarity may be derived by

$$pV = nRT; \frac{n}{V} = \frac{p}{RT}$$

$$\frac{n}{V} = \frac{0.8}{0.0821 \times 298} = 0.0327$$

Rate of reaction $= \frac{\text{Change in molarity}}{\text{Time in second}} = \frac{0.0327}{50 \times 60}$

$$= 1.09 \times 10^{-5}\,mol\,L^{-1}s^{-1}$$

44. (6) Rate constant $= 1 \times 10^7\,mol\,L^{-1}s^{-1}$

For zero order reaction,

$$t = \frac{x}{k} = \frac{\text{concentration decompose}}{\text{rate constant}} \qquad \dots(i)$$

$\because$ 0.05 mL has 3×10^{-6} mole of H^+

$\therefore$ 1000 mL has $\frac{3 \times 10^{-6} \times 10^3}{0.05} = 0.6 \times 10^{-1}$ mol L of H^+

$\therefore$ By Eq. (i) $t = \frac{0.6 \times 10^{-1}}{1 \times 10^7} = 6 \times 10^{-9}s$

45. (1) $\frac{dx}{dt} = k[A]^a[B]^b$

$$0.25 = k(1)^a(1)^b \qquad \dots(i)$$

$$0.50 = k(2)^a(1)^b \qquad \dots(ii)$$

$$0.25 = k(1)^a(2)^b \qquad \dots(iii)$$

Dividing Eq. (ii) by Eq. (i) and Eq. (iii) by Eq. (i)

$$2 = (2)^a \Rightarrow a = 1$$

$$1 = (2)^b$$

$$2° = (2)^b \Rightarrow b = 0$$

Thus, $\qquad \frac{dx}{dt} = k[A]$

Hence, order of reaction with respect to (A) is one.

Rachna Rani

Assertion-Reason

Collection of Best Assertion-Reason Problems for AIIMS, MGIMS and Other Medical Entrances

Direction **(Q. Nos. 1-25)** Read the Assertion and Reason carefully to mark the correct option out of the options given below.

(a) Both the Assertion and the Reason are true and the Reason is a correct explanation of the Assertion
(b) Both the Assertion and the Reason are true but the Reason is not a correct explanation of the Assertion
(c) The Assertion is true but the Reason is false
(d) The Assertion is false but Reason is true
(e) Both the Assertion and Reason are false

1. **Assertion** (A) C—H bonds in ethyne are shorter than C—H bonds in ethene.

Reason (R) Carbon atom in ethene is *sp* hybridised while it is sp^2 in ethyne. **[AIIMS 2007]**

2. **Assertion** (A) H—S—H bond angle in H_2S is closer to 90° but H—O—H bond angle in H_2O is 104.5°.

Reason (R) *lp-lp* repulsion is stronger in H_2S than in H_2O. **[AIIMS 2007]**

3. **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. **[AIIMS 2003]**

4. **Assertion** (A) In the following ion, the bond represented by an arrow is a coordinate bond.

$$\left[\begin{array}{c} \text{Cl} \\ | \\ \text{Cl} \rightarrow \overset{\displaystyle \text{Cl}}{\underset{\displaystyle \text{Cl}}{\text{P}}} \leftarrow \text{Cl} \\ | \\ \text{Cl} \end{array} \right]^{-}$$
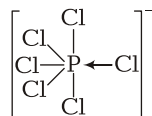
Reason (R) A coordinate bond results from the sharing of pair of electrons between two atoms where each atom contributes one electron to the bond.

5. **Assertion** (A) An ionic bond is formed when a metal atom transfers one or more electrons to a non-metal atom.

Reason (R) As a result of electron transfer, the metal atom becomes cation and the non-metal atom becomes anion.

6. **Assertion** (A) The solubility order of NaCl in different solvents is given below

$$H_2O > CH_3CH_2OH > CH_3OCH_3$$
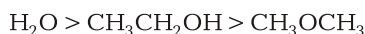
Reason (R) For a given solute, greater the value of dielectric constant of the solvent, greater the force of attraction between positive and negative ions.

7. **Assertion** (A) If the anion and the cation are of comparable size, the anionic radius will influence the lattice energy.

Reason (R) Lattice energy decreases much more than hydration energy with increase in ionic size.

8. **Assertion** (A) PF_3 obeys octet rule but PF_5 does not.

Reason (R) 3*d*-orbitals play crucial role during formation of PF_5.

9. **Assertion** (A) In SF_6, there are six S—F bonds, made up of 12 shared electrons.

Reason (R) Sulphur has 6 electrons in its outermost shell.

ASSERTION-REASON

10. **Assertion** (A) H—O—Cl has more stable atomic skeleton than H—Cl—O.

Reason (R) The atomic skeleton is more stable in which the sum of electronegativity difference of adjacent atoms is maximum.

11. **Assertion** (A) In between the following structures, structure I is more favourable than II

$$\ominus \overset{..}{\underset{..}{:N}}=\overset{\oplus}{N}=\overset{..}{\underset{..}{O}} \qquad :N=N=\overset{..}{\underset{..}{O}}:\ominus$$
$$\text{(I)} \qquad\qquad\qquad \text{(II)}$$

Reason (R) Oxygen is less electronegative element than nitrogen.

12. **Assertion** (A) F—N—F bond angles in NF_3 is 102° 30′ while H—N—H bond angle in NH_3 is 107°48′.

Reason (R) Repulsion between bond pairs is more in NF_3 than NH_3.

13. **Assertion** (A) F_3^- is more stable than I_3^-.

