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EXEMPLAR SIMPLIFIED
CONCEPT MAP
DO YOU KNOW

FROM THE EDITOR'S DESK
PLAN-n-PLAY
YOUR ROAD MAP TO CAPTURE
JEE 2017

CHEMISTRY CONCENTRATE
ATOMIC SPHERE IN QUANTUM MECHANICAL VIEW
CRYOSCOPY

JEE ADVANCED DRILL
SOLUTIONS

METICULOUS ANALYSIS
REACTION INTERMEDIATES

EXPLICATION
ELEMENTS :
HOW THEY WERE DISCOVERED?

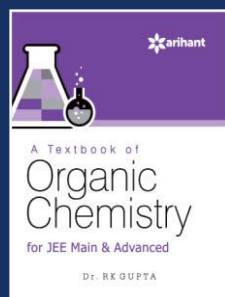**PRACTICE PAPER** **NEET** (Phase II)

SOLVED PAPERS
JEE ADVANCED
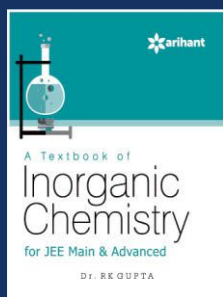PAPER 1 & 2

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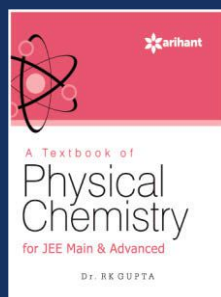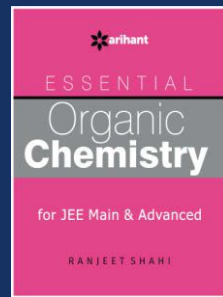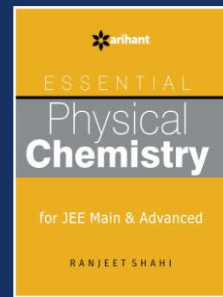| B001 ₹775.00 | B002 ₹765.00 | B003 ₹640.00 | B088 ₹895.00 | B071 ₹755.00 |

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Issue 8   **Vol 2**

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FROM THE EDITOR'S DESK

The beginning of new session is the most auspicious time for all of us. It's the time when each one of us enters the portals of educational institutions with a new dream or hope. The shaping of dreams requires positive thoughts and energy for its real appearance. It is well said, 'if we sow good thoughts in our mind, we reap good actions resulting to fulfilling of our dreams'. It is good to have a dream but always remember!

"The size of your success is determined by the size of your belief."

David J Schwantz

PLAN-*n*-PLAY
YOUR ROAD MAP TO CAPTURE
JEE 2017

As written in quote above **"the size of UR success is connected with the size of self-belief U have"**. All of us know that every success has a concrete plan in its base, so it is essential to develop an action plan, which have the ability to convert goals into reality. An action plan in real sense defines the exact pathway of our motion in order to accomplish our mission. In my opinion true self-belief is one of the foundation stones of planning.

For a real student of science development of action plan should not be a tough job. As the circumstances, capacities and needs vary from person to person hence such an action plan which completely fits into someone's need is very difficult to design. However, here we can discuss the methodologies to develop a generalised plan, which is flexi enough to be customised according to your needs.

After years of experimentation and thinking I succeeded in developing a full proof plan which is self-sustaining and works on **self-pressure creation technique.** It has some sort of inspiration from professional studies. The step-wise approach to formulate such a plan is as follows

Step 1 *Accumulation of rough work volume and calculation of tentative time available in a year.*
This can be exemplified as—Suppose we are in the first week of April then we have 11 months till 1st of March as the time available. It comes of about 330 days in total. Physics,

Chemistry and Mathematics include about 48 chapters in total (approx. estimated for one class only either 11th or 12th). Thus, we have roughly 6.8 days available to complete 1 chapter.

Step 2 *Target Fixation* 1 (*Generalised Monthly Target Fixation*)
In broad sense it looks very simple as 7 days (approx.) are available for 1 chapter of any of the subjects. But in this step we look for first minor detail of the work volume. The rough estimates calculated in step 1 were stipulated for one time study of the lesson only. We also know that one time learning of the chapters is insufficient to give requisite results. That means we actually require atleast 2 months for revision and atleast last 15-20 days for rapid revision. Hence, in real sense the tentative available time can be splitted into
(a) Learning phase
(b) Consolidation phase for (6-8 weeks)
(c) Rapid review or revision phase (last 2-3 weeks)
From this splitting it is very clear that the real learning phase is squeezed to 8 months (i.e. 240 days) from roughly estimated 330 days. This simply indicates that the rough estimate of 7 days per chapter now becomes 240/48 = 5 days per chapter. Now, for actual calculation we have to remove atleast 30 days from the scheduled time of learning phase in lieu of festivals or other kind of holidays during which it is very difficult to study with proper strength. So,

☒ FROM THE EDITOR'S DESK

practically we have approximately 7 months or 210 days in a year to complete our syllabus atleast once that means we have only about 4 days (210/48) per chapter to the max. As I told in the beginning it is a **self-pressure creation technique** so it is the beginning of pressure building.

> The learning and consolidation phases have specific meanings related to their names. **The learning phase** is the basic phase in which the focus is on learning fundamentals and practice while the **consolidation phase** is related to the consolidation of the studies. The **rapid review phase** is in fact the part of **consolidation phase,** but here we go for rapid revisions for consolidation while a slow revision features proper **consolidation phase**.

Step 3 *Target Fixation 2 (Specific Monthly Target Fixation)*
The generalised time distribution given in Step 2 requires further attention according to your need. Here adjustments according to your class and requirements (work volume) are to be made. e.g. The generalised time distribution may vary for a class 11th student as compared to a class 12th or 12th pass student as

In Class 11th	In Class 12th
Start date Either Ist week of April or Ist week of July (as class 10th results are declared in June)	**Start date** Ist week of April
Finish date	Finish date
(i) For learning phase: Either November end or January end to the max. *For those who start late the time availability is reduced by 60 days atleast.*	(i) For learning phase: By November 15th (max)
(ii) For consolidation phase: December and January for those having start date in April. *The consolidation phase may squeezed to 15 days or so for those who start late. Here, it is advisable to mix it up with rapid review phase for better results.*	(ii) For consolidation phase: Maximum by December end
(iii) Rapid review phase: Month of February for those who start early *Practically, it is not available for those who start late.*	(iii) For rapid review of class 11th syllabus : By 25th of January (max)
	(iv) Rapid review and board practice: In the last week of January and complete February.

For Class 12th students Board Exams takes place in the Month of March
After the Boards till JEE Mains rapid review is required with more emphasis on class 11th syllabus as compared to class 12th syllabus.

REMEMBER!

> For the preparation of an objective examination last 2 days must be proper relaxing type with 6-7 hrs of sleep and cool mind.

From the above work distribution following conclusion can be drawn

1. Class 11th requires much more attention, time and space as after covering it once properly in Ist year, the requirement of revising the same before JEE Mains exam already exists. Due to which, minor adjustment are to be made, in class 12th time distribution. "**So never think class 11th is the rest year**".

2. The time pressure problem is visible for late starters as their scheduled time of learning is squeezed by atleast 60 days. Thus, they don't have time for proper consolidation and the time pressure shift is visible on class 12th.

3. Such late starters usually say "**Sir meri Class 11th zara weak hai**". In reality it is not "**zara weak**", rather it is "**very weak**" and repairing for such a weakness requires much more strength and determination. Thus, **the situation is very delicate also as this repairing cannot be done at the cost of class 12th studies.**

   Mantra *For such students it is advisable to use 25 days of January (as visible in class 12th time distribution above) very effectively with honesty along with the time available between their last board exam and JEE mains to remove their this weakness.*

4. Those students, who, start early in class 11th are in a better situation both study wise as well as psychologically as compared to late starters.

FOR CLASS 12TH PASSED STUDENTS

For a normal class 12th student the schedule remains more or less the same as written above. However, this time distribution requires major changes for a class 12th pass student. For them the problem lies in the fact that they have to cover up almost double the syllabus within the same stipulated time. The tentative time distribution for a class 12th pass student is as follows

• **Start date** Either last week of June or first week of July.
• **Finish date**
   (i) For learning phase — By the end of January or mid February (Max).
   (ii) For consolidation phase — By the 3rd week of March (Max).
   (iii) Period for rapid review — Last week of March + Days of April till exam.

The conclusions drawn from the above time distribution are

1. The learning phase is jam packed as approx. 96 chapters to be covered in 210 days, i.e. 2 days approx. for one chapter.

2. A genuine pace is required right from the beginning so work distribution must be in accordance with the available time span.

3. The consolidation time is also reduced while the work volume is doubled.

4. *The above given charts clearly indicate that the preparation for JEE is easiest for a student if it begins from class 11th (April) and most tedious for a 12th pass out student.*

Step 4 *Matching of Time Availability with Work Volume*
After getting almost accurate time availability and as we already have work volume we can develop a synchronised plan which fulfills all our demands and suits to all needs.

The procedure requires calenderwise allotment of work and can be moulded month wise, week wise or day wise. A sample of week wise such a work distribution is given below. Accordingly, you can also prepare the same for yourself and it can easily change into month wise or day wise pattern.

The week wise study planner for the learning phase targeting towards JEE 2017 can be

1st week	Stoichiometry
2nd week	Stoichiometry, Solutions
3rd week	Solutions, Solid State
4th week	Solid State, Chemical Kinetics
5th week	Chemical Kinetics
6th week	Chemical Thermodynamics
7th week	Chemical Thermodynamics, Electrochemistry
8th week	Electrochemistry, Surface Chemistry
9th week	Atomic Structure
10th week	Nuclear Chemistry, Chemical bonding
11th week	Chemical Bonding
12th week	Nomenclature of Organic Compounds
13th week	Isomerism
14th week	General Organic Chemistry
15th week	General Organic Chemistry, Hydrocarbons
16th week	Hydrocarbons, Alkyl halides
17th week	Aryl Halides
18th week	Alcohols, Phenols, Ethers
19th week	Aldehydes, Ketones
20th week	Carboxylic Acids and Its Derivative
21st week	Organic Compounds Containing Nitrogen
22nd week	Polymers, s-Block Elements
23rd week	s-Block Elements, p-Block Elements
24th week	p-Block Elements
25th week	p-Block Elements, Transition Elements
26th week	Transition Elements
27th week	Coordination Compounds, Analytical Chemistry
28th week	Gaseous State
29th week	Chemical Equilibrium
30th week	Chemistry : Ionic Equilibrium

MENTORS ADVICE

1. In general chemistry, **Stoichiometry**, **Photoelectric effect, Bohr's model, Hydrogen spectrum, quantum numbers, Periodic properties, Hybridisation, VSEPR theory, Dipole moment, Resonance** and **MOT** are the concepts of importance as most of the direct questions in JEE are asked from these concepts frequently. Remember all of these topics belong to class 11th syllabus and the approximate coverage of this portion in JEE reaches to approximately 15%.

2. *For stoichiometric calculations develop your own shot cuts, and it is also suggestive to use approximation technique in calculations to save time.* Atomic structure has overlapping with the Modern physics portion of Physics so in depth study of this portion will prove very helpful in gripping the Modern Physics portion as well.

3. Physical chemistry has many similarities with physics in nature, so, take physics like approach to capture this portion of chemistry.

4. The topics of interest are **gas laws and gas equation especially van der Waals' modification, concept of entropy, Gibbs free energy**, various enthalpy related problems in connection with chemical equations, Le **chatelier principle, solubility product, common ion effect, pH, buffers, salt hydrolysis and its applications, electrochemical series and its applications, electrochemical cells, Nernst equation and batteries (especially corrosion).**

5. Direct questions can be easily framed on these topics. Some questions of mixed nature are also seen. For topics mentioned above learning with direct solved examples will be beneficial.

6. It is advisable to take electrochemistry with redox as latter is helpful in understanding the former. Try to develop direct formulas for solubility product, pH, and salt hydrolysis to save time.

7. Inorganic chemistry is very vast and requires picturisation technique to capture, i.e. repeated readings (without memorisation) are required to capture the topics.

8. The topics of special interest are H_2O_2, **s-block elements** (especially Li, Na, K, Be, Mg and Ca) and their compounds, among **p-block B, C, N, O, F, P, S, Cl** and **Xe** with especial reference to **oxy acids of N, P, S, Inter halogen compounds** and compounds of Xe.

9. The emphasis must be laid on the structures in case of oxy acids and compounds of Xe.

10. The study about compounds like NH_3, HNO_3, H_2SO_4, H_3PO_4 from properties point of view is very important.

11. In case of HNO_3 emphasise more on type of nitrogen oxide or related product formed during the reaction rather than the oxidation product.

12. Elements of 2nd period are called naughty elements as all of these show different properties than the fellow members of their group due to their small size. Most of the questions framed and asked on these elements only.

13. Questions on **Boron** are very frequent.

14. The other topics of special interest in physical and inorganic chemistry are **solid state**, **colligative properties**, **chemical kinetics** with special emphasis on **order and molecularity of reactions, pseudounimolecular reactions, radioactivity in relation to chemical kinetics, catalysis in general, colloidal state, lanthanide contraction, variable oxidation states in transition elements, nomenclature and Isomerism in coordination compounds, VBT** and **CFT in coordination compounds.**

15. In organic chemistry, initial chapters are the fundamental chapters of this segment. **IUPAC nomenclature** and **electron displacement in a molecule** gives idea of structures of organic compounds, while Isomerism indicates the relationship between the structure and the reactions of organic compounds. The exposure to type of organic reactions is required then to develop the complete logic.

16. The chapters of utmost importance are **Hydrocarbons** and **Aldehydes** and **Ketones**.

17. The chapters of moderate importance are **halogen compounds**, Alcohol, Phenol and **Ethers**, **Carboxylic acids** and their derivatives and **Nitrogen compounds**. Questions on trends in the acidic and basic strength are frequently asked.

18. Chapters like Biomolecules, Polymers and Chemistry in every day life although look unimportant but every year 1-2 questions each from these chapters are visible in JEE and other competitions. Hence a proper capturing of these chapters is also essential.

REMEMBER!

1. Flexibility is the prime feature of this action plan. If your daily targets or weekly targets are fixed then the number of hours of study becomes immaterial.

2. Close monitoring along with regular adjustments are required while executing the action plan.

3. *As the plan is based on **self-pressure creation technique** so each time your failing in hitting the target will automatically builts pressure over you.*

4. Select one person who is going to stay with you all throughout your preparation as your mentor. He / She can be your senior, teacher, parents relative, friends or any other person, who understand the importance of JEE in your life. Discuss all your plans, progress and status of study with your mentor regularly and take advice for improvement from time to time.

5. Remove the fear of mistakes from your mind. Remember mistakes are the best teachers. Mistakes are helpful in eliminating wrong paths and guide you towards the right path. With fewer mistakes you also have few chances of finding the right path to new skills and ideas. *For proper making and execution of action plan, it is very important that you must do mistakes, identify them and then* rectify them with your abilities. Regarding mistakes it is rightly said by **Thomas A. Edison**

"I haven't failed. I've found 10,000 ways that don't work"

CHEMISTRY
CONCENTRATE
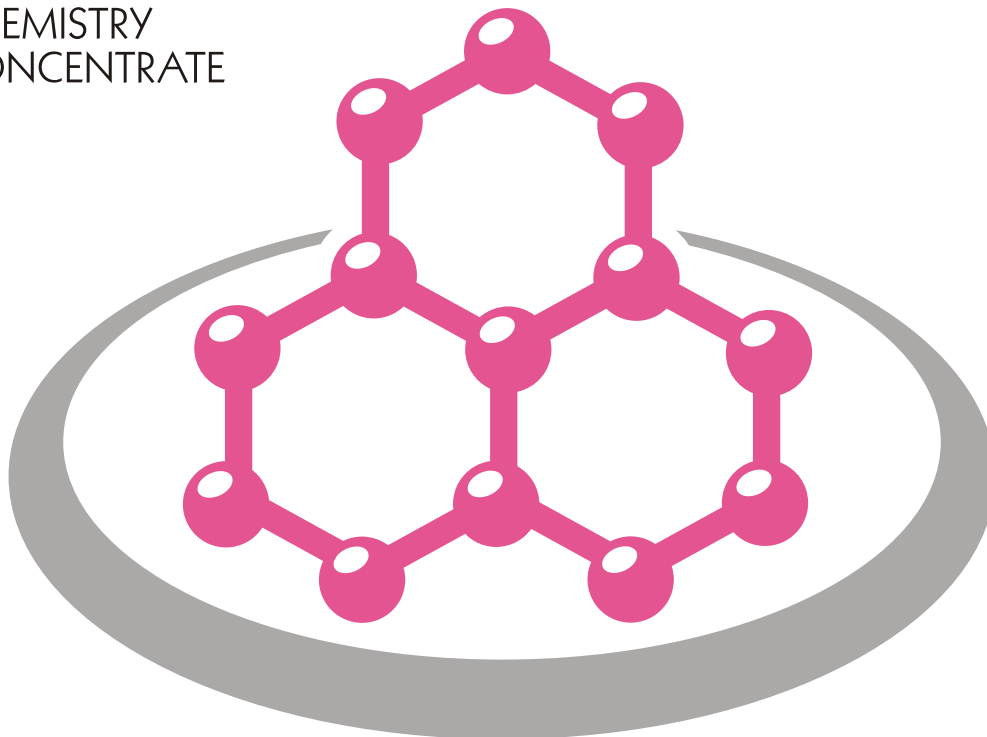
ATOMIC SPHERE IN
QUANTUM MECHANICAL VIEW

Bohr's theory for the structure of hydrogen atom was highly successful. This success soon led to extend the same model to more complex atoms by him and others. However, that line spectra for elements other than hydrogen atom had more lines that could not be explained by the simple Bohr's model. Thus, totally different approach was needed to explain behaviour of electron in atoms or ions with more than one electron.

de-Broglie Concept

- In the direction of finding solution to the problems related to structure of elements having more than one electron, Louis de-Broglie posed the revolutionary question : If light can be viewed in terms of both wave and particle properties, why can't particles of matter, such as electron, be treated the same way?

- In few years de-Broglie's postulate was confirmed experimentally. This led to the development of a whole new discipline, first called wave mechanics, more commonly known today as *quantum mechanics*.