Reason (R) Iodine can expand its octet but fluorine cannot.

14. **Assertion** (A) The HF_2^- ions exist in the solid state and also in liquid HF solution, but not in dilute aqueous solution.

Reason (R) Due to hydrogen bonding, HF_2^- ions held together in liquid HF solution and in solid state.

15. **Assertion** (A) $BaSO_4$ is a covalent compound and soluble in water.

Reason (R) Lattice energy of $BaSO_4$ is smaller than its hydration energy.

16. **Assertion** (A) Pb^{2+} ion is more stable than Pb^{4+} ion.

Reason (R) Pb^{2+} ion is formed more readily than Pb^{4+} ion.

17. **Assertion** (A) $BaCl_2$ is an ionic compound.

Reason (R) There is sufficient difference between electronegativities of Ba and Cl.

18. **Assertion** (A) Single bonded compounds are less reactive than double bonded compounds.

Reason (R) Sigma bond is more stronger than pi-bond.

19. **Assertion** (A) NaCl in solid form behaves as an insulator while in molten state, it conducts electricity.

Reason (R) NaCl dissociates into Na^+ and Cl^- ions which can move freely and conduct electricity.

20. **Assertion** (A) NaCl has higher melting point than $MgCl_2$ and $AlCl_3$.

Reason (R) NaCl has more covalent character than $MgCl_2$ and $AlCl_3$.

21. **Assertion** (A) $AlCl_3$ is a covalent compound while $AlCl_3 \cdot 6H_2O$ is an ionic compound.

Reason (R) In the presence of polar medium, ionic character increases in the molecule.

22. **Assertion** (A) $(CH_3)_3N$ is more basic than $(SiH_3)_3N$.

Reason (R) In $(SiH_3)_3N$, d-orbitals of Si-atom and lone pair of electrons present on N-atom form pπ-$d\pi$ bonding.

23. **Assertion** (A) $SnCl_2$ is a solid while $SnCl_4$ is a volatile liquid.

Reason (R) $SnCl_2$ is more ionic than $SnCl_4$.

24. **Assertion** (A) Increasing order of bond dissociation energy of the following is
$$Cl_2 < O_2 < N_2$$
Reason (R) Bond order of N_2, O_2, F_2 and Cl_2 are 3, 2 and 1 respectively.

25. **Assertion** (A) Boiling point of thioethers (R—S—R) is lesser than that of ethers (R—O—R).

Reason (R) Boiling point is inversely proportional to molecular weight.

Answer *with* Explanations

1. *(c)* Carbon atom in ethene is sp^2 hybridised while it is sp in ethyne.

2. *(c)* lp-lp repulsion is stronger in H_2O than in H_2S.

3. *(e)* **Correct** (A) The O—O bond length in O_2F_2 is shorter than that in H_2O_2.

Correct (R) H_2O_2 is a covalent compound.

**4.** *(c)* A coordinate bond results when both electrons originate from one atom and these electrons are completely donated to the other atom. The bond formation in this process is known as coordinate bond and shown by arrow '←' which points direction of electron donation, from donor to acceptor.

5. *(a)* As ionic bond is formed between two oppositely charged ions. Hence, both (A) and (R) are correct and (R) is the correct explanation of (A).

6. *(c)* For a given solute, greater the value of dielectric constant of the solvent, smaller the force of attraction between oppositely charged ions hence, greater the solubility.
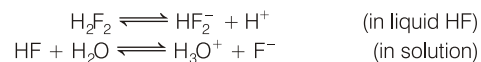
7. *(d)* **Correct** (A) If the anion and the cation are of comparable size, the cationic radius will influence the lattice energy.

8. **(a)** PF_5 is one of the exception of octet rule. In this case an electron from $3s$ orbital excite and jump to the $3d$ orbital thus making 5 electrons available for sharing and hence forming the PF_5 molecule

(Ground state)   (Excited state)
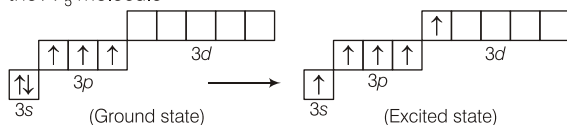
9. **(b)** Compounds having more than four covalent bonds violate from octet rule, these become very common in the elements after the first two periods of eight elements in the periodic table.

10. **(a)** $\overset{2.20}{H} — \overset{3.44}{O} — \overset{3.16}{Cl}$; $\Sigma = (3.44 - 2.20) + (3.44 - 3.16) = 1.52$

$\overset{2.20}{H} — \overset{3.16}{Cl} — \overset{3.44}{O}$; $\Sigma = (3.16 - 2.20) + (3.44 - 3.16) = 1.24$

11. **(e)** Structure II is more favourable than I. Since, oxygen is more electronegative element than nitrogen, the structure that places a negative formal charge on oxygen is lower in energy than the structure that has a negative formal charge on nitrogen.

12. **(c)** Due to high electronegativity of F, it pulls the bonding electrons farther away from N than in NH_3. Hence, repulsion between bond pairs is less in NF_3 than in NH_3 and the lone pair in NF_3 causes a greater distortion from tetrahedral and gives a F—N—F bond angles of $102°30'$ compared with $107°48'$ in NH_3.

13. **(d)** I_3^- is more stable than F_3^-. Iodine can expand its octet whereas fluorine cannot. Thus, in I_3^-, octet rule is not violated but in F_3^-, octet rule is violated.