- de-Broglie's suggestion can be explained by combining Planck's quantum theory $(E = h\nu)$ with Einstein's mass-energy equation $(E = mc^2)$

$$E = h\nu = \frac{hc}{\lambda} \qquad \qquad \ldots(i)$$

$$E = mc^2 \qquad \qquad \ldots(ii)$$

From Eqs. (i) and (ii), we get

$$\frac{hc}{\lambda} = mc^2$$

or
$$\lambda = \frac{h}{mc} = \frac{h}{p}$$

$$= \frac{h}{\sqrt{2m(KE)}}; \qquad (KE = \text{Kinetic energy})$$

where, kinetic energy $(KE) = \dfrac{p^2}{2m}$

$$\Rightarrow \qquad p = \sqrt{2m(KE)}$$

CHEMISTRY CONCENTRATE

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de-Broglie Vs charged particles and gaseous molecules

- For a gas molecule, $\lambda = \dfrac{h}{mv_{rms}} = \dfrac{h}{\sqrt{3mkT}}$ $\qquad \left[v_{rms} = \sqrt{\dfrac{3kT}{m}} \right]$

  or $\qquad\qquad \lambda = \dfrac{h}{\sqrt{2m(KE)}}$ $\qquad \left[\because KE = \dfrac{3}{2}kT \right]$

  where, m = mass of gas molecule,
  $\quad v_{rms}$ = root mean square velocity of gas molecule
  $\quad k$ = Boltzmann constant
  $\quad T$ = Temperature of gas in kelvin

- For charged particle, $KE = \dfrac{1}{2}mv^2 = qV$ $\qquad$ …(i)

  where, q and V are charge and potential of charged particle, respectively.

  From Eq. (i), $\quad \dfrac{1}{2}\dfrac{m^2v^2}{m} = qV \quad$ or $\quad \dfrac{1}{2}\cdot\dfrac{p^2}{m} = qV \qquad [\because p = mv]$

  or $\qquad\qquad p = \sqrt{2mqV}$ or $\lambda = \dfrac{h}{p} = \dfrac{h}{\sqrt{2mqV}}$

  Note Particles with very small sizes such as electron or photon have measurable wavelengths while that of large sizes such as cricket ball have wavelengths too short to be observed.

Example ❶ If an electron is moving with a velocity 10^{10} cm s^{-1}, calculate its corresponding wavelength.

(a) 7.27×10^{-10} cm $\qquad$ (b) 7.27×10^{-12} cm
(c) 7.27×10^{-8} cm $\qquad$ (d) 7.27×10^{-9} cm

Sol. (a) Velocity of electron = 10^{10} cm s^{-1}

Mass of the electron = 9.1×10^{-28} g

Planck's constant, $h = 6.62 \times 10^{-27}$ erg-s

Now, according to de-Broglie equation,

$$\lambda = \frac{h}{mv} = \frac{6.62 \times 10^{-27}}{9.10 \times 10^{-28} \times 10^{10}} = 7.27 \times 10^{-10} \text{ cm}$$

Example ❷ Determine the de-Broglie wavelength (Å) associated with He atom at 500 K.

(a) 0.123 Å $\qquad$ (b) 0.565 Å
(c) 0.456 Å $\qquad$ (d) 0.759 Å

Sol. (b) For a gaseous atom, $v_{rms} = \sqrt{\dfrac{3RT}{M}} = \sqrt{\dfrac{3 \times 8.314 \times 500}{4 \times 10^{-3}}}$

$$= 1766 \text{ ms}^{-1}$$

Mass of He atom = $\dfrac{4 \times 10^{-3}}{6.023 \times 10^{23}}$

$$= 6.64 \times 10^{-27} \text{ kg}$$

$\therefore$ de-Broglie wavelength $(\lambda) = \dfrac{h}{mv}$

$$= \frac{6.626 \times 10^{-34}}{6.64 \times 10^{-27} \times 1766}$$

$$= 5.65 \times 10^{-11} \text{ m} = 0.565 \text{ Å}$$

Example ❸ Calculate the wavelength associated with an electron accelerated from rest by a potential of 10000 volt.

(a) 0.456 Å $\qquad$ (b) 0.223 Å
(c) 0.123 Å $\qquad$ (d) 0.789 Å

Sol. (c) As, $\lambda = \dfrac{h}{mv} = \dfrac{h}{\sqrt{2m(KE)}}$

or $\qquad mv = \sqrt{2m(KE)} = \sqrt{2\,meV}$

$$\sqrt{2mev} = \sqrt{2 \times 9.1 \times 10^{-31} \times 1.6 \times 10^{-19} \times 10000}$$

$$= 5.396 \times 10^{-23} \text{ kg m s}^{-1}$$

$\therefore \qquad \lambda = \dfrac{h}{mv} = \dfrac{6.63 \times 10^{-34} \text{ Js}}{5.396 \times 10^{-23} \text{ kg ms}^{-1}}$

$$= 1.23 \times 10^{-11} \text{ m}$$

$$= 0.123 \times 10^{-10} \text{ m}$$

$$= 0.123 \text{ Å}$$

Heisenberg's Uncertainty Principle

- After few years of de-Broglie hypothesis about wave nature of the electron, Werner Heisenberg proposed the **uncertainty principle**.

- Heisenberg uncertainty principle states that, *the exact position and exact velocity (or momentum) of a subatomic particle can not be measured simultaneously*.

- This limitation does not cause any problem for a macroscopic object because the energy of photons used to locate such an object, does not cause any measurable change in the position (momentum) of that object.

- However, the act of measurement would affect the position and momentum of the electron because electron has very small size and mass. High energy photons would be required to locate the small electron; When such photons collide with the electron, the momentum of the electron would be changed. If lower energy photons were used to locate the electron, less effect is obtained on the momentum of the electron.

- Hence, less energised photons are not able to locate the position of an electron precisely.

The uncertainties of position Δx and momentum $(\Delta p = m\Delta v)$ are related as

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

or $\qquad \Delta x \cdot m\Delta v \geq \dfrac{h}{4\pi}$

or $\qquad \Delta x \cdot m \cdot \dfrac{\Delta v}{\Delta t} \cdot \Delta t \geq \dfrac{h}{4\pi}$

or $\qquad \Delta x \cdot m\Delta a \cdot \Delta t \geq \dfrac{h}{4\pi} \quad \left(\dfrac{\Delta v}{\Delta t} = \Delta a, a = \text{acceleration} \right)$

or $\qquad \Delta x \cdot F \cdot \Delta t \geq \dfrac{h}{4\pi} \qquad\qquad (\because F = m \cdot \Delta a)$

or $\quad \Delta E \cdot \Delta t \geq \dfrac{h}{4\pi}$ $\quad (\because \Delta E = F \cdot \Delta x, \ E = \text{Energy})$

Hence, energy can be uncertained for a period given by,

$$\Delta t = \frac{h}{4\pi \Delta E}$$

📝 Teacher's NOTE

In simple terms the representation $\Delta x \cdot \Delta p \geq \dfrac{h}{4\pi}$, signifies that "for smaller entities like electron if we try to judge the position and momentum simultaneously then there must occur a minimum error with the value $\dfrac{h}{4\pi}$."

Example ④ If the uncertainties in position and velocity of a particle are 10^{-10} m and 5.27×10^{-24} m s^{-1} respectively, calculate the mass of the particle.

    (a) 99 g   (b) 60 g
    (c) 50 g   (d) 40 g

Sol. **(a)** According to Heisenberg's uncertainty principle,

$$\Delta x \cdot m \cdot \Delta v \geq \frac{h}{4\pi}$$

or $\quad m = \dfrac{h}{4\pi \Delta x \cdot \Delta v}$

(neglecting greater than (>) sign)

or $\quad m = \dfrac{6.625 \times 10^{-34}}{4 \times 3.143 \times 10^{-10} \times 5.270 \times 10^{-24}}$

$\quad\quad\quad = 0.099$ kg

or $\quad m = 99$ g

Tips to differentiate between quantum and classical mechanical equations of particles

- Mechanics means study of motion for any species.
- The study of motion for very small species or micro species (e.g. electron, photon, gaseos atoms or molecules) is done under the branch, quantum mechanics while the study for motion of larger species or macro species (e.g., ball, car) is done under the branch classical mechanics.
- In order to explain the mechanics of microspecies in quantum mechanics Planck's constant is always introduced to the corresponding quantity equations such as wavelength, $\left(\lambda = \dfrac{h}{p}\right)$, orbital angular momentum $= \left(\dfrac{h}{2\pi} \sqrt{l(l+1)}\right)$, etc.
- In order to explain the mechanics of macrospecies in classical mechanics Planck's constant is omitted as size of particle is large and show too short wavelengths to be observed.
  e.g. Orbital angular momentum for a ball $= mvr$, kinetic energy $\quad\quad = \dfrac{1}{2} mv^2$

Schrödinger Wave Equation

- In 1926, Erwin Schrödinger combined de-Broglie hypothesis with classical equations for wave motion. From these and other ideas he derived a new equation called the *wave equation*.
- The solutions of this wave equation are called *wave functions* and are represented by Greek letter, ψ.
- The wave functions predict the allowed energy states of an electron and probability of finding that electron in a given region of space.
- The wave function has no direct physical meaning. However, the square of wave function, ψ^2, can be represented in three dimensional region of the atom, where an electron with a given energy state is most likely to be found.
- Thus, ψ^2 is probability of finding the electron in a given region of space. This probability is known as *probability density*. If volume is in the multiple of ψ^2, such as $\psi^2 \, dV$, then $\psi^2 dV$ is simply termed as probability of finding an electron within volume dV.
- Solving the Schrödinger wave equation results in a set of wave functions called orbitals. Each orbital contains information about the region of space where an electron of a given energy is most likely located.
- Another way to represent the probability of finding an electron, is to draw a surface within which there is 90% probability that the electron will be found.
- A 100% probability is not choosen because such a surface would not have definite boundary.

Schrödinger Wave Equation in Cartesian Coordinates

- As in classical mechanics, various quantities (energy, momentum etc) correspond to observable properties. Similarly, in quantum mechanics various operators (energy operator, momentum operator) corresponds to observable properties of electron.
- Schrödinger gave a generalised wave equation for an electron using energy operators.

Total energy operator $(\hat{H}) =$ Kinetic energy operator $(\hat{T}) +$ Potential energy operator $(\hat{V})$

or $\quad\quad \hat{H} = \hat{T} + \hat{V}$

or $\quad\quad \hat{H}\psi = \hat{T}\psi + \hat{V}\psi$

$$\underbrace{E\psi}_{\hat{H}} = \underbrace{-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi}_{\hat{T}} + \underbrace{V(x, y, z)\psi}_{\hat{V}}$$

or $\quad \dfrac{\partial^2 \psi}{\partial x^2} + \dfrac{\partial^2 \psi}{\partial y^2} + \dfrac{\partial^2 \psi}{\partial z^2} + \dfrac{8\pi^2 m}{h^2}(E - V)\psi = 0$

▣ CHEMISTRY CONCENTRATE

📝 Teacher's **NOTE**

Simple interpretation of Schrödinger wave equation This equation in very simple terms explains the 3D existence of an atom, i.e. an entity like atom has its existence along the x, y and z-axis. The x, y and z terms shown in the equation signify the same while E and V terms signify energy.

Relationship between Cartesian and Polar Coordinates

• For better results Schrödinger used spherical polar coordinate system (r, θ, φ) rather than cartesian coordinate system (x, y, z).
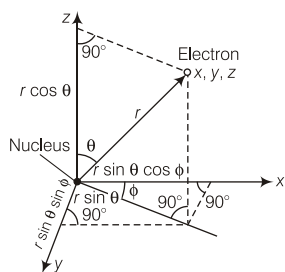
• This is because cartesian coordinate system involves three variables (x, y, z) whereas spherical polar coordinate system can be represented in terms of two functions, R that depends only on r and a second function Y, which depends upon two angles θ and ϕ.

Here, $x = r \sin \theta \cdot \cos \phi$, $y = r \sin \theta \cdot \sin \phi$, $z = r \cos \theta$ and $r^2 = x^2 + y^2 + z^2$

Hence, $\psi (r, \theta, \phi) = R(r) Y(\theta, \phi)$

Here, $R(r)$ = Radial wave function

$Y(\theta, \phi)$ = Angular wave function.

The angular and radial wave function of different orbitals of a H-like species are given below.

Orbital	Angular part $Y(\theta, \phi)$	Radial part $R(r)$
$1s$	$\left(\dfrac{1}{4\pi}\right)^{1/2}$	$2\left(\dfrac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
$2s$	$\left(\dfrac{1}{4\pi}\right)^{1/2}$	$\dfrac{1}{2\sqrt{2}}\left(\dfrac{Z}{a_0}\right)^{3/2}\left(2 - \dfrac{Zr}{a_0}\right)e^{-Zr/2a_0}$
$2p$	$\left(\dfrac{3}{4\pi}\right)^{1/2} \sin \theta \cdot \cos \phi$	$\dfrac{1}{2\sqrt{6}}\left(\dfrac{Zr}{a_0}\right)^{5/2} e^{-Zr/2a_0}$

Here, Z = atomic number of species.

Note Radial wave function depends upon quantum numbers n and l while angular wave function depends upon quantum numbers l and m.

Radial and angular nodes for different orbitals

For an s-orbital, number of nodes = $(n - 1)$ i.e. 1s orbital do not contain any node, 2s orbital contains one node, 3s orbital contains 2 nodes and so on. Infact nodes are of two types, i.e.
 (i) Radial nodes
(ii) Angular nodes

A **radial node** is the spherical region around nucleus where probability of finding an electron is zero as shown in the figure of 2s orbital. Similarly, if such a distribution is seen at an angle from the nucleus, the node is called **angular node.**

Spherical s orbitals symmetrically disposed about the nucleus
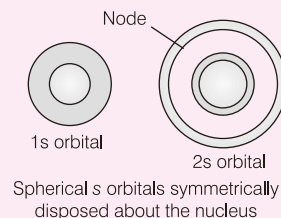
For an orbital, number of nodes are calculated as

Number of radial nodes = $n - l - 1$
Number of angular nodes = l, Total nodes = $n - 1$
For example, in 3p orbitals
Angular node = 1, Radial nodes = $3 - 1 - 1 = 1$
So, total nodes = 2 (one radial, one angular)

## Plots of Radial Probability Function, $R(r)$ *versus* Distance (r) From the Nucleus

(i) **For 1s** ($n = 1, l = 0$)

Conclusion The value of $R(r)$ which is equal to $4\pi r^2 dr \psi^2$, is zero at $r = 0$. Then, it increases as r increases, passes through a maximum (peak) at $r = 0.529$ Å, which is equal to Bohr's first orbit radius. Then, it falls to zero as r tends to infinity. Thus, for 1s electron $R = 0$ at $r = 0$ and R is maximum at $r = 0.529$ Å.
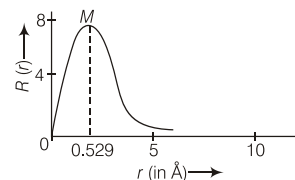

(ii) **For 2s** ($n = 2, l = 0$)

Conclusion The value of $R(r)$ is zero at $r = 0$. The value of $R(r)$ increases as r increases, passes through a maximum at $r = 0.529$ Å and falls to zero again at $r = 1.058$ Å. $R(r)$ reaches at second highest at $r = 5 \times 0.529$ Å and then finally approaches to zero as r tends to infinity. The distance i.e., 1.058 Å at which the probability of finding an electron is zero is called node. Thus, there is a space around nucleus containing nodes known as nodal plane where probability of finding electron is zero.
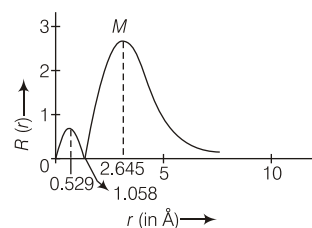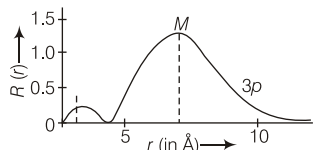

(iii) **For 2p** ($n = 2, l = 1$)

Conclusion The probability of finding the electron at the origin (nucleus) is zero i.e. electron can never be found at the nucleus.
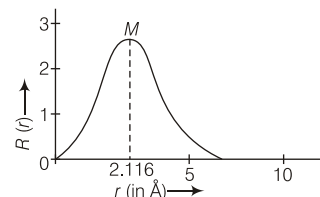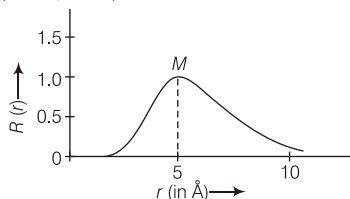
(iv) **For 3s**$(n = 3, l = 0)$
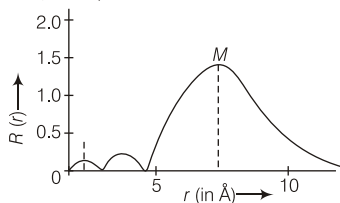
Conclusion The distance for maximum probability in an orbital increases with the value of n (principal quantum number). e.g. $1s < 2s < 3s$.

(v) **For 3p** $(n = 3, l = 1)$

Conclusion It is similar to the graph in case of $2s$-orbitals, but it is more broader than $2s$. Hence, as value of principal quantum number increases, broadness of graph also increases.

(vi) **For 3d** $(n = 3, l = 2)$

Conclusion The total number of peaks for s, p and d orbitals are n, $(n - 1)$ and $(n - 2)$ respectively.

Example 5 P is the probability of finding the $1s$ electron of hydrogen atom in a spherical shell of infinitesimal thickness, dr, at a distance r from the nucleus. The volume of this shell is $4\pi r^2 dr$. The qualitative sketch of the dependence of P on r is **(IIT JEE 2016)**
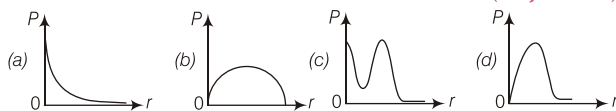
Sol. **(d)** You may go through following steps in order to solve this problem.

Step 1 Write down the formula of probability (P) of finding the $1s$ electron of hydrogen atom in volume $4\pi r^2 dr$ $P = \psi^2(r)4\pi r^2 dr$

Step 2 Put the value of $\psi(r)$ in the above formula
For $1s$ electron radial part of wave function is,

$$\psi(r) = 2\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

$$\therefore \quad P = \left(2\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}\right)^2 4\pi r^2 dr$$

or $$P = 16\pi r^2 \left(\frac{1}{a_0}\right)^3 e^{-2r/a_0} \, dr$$

Step 3 Put different values of r in the expression of p and check which is suitable for these values. In order to easy calculation try to find out the distances where probability becomes zero.

At $r = 0$, $P = 16\pi(0)^2 \times \left(\frac{1}{a_0}\right)^3 e^0 dr = 0$

At $r = \infty$, $P = 16\pi(\infty)^2 \times \left(\frac{1}{a_0}\right)^3 e^{-\infty} dr = 0$

$$\left[\because e^{-\infty} = \frac{1}{e^{\infty}} = \frac{1}{\infty} = 0\right]$$

In option (a), Probability is not zero at $r = 0$. Hence, it is an incorrect option.

In option (b), Probability is zero at $r = 0$ and at some finite value of r. Hence, it is an incorrect option.

In option (c), Probability is not zero at $r = 0$ and it is zero at some finite value of r. Hence, it is an incorrect option.

In option (d), Probability is zero at $r = 0$ and $r = \infty$. Hence, it is correct.

Example 6 The Schrödinger wave equation for $2s$ orbital of hydrogen atom is $\psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2 - \frac{r}{a_0}\right)e^{-r/2a_0}$

where, a_0 is Bohr's radius. Let the radial node in $2s$ be at r_0. Find r in terms of a_0.

(a) $r = a_0$　　　　　　　　(b) $r = 2a_0$

(c) $r = 3a_0$　　　　　　　　(d) $r = \dfrac{a_0}{2}$

Sol. **(b)** The probability of finding electron is zero at radial node. Hence, ψ_{2s}^2 must be zero at $r = r_0$.

$$\psi_{2s}^2 = \left(\frac{1}{4\sqrt{2\pi}}\right)^2\left(\frac{1}{a_0}\right)^3\left(2 - \frac{r_0}{a_0}\right)^2 e^{-r_0/a_0} = 0$$

As $\dfrac{1}{4\sqrt{2\pi}}$ and e^{-r_0/a_0} can not be zero, hence

$$\left(2 - \frac{r_0}{a_0}\right)^2 = 0$$

or $$\frac{r_0}{a_0} = 2$$

or $$r_0 = 2a_0$$

BEYOND HORIZONS

Chemists have successfully married chemistry and biology to create reactions never before possible. They did this by replacing the iron normally found in the muscle protein myoglobin with iridium, a noble metal not known to be used by living systems. The iridium-enhanced myoglobin was then tested and found that it led to a new type of chemical reaction for this protein, the conversion of a carbon-hydrogen bond to a carbon-carbon single bond. The bionic enzyme, an artificial metalloenzyme, was thus capable of catalyzing a reaction for which there is no known natural or engineered enzyme.

◼ CHEMISTRY CONCENTRATE

Quantum Numbers

When Schrödinger and others were doing calculations related to quantum mechanics, they found a set of three integers, called quantum numbers-principal quantum number (n), azimuthal quantum number (l) and magnetic quantum number (m_l). The need for a fourth quantum number, spin quantum number (m_s), was identified in subsequent work by others. Thus, a set of four quantum numbers, n, l, m_l and m_s, is used to denote the energy and the shape of the electron cloud for each electron.

Principal quantum number (n)	Azimuthal quantum number (l)	Magnetic quantum number (m_l)	Spin quantum number (m_s)
First Bohr described the quantisation of energy of an electron in an atom in terms of n as $mvr = \dfrac{nh}{2\pi}$ Here, $n = 1, 2, 3...$	First, Sommerfeld described motion of an electron in an elliptical path within an atom in terms of l as $mvr = \dfrac{h}{2\pi}\sqrt{l(l+1)}$	m_l describes degree of freedom of electrons i.e orientation of electrons in three-dimensional space, particularly under the influence of applied magnetic field.	In a magnetic field, electron behaves as if it was spinning rapidly about its own axis. This conclusion is reached as a result of the discovery that the electron itself, is a tiny magnet, the magnetic field being due to its apparent spin about its own axis as shown below. fig. Electron axis with clockwise spin / Electron with anticlockwise spin ←spinning→
The values of n for a circular orbit indicates roughly the binding force and distance between electron and nucleus. Hence, n represents the size of orbit.	According to this modification, the electrons in any particular energy levels could have either a circular path or a variety of elliptical paths about the nucleus.	The splitting of spectral lines of a source in a strong magnetic field was first studied by Zeeman and therefore known as Zeeman effect. This phenomenon indicates that energy levels get split when the emitting atoms are placed in a strong magnetic field.	The spin quantum number m_s can have two values either $+\dfrac{1}{2}$ or $-\dfrac{1}{2}$. These values do not denote any specific direction i.e. $+\dfrac{1}{2}$ or $-\dfrac{1}{2}$ may be assigned to either direction of spin i.e. clockwise or anticlockwise.
Size and energy of orbit increases as the value of n increases.	For a given value of n the possible values of the angular or azimuthal quantum number l are 0, 1, 2, … $(n-1)$ for e.g., $n = 2; l = 0, 1$	Mathematically, $mvr = \dfrac{m_l}{2\pi}$	Mathematically, $m_s = \sqrt{s(s+1)}\dfrac{h}{2\pi}$
$n \to 1\ 2\ 3\ 4$ Letter designation $\to$ K L M N Maximum no. of electrons $(2n^2) \to 2\ 8\ 18\ 32$		The value of m_l for a given value of l are $-l, … 0, … +l$ e.g., $l = 2; m_l = -2, -1, 0, 1, 2$ Total possible values of $m_l = 2l+1$	
The value of n predicts the number of peaks of amplitude in a standing wave pattern of electron. The more peaks there are, the higher are the energies of that state.	In modern terminology, each value of l denotes a specific orbital designation by orbitals s, p, d, f, g etc. e.g. $l = 0 \to s$-orbital; $l = 1 \to p$-orbital $l = 3 \to d$-orbital; $l = 4 \to f$-orbital	If m_l has positive value, means orbital angular momentum component is in the direction of applied magnetic field and vice-versa.	If we assign $+\dfrac{1}{2}$ to clockwise. Direction $-\dfrac{1}{2}$ is automatically assigned to anticlockwise direction.
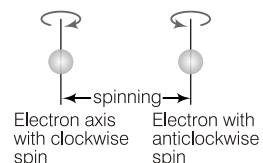
Example 7 Which of the following sets of quantum number is not possible ?

(a) $n = 4, l = 1, m = 0, s = +\dfrac{1}{2}$ (b) $n = 4, l = 3, m = -3, s = -\dfrac{1}{2}$

(c) $n = 4, l = 0, m = 0, s = -\dfrac{1}{2}$ (d) $n = 4, l = 1, m = +2, s = -\dfrac{1}{2}$

Sol. **(d)** m has values $-l$ to $+l$ including zero. Thus, if $l = 1$, the possible values m are $-1, 0$ and $+1$ but not $+2$ as given in set (d). Thus, set (d) is not possible.

Example 8 The correct set of four quantum number for the valence electrons of rubidium atom ($Z = 37$) is **[JEE Main 2013]**

(a) $5, 0, 0, +\dfrac{1}{2}$ (b) $5, 1, 0, +\dfrac{1}{2}$

(c) $5, 1, 1, +\dfrac{1}{2}$ (d) $5, 0, 1, +\dfrac{1}{2}$

Sol. **(a)** Rb (37) = [Kr], $5s^1$

Since, the last electron or valence electron enters in $5s$-subshell therefore quantum numbers are; $n = 5, l = 0$ (for s-orbital) $m = 0$

$(\because m_l = -l$ to $+l)$, $m_s = +\dfrac{1}{2}$ or $-\dfrac{1}{2}$

Smart Practice

1. A stream of electrons from a heated filament was passed between two charged plates kept at a potential difference V esu. If e and m are charge and mass of an electron, respectively, then the value of $\dfrac{h}{\lambda}$ (where, λ is wavelength associated with electron wave) is given by **[JEE Main 2016]**

(a) $2\,meV$
(b) $\sqrt{meV}$
(c) $\sqrt{2\,meV}$
(d) meV

2. The number of radial nodes in $3s$ and $2p$ respectively are **[JEE Main 2005]**

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

3. Which of the following particles moving with same velocity would be associated with smallest de-Broglie wavelength?

(a) Helium molecule
(b) Oxygen molecule
(c) Hydrogen molecule
(d) Carbon molecule

4. Which of the following radial distribution graphs correspond to $n = 3, l = 2$ for an atom?
$(R(r) = 4\pi r^2\, dr\ \psi^2)$

(a) $R\,(r)$
(b) $R\,(r)$
(c) $R\,(r)$
(d) $R\,(r)$
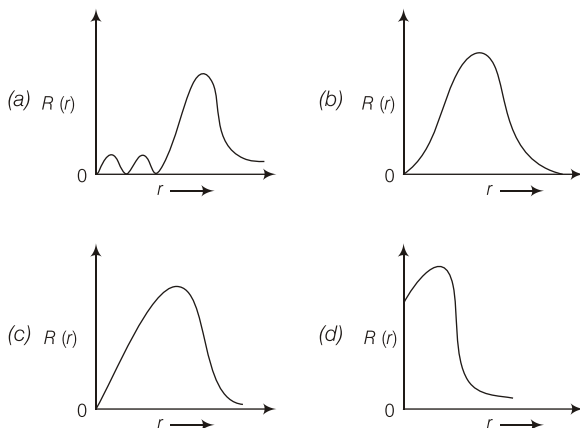
5. The quantum numbers $+\dfrac{1}{2}$ and $-\dfrac{1}{2}$ for two electron represent

(a) rotation of electrons in clockwise and anticlockwise direction respectively
(b) rotation of electrons in anticlockwise and clockwise direction respectively
(c) Two quantum mechanical spin states which have no classical analogue
(d) Magnetic moment of electron pointing up and down respectively

6. For an electron in hydrogen atom, the wave function ψ is proportional to e^{-t/a_0}, where a_0 is the Bohr's radius. What is the ratio of the probability of finding the electron at the nucleus to the probability of finding it at a_0?

(a) e
(b) e^2
(c) $\dfrac{1}{e^2}$
(d) Zero

7. A particle A moving with a certain velocity has the de-Broglie wavelength equals to 1Å. For particle B with 25% mass of A and 75% velocity of A, calculate de-Broglie wavelength.

(a) 3 Å
(b) 5.33 Å
(c) 6.88 Å
(d) 0.48 Å

8. The uncertainty in position of an electron $(m = 9.1 \times 10^{-28}\,g)$ moving with a velocity 3×10^4 cm/s accurate upto 0.001% will be

(a) 3.84 cm
(b) 1.92 cm
(d) 7.68 cm
(d) 5.76 cm

9. The radial wave equation for hydrogen atom is given as : $\psi = \dfrac{1}{16\sqrt{4}}\left(\dfrac{1}{a_0}\right)^{3/2}[(x-1)\,(x^2 - 8x + 12)]_e^{-x/2}$ where, $x = \dfrac{2r}{a_0}$; $a_0 = $ radius of first Bohr orbit.

The minimum and maximum position of radial nodes from nucleus are

(a) $a_0, 3a_0$
(b) $\dfrac{a_0}{2}, 3a_0$
(d) $\dfrac{a_0}{2}, a_0$
(d) $\dfrac{a_0}{2}, 4a_0$

10. Calculate the uncertainty in velocity of a cricket ball of mass 150 g if the uncertainty in its position is of the order of 1 Å ($h = 6.6 \times 10^{-34}$ kg-m^{2}s^{-1})

(a) 3.499×10^{-24} m/s
(b) 5.029×10^{-23} m/s
(c) 3.499×10^{-25} m/s
(d) 5.029×10^{-22} m/s

Answers with Explanation

1. **(c) Strategy** *As you can see in options, kinetic energy (eV) term is given, and we have to find out relation between $\dfrac{h}{\lambda}$ and energy. For this, we shall use de-Broglie wavelength (λ) and kinetic energy term in eV.*

$$\lambda = \frac{h}{p} \text{ or } p = \frac{h}{\lambda} \qquad \ldots(i)$$

Kinetic energy $= \dfrac{p^2}{2m}$

$\Rightarrow \qquad eV = \dfrac{p^2}{2m}$

or $\qquad p = \sqrt{2meV} \qquad \ldots(ii)$

From Eq. (i) and (ii), we get

$$\frac{h}{\lambda} = \sqrt{2meV}$$

2. **(a)** The number of radial nodes is given by expression $(n - l - 1)$

Where, $n =$ Principal quantum number

$l =$ Azimuthal quantum number

For $3s$, Number of radial nodes $= 3 - 0 - 1 = 2$

For $2p$, Number of radial nodes $= 2 - 1 - 1 = 0$

3. **(b)** According to de-Broglie,

$$\lambda = \frac{h}{mv}$$

or $\qquad \lambda \propto \dfrac{1}{m} \qquad$ (If $v =$ constant)

Hence, the larger mass will be associated with smaller de-Broglie wavelength.

Species	Mass
Helium molecule	$4\ \text{g mol}^{-1}$
Oxygen molecule	$32\ \text{g mol}^{-1}$
Hydrogen molecule	$2\ \text{g mol}^{-1}$
Carbon molecule	$24\ \text{g mol}^{-1}$

As oxygen molecule has largest mass, hence, will show smallest de-Broglie wavelength.

4. **(c)** For $n = 3, l = 2$; Subshell will be $3d$, Hence, correct option will be (c).

5. **(c)** Spins of electron $\left(\text{either} +\dfrac{1}{2} \text{or} +\dfrac{1}{2}\right)$ produce angular momentum equal to Z-component of angular momentum which is given as $m_s\left(\dfrac{h}{2\pi}\right)$.

6. **(d)** $\psi \propto e^{-t/a_0}$ or $\psi = Ke^{-t/a_0}$

Let probability of finding the electron at a_0 i.e. at Bohr's radius $= x$

As we know that probability of finding an electron at nucleus is always zero.

Hence ratio $= \dfrac{0}{x} = 0$ (except $x = 0$)

7. **(b)** Given, $\lambda_A = 1\,\text{Å}$

Mass of B $(M_B) = 25\%$ of A

Velocity of B $(v_B) = 75\%$ of A

Let velocity and mass of A are 100 units for each thus,

$$M_B = 25\,\text{units}$$
$$v_B = 75\,\text{units}$$
$$\lambda_A = \frac{h}{m_A v_A}$$

and $\qquad \lambda_B = \dfrac{h}{m_B v_B}$

$$\frac{\lambda_A}{\lambda_B} = \frac{m_B v_B}{m_A v_A}$$

$$\frac{1 \times 10^{-10}}{\lambda_B} = \frac{m_A \times 3v_A}{m_A \times 4 \times v_A \times 4}$$

$$\lambda_B = \frac{16 \times 10^{-10}}{3} = 5.33\,\text{Å}$$

8. **(b)** Uncertainty in velocity

$$(\Delta v) = 3 \times 10^4 \times \frac{0.001}{100} = 0.3\,\text{cm/s}$$

$$\Delta x \cdot \Delta v = \frac{h}{4\pi m} = \frac{6.6 \times 10^{-27}}{4 \times 3.14 \times 9.1 \times 10^{-28}}$$

or $\qquad \Delta x = \dfrac{6.6 \times 10^{-27}}{4 \times 3.14 \times 9.1 \times 10^{-28} \times 0.3} = 1.92\,\text{cm}$

9. **(b)** At radial node, $\psi = 0$

$\therefore \qquad \dfrac{1}{16\sqrt{4}}\left(\dfrac{1}{a_0}\right)^{3/2}[(x-1)(x^2 - 8x + 12)]e^{-\frac{x}{2}} = 0$

$\because \qquad \dfrac{1}{16\sqrt{4}}\left(\dfrac{1}{a_0}\right)^{3/2} e^{-\frac{x}{2}} \neq 0$

$\therefore \qquad (x - 1)(x^2 - 8x + 12) = 0$

When $x - 1 = 0$

$$x = 1$$

i.e. $\qquad \dfrac{2r}{a_0} = 1;\ \ r = \dfrac{a_0}{2} \qquad$ (Minimum)

When $\qquad x^2 - 8x + 12 = 0$

$$(x - 6)(x - 2) = 0$$
$$x - 2 = 0$$

$\dfrac{2r}{a_0} = 2$ i.e. $r = a_0 \qquad$ (Middle)

$$x - 6 = 0$$
$$x = 6$$
$$\frac{2r}{a_0} = 6$$

or $\qquad r = 3a_0 \qquad$ (Maximum)

10. **(a)** Given, $m = 150\,\text{g} = 0.150\,\text{kg}$

$$\Delta x = 1\,\text{Å} = 10^{-10}\,\text{m}$$
$$\Delta x \cdot m \cdot \Delta v = \frac{h}{4\pi}$$

or $\qquad \Delta v = \dfrac{h}{4\pi \cdot \Delta x \cdot m}$

$$= \frac{6.6 \times 10^{-34}}{4 \times 3.143 \times 10^{-10} \times 0.150}$$

$$= 3.499 \times 10^{-24}\,\text{ms}^{-1}$$

▣ EXAM SPECTRUM

JEE Advanced 2016
PAPER 1 (Online)
FULLY SOLVED

── SECTION 1 (MM : 15) ──

- This section contains **FIVE** questions.
- Each question has **FOUR** options (a), (b), (c) and (d). Only one of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in one of the following categories.
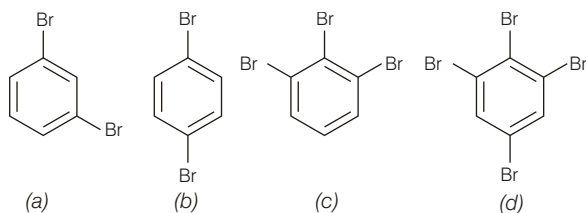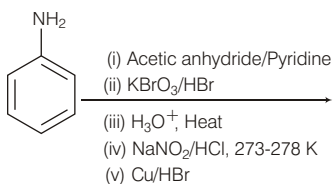 Full Marks : + 3, If only the bubble corresponding to the correct option is darkened.
  Zero Marks : 0, If none of the bubbles is darkened.
  Negative Marks : − 1, In all other cases.

EXAM CRUX

- There were total 36 questions asked in JEE Advanced 2016 paper from paper-1 and paper-2. Out of 18 questions, 4 questions were numerical based while 14 questions were theory based. Overall paper was quite tough and need a good knowledge of subject to solve.
- According to chapterwise distribution, number of questions were asked as:

From Class XI

- Structure of Atom-2Qs, Periodic Properties-1Q, Chemical Bonding-1Q The p-block elements 1Q.
- State of Matter-1Q, Thermodynamics-1Q, Redox Reactions-1Q, Some basic principles and Techniques and Hydrocarbons 2Qs.

From Class XII

- General Principles and Processes of Isolation of Elements-1Q, Aldehydes, Ketones and Carboxylic Acids-2Qs. Coordination Compounds-2Qs, Chemical Kinetics-1Q, Solutions-1Q, Amines-1Q and Polymers-1Q.
- Thus, approx-44% of paper came from Class XI and 56% from Class XII.
- Out of which 18 questions were asked in paper 1.
- Maximum questions were asked from Physical and Inorganic Chemistry rather than organic Chemistry in this paper.