14. **(a)** In aqueous solution, there is hydrogen bonding, but each HF molecule being stronger acid than H_2O, forms H_3O^+ and F^-.

$$H_2F_2 \rightleftharpoons HF_2^- + H^+ \qquad \text{(in liquid HF)}$$
$$HF + H_2O \rightleftharpoons H_3O^+ + F^- \qquad \text{(in solution)}$$

15. **(e)** $BaSO_4$ is an ionic compound and it is insoluble in water because lattice energy of $BaSO_4$ is greater than its hydration energy.

16. **(b)** s-electrons of valence shell of Pb become inert and do not take part in bond formation due to inert pair effect.

17. **(a)** Ionic bond is formed between two oppositely charged ions where, there is sufficient difference between electronegativities of their corresponding atoms.

18. **(b)** Double bond contains one π-bond which is more reactive due to its low bond energy.

19. **(a)** Both (A) and (R) are correct and (R) is the correct explanation of (A).

20. **(c)** NaCl is more electrovalent than $MgCl_2$ and $AlCl_3$.

21. **(a)** According to Fajans' rule, ionic character increases in the molecule in the presence of polar medium.

22. **(a)** Both (A) and (R) are correct and (R) is the corr.

23. **(b)** In $SnCl_2$, effective electrostatic forces of attraction are stronger than van der Waals' forces of attraction between $SnCl_4$ molecules.

24. **(a)** Bond dissociation energy $\propto$ Bond order

25. **(e)** Boiling point is directly proportional to molecular weight. Since, thioether has more molecular weight than ether hence, boiling point of thioether is more than that of ether.

DPP
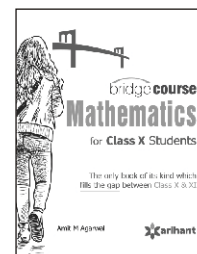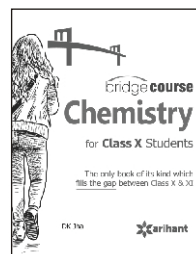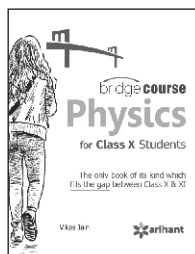
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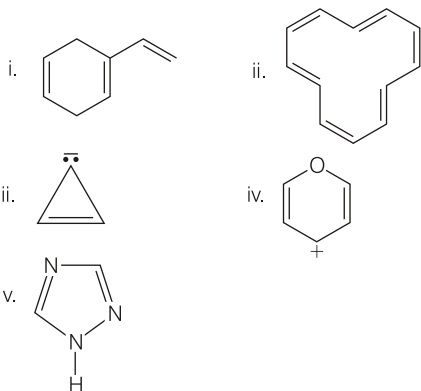
COURTESY : Ranjeet Shahi

Aromaticity

Subjective Questions

**Direction** (Q. Nos. 1-5) These questions are subjective in nature, need to be solved completely on notebook.

1. Label each of the following compound as aromatic, antiaromatic or non-aromatic.

i.

ii.

iii.

iv.

v.

2. The heterocyclic compound shown below has a tautomer which is highly stable and it tautomerises readily in acidic medium. Draw the structure of that tautomer and give reason for its higher stability.
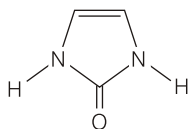
3. Label each of the following compounds or ions below as aromatic, antiaromatic or non-aromatic.

i.

ii.

iii.

iv.

v.
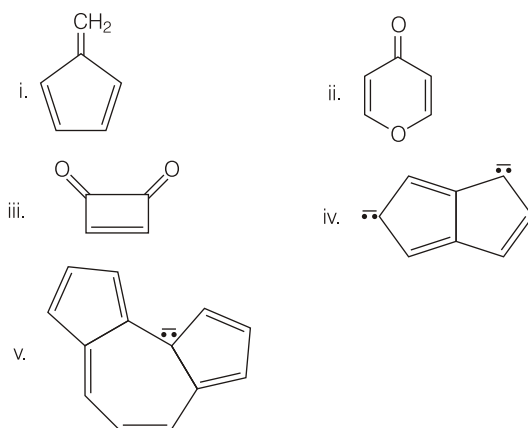
4. Most diazo compounds, such as CH_2N_2, are exceedingly unstable but diazocyclopentadiene (shown below) is quite stable. Provide reasonable explanation for that
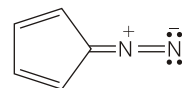
Diazocyclopentadiene

5. Explain each of the following processes applied to cyclooctatetraene and decide whether the species formed is aromatic or not.
  (i) Addition of one electron to form $C_8H_8^-$
  (ii) Addition of two electrons to form $C_8H_8^{2-}$
  (iii) Removal of one electron to form $C_8H_8^+$
  (iv) Removal of two electrons to form $C_8H_8^{2+}$

THE MOST SUCCESSFUL WAY OF **JEE PREPARATION** NOW ON YOUR TABLE

Only One Option Correct Type

Direction (Q. Nos. 6-13) This section contains 8 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which only one option is correct.