Difficulty Level

- Around 55% of questions can be considered as tough; 25% were relatively moderate and 20% are considered easy by the Arihant team. Overall, this year paper was tough as compare to previous year paper.

1. P is the probability of finding the 1s electron of hydrogen atom in a spherical shell of infinitesimal thickness, dr, at a distance r from the nucleus. The volume of this shell is $4\pi r^2 dr$. The qualitative sketch of the dependence of P on r is
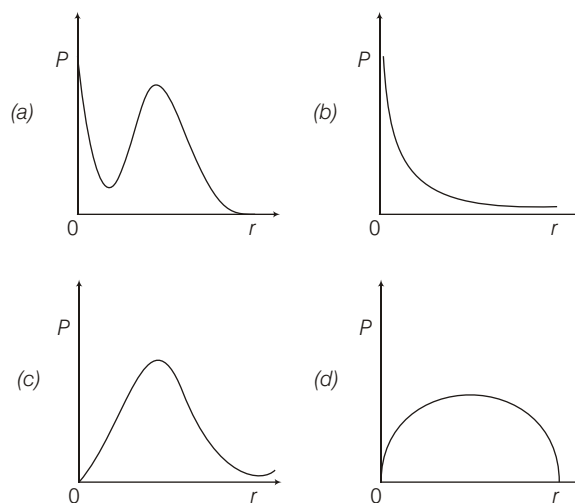
☒ EXAM SPECTRUM

2. One mole of an ideal gas at 300 K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm. In this process, the change in entropy of surroundings (ΔS_{surr}) in JK^{-1} is (1 L atm = 101.3 J)

(a) 5.763　　(b) 1.013　　(c) – 1.013　　(d) – 5.763

3. Among $[Ni(CO)_4]$, $[NiCl_4]^{2-}$, $[Co(NH_3)_4Cl_2]$ Cl, $Na_3[CoF_6]$, Na_2O_2 and CsO_2, the total number of paramagnetic compounds is

(a) 2　　　(b) 3　　　(c) 4　　　(d) 5

4. The increasing order of atomic radii of the following group 13 elements is

(a) Al < Ga < In < Tl　　(b) Ga < Al < In < Tl
(c) Al < In < Ga < Tl　　(d) Al < Ga < Tl < In

5. On complete hydrogenation, natural rubber produces

(a) ethylene-propylene copolymer
(b) vulcanised rubber
(c) polypropylene
(d) polybutylene

─ SECTION 2 (MM : 32) ─

- This section contains **EIGHT** questions.
- Each question has **FOUR** options (a), (b), (c) and (d). **ONE OR MORE THAN ONE** of these four options is (are) correct.
- For each question, darken the bubble(s) corresponding to all the correct option(s) in the ORS.
- For each question, marks will be awarded in **one of the following categories**:
  Full Marks　　: + 4, If only the bubble(s) corresponding to all the correct option(s) is (are) darkened.
  Partial Marks　: + 1, For darkening a bubble corresponding **to each correct option** provided **NO** incorrect option is darkened.
  Zero Marks　　:　0, If none of the bubbles is darkened.
  Negative Marks　: − 2, In all other cases.
  For example, if (a), (c) and (d) are all the correct options for a question, darkening all these three will result in + 4 marks; darkening only (a) and (d) will result in + 2 marks; and darkening (a) and (b) will result in − 2 marks, as a wrong option is also darkened.

6. The product(s) of the following reaction sequence is (are)

(i) Acetic anhydride/Pyridine
(ii) KBrO_3/HBr
(iii) H_3O^+, Heat
(iv) NaNO_2/HCl, 273-278 K
(v) Cu/HBr

(a)　　　(b)　　　(c)　　　(d)

7. The correct statement(s) about the following reaction sequence is (are)

Cumene (C_9H_{12}) $\xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } O_2}$ P $\xrightarrow{CHCl_3/NaOH}$

Q (major) + R (minor), Q $\xrightarrow[PhCH_2Br]{NaOH}$ S
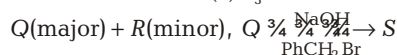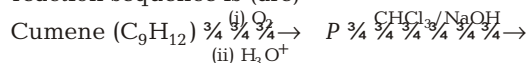
(a) R is steam volatile
(b) Q gives dark violet colouration with 1% aqueous FeCl_3 solution
(c) S gives yellow precipitate with 2, 4-dinitrophenylhydrazine
(d) S gives dark violet colouration with 1% aqueous FeCl_3 solution

8. The crystalline form of borax has

(a) tetranuclear $[B_4O_5(OH)_4]^{2-}$ unit
(b) all boron atoms in the same plane
(c) equal number of sp^2 and sp^3 hybridised boron atoms
(d) one terminal hydroxide per boron atom

9. The reagent(s) that can selectively precipitate S^{2-} from a mixture of S^{2-} and SO_4^{2-} in aqueous solution is (are)

(a) CuCl_2　　　　　(b) BaCl_2
(c) Pb(OOCCH_3)_2　(d) Na_2[Fe(CN)_5NO]

10. A plot of the number of neutrons (n) against the number of protons (p) of stable nuclei exhibits upward deviation from linearity for atomic number, $Z > 20$. For an unstable nucleus having n/p ratio less than 1, the possible mode(s) of decay is (are)

(a) β^- - decay (β - emission)
(b) orbital or K-electron capture
(c) neutron emission
(d) β^+ - decay (positron emission)

11. Positive Tollen's test is observed for

(a)　　　(b)　　　(c)　　　(d)
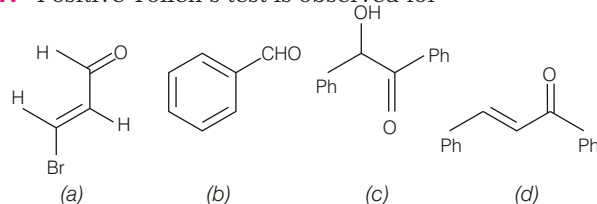
12. The compound(s) with two lone pairs of electrons on the central atom is (are)

(a) BrF_5 (b) ClF_3 (c) XeF_4 (d) SF_4

13. According to the Arrhenius equation

(a) a high activation energy usually implies a fast reaction

(b) rate constant increases with increase in temperature. This is due to a greater number of collisions whose energy exceeds the activation energy

(c) higher the magnitude of activation energy, stronger is the temperature dependence of the rate constant

(d) the pre-exponential factor is a measure of the rate at which collisions occur, irrespective of their energy

SECTION 3 (MM : 15)

- This section contains **FIVE** questions.
- The answer to each question is a **SINGLE DIGIT INTEGER** ranging from 0 to 9, both inclusive.
- For each question, darken the bubble corresponding to the correct integer in the ORS.
- For each question, marks will be awarded in **one of the following categories**:
  Full Marks   : +3, If only the bubble corresponding to the correct answer is darkened.
  Zero marks   : 0, In all other cases.

14. In the following monobromination reaction, the number of possible chiral product(s) is (are)...

$CH_2CH_2CH_3$

H —— Br $\xrightarrow[300^\circ C]{Br_2 \text{ (1.0 mole)}}$

CH_3

(1.0 mole) (Enantiomerically pure)
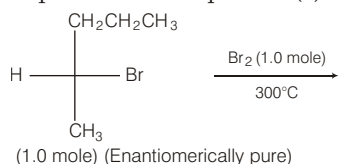
15. The mole fraction of a solute in a solution is 0.1. At 298 K, molarity of this solution is the same as its molality. Density of this solution at 298 K is 2.0 g cm^{-3}. The ratio of the molecular weights of the solute and solvent, $\left(\dfrac{m_{solute}}{m_{solvent}}\right)$ is ... .

16. The possible number of geometrical isomers for the complex $[CoL_2Cl_2]^-$ ($L = H_2NCH_2CH_2O^-$) is (are) ...

17. In neutral or faintly alkaline solution, 8 moles of permanganate anion quantitatively oxidise thiosulphate anions to produce X moles of a sulphur containing product. The magnitude of X is ... .

18. The diffusion coefficient of an ideal gas is proportional to its mean free path and mean speed. The absolute temperature of an ideal gas is increased 4 times and its pressure is increased 2 times. As a result, the diffusion coefficient of this gas increases x times. The value of x is ...
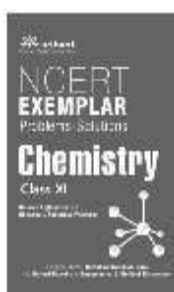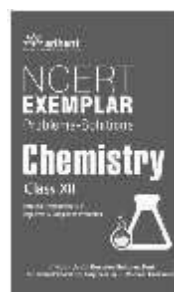
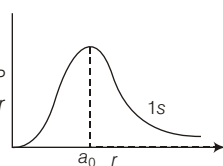# Answers with Explanation

1. *(c)* For 1s electron, radial part of the wave function is given as,

$$\psi(r) = 2 \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

$$\therefore\ P = (\psi(r))^2 4\pi r^2 dr = 16\pi r^2 \left(\frac{1}{a_0}\right)^3 e^{\frac{-2r}{a_0}} dr$$

At $r = 0$, $P = 16\pi(0)^2 \times \left(\frac{1}{a_0}\right)^3 e^0 dr = 0$

At $r = \infty$, $P = 16\pi(\infty)^2 \times \left(\frac{1}{a_0}\right)^3 e^{-\infty} dr = 0$ $[\because e^{-\infty} = 0]$

Hence, graph (c) is correct.

This graph shows the probability of finding the electron within the shell at various distances from the nucleus (radial probability).

The maximum peak of the curve shows maximum radial probability of finding an electron for a given distance from the nucleus. This distance is equal to Bohr's radius (a_0).

2. *(c)* **Key Concept** *For isothermal process, change in internal energy is zero*

i.e. $\Delta U = nC_v\, \Delta T = 0$ [as $\Delta T = T_2 - T_1 = 0$]
By first law of thermodynamics,

$$\Delta E = q + W$$
$$\therefore\quad q = -W$$
$$-q_{irrev} = W_{irrev} = p\Delta V = 3(2-1) = 3\,L\,atm$$

Also, $\Delta S_{surr} = \dfrac{q_{irrev}}{T} = \dfrac{(-3 \times 101.3)\,J}{300\,K} = -\dfrac{303.9\,J}{300\,K}$

$$= -1.013\,JK^{-1}$$

3. *(b)* **Key Concept** Paramagnetic compounds are those compounds that contains atleast one unpaired electron.

Superoxide (O_2^-) is also paramagnetic in nature as it contains one unpaired electron

$$O_2 = \left[:\ddot{O}-\dot{\ddot{O}}:\right]^-\ \text{Unpaired electron}$$

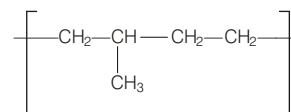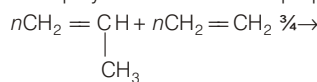| Compound	Hybridisation	Unpaired electron(s)	Magnetic character
$Ni(CO)_4$	sp^3	—	Diamagnetic
$[NiCl_4]^{2-}$	sp^3	2	Paramagnetic
$[Co(NH_3)_4Cl_2]\,Cl$	sp^3d^2	—	Diamagnetic
$Na_3[CoF_6]$	sp^3d^2	3	Paramagnetic
Na_2O_2	—	—	Diamagnetic (O_2^{2-})
CsO_2	—	1	Paramagnetic
			O_2^- (superoxide ion is paramagnetic)

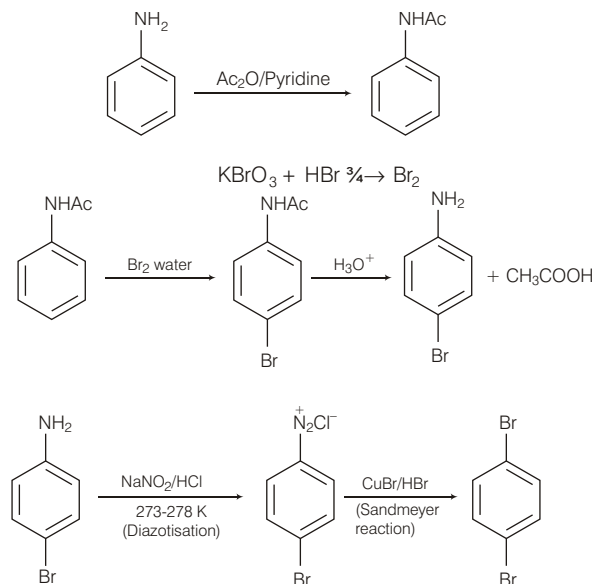Thus, only $[NiCl_4]^{2-}$, $Na_3[CoF_6]$ and CsO_2 are paramagnetic in nature.

4. *(b)* As we move down the group, atomic radius increases but due to poor shielding of *d*-orbital electrons in Ga, atomic radius of Ga is smaller than that of Al. Thus, the correct increasing order is Ga < Al < In < Tl.

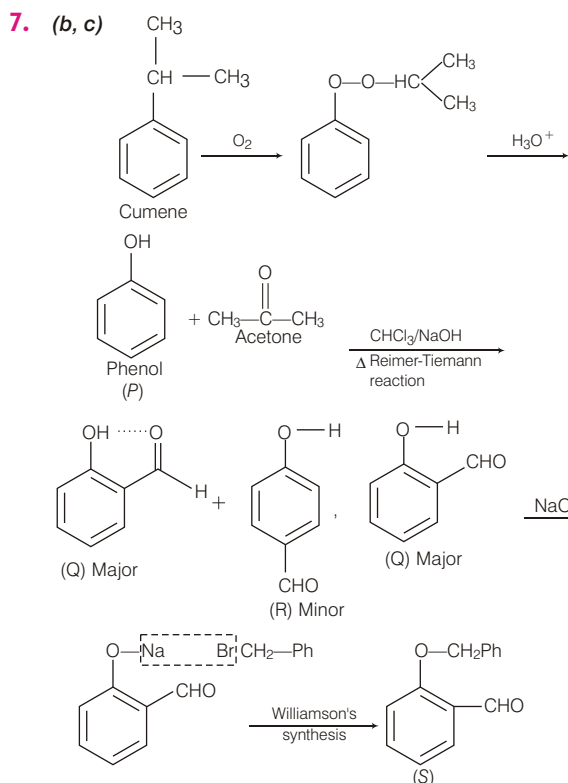**5.** *(a)* Natural rubber is formed by the polymerisation of isoprene.
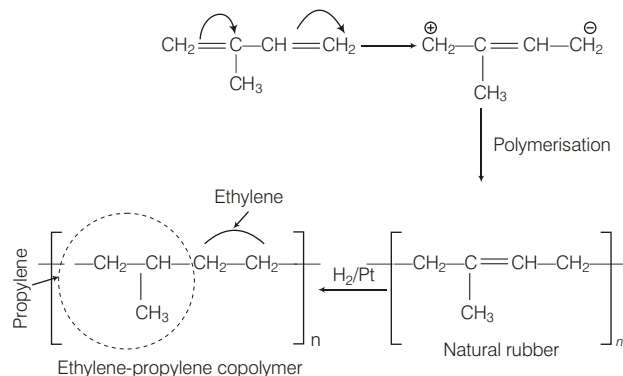

This co-polymer is formed from propylene and ethylene.

$$nCH_2 = \underset{\underset{CH_3}{|}}{C}H + nCH_2 = CH_2 \longrightarrow$$

6. *(b)* **Key Concept** Ac is CH_3CO (acetyl), it protects $-NH_2$ group from being oxidised.

7. **(b, c)**

Cumene → Phenol (P) + Acetone

CH_3-C-CH_3

Phenol (P) — $\xrightarrow[\text{reaction}]{\text{CHCl}_3/\text{NaOH}}{\Delta \text{ Reimer-Tiemann}}$

(Q) Major , (R) Minor — $\xrightarrow{\text{NaOH}}$ (Q) Major

$\xrightarrow[\text{synthesis}]{\text{Williamson's}}$ (S)

(a) R is not steam volatile, but Q is steam volatile thus, incorrect.

(b) Q has enolic group thus, gives violet colour with 1% aqueous $FeCl_3$ solution thus, correct.

(c) S has carbonyl group hence, gives yellow precipitate with 2, 4-DNP thus, correct.

(d) S does not give colour with $FeCl_3$ thus, incorrect.

8. **(a, c, d)** $Na_2B_4O_7 \times 10H_2O$ (borax) is actually made of two tetrahedral and two triangular units, and is actually written as $Na_2[B_4O_5(OH)_4] \times 5H_2O$.
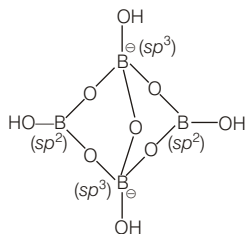
(a) It is a tetranuclear unit. Thus, correct.

(b) Boron atoms are in different planes thus, incorrect.

(c) Two sp^2 and two sp^3 hybridised B atoms. Thus, correct.

(d) Each boron has one ¾ OH group. Thus, correct.

9. **(a)** $S^{2-} + CuCl_2 \xrightarrow{\text{ }} CuS\downarrow$ (black ppt.)

$SO_4^{2-} + CuCl_2 \xrightarrow{\text{ }}$ Soluble

It concludes that

(a) $CuCl_2$ selectively precipitates S^{2-}.

(b) $S^{2-} + BaCl_2 \xrightarrow{\text{ }} BaS\downarrow$ (soluble)

$SO_4^{2-} + BaCl_2 \xrightarrow{\text{ }} BaSO_4\downarrow$ (white ppt.)

Precipitates SO_4^{2-} but not S^{2-}.

(c) $S^{2-} + Pb^{2+} \xrightarrow{\text{ }} PbS\downarrow$ (black ppt.)

$SO_4^{2-} + Pb^{2+} \xrightarrow{\text{ }} PbSO_4\downarrow$ (white ppt.)

S^{2-} and SO_4^{2-}, both are precipitated.

(d) $S^{2-} + Na_2[Fe(CN)_5]NO \xrightarrow{\text{ }} Na_4[Fe(CN)_5]NOS]$
Sodium nitroprusside (Purple colour)
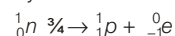
But does not give any colour with SO_4^{2-}.

10. **(b, d)** For the elements with atomic number (Z) larger than 20, Neutrons (n) > Protons (p)

Thus, $\dfrac{n}{p} > 1$

Thus, there is upward deviation from linearity.

If $n < p$, Thus $\dfrac{n}{p} < 1$, then

(a) By β^- - decay

$^1_0n \xrightarrow{\text{ }} ^1_1p + ^{\ 0}_{-1}e$

neutron changes to proton. Thus, $\left(\dfrac{n}{p}\right)$ ratio further decreases below 1.

Thus, this decay is not allowed.

(b) By orbital or K- electron capture

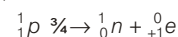$^1_1p + ^{\ 0}_{-1}e \xrightarrow{\text{ }} ^1_0n$

proton changes to neutron, hence, $\left(\dfrac{n}{p}\right)$ ratio increases.

Thus, stability increases. Hence, correct.

(c) Neutron emission further decreases the $\dfrac{n}{p}$ ratio.
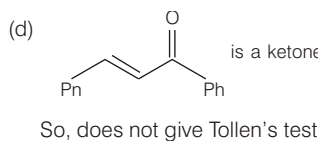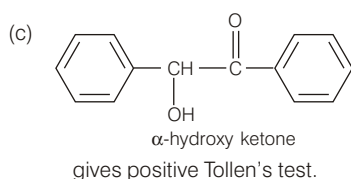
(d) By β^+-emission,

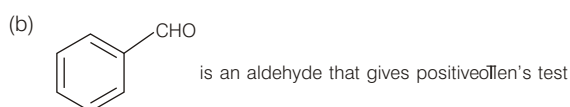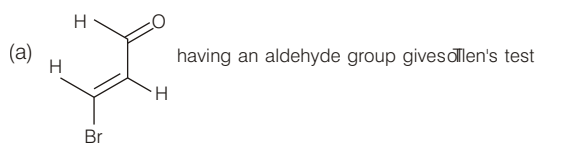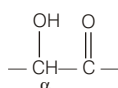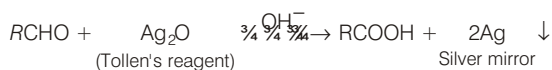$^1_1p \xrightarrow{\text{ }} ^1_0n + ^{\ 0}_{+1}e$

proton changes to neutron.

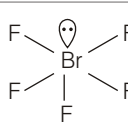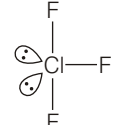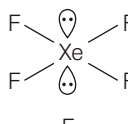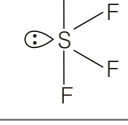Thus, $\dfrac{n}{p}$ ratio increases. Hecne, correct.
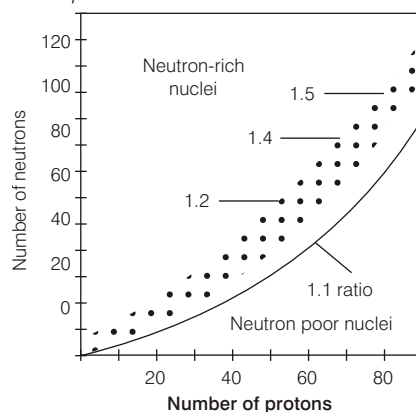
Plot of the number of neutrons against the number of protons in stable nuclei (shown by dots).

EXAM SPECTRUM

11. **(a, b, c)** **Key Concept** *Tollen's test is given by all aldehydes and all reducing sugars as glucose, fructose and α-hydroxy ketones.*

$$RCHO + \quad Ag_2O \quad \xrightarrow{OH^-} RCOOH + \quad 2Ag \quad \downarrow$$
(Tollen's reagent) Silver mirror

(a) having an aldehyde group gives Tollen's test

(b) is an aldehyde that gives positive Tollen's test

(c) α-hydroxy ketone gives positive Tollen's test.

(d) is a ketone

So, does not give Tollen's test

12. **(b,c)**

Compound	Hybridisation	Structure	Lone pair on central atom
BrF_5	sp^3d^2		1
ClF_3	sp^3d		2
XeF_4	sp^3d^2		2
SF_4	sp^3d		1

Only ClF_3 and XeF_4 have two lone pairs.

13. **(b,c,d)** Rate constant, $k = Ae^{-E_a/RT}$ where, E_a = activation energy and A = pre-exponential factor

(a) If E_a is high, it means lower value of k hence, slow reaction. Thus, incorrect.

(b) On increasing temperature, molecules are raised to higher energy (greater than E_a), hence number of collisions increases. Thus, correct.

(c) $\log k = \log A - \dfrac{E_a}{RT}$

$$\dfrac{d(\log k)}{dT} = \dfrac{E_a}{RT^2} \qquad \left[\dfrac{d(\log A)}{dT} = 0; \log A \text{ is constant} \right]$$

Thus, when E_a is high, stronger is the temperature dependence of the rate constant. Thus, correct.

(d) Pre-exponential factor (A) is a measure of rate at which collisions occur. Thus, correct.

14. **(5)** **Thinking Process** *Given compound undergoes free-radical bromination under given conditions,*
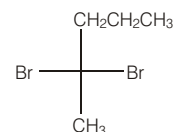
As there are many replaceable hydrogen atoms are present. Hence, there are possibility to obtain many products.

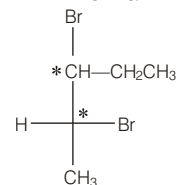*Replace all the hydrogen atoms one by one and find out total number of chiral products.*
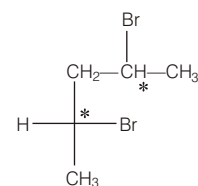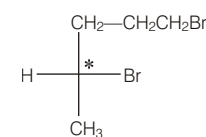
C^* is chiral carbon.
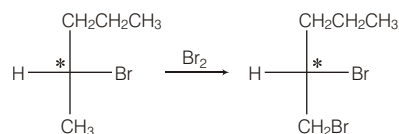
I. Chiral

II. Achiral

III. Chiral

IV. Chiral

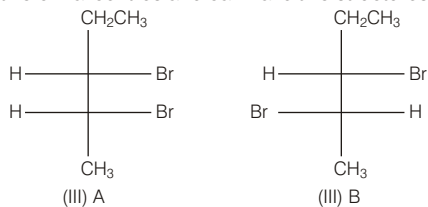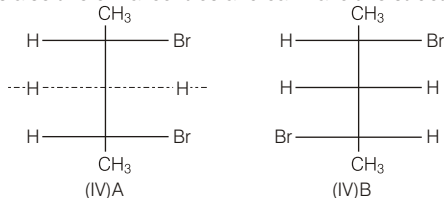**V. Chiral**

(III)   has two chiral centres and can have two structures.

(III) A

(III) B

(IV)   has also two chiral centres and can have two structures.

(IV)A

(IV)B

Compound IVA has plane of symmetry thus, achiral.

Thus, chiral compounds are five.

I, III A, III B, IV B and V.

15.   (9) Moles of solute, $n_1 = \dfrac{w_1}{m_1}$

Moles of solvent, $n_2 = \dfrac{w_2}{m_2}$

Mole fraction, χ_1 (solute) = 0.1
Mole fraction, χ_2 (solvent) = 0.9

$\therefore$ $\dfrac{\chi_1}{\chi_2} = \dfrac{n_1}{n_2} = \dfrac{w_1}{m_1} \times \dfrac{m_2}{w_2} = \dfrac{1}{9}$

Molarity $= \dfrac{\text{Solute (moles)}}{\text{Volume (L)}}$

$= \dfrac{w_1 \times 1000 \times 2}{m_1 (w_1 + w_2)}$

Volume $= \dfrac{\text{Total mass of solution}}{\text{Density}}$

$= \left(\dfrac{w_1 + w_2}{2}\right) \text{mL}$

Molality $= \dfrac{\text{Solute (moles)}}{\text{Solvent (kg)}} = \dfrac{w_1 \times 1000}{m_1 \times w_2}$

Given, molarity = molality

hence, $\dfrac{2000 w_1}{m_1 (w_1 + w_2)} = \dfrac{1000 w_1}{m_1 w_2}$

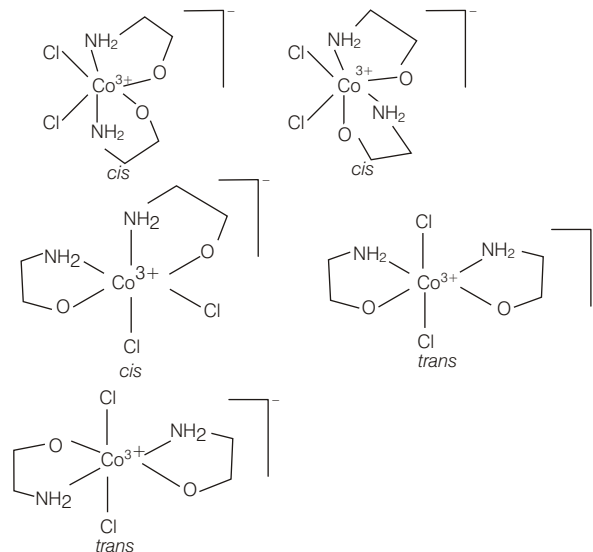$\therefore$ $\dfrac{w_2}{w_1 + w_2} = \dfrac{1}{2}$

Thus, $w_1 = w_2 = 1$

$\therefore$ $\dfrac{w_1 m_2}{m_1 w_2} = \dfrac{1}{9}$

Thus, $\dfrac{m_1 \text{(solute)}}{m_2 \text{(solvent)}} = 9$

16.   (5) Ligand is $\underset{\overset{|}{CH_2\overset{\ominus}{O}}}{CH_2{-}NH_2}$

Geometrical isomers are

17.   (6) In neutral or faintly alkaline solution, MnO_4^- is reduced to MnO_2 and $S_2O_3^{2-}$ is oxidised to SO_4^{2-}.

Thus,

$4MnO_4^- + \dfrac{3}{2} S_2O_3^{2-} \longrightarrow 3SO_4^{2-} + 4MnO_2$

or $8MnO_4^- + 3S_2O_3^{2-} \longrightarrow 6SO_4^{2-} + 8MnO_2$
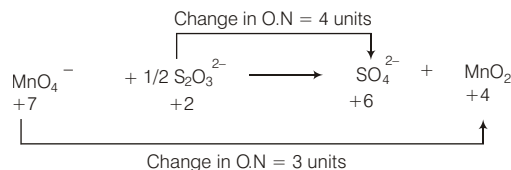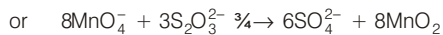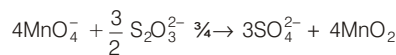
Thus, moles of SO_4^{2-} formed by 8 moles of $MnO_4^- = 6$

18.   (4) Key Concept Diffusion coefficient (DC) μ λ (mean free path)

DC μ U_{mean}

Thus, (DC) μ λ U_{mean}

But, $\lambda = \dfrac{RT}{\sqrt{2}\, N_0 \sigma p}$

$\lambda \mu \dfrac{T}{p}$

and $U_{mean} = \sqrt{\dfrac{8RT}{\pi M}}$

$U_{mean} \mu \sqrt{T}$

$\therefore$ DC μ $\dfrac{(T)^{3/2}}{p}$

$\dfrac{(DC)_2}{(DC)_1} (x) = \left(\dfrac{p_1}{p_2}\right)\left(\dfrac{T_2}{T_1}\right)^{3/2}$

$= \left(\dfrac{p_1}{2 p_1}\right)\left(\dfrac{4 T_1}{T_1}\right)^{3/2}$

$= \left(\dfrac{1}{2}\right)(8) = 4$

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B095 ₹665	**B097** ₹665	**C134** ₹665

MEDICAL ENTRANCES

CHAPTERWISE TOPICWISE Questions-Solutions **PHYSICS** FOR Medical Entrances 2015-2005 — *Highly Useful for CBSE-AIPMT, AIIMS & Other Medical Entrances* — Digvijay Singh	CHAPTERWISE TOPICWISE Questions-Solutions **CHEMISTRY** FOR Medical Entrances 2015-2005 — *Highly Useful for CBSE-AIPMT, AIIMS & Other Medical Entrances* — Preeti Gupta	CHAPTERWISE TOPICWISE Questions-Solutions **BIOLOGY** FOR Medical Entrances 2015-2005 — *Highly Useful for CBSE-AIPMT, AIIMS & Other Medical Entrances* — Sudhakar Banerjee
B096 ₹650	**B098** ₹650	**B074** ₹650

Accurate Collection of all the Questions-Solutions asked in last 10 Years' Engineering & Medical Entrances

arihant

EXAM SPECTRUM

JEE Advanced 2016
PAPER II (Online)
FULLY SOLVED

─ **SECTION 1 (MM : 18)** ─

- This section contains **SIX** questions.
- Each question has **FOUR** options (a), (b), (c) and (d). ONLY ONE of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in ORS.
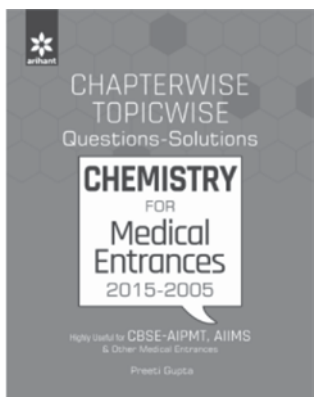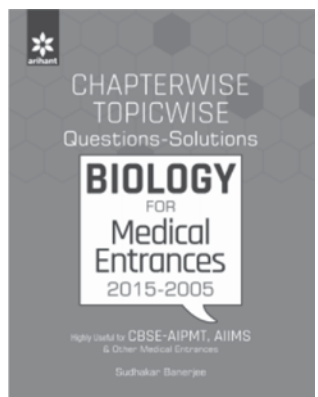- For each question, marks will be awarded in **one of the following categories.**
  Full Marks   : + 3, If the bubble corresponding to the answer is darkened.
  Zero Marks   :   0, If none of the bubbles is darkened.
  Negative Marks : −1, In all other cases.

EXAM CRUX

- There were total 18 questions asked in JEE Advanced 2016 paper II. Out of 18 questions, 6 questions were numerical based while 12 questions were theory based. Overall paper was quite tough and need a good knowledge of subject to solve.
- According to chapterwise distribution, number of questions were asked as:

From Class XI

- Chemical Bonding and Molecular Structure–1Q, Equilibrium–2QS, The *p*-block elements–1Q Some Basic Concepts of Chemistry–1Q.

From Class XII

- General Principles and Processes of Isolation of Elements–3Qs Aldehydes, Ketones and Carboxylic Acids–2Qs. Coordination Compounds–1Q, Biomolecules–2Qs, The Solid State, Solutions, Electrochemistry and Haloarenes and Polymers–1Q from each chapter.
- Thus, approx–30% of paper came from Class XI and 70% from Class XII.
- Maximum questions were asked from Physical and Organic Chemistry rather than Inorganic Chemistry in this paper.

Difficulty Level

- Around 60% of questions can be considered as tough; 20% were relatively moderate and 20% are considered easy by the Arihant team. Overall, this year paper was tough as compare to previous year paper.

1. The correct order of acidity for the following compounds is
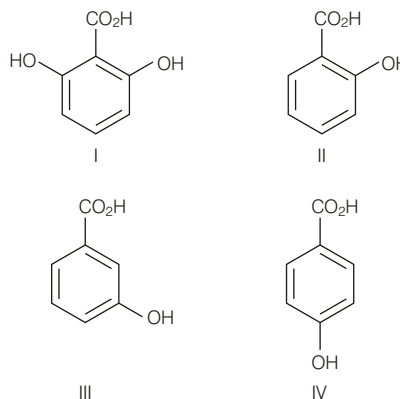
(a) I > II > III > IV
(b) III > I > II > IV
(c) III > IV > II > I
(d) I > III > IV > II

⬛ EXAM SPECTRUM

2. The major product of the following reaction sequence is

(i) HCHO (Excess)/NaOH, Heat
(ii) HCHO/H$^+$ (Catalytic amount)

(a)

(b)

(c)

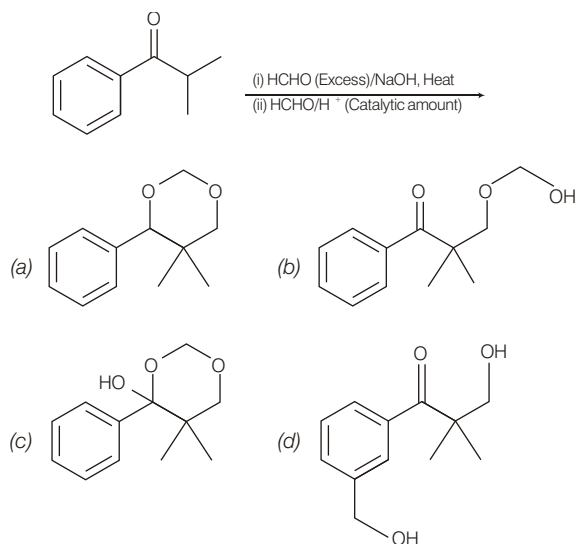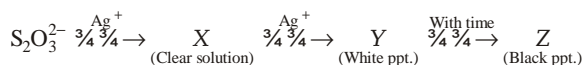(d)

3. In the following reaction sequence in aqueous solution, the species X, Y and Z, respectively, are

$$S_2O_3^{2-} \xrightarrow[\text{(Clear solution)}]{Ag^+} X \xrightarrow[\text{(White ppt.)}]{Ag^+} Y \xrightarrow[\text{(Black ppt.)}]{\text{With time}} Z$$

(a) $[Ag(S_2O_3)_2]^{3-}$, $Ag_2S_2O_3$, Ag_2S
(b) $[Ag(S_2O_3)_3]^{5-}$, Ag_2SO_3, Ag_2S
(c) $[Ag(SO_3)_2]^{3-}$, $Ag_2S_2O_3$, Ag
(d) $[Ag(SO_3)_3]^{3-}$, Ag_2SO_4, Ag

4. The qualitative sketches I, II and III given below show the variation of surface tension with molar concentration of three different aqueous solutions of KCl, CH_3OH and $CH_3(CH_2)_{11}OSO_3^-Na^+$ at room temperature.
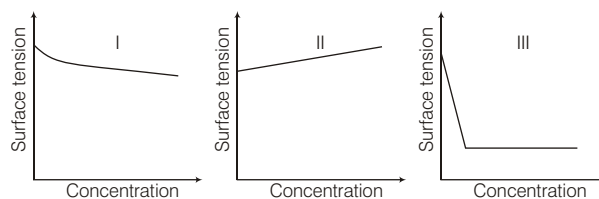
The correct assignment of the sketches is

(a)	I : KCl	II : CH_3OH	III : $CH_3(CH_2)_{11}$ OSO_3^- Na$^+$
(b)	I : $CH_3(CH_2)_{11}$ OSO_3^- Na$^+$	II : CH_3OH	III : KCl
(c)	I : KCl	II : $CH_3(CH_2)_{11}$ $OSO_3^-Na^+$	III : CH_3OH
(d)	I : CH_3OH	II : KCl	III : $CH_3(CH_2)_{11}$ OSO_3^- Na$^+$

5. The geometries of the ammonia complexes of Ni^{2+}, Pt^{2+} and Zn^{2+}, respectively, are

(a) octahedral, square planar and tetrahedral
(b) square planar, octahedral and tetrahedral
(c) tetrahedral, square planar and octahedral
(d) octahedral, tetrahedral and square planar

6. For the following electrochemical cell at 298 K,

$$Pt(s) \mid H_2(g, 1 \text{ bar}) \mid H^+(aq, 1 \text{ M}) \parallel M^{4+}(aq), M^{2+}(aq) \mid Pt(s)$$

$E_{cell} = 0.092$ V when $\dfrac{[M^{2+}(aq)]}{[M^{4+}(aq)]} = 10^x$

Given, $E^\circ_{M^{4+}/M^{2+}} = 0.151$ V; $2.303\dfrac{RT}{F} = 0.059$ V

The value of x is

(a) – 2   (b) – 1   (c) 1   (d) 2

SECTION 2 (MM : 32)

- This section contains **EIGHT** questions.
- Each question has **FOUR** options (a), (b), (c) and (d). **ONE OR MORE THAN ONE** of these four options is (are) correct.
- For each question, darken the bubble(s) corresponding to all the correct option(s) in the ORS.
- For each question, marks will be awarded in **one of the following categories**:
  Full Marks   : + 4, If only the bubble corresponding to all the correct option(s) is (are) darkened.
  Partial Marks   : + 1, For darkening a bubble corresponding to **each correct option,** provided no incorrect option is darkened.
  Zero Marks   : 0, If none of the bubbles is darkened.
 Negative Marks   : − 2, In all other cases.