6. Arrange the following compounds in the increasing order of polarity.
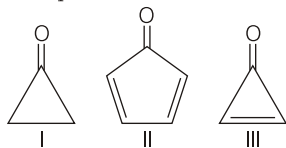
(a) I < II < III   (b) III < II < I
(c) II < I < III   (d) III < I < II

7. In principle, what is true regarding benzene and 1, 3, 5-cyclohexatriene?

(a) Theoretically they are the same molecules
(b) Both have same lengths of all of their C—C bonds
(c) Both have same enthalpy of hydrogenation
(d) Cyclohexatriene has two different C—C bond lengths while benzene has only one type of C—C bond length whose value is between those of cyclohexatriene

8. Enthalpy of hydrogenation of cyclohexene is -119 kJ/mol and that of benzene is -208 kJ/mol. Based on these information, resonance energy of benzene can be calculated to be

(a) -119 kJ/mol   (b) -238 kJ/mol
(c) -149 kJ/mol   (d) -565 kJ/mol

9. Select the species which is not aromatic.
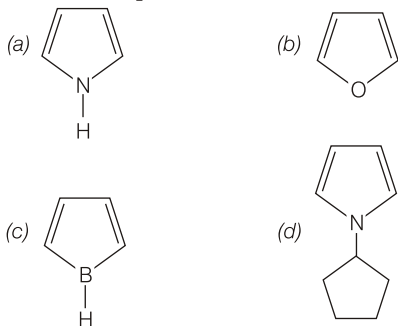
10. Consider the following bromides,
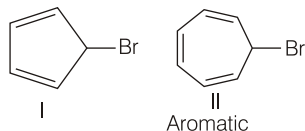
If the above bromides undergo heterolytic fission of C—Br bonds, the preferred mode of decomposition would be

(a) Both decomposes to forms Br^-
(b) Both decomposes to forms Br^+
(c) I decomposes to give Br^- and II gives Br^+
(d) I decomposes to give Br^+ while II gives Br^-

11. Which is not true regarding 1, 3, 5, 7-cyclooctatetraene?

(a) It decolourises purple colour of cold, dilute, alkaline $KMnO_4$ (Baeyer's reagent)
(b) It decolourises brown colour of Br_2-H_2O solution
(c) It is absorbed in cold, concentrated H_2SO_4 solution
(d) It is an aromatic system

12. The following compound, when treated with excess of $AgBF_4$ gives a red precipitate leaving a highly conducting filtrate, due to

Red ppt. + Conducting solution
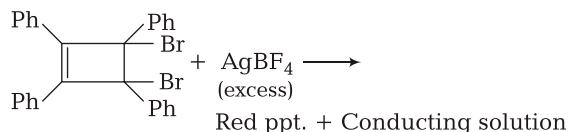
(a) A dianion aromatic system is formed
(b) A dication aromatic system is formed
(c) A covalent ditetrafluoroborate compound is formed
(d) An aromatic salt precipitate which is red coloured

13. When potassium metal is added to 1, 3, 5, 7-cyclooctatetraene, a highly conducting salt is formed without evolution of H_2 gas because

(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}
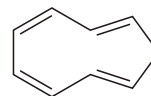(d) oxidation of cyclooctatetraene into $C_8H_8^{2+}$

One or More than One Options Correct Type

Direction (Q. Nos. 14-17) This section contains 4 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which one or more than one are correct.

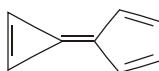**14.** Which of the following species is/are aromatic?
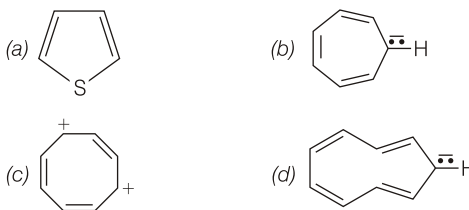
15. What makes the following compound aromatic?

(a) Add one electron to π-bond to give $C_9H_{10}^-$
(b) Add two electrons to π-bond to give $C_9H_{10}^{2-}$
(c) Remove an ion, H^+, from sp^3 carbon
(d) Remove an ion, H^+ from sp^2 carbon

16. What is true about the compound calicene?

(a) It is highly soluble in water

(b) It exists mainly as dipolar ion with +ve charge in the three membered ring while –ve charge in five membered ring

(c) It exists mainly as dipolar ion with –ve charge in the three membered ring and +ve charge in five membered ring

(d) In solution it shows very high electrical conductivity

**17.** Which of the following species is/are antiaromatic?

(a)

(b)

(c)

(d)
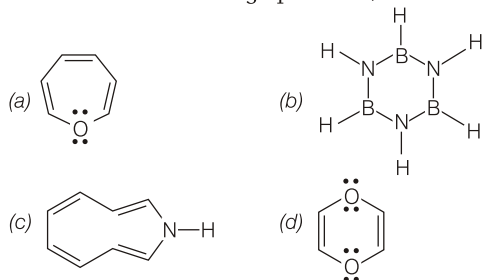
Statement Type

Direction (Q. Nos. 18-21) **This section is based on Statement I and Statement II. Select the correct answer from the codes given below.**

(a) Both Statement I and Statement II are correct and Statement II is the correct explanation of Statement I

(b) Both Statement I and Statement II are correct and Statement II is not the correct explanation of Statement I

(c) Statement I is correct but Statement II is incorrect

(d) Statement I is incorrect but Statement II is correct

18. **Statement I** Benzene has very high stability than a general triene.

Statement II Benzene is a completely conjugated system.

19. **Statement I** Pyrene, although aromatic, decolourise brown colour of bromine water.

Pyrene
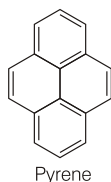
Statement II It has one pi-bond extra which is not the part of aromatic system.

20. **Statement I** The following compound is optically active.
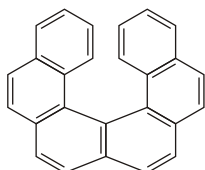
Statement II It has a chiral carbon.