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7. According to molecular orbital theory, which of the following statements is(are) correct?

(a) C_2^{2-} is expected to be diamagnetic

(b) O_2^{2+} is expected to have a longer bond length than O_2

(c) N_2^+ and N_2^- have the same bond order

(d) He_2^+ has the same energy as two isolated He atoms

8. The correct statement(s) for cubic close packed (ccp) three dimensional structure is (are)
   (a) The number of the nearest neighbours of an atom present in the topmost layer is 12
   (b) The packing efficiency of atom is 74%
   (c) The number of octahedral and tetrahedral voids per atom are 1 and 2, respectively
   (d) The unit cell edge length is $2\sqrt{2}$ times the radius of the atom

9. Reagent(s) which can be used to bring about the following transformation is (are)
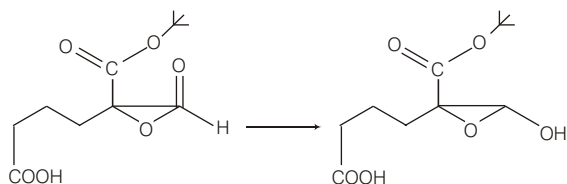
   (a) $LiAlH_4$ in $(C_2H_5)_2O$
   (b) BH_3 in THF
   (c) $NaBH_4$ in C_2H_5OH
   (d) Raney Ni/H_2 in THF

10. Extraction of copper from copper pyrite $(CuFeS_2)$ involves
    (a) crushing followed by concentration of the ore by froth-floatation
    (b) removal of iron as slag
    (c) self reduction step to produce 'blister copper' following evolution of SO_2
    (d) refining of 'blister copper' by carbon reduction

11. The nitrogen containing compound produced in the reaction of HNO_3 with P_4O_{10}
    (a) can also be prepared by reaction of P_4 and HNO_3
    (b) is diamagnetic

(c) contains one N¾N bond
(d) reacts with Na metal producing a brown gas

12. Mixture(s) showing positive deviation from Raoult's law at 35°C is (are)
    (a) carbon tetrachloride + methanol
    (b) carbon disulphide + acetone
    (c) benzene + toluene
    (d) phenol + aniline

13. For 'invert sugar', the correct statement(s) is (are) (Given: specific rotations of (+)-sucrose, (+)-maltose, L-(−)-glucose and L-(+)-fructose in aqueous solution are $+66°$, $+140°$, $-52°$ and $92°$, respectively)
    (a) Invert sugar is prepared by acid catalysed hydrolysis of maltose
    (b) Invert sugar is an equimolar mixture of D-(+)-glucose and D-(−)-fructose
    (c) Specific rotation of invert sugar is − 20°
    (d) On reaction with Br_2 water, invert sugar forms saccharic acid as one of the products

14. Among the following reactions(s), which gives(give) *tert*-butyl benzene as the major product?
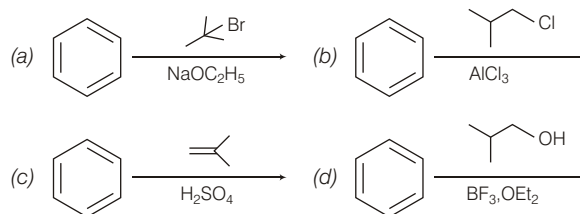
SECTION 3 (MM : 12)

- This section contains **FOUR** questions.
- Based on each paragraph, there are TWO questions.
- Each question has FOUR options (a), (b), (c) and (d). ONLY ONE of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in **one of the following categories**:
  Full Marks   : +3, If only the bubble corresponding to the correct answer is darkened.
  Zero Marks   : 0, In all other cases.

Paragraph 1

Directions (Q. Nos. 15-16) Thermal decomposition of gaseous X_2 to gaseous X at 298 K takes place according to the following equation:

$$X_2(g) \rightleftharpoons 2X(g)$$

The standard reaction Gibbs energy, $\Delta_r G°$, of this reaction is positive. At the start of the reaction, there is one mole of X_2 and no X. As the reaction proceeds, the number of moles of X formed is given by β. Thus, $β_{equilibrium}$ is the number of moles of X formed at equilibrium. The reaction is carried out at a constant total pressure of 2 bar. Consider the gases to behave ideally. (Given, $R = 0.083$ L bar K^{-1} mol^{-1})

▣ EXAM SPECTRUM

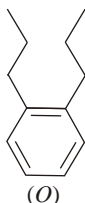**15.** The equilibrium constant K_p for this reaction at 298 K, in terms of $\beta_{equilibrium}$ is

(a) $\dfrac{8\,\beta^2_{equilibrium}}{2 - \beta_{equilibrium}}$

(b) $\dfrac{8\,\beta^2_{equilibrium}}{4 - \beta^2_{equilibrium}}$

(c) $\dfrac{4\,\beta^2_{equilibrium}}{2 - \beta_{equilibrium}}$

(d) $\dfrac{4\,\beta^2_{equilibrium}}{4 - \beta^2_{equilibrium}}$

16. The incorrect statement among the following for this reaction, is

(a) Decrease in the total pressure will result in the formation of more moles of gaseous X

(b) At the start of the reaction, dissociation of gaseous X_2 takes place spontaneously

(c) $\beta_{equilibrium} = 0.7$

(d) $K_C < 1$

Paragraph 2

Directions (Q. Nos. 17-18) Treatment of compound *O* with $KMnO_4 / H^+$ gave *P*, which on heating with ammonia gave *Q*. The compound *Q* on treatment with $Br_2 / NaOH$ produced *R*. On strong heating, *Q* gave *S*, which on further treatment with ethyl 2-bromopropanoate in the presence of KOH followed by the acidification, gave a compound *T*.

(O)

17. The compound *R* is

(a)

(b)

(c)

(d)
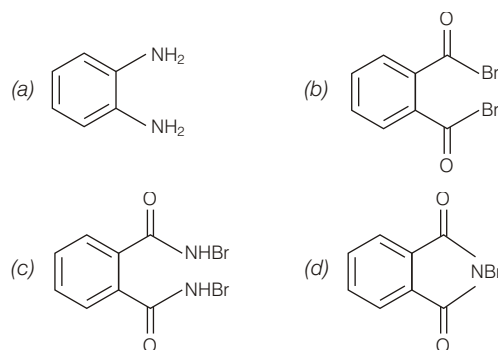
18. The compound *T* is

(a) glycine

(b) alanine

(c) valine

(d) serine

Answers with Explanation

1. **(a)** **Thinking Process** —OH *group displays both kinds of effect; an electron withdrawing acid-strengthening inductive effect from the meta-position and an electron-releasing acid weakening resonance effect from the para-position (at this position, resonance effect overweighs the inductive effect). Thus,* III > IV.

o-hydroxybenzoic acid (II) *is far stronger than the corresponding meta and para isomers as the carboxylate ion is stabilised by intramolecular H-bonding.*

2,6-dihydroxybenzoic acid (I) forms carboxylate ion which is further stabilised by intramolecular H-bonding, Thus, correct order is I > II > III > IV
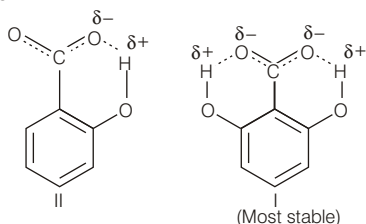
2. **(a)** **Key Concept** Alkali abstracts proton from α-position of carbonyl group and generates carbanion.

This carbanion attacks at electron deficient carbon of carbonyl group and further gives Crossed-aldol reaction.

α-carbon has no H-atom hence, next reaction with HCHO is Crossed Cannizzaro reaction

(By reduction)   (By oxidation)
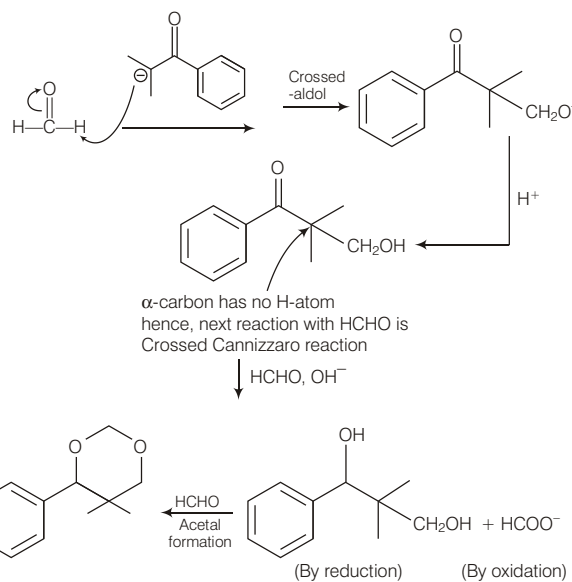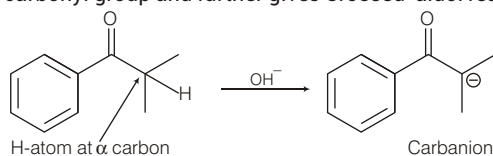
3. **(a)** $2S_2O_3^{2-} + Ag^+ \longrightarrow [Ag(S_2O_3)_2]^{3-}$
(Clear solution)

$[Ag(S_2O_3)_2]^{3-} + 3Ag^+ \longrightarrow 2Ag_2S_2O_3$
(White ppt.)

$Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S + H_2SO_4$
(Black ppt.)
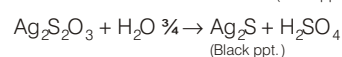
4. **(d)** I (CH₃OH) : Surface tension decreases as concentration increases.

II (KCl) : Surface tension increases with concentration for ionic salt.

III [CH₃(CH₂)₁₁OSO₃⁻ Na⁺] : It is an anionic detergent.

There is decrease in surface tension before micelle formation, and after CMC (Critical Micelle Concentration) is attained, no change in surface tension is observed.

5. **(a)**

Compound	Hybridisation	Geometry
$[Ni(NH_3)_6]^{2+}$	sp^3d^2	octahedral
$[Pt(NH_3)_4]^{2+}$	dsp^2	square planar
$[Zn(NH_3)_4]^{2+}$	sp^3	tetrahedral

6. **(d)** Strategy *Find out* $E_{cell}^°$, $E_{cell}^° = E_{right}^° - E_{left}^°$

Apply Nernst equation; $E_{cell} = E_{cell}^° - \dfrac{0.059}{n} \log \dfrac{[M^{2+}][H^+]^2}{[M^{4+}] \, p_{H_2}}$

Put $\dfrac{[M^{2+}][H^+]^2}{[M^{4+}] \, p_{H_2}} = K$ *and find the value of x.*

Oxidation at anode

$$H_2(g) \longrightarrow 2H^+(aq) + 2e^-; \quad E_{SHE}^° = 0.00 \text{ V}$$

Reduction at cathode

$$M^{4+}(aq) + 2e^- \longrightarrow M^{2+}(aq); E_{M^{4+}/M^{2+}}^° = 0.151 \text{ V}$$

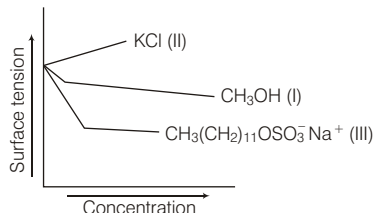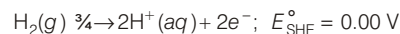Net: $M^{4+}(aq) + H_2(g) \longrightarrow M^{2+}(aq) + 2H^+(aq)$;
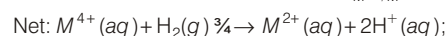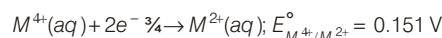
$$K = \dfrac{[M^{2+}][H^+]^2}{[M^{4+}] \, p_{H_2}}; (E_{cell}^° = 0.151 \text{ V}) = \dfrac{[M^{2+}]}{[M^{4+}]}$$

$$E_{cell} = E_{cell}^° - \dfrac{0.059}{2} \log K$$

$$0.092 = 0.151 - \dfrac{0.059}{2} \log \dfrac{[M^{2+}]}{[M^{4+}]}$$

$$0.059 = \dfrac{0.059}{2} \log 10^x$$

∴ $\log 10^x = 2$

∴ $x = 2$

7. **(a,c)**

Species	Number of electrons	Molecular orbital electronic configuration (MOEC)	N_B	N_A	BO	Magnetic character
C_2^{2-}	14	$\sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2, \pi 2p_x^2 \approx \pi 2p_y^2, \sigma 2p_z^2$	10	4	3	Diamagnetic
O_2^{2+}	14	$\sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2, \pi 2p_x^2 \approx \pi 2p_y^2, \sigma 2p_z^2$	10	4	3	Diamagnetic
O_2	16	$\sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2, \sigma 2p_z^2, \pi 2p_y^2 \approx \pi 2p_x^2, \pi^*2p_x^1 \approx \pi^*2p_y$	10	6	2	Paramagnetic
N_2^+	13	$\sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2, \pi 2p_x^2 \approx \pi 2p_y^2, \sigma 2p_z^1$	9	4	2.5	Paramagnetic
N_2^-	15	$\sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2, \sigma 2p_z, \pi 2p_y^2 \approx \pi 2p_x^2, \pi^*2p_x^1 \approx \pi^*2p_y$	10	5	2.5	Paramagnetic
He_2^+	3	$\sigma 1s^2, \sigma^*1s^1$	2	1	0.5	Paramagnetic

Thus, (a) is correct.

(b) Bond order of $O_2^{2+} > O_2$ thus, bond length of $O_2^{2+} < O_2$ thus, incorrect.

(c) N_2^+ and N_2^- have same bond order thus, correct.

(d) He_2^+ with bond order equal to 0.5 is more stable thus, less energised than isolated He atoms. Thus, (d) is incorrect.

8. **(b,c,d)**

(a) Nearest neighbour in the topmost layer of ccp structure is 9 thus, incorrect.

(b) Packing efficiency is 74% thus, correct.

(c) Tetrahedral voids = 2. Octahedral voids = 1 per atom thus, correct.

(d) Edge length, $a = \dfrac{4}{\sqrt{2}} r = 2\sqrt{2}r$ thus, correct.

Explanation Edge length $= a$; Radius $= r$, $AC^2 = AB^2 + BC^2$, $(4r)^2 = a^2 + a^2 = 2a^2$

$$4r = \sqrt{2}a \, Þ \, r = \dfrac{\sqrt{2}}{4} a = \dfrac{a}{2\sqrt{2}}, \quad a = 2\sqrt{2} \, r$$

In ccp structure, number of spheres is 4.

Hence, volume of 4 spheres $= 4\left(\dfrac{4}{3} \pi r^3\right)$ Total volume of unit cell $= a^3 = (2\sqrt{2}r)^3$ % of packing efficiency

$$= \dfrac{\text{Volume of 4 spheres}}{\text{Volume of unit cell}} = \dfrac{4\left(\dfrac{4}{3} \pi r^3\right)}{[2(\sqrt{2}r)]^3} \times 100 = 74.05\% \simeq 74\%$$
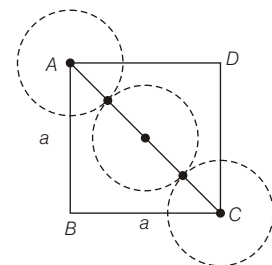
9. **(c)** Only ¾ CHO group is to be reduced to ¾ CH_2OH.
It can be done using $NaBH_4$ in C_2H_5OH.
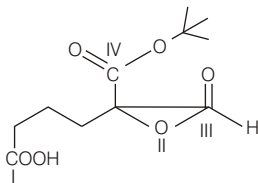
(a) $LiAlH_4/(C_2H_5)_2O$ reduces I, II and III into ¾ CH_2OH, and IV into diol.

(b) BH_3/THF show same properties as explained in option (a).

(c) $NaBH_4/C_2H_5OH$ reduces III into ¾ CH_2OH as it selectively reduce the carbonyl group.

(d) Raney nickel, same as (a) and (b).

Thus (c) is correct reagent.

10. **(a,b,c)** Extraction of copper is done from copper pyrite by going through following steps:

Step I Crushing (grinding) followed by concentration of ore by froth-floatation process.

Step II Roasting of ore in the presence of SiO_2 which removes iron as slag ($FeSiO_3$).

$$2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$$
$$2FeS + 3O_2 \longrightarrow 2SO_2 + 2FeO$$
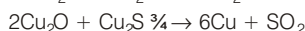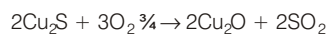$$FeO + SiO_2 \longrightarrow FeSiO_3 (Slag)$$
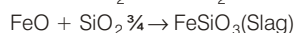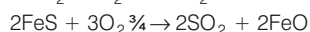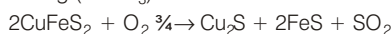
Step III Self-reduction in Bessemer converter

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$
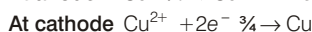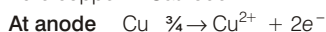$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$$

Copper obtained is blister copper (98% pure).

Step IV Refining of blister copper is done by electrolysis

Impure copper—Anode

Pure copper— Cathode

At anode $Cu \longrightarrow Cu^{2+} + 2e^-$

At cathode $Cu^{2+} + 2e^- \longrightarrow Cu$

Carbon-reduction method is not used. Thus, (d) is incorrect.

11. **(b,d)** P_4O_{10} is a dehydrating agent and converts HNO_3 into N_2O_5

$$2HNO_3 \longrightarrow N_2O_5 + H_2O$$
$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$$
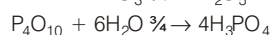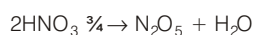
(a) $P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$

Thus, (a) is incorrect.