21. **Statement I** Furan is an aromatic system, has resonance energy comparable to that of benzene.

Statement II Furan decolourises the brown colour of bromine water solution.

(Furan)
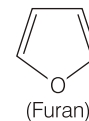
One Integer Value Correct Type

Direction (Q. Nos. 22-25) **This section contains 4 questions. When worked out will result in an integer from 0 to 9 (both inclusive).**

22. From the list below, how many of them are aromatic?

I.   II.   III.

IV.   V.   VI.

VII.   VIII.   IX.

X.   XI.
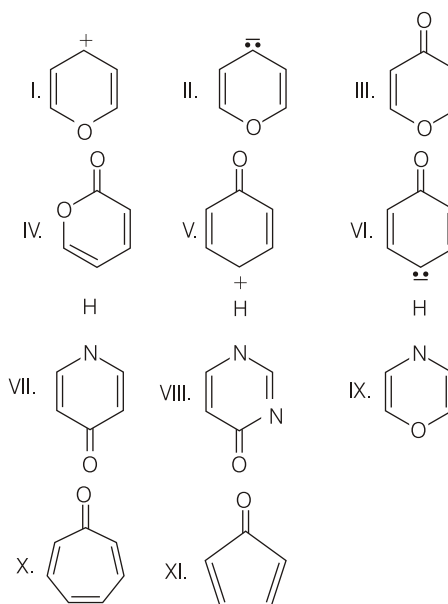
23. Cyclobutene when refluxed in presence of potassium metal, evolve hydrogen gas and an aromatic system is formed. How many pi-electrons are involved in the above formed aromatic system?

24. In the molecule shown below, how many lone pairs of the valence shell are not the part of aromatic system?

25. The compound below has four phenyl rings, but very less stable due to an opposing factor of stability. Therefore, this compound absorb bromine in dark. How many bromine molecules, when added to this molecule, would make it stable and prevent further bromine addition? **[IIT JEE 2005]**

DPP THE MOST SUCCESSFUL WAY OF **JEE PREPARATION** NOW ON YOUR TABLE
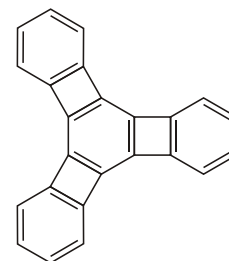
Answer *with* Explanations

1. (i) Non-aromatic does not has $(4n + 2)$ delocalised pi-electrons in close cyclic loop.

(ii) Antiaromatic has 4n pi-electrons delocalised in a closed, cyclic loop.

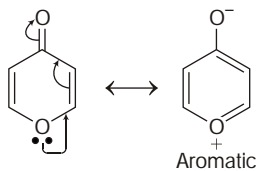(iii) Antiaromatic has 4n pi-electrons delocalised in a closed cyclic loop.

(iv) Aromatic
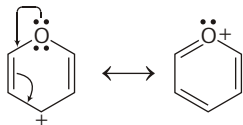
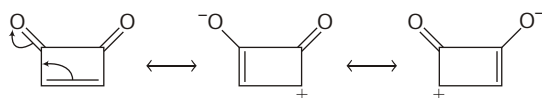Has $(4n + 2)$ pi-electrons in a closed, cyclic loop as well as they are conjugated.

(v) Aromatic

2.

Tautomer II is much more stable than I due to aromaticity in II.
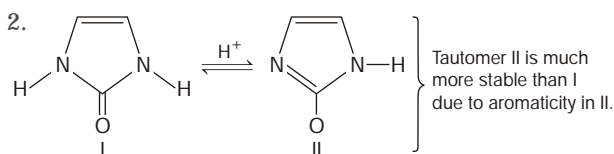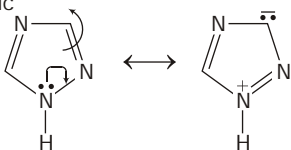
3. (i) Non-aromatic, the two pi-bonds of ring do not form close loop delocalised system.

(ii) Aromatic

Aromatic

(iii) Aromatic

Satisfy $4n + 2 (n = 0)$ rule

(iv) Aromatic
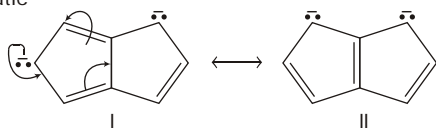
Both rings in II behave like cyclopentadienyl (aromatic) anions.

(v) Aromatic
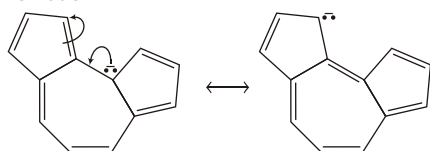
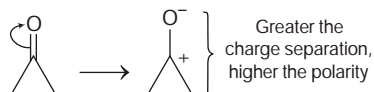

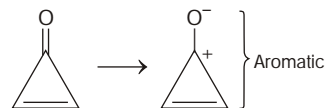Behaves like monocyclic ring with $4n + 2$ $(n = 3)$ delocalised pi-electrons.

**4.** One of its resonance structure makes cyclopentyl ring aromatic as:

Aromatic ring

5.
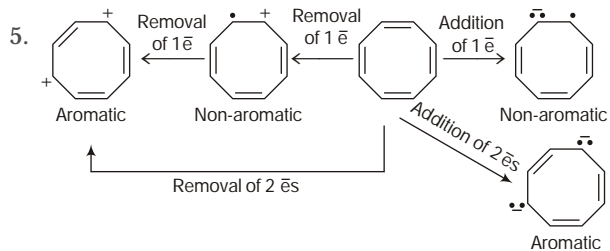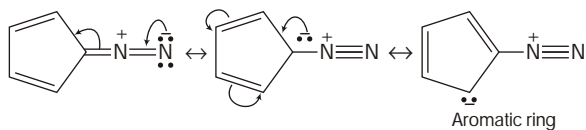
6. (c) Polarity of carbonyls is mainly due to following charge separation
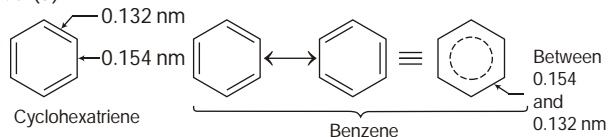

Greater the charge separation, higher the polarity

III forms aromatic cation on charge separation, most polar

Aromatic
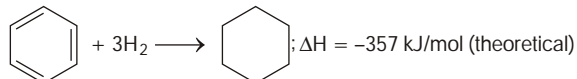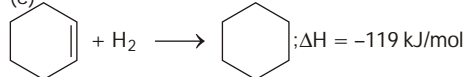
II forms anti-aromatic cation on charge separation, has least tendency for charge separation, least polar.

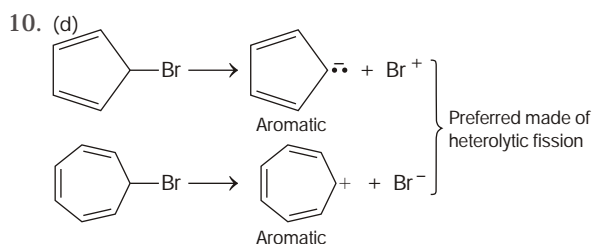Anti-aromatic

7. (d)

Between 0.154 and 0.132 nm
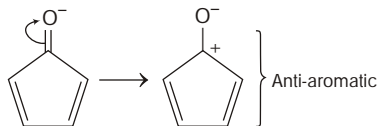
8. (c)
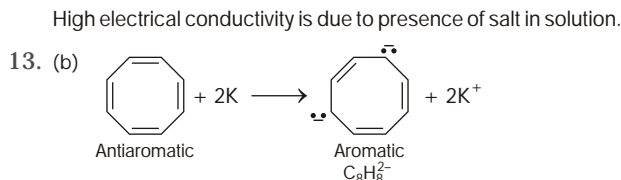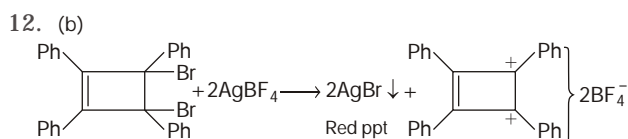

$\Delta H_{RE} = \Delta H_{Theo} - \Delta H_{exp} = -357 - (-208) = -149\,kJ/mol$

9. (c) It is a conjugated system but has only 4π electrons, does not satisfy Huckel rule.

10. (d)

Preferred made of heterolytic fission

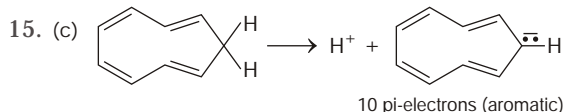**11.** (d) Cyclooctatetraene has 8 delocalised pi-electrons, does not satisfy Huckel rule, not aromatic. Hence, it gives all the reactions of alkenes.

12. (b)

High electrical conductivity is due to presence of salt in solution.

13. (b)

Antiaromatic   Aromatic
$C_8H_8^{2-}$

14. (a, c, d) All (a), (c), (d), satisfy Huckel $(4n + 2)\pi$ electron rule.
(b) is antiaromatic as it has $8\pi e^-$ (4n).

15. (c)

10 pi-electrons (aromatic)

16. (a, b, d) The compound has following resonance structures due to stable dipolar ion, positive charge in three membered ring and negative charge in five membered ring, it dissolve in water, highly conducting.
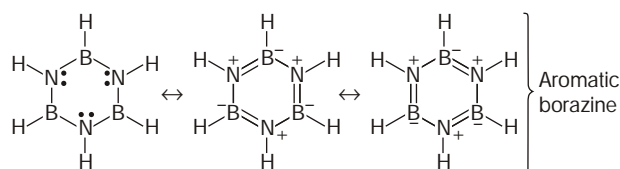

Unstable   Both rings anti-aromatic

Both rings aromatic   Stable

17. (a, d)
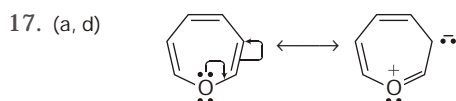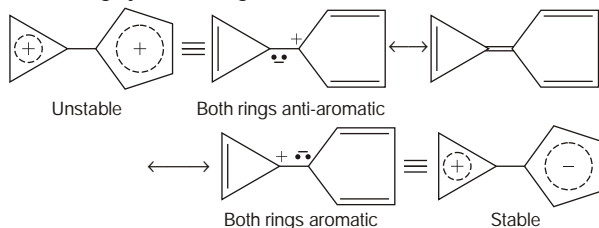
Has eight delocalised pi-electrons p-satisfy 4n pi-electrons rule, hence antiaromatic.

Has eight delocalised pi-electrons, satisfy 4n pi-electrons rule,
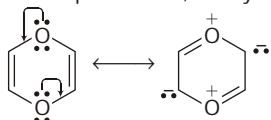

hence, antiaromatic. b and c are both aromatic.

Aromatic borazine

18. (b) The unusual stability of benzene is due to aromaticity in it, conjugation is one of the requirement of aromaticity.