(b) N_2O_5 has no unpaired electron and is thus, diamagnetic thus, (b) is correct.

(c)
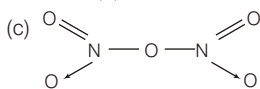
There is no N—N bond, thus, (c) is incorrect.

(d) $N_2O_5 + Na \longrightarrow NaNO_3 + NO_2$

NO_2 vapours are of brownish colour.

Thus, (d) is correct.

12. **(a,b)** **Key Concept** When intermolecular attraction between two components A and B in the mixture is same as between A and A or B and B, then it is a case of ideal solution and this solution obeys Raoult's law.

When intermolecular attraction between A and B in a mixture is smaller than that of between A and A or B and B, then mixture is more vapourised, boiling point is lowered. It is a case of positive deviation from Raoult's law.

When intermolecular attraction between A and B is higher than that of between A and A or B and B, then mixture is less vaporised, boiling point is increased. It is a case of negative deviation from Raoult's law.

(a) Methanol molecules (CH_3OH) show hydrogen bonding. In a mixture of CCl_4 and CH_3OH, extent of H-bonding is decreased. Mixture is more vapourised thus, positive deviation from Raoult's law.

(b) Acetone molecules have higher intermolecular attraction due to dipole-dipole interaction. With CS_2, this interaction is decreased thus, shows positive deviation.

(c) Mixture of benzene and toluene forms ideal solution.

(d) Phenol and aniline have higher interaction due to inter-molecular H-bonding. Hence, shows negative deviation.

13. **(b,c)** **Key Concept** If there is specific rotation from $(+)$ to $(-)$, then inverted sugar is formed.

(a) $\underset{\underset{140°}{(+)Maltose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\underset{52°}{D(+)}}{Glucose}$

(b) $\underset{\underset{+66°}{(+)Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\underset{52°}{D(+)}}{Glucose} + \underset{\underset{-92°}{L(-)}}{Fructose}$
$$\underset{-20° for\ 1\ mole\ mixture}{-40° for\ 2\ moles\ mixture}$$
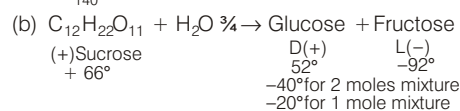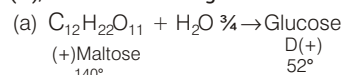
There is formation of inverted sugar. Thus, correct.

(c) Specific rotation of inverted sugar is $-20°$ per mole. Thus, correct.

(d) Br_2 water is a weak oxidising agent. It oxidises specifically ¾ CHO to ¾ COOH, ¾ CH_2OH group is not affected.
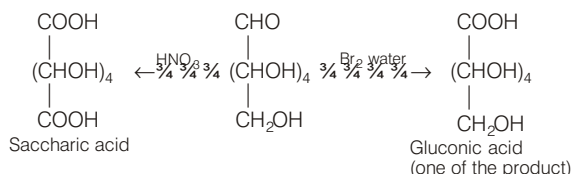
HNO_3 (a strong oxidising agent) oxidises inverted sugar to saccharic acid. Thus, incorrect.

14. **(b,c,d)**

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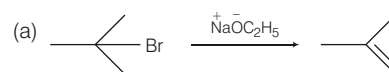
$C_2H_5O^-$ (a strong nucleophile) shows E1 reaction to form isobutene as the major product.

(b)

(c)

Tertiary butyl benzene

(d)

Tertiary butyl benzene

15. **(b)**

$$X_2(g) \rightleftharpoons 2X(g)$$

At $t = 0$ 1   0

At equilibrium $\left(1 - \dfrac{x}{2}\right)$ x (where, $x = \beta_{eq}$)

Total moles at equilibrium

$$= \left(1 + \frac{x}{2}\right)$$

Mole fraction, $X_2(g) = \dfrac{\left(1 - \dfrac{x}{2}\right)}{\left(1 + \dfrac{x}{2}\right)}$; $X(g) = \left(\dfrac{x}{1 + \dfrac{x}{2}}\right)$ and $p = 2$ bar

Partial pressure, $(px_2) = \left(\dfrac{1 - \dfrac{x}{2}}{1 + \dfrac{x}{2}}\right) \cdot p$

and $p_X = \dfrac{p \cdot x}{\left(1 + \dfrac{x}{2}\right)}$

∴ $K_p = (px)^2 / px_2$

$$= \frac{\left[px / \left(1 + \dfrac{x}{2}\right)\right]^2}{p\dfrac{(1 - x/2)}{\left(1 + \dfrac{x}{2}\right)}} = \frac{4px^2}{(4 - x^2)} = \frac{8\beta_{eq}^2}{(4 - \beta_{eq}^2)}$$

16. **(c)**

(a) $K_p = \dfrac{4px^2}{(4 - x^2)} = px^2$ $[\because 4 >>> x]$
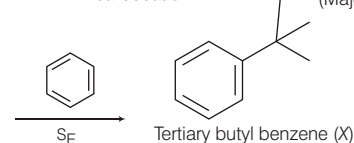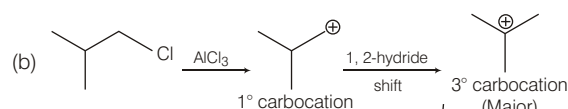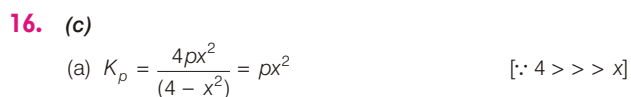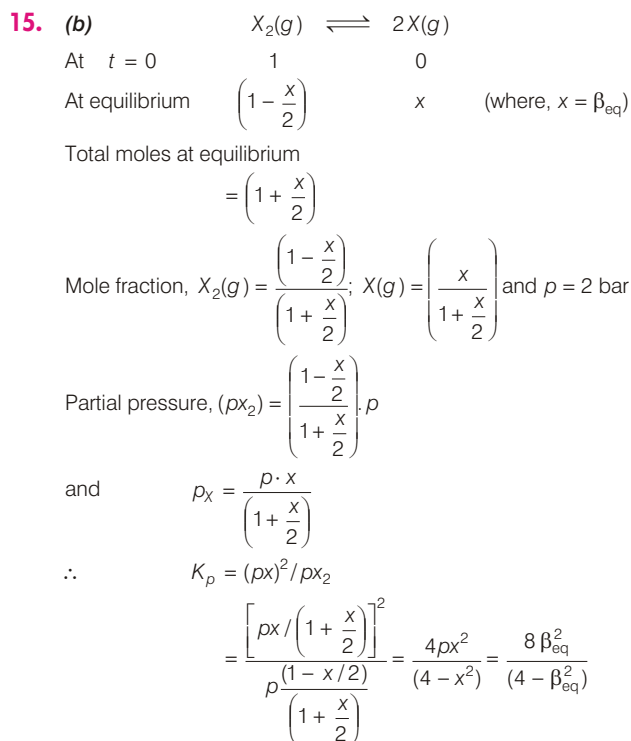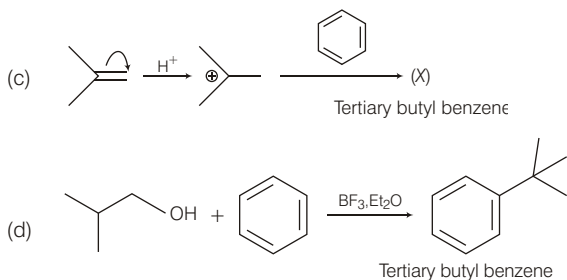
∴ $x \propto \sqrt{\dfrac{1}{p}}$

If p decreases, x increases. Equilibrium get shifted in the forward direction. Thus, statement (a) is correct.

(b) At the start of the reaction, $Q = 0$ where, Q is the reaction quotient

$$\Delta G = \Delta G° + 2.303\, RT \log Q$$

Since, $\Delta G° < 0$, thus ΔG is –ve.

Hence, dissociation takes place spontaneously. Thus, (b) is correct.

(c) If we use $x = 0.7$ and $p = 2$ bar

then $K_p = \dfrac{4 \times 2(0.7)^2}{[4 - (0.7)^2]} = 1.11 > 1$

Thus, (c) is incorrect.

(d) At equilibrium, $\Delta G = 0$

∴ $\Delta G° = -2.303RT \log K_p$

Since, $\Delta G° = +$ ve

Hence, $K_p < 1$

$$K_C = \frac{K_p}{(RT)}$$

∴ $K_C < 1$. Thus, (d) is correct.

17. **(a)** **Key Concept** Any alkyl group with atleast one H at α-carbon, e.g. — CH_2OH, — CH_2NH_2, — CH_2Cl is oxidised to — $COOH$ by MnO_4^-/H^+.

Thus, (O) is converted to (P).

18. **(a)** **Key Concept**

(i) $RCONH_2 \xrightarrow{Br_2 / NaOH} RNH_2$
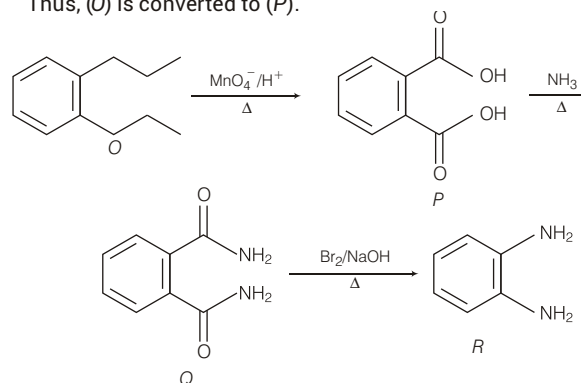
It is called Hofmann bromamide degradation reaction. Thus, (Q) changes to (R).

(ii) Conversion of (S) into (T) through S_1, S_2 is called Gabriel phthalimide reaction. P is formed by cleavage of amide linkage in Gabriel phthalimide reaction.

◩ METICULOUS ANALYSIS

REACTION
INTERMEDIATES

⌄

Coverage of Special Topics for JEE Advanced

All organic compounds are made up of covalent bonds. During the course of a chemical reaction, short-lived reactive intermediates are formed. These intermediates can be formed either by homolytic and heterolytic bond fissions or by course of some other reaction conditions.

The main types of reactive intermediates of interest to organic chemists are carbocations, carbanions, radicals carbenes, nitrenes, arynes, nitrenium ions and diradicals. We shall read some important reactive intermediates in this article.

(A) Carbocations

- These have atleast one carbon atom with a positive charge and have 6 electrons in the valence shell.
- These are sp^2-hybridised and trigonal planar in shape.
- These are diamagnetic in nature.
- These are intermediates in many kinds of reactions. The more stable ones have been prepared in solution and in some cases even as solid salts. In solution, the carbocations may be free (this is more likely in polar solvents, in which it is solvated) or it may exist as an ion pair, which means that it is closely associated with a negative ion, called a counter ion. Ion pairs exist in **non-polar solvents.**
- These are formed by the heterolytic fission or by the addition of a proton to an unsaturated system

REMEMBER
Whatever the process used, carbocations are most often short-lived transient species and react further without isolated.

Classification of Carbocations

(I) **Classical carbocations** In these, the positive charge is localised on one carbon atom or delocalised by resonance involving an unshared pair of electrons or a double or triple bond at the allylic position. These can be 1°, 2° or 3°.

e.g.

(II) **Non-classical carbocations** In these, the positive charge is delocalised by double or triple bond that is not at the allylic position or by a single bond.

e.g.

7-norbornenyl carbocation

(Cyclopropyl methyl carbocation)

(2-phenyl ethyl carbocation)

Order of Stability of Carbocations

Stability $\propto$ Resonance $\propto$ Hyperconjugation

$$\propto + I\text{-effect} \propto \frac{1}{- I\text{-effect}}$$

The order of stability for various carbocations is:

$$\overset{\oplus}{Ph_3 C} > \overset{\oplus}{Ph_2 CH} > \overset{\oplus}{Ph\,CH_2} > \overset{\oplus}{(CH_3)_3 C}$$

$$> \overset{\oplus}{C H_2} - CH = CH_2 > \overset{\oplus}{R_2 C H} > \overset{\oplus}{R\,CH_2}$$

$$> \overset{\oplus}{CH_3} > \overset{\oplus}{CH_2} = CH > \overset{\oplus}{\bigcirc}$$

TYPE 1 Problem Based on Finding Stability of Carbocations

Example 1 The order of stability of the following carbocations is   [IIT JEE 2013]

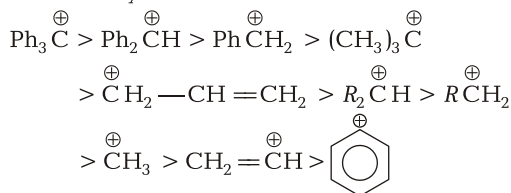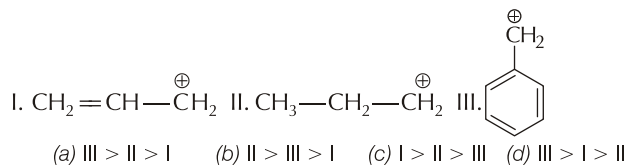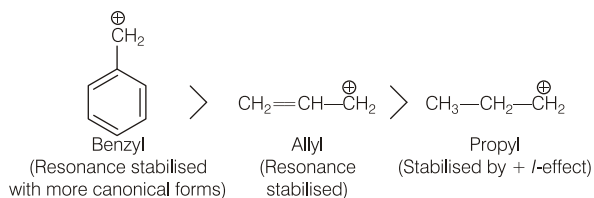I. $CH_2 = CH - \overset{\oplus}{C H_2}$ II. $CH_3 - CH_2 - \overset{\oplus}{C H_2}$ III.

(a) III > II > I   (b) II > III > I   (c) I > II > III   (d) III > I > II

Sol. **(d)** The order of stability of carbocations will be

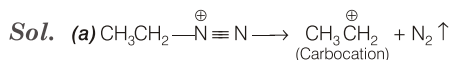| Benzyl	Allyl	Propyl
(Resonance stabilised with more canonical forms)	(Resonance stabilised)	(Stabilised by + I-effect)

TYPE 2 Problem Based on Finding Reactive Intermediate

**Example 2** Name the intermediate (I) species formed in the following reaction.

$$CH_3CH_2 - \overset{\oplus}{N} \equiv N \longrightarrow (I) + :N \equiv N:$$
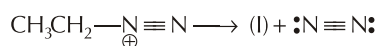
(a) Carbocation   (b) Carbanion
(c) Radical   (d) None of these

Sol. **(a)** $CH_3CH_2 - \overset{\oplus}{N} \equiv N \longrightarrow \underset{\text{(Carbocation)}}{CH_3 CH_2^+} + N_2 \uparrow$
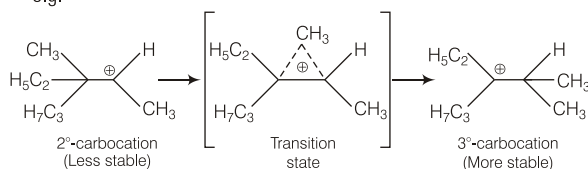

Rearrangement in Carbocations

- As carbocations are stabilised by + I-effect, resonance and hyperconjugation so, carbocations become more stable as you increase the number of electron donating groups or conjugation attached to them.
- If a possibility exists when an unstable carbocation can be transformed into a more stable carbocation, then rearrangement occurs. These possibilities are given below:

 (i) **By hydride transfer** One rearrangement pathway where an unstable carbocation can be transformed into a more stable carbocation is called a hydride shift.

e.g.

| 2°-carbocation (Less stable)	Transition state	3°-carbocation (More stable)
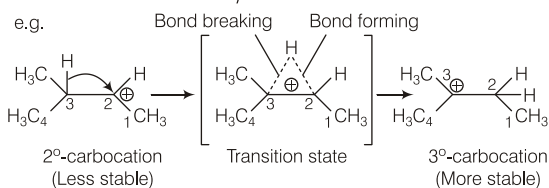
In the above rearrangement,

- The bonding pair of electrons of C—H bond is transferred to the empty p-orbital on the carbocation.
- In transition state, both carbons, i.e. C_2 and C_3, contain partial positive charge.
- The C_2—H bond shortens and the C_3—H bond weakens, we end up with a carbocation on C_3 (a 3°-carbocation) in the product which is more stable.
- If we do not have hydride ion at the adjacent position to the carbocation, smaller group among the adjacent groups, will migrate in order to get more stable carbocation.

e.g.

2°-carbocation (Less stable)	Transition state	3°-carbocation (More stable)

 (ii) **By resonance** If after hydride shift, resulting carbocation stabilises by resonance then, carbocation rearrangement occurs.

e.g.

2°-carbocation	2°-carbocation (Resonance stabilised)
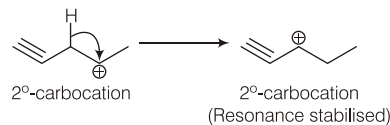
Note Rearrangement always occurs between adjacent carbon atoms, i.e. $C_1 - C_2$ or $C_2 - C_3$ etc.