19. (a) One of the resonance structure shown below indicates clearly that the central pi-bond is not involved in aromaticity, show the general reactions of a typical alkene.

Not the part of aromatic system
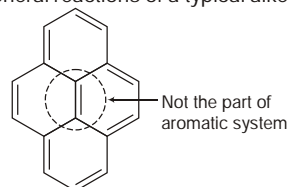
20. (c) Due to proximity of the two phenyl rings, their hydrogens come very close, repels one-another and destroy the planarity making the system non-superimposable on mirror images.
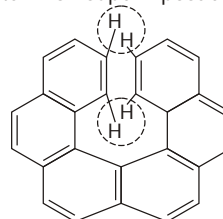
H—H repulsions shown here destroy planarity of the two rings and the system becomes non-superimposable on mirror image.

21. (d)
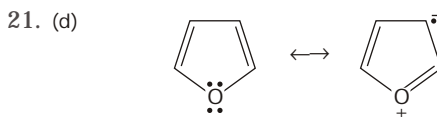
Due to above resonance, furan acquires 6π electrons and show aromaticity but to a very small extent due to development of positive charge on electronegative oxygen atom. Hence, resonance stabilisation of furan is much less than benzene. Due to this reason, furan show, to some extent, reactions of alkene.

22. (7) I, III, IV, VI, VII, VIII and X satisfy Huckel $(4n + 2)$ rule, hence aromatic. II, V and IX are non-aromatic while XI is antiaromatic..

23. (6)

Cyclobutene   Aromatic dianion
(It has 6 delocalised pi-electrons)
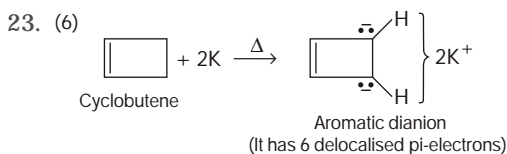
24. (5) The lone pairs which are not involved in aromaticity are circled in the corresponding molecule shown in right hand side.

25. (3) It has three antiaromatic (cyclobutadiene) rings which makes it unstable. If 3 molecules of Br_2 are added to central benzene, anti-aromaticity would be removed completely.
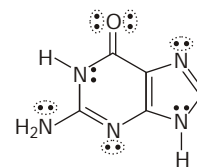
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Just Solve & Send
Knowledge Coefficient
Quizzer (No.12)

1. A 0.750 g sample of solid benzoic acid, $C_7H_6O_2$, was placed in a 0.500 L pressurised reaction vessel filled with O_2 at 10.0 atm pressure and 25°C. To the extent of the availability of oxygen, the benzoic acid was burned completely to water and CO_2. The vapour p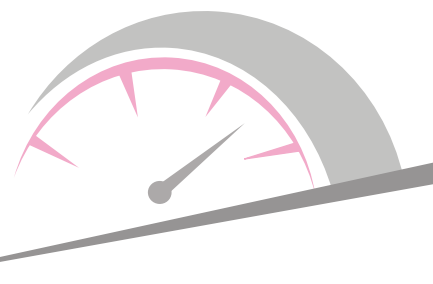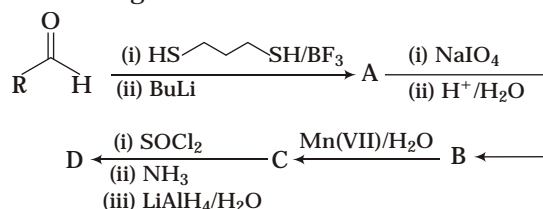ressure of water at 25°C is 23.8 torr. Neglect both the volume occupied by non-gaseous substance and the solubility of CO_2 in H_2O. The final mole fraction (χ) of CO_2 and H_2O vapour in the resulting gas mixture brought to the initial temperature are respectively
   - (a) 2.13, 0.032
   - (b) 0.213, 0.0032
   - (c) 0.213, 0.032
   - (d) 21.3, 0.32

2. Which of the following represents the proper structure of the final major product D, obtained after the following series of reactions?

   R–CHO $\xrightarrow[\text{(ii) BuLi}]{\text{(i) HS} \sim \text{SH/BF}_3}$ A $\xrightarrow[\text{(ii) H}^+/\text{H}_2\text{O}]{\text{(i) NaIO}_4}$ B

   D $\xleftarrow[\substack{\text{(ii) NH}_3 \\ \text{(iii) LiAlH}_4/\text{H}_2\text{O}}]{\text{(i) SOCl}_2}$ C $\xleftarrow{\text{Mn(VII)/H}_2\text{O}}$ B

   - (a) R~NH₂
   - (b) R–CH(R)–NH₂
   - (c) R–C(O)–NH₂
   - (d) R~N(R)(R)

3. Evaluate the concentration overpotential at a cadmium amalgam electrode, the diffusion flux of Cd^{2+} ions and the current per square centimeter for 298.15 K. Assume that $d = 200\,\mu m$, the concentration at the electrode is 0.0100 mol L^{-1} and the concentration in the bulk is 0.0200 mol L^{-1}. The diffusion coefficient for Cd^{2+} ions at this temperature equal to 8.7×10^{-10} m^{2}s^{-1}.
   - (a) 4.8×10^{-7} A cm^{-2}
   - (b) 6.8×10^{-9} A cm^{-2}
   - (c) 8.4×10^{-7} A cm^{-2}
   - (d) 0.8×10^{-7} A cm^{-2}

4. A 0.63% by weight aqueous tin(II) fluoride, SnF_2, solution is used as an oral rinse in dentistry to decrease tooth decay. Large quantities of tin are produced commercially by the reduction of cassiterite, SnO_2, the principal tin ore with carbon,
 $$SnO_2\,(s) + 2C\,(s) \longrightarrow Sn(s) + 2CO(g)$$
   Once purified, the tin is reacted with hydrogen fluoride vapour to produce SnF_2. Consider that one metric ton of cassiterite ore is reduced with sufficient carbon to tin metal in 80% yield. The tin is purified and reacted with sufficient hydrogen fluoride to produce SnF_2 in 94% yield. Calculate how many 250 mL bottles of 0.63% SnF_2 solution could be prepared from the one metric ton of cassiterite by these steps.
   - (a) 4.99×10^4 bottles
   - (b) 9.49×10^4 bottles
   - (c) 4.99×10^5 bottles
   - (d) 9.49×10^5 bottles

5. The standard state enthalpy change of combustion of methane at 298.15 K equals to 890.36 kJ mol^{-1}, with liquid water as one of the products. The enthalpy change of formation of methane at 298.15 K using the enthalpy changes of formation of H_2O and CO_2 is
   - (a) 748.2 kJ mol^{-1}
   - (b) 74.82 kJ mol^{-1}
   - (c) – 74.82 kJ mol^{-1}
   - (d) – 7.48 kJ mol^{-1}

6. Consider the following reaction,

   $\xrightarrow{\text{NH}_2\text{OH}}$ A $\xrightarrow[\text{(ii) Hydrolysis}]{\text{(i) CH}_3\text{COCl}}$ B
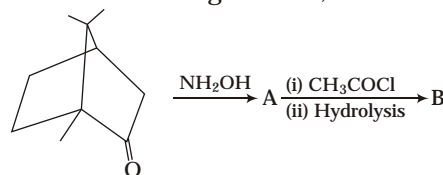
   Identify the structure of compound B.

   (a)   (b)

   (c)   (d)

7. By a process equivalent to base dissociation, glycine can acquire an additional proton to form $\overset{\oplus}{N}H_3CH_2COOH$. The resulting cation may be considered to be a diprotic acid, since one proton from the —COOH group and one proton from the $\overset{\oplus}{—NH_3}$ group may be lost. The pK_a value for these processes are 2.35 and 9.78, respectively. In a 0.0100 M solution of neutral glycine, the % of the glycine is in the cationic form at equilibrium is
   (a) 1.9%
   (b) 0.19%
   (c) 0.0019%
   (d) 0.019%

8. The specific heat of a liquid was measured by placing 100 g of the liquid in a calorimeter. The liquid was heated by an electric immersion coil. The heat capacity of the calorimeter together with the coil was previously determined to be 31.4 J/K. With the 100 g sample is placed in the calorimeter, a current of 0.500 A was passed through the immersion coil for exactly 3 min. The voltage across the terminals of the coil was measured to be 1.50 V. The temperature of the sample rose by 0.800°C. The specific heat capacity of liquid is

   (a) 0.138 J/g-K
   (b) 13.8 J/g-K
   (c) 1.38 J/g-K
   (d) 3.18 J/g-K

9. At 20°C and a total pressure of 760 torr, 1 L of water dissolves 0.043 g of pure oxygen or 0.019 g of pure nitrogen. Assuming that dry air is composed of 20% oxygen and 80% nitrogen by volume, the masses of oxygen and nitrogen dissolved by 1 L of water at 20°C exposed to air at a total pressure of 760 torr respectively ae
   (a) 0.086 g/L, 0.0015 g/L
   (b) 0.86 g/L, 0.015 g/L
   (c) 0.0086 g/L, 0.015 g/L
   (d) 0.86 g/L, 0.0015 g/L

10. A cubical cell 0.100 m on a side is filled with C_6H_6. The top surface is maintained at 25.0°C and the bottom surface is maintained at 15.0°C. After some time, the system will reach a steady state in which the state of the system does not change with time although heat is flowing. The amount of heat flowing through the benzene per hour after a steady state is achieved, neglecting convection, is
   (a) 844 J
   (b) 544 J
   (c) 644 J
   (d) 445 J

KNOWLEDGE
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Quizzer (No. 12)

Q. No.	a.	b.	c.	d.	Q. No.	a.	b.	c.	d.
1.	○	○	○	○	6.	○	○	○	○
2.	○	○	○	○	7.	○	○	○	○
3.	○	○	○	○	8.	○	○	○	○
4.	○	○	○	○	9.	○	○	○	○
5.	○	○	○	○	10.	○	○	○	○

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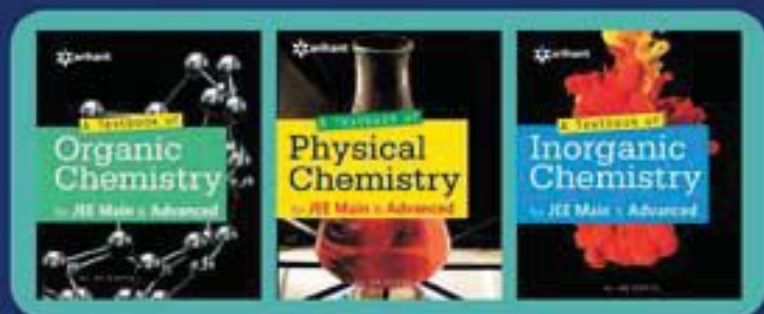Informatics Practices, Computer Science, English core, Hindi Core.

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