TYPE 3 Problem Based on Rearrangement of Carbocations

Example 3 In the following carbocation; H/CH_3 that is most likely to migrate to the positively charged carbon is   [IIT JEE 2009]
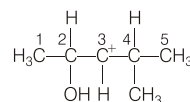
(a) CH_3 at C-4   (b) H at C-4   (c) CH_3 at C-2   (d) H at C-2

▣ METICULOUS ANALYSIS

Sol. *(d)* H at C-2 will migrate giving resonance stabilised carbocation.

$$H_3C-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{\overset{\oplus}{C}}}-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3 \xrightarrow[\text{shift}]{H^-} H_3C-\overset{\oplus}{\underset{\underset{OH}{|}}{C}}-CH_2-CH\,(CH_3)_2$$
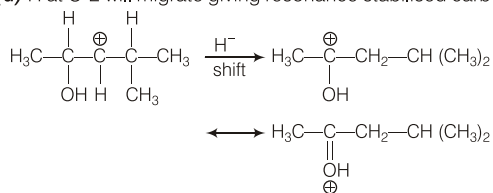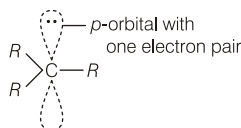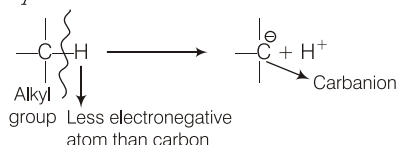
$$\longleftrightarrow H_3C-\overset{}{\underset{\underset{\overset{OH}{\oplus}}{\|}}{C}}-CH_2-CH\,(CH_3)_2$$

(B) **Carbanions**

$$\underset{R}{\overset{R}{>}}C\overset{\cdot\cdot}{\underset{}{\Big\vert}}-R \quad \begin{matrix} \text{— }p\text{-orbital with}\\ \text{one electron pair}\end{matrix}$$
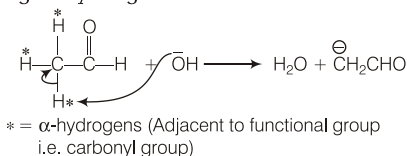
• These have atleast one carbon atom with a negative charge and have 8 electrons in their valence shells.
• These are sp^3-hybridised and trigonal pyramidal in shape.
• These are diamagnetic in nature.
• These combine with the electrophile that can accept a pair of electrons.
• These are formed by the following methods:
  (i) By heterolysis of covalent bond

$$-\overset{|}{\underset{|}{C}}\{H \longrightarrow -\overset{|}{\underset{|}{\overset{\ominus}{C}}} + H^+$$

Alkyl group Less electronegative atom than carbon Carbanion

  (ii) By the treatment of α-hydrogen containing aldehydes having α-hydrogen with $\bar{O}H$ ions

$$\overset{*}{H}-\overset{\overset{*}{\overset{H}{|}}}{\underset{\underset{H*}{|}}{C}}-\overset{\overset{O}{\|}}{C}-H + \bar{O}H \longrightarrow H_2O + \overset{\ominus}{C}H_2CHO$$

  * = α-hydrogens (Adjacent to functional group i.e. carbonyl group)

  (iii) By the addition of anions to alkenes and alkynes

$$\overset{}{>}C=C\overset{}{<} + X\bar{\,} \longrightarrow \overset{}{>}\underset{\underset{X}{|}}{C}-\overset{\ominus}{C}\overset{}{<}$$
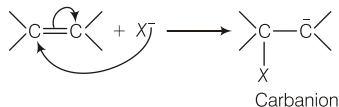
Carbanion

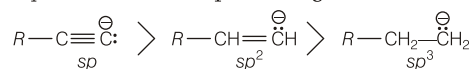## **Order of Stability for Carbanions**

• Stability ∝ Resonance ∝ Hyperconjugation
$$\propto -I\text{- effect} \propto \frac{1}{+\,I\text{-effect}}$$

• *The order of stability for various carbanions is*

$$Ph_3\overset{\ominus}{C} > Ph_2\overset{\ominus}{C}H > Ph\overset{\ominus}{C}H_2 > \overset{\ominus}{C}H_2-CH=CH_2$$

$$> \underset{\bigcirc}{\overset{\ominus}{\bigcirc}} > HC-\overset{\ominus}{C} > \underset{\underset{\ominus}{CH}}{\overset{CH_2}{\|}} > \overset{\ominus}{C}H_3$$

$$> CH_3-\overset{\ominus}{C}H_2 > (CH_3)_2\overset{\ominus}{C}H > (CH_3)_3\overset{\ominus}{C}$$

• Stability of carbanion ∝ percentage of s-character

$$\underset{sp}{R-C\equiv\overset{\ominus}{C}:} > \underset{sp^2}{R-CH=\overset{\ominus}{C}H} > \underset{sp^3}{R-CH_2-\overset{\ominus}{C}H_2}$$
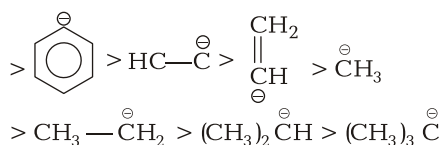
TYPE 4 Problems Based on Finding Stability of Carbanions

Example 4 The correct stability order of the following resonance structures is [IIT JEE 2009]

I. $H_2C=\overset{\oplus}{N}=\overset{\ominus}{N}$ II. $H_2\overset{\oplus}{C}-N=\overset{\ominus}{N}$

III. $H_2\overset{\ominus}{C}-\overset{\oplus}{N}\equiv N$ IV. $H_2\overset{\ominus}{C}-N=\overset{\oplus}{N}$

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

Sol. *(b)* I is most stable as it has more covalent bonds and it contains negative charge on more electronegative atom, i.e. nitrogen.
• III is more stable than II and IV due to greater number of covalent bonds.
• Between II and IV, II is more stable since, it has negative charge on more electronegative atom and positive charge on more electropositive atom.
Hence, overall stability order is I > III > II > IV

Stability of Carbanions in Terms of Acidity

▪ Carbanion possesses an unshared pair of electrons and is therefore act as a base or a nucleophile. The stability of the carbanion is directly related to the strength of the conjugate acid. The weaker the acid, the greater the basic strength and the lower the stability of carbanion.
▪ Stability of carbanion ∝ Acidic strength ∝ $\dfrac{1}{\text{Basic strength}}$.
▪ By stability, here we mean stability towards a proton donor species: the lower the stability, the more willing the carbanion is to accept a proton from any available source and hence, to end its existence as a carbanion.
▪ Thus, the determination of the order of stability of a series of carbanions is equivalent to a determination of the order of strengths of the conjugative acids, and one can obtain information about relative stability carbanions of from a table of acidic strength.

Example 5 Give reason for the following.

$CH_2=\overset{\ominus}{C}H$ is more basic than $HC\equiv\overset{\ominus}{C}$ [IIT JEE 2000]

Sol. Stability of carbanion ∝ percentage of s-character

$$\underset{sp^2}{CH_2=\overset{\ominus}{C}H} \Rightarrow s\text{-character \%} = \frac{1}{1+2}\times100$$

$$= \frac{1}{3}\times100 = 33.33$$

$$\underset{sp}{HC\equiv\overset{\ominus}{C}} \Rightarrow s\text{-character \%} = \frac{1}{1+1}\times100$$

$$= \frac{1}{2}\times100 = 50\%$$

Hence, $HC\equiv\overset{\ominus}{C}$ is more stable than $CH_2=\overset{\ominus}{C}H$, which results availability of non-bonding electrons in $CH_2=\overset{\ominus}{C}H$ is more than that in $HC\equiv\overset{\ominus}{C}$. Hence, $CH_2=\overset{\ominus}{C}H$ is more basic than $HC\equiv\overset{\ominus}{C}$.

Example 6 The correct order of basicities of the following compounds is   **[IIT JEE 2001]**

I. $H_3C-C\overset{NH}{\underset{NH_2}{\big\backslash}}$ II. $CH_3-CH_2NH_2$

III. $(CH_3)_2NH_2$ IV. CH_3CONH_2

   (a) II > I > III > IV   (b) I > III > II > IV
   (c) III > I > II > IV   (d) I > II > III > IV
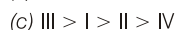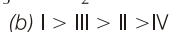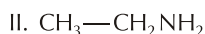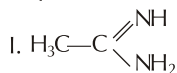
Sol. **(b)** I is most basic due to the formation of resonance stabilised conjugate acid.

$H_3C-C\overset{NH}{\underset{NH_2}{\big\backslash}}$ $\xrightarrow{H^+}$ $H_3C-C\overset{+NH_2}{\underset{NH_2}{\big\backslash}}$ ⟷ $H_3C-C\overset{NH_2}{\underset{\oplus NH_2}{\big\backslash}}$

Resonance stabilised conjugate acid
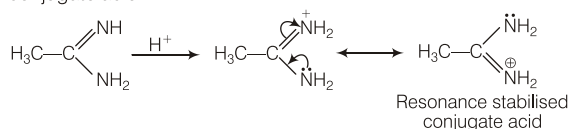
• IV is amide, least basic.

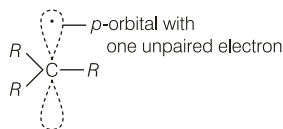$CH_3-\overset{O}{\overset{\|}{C}}-NH_2$ ⟷ $CH_3-\overset{O^-}{\overset{\|}{C}}=\overset{+}{N}H_2$

lone pair involves in delocalisation.

• Between alkyl amines, 2° is more basic than 1° amine. Hence, overall order of basic strength is I > III > II > IV.
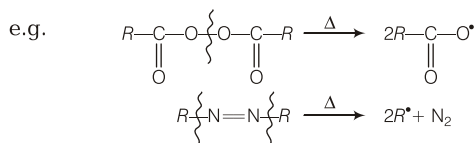
(C) Free Radicals

$R-\overset{R}{\underset{R}{C}}$ — *p*-orbital with one unpaired electron

• These are atoms or groups containing a free or an odd electron.
• These can be sp^3 or sp^2-hybridised and hence, can have corresponding pyramidal or planar shape.
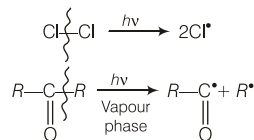
Planar (sp^2)   Pyramidal (sp^3)
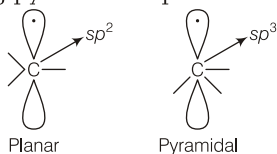
• As these have one unpaired electron, these are paramagnetic in nature.
• These can be prepared by the following methods:
  (i) **Thermal cleavage** When organic molecules are subjected to high temperature in the gas phase, result in the formation of free radicals.
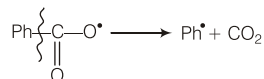
e.g.

$R-\overset{O}{\overset{\|}{C}}-O\{O-\overset{O}{\overset{\|}{C}}-R \xrightarrow{\Delta} 2R-\overset{O}{\overset{\|}{C}}-O^\bullet$

$R\{N=N\{R \xrightarrow{\Delta} 2R^\bullet + N_2$

(ii) **Photochemical cleavage** The energy corresponding to the light of 600 to 300 nm is 48 to 96 kcal mol^{-1} (200 to 400 kJ mol^{-1}), which is of the order of magnitude of covalent bond energies.
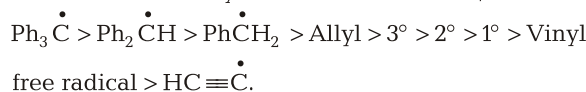
e.g.

$Cl\{Cl \xrightarrow{h\nu} 2Cl^\bullet$

$R-\overset{O}{\overset{\|}{C}}\{R \xrightarrow[\text{Vapour phase}]{h\nu} R-\overset{O}{\overset{\|}{C}}^\bullet + R^\bullet$

(iii) **By other radicals**

$Ph\{\overset{O}{\overset{\|}{C}}-O^\bullet \longrightarrow Ph^\bullet + CO_2$

Order of Stability of Free Radicals

• Stability ∝ Resonance ∝ Hypercongugation
 $$\propto +I\text{-effect} \propto \frac{1}{-I\text{-effect}}$$

• *The order of stability for various radicals is,*
  $Ph_3\overset{\bullet}{C} > Ph_2\overset{\bullet}{C}H > Ph\overset{\bullet}{C}H_2 > Allyl > 3° > 2° > 1° > Vinyl$
  $free\ radical > HC\equiv\overset{\bullet}{C}.$

• Vinyl free radical is least stable as it does not show resonance or hypercongugation.

ANALYSIS OF BOND STRENGTH IN TERMS OF BOND DISSOCIATION ENERGY

■ Bond dissociation energy is the energy required for the breaking of a particular bond in a molecule in its gaseous state or it is the standard enthalpy change, when a bond is cleaved by homolysis.

$$A\{B \longrightarrow A^\bullet + B^\bullet;\ \Delta H = x\ \text{kcal mol}^{-1}$$
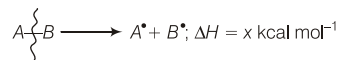
Here, positive value of ΔH indicates that energy has to be supplied in order to break the covalent bond between A and B.

■ Therefore, the bond dissociation energy reflects the stability of the radicals formed, the less is the bond dissociation energy, more will be the stability of radical.
■ Bond dissociation energy provides an accurate assessment of the energy required to break a particular bond homolytically. Bond energy (or average bond energy) is used to estimate the change in energy for transformations from one stable species to another especially in cases where π-bonds are broken and formed.
■ However, in reactions where multiple bonds are broken, the bond dissociation energy of a particular bond can be changed dramatically by the cleavage of one of the bonds within the molecule. That is, once the first bond is broken, the remaining bond dissociation energies are often altered.
■ The bond energy and bond dissociation energy are the same for the bond in a diatomic molecules but these are different for a bond in a polyatomic molecules.
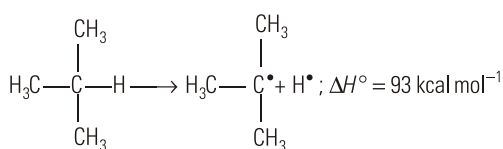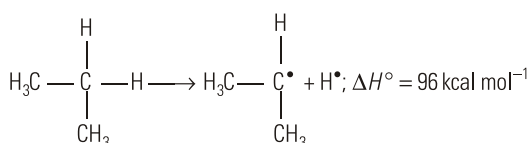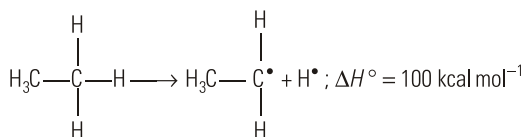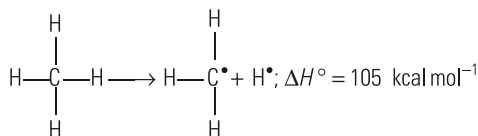
🗒 METICULOUS ANALYSIS

e.g.

Species	Homolytic fission	Bond dissociation energy (BDE)
H—O—H	H—O⟨H⟩ ⟶ H—Ö⟨ + H•	119.9 kcal mol^{-1}
•Ö—H	•Ö⟨H⟩ ⟶ ••Ö + H•	101.2 kcal mol^{-1}

Average BDE = $(119.9 + 101.2)/2$ kcal mol^{-1} = 110.6 kcal mol^{-1}

Here, 110.6 kcal mol^{-1} is the bond energy.

- The bond dissociation energy is important in terms of finding stability of substituted radicals. The less is the bond dissociation energy, more will be the stability of radical.
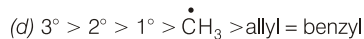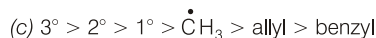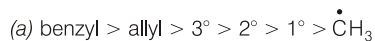
$$H{-}\underset{H}{\overset{H}{C}}{-}H \longrightarrow H{-}\underset{H}{\overset{H}{C}}{}^{\bullet} + H^{\bullet};\ \Delta H° = 105\ \text{kcal mol}^{-1}$$

$$H_3C{-}\underset{H}{\overset{H}{C}}{-}H \longrightarrow H_3C{-}\underset{H}{\overset{H}{C}}{}^{\bullet} + H^{\bullet};\ \Delta H° = 100\ \text{kcal mol}^{-1}$$

$$H_3C{-}\underset{CH_3}{\overset{H}{C}}{-}H \longrightarrow H_3C{-}\underset{CH_3}{\overset{H}{C}}{}^{\bullet} + H^{\bullet};\ \Delta H° = 96\ \text{kcal mol}^{-1}$$

$$H_3C{-}\underset{CH_3}{\overset{CH_3}{C}}{-}H \longrightarrow H_3C{-}\underset{CH_3}{\overset{CH_3}{C}}{}^{\bullet} + H^{\bullet};\ \Delta H° = 93\ \text{kcal mol}^{-1}$$

Hence, stability of radicals 3° > 2° > 1°.

TYPE 5 Problem Based on Finding Stability of Free Radicals

Example 7 The stability of the free radicals, allyl, benzyl, 3°, 2° and 1° and $\overset{\bullet}{C}H_3$ is in the order

(a) benzyl > allyl > 3° > 2° > 1° > $\overset{\bullet}{C}H_3$

(b) allyl > 3° > benzyl > 2° > 1° > $\overset{\bullet}{C}H_3$

(c) 3° > 2° > 1° > $\overset{\bullet}{C}H_3$ > allyl > benzyl

(d) 3° > 2° > 1° > $\overset{\bullet}{C}H_3$ > allyl = benzyl

Sol. **(a)** Stability of free radical ∝ Resonance ∝ Hyperconjugation Resonance dominates over hyperconjugation. Hence, benzyl and allyl radicals are more stable than 3°, 2°, 1° and $\overset{\bullet}{C}H_3$ radicals.
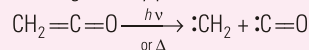
∴ Order of stability is

$$\underset{\substack{\text{Resonance}\\\text{stabilised}}}{\underline{\text{Benzyl} > \text{Allyl}}} > \underset{\substack{\text{Hyperconjugation}\\\text{stabilised}}}{\underline{3° > 2° > 1°}} > \overset{\bullet}{C}H_3 \longrightarrow \underset{\text{nor hyperconjugation}}{\overset{\text{Neither resonance}}{}}$$
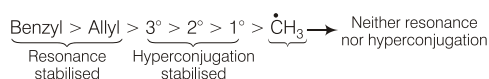
Intermediate : Neutral Molecules

Carbenes

- The neutral divalent carbon species in which two non-bonding electrons are present along with two bonding pairs are called carbenes. These are generally produced either by photolysis.

$$CH_2{=}C{=}O \xrightarrow[\text{or }\Delta]{h\nu} :CH_2 + :C{=}O$$

- decreasing order of stability of carbenes

$$:CH_2 > :CF_2 > :CCl_2 > :CBr_2$$

- Carbenes can be categorised to singlet and triplet carbenes
- Distinguish between singlet and triplet carbenes

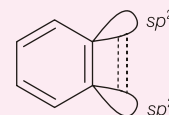| Singlet	Triplet
Central C-atom is sp^2 hybridised.	Central C-atom is sp hybridised.
Unhybridised orbital contains no electron and a hybridised orbital contains two electrons	Unhybridised orbitals contain 1 electron each.
Bond structure, less stable the singlet	Has linear structure, more stable than singlet carbene.

Nitrenes Neutral monovalent nitrogen species in which nitrogen has two unshared pair of electrons with a monovalent atom or group attached is called nitrenes.

- These are produced by thermolysis of azides
- Nitrenes obey Hund's rule
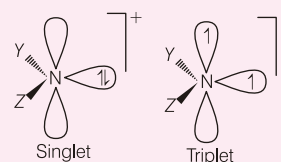
Arynes A formal carbon-carbon triple bond containing aromatic molecule is called aryne. The best known example is benzyne.

Nitrenium ions These are nitrogen containing organic compounds in which the nitrogen atom has an incomplete (sextet) electron shell and a formal positive charge.

- These ions exist in two electronic states
  - The singlet state – The triplet state
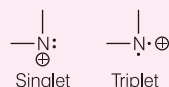
Diradicals The species with a pair of degenerate (equal energy) molecular orbitals and two electrons
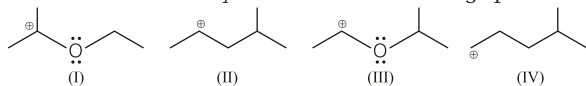
Three possible diradical rearrangements are
- The singlet state
- The triplet state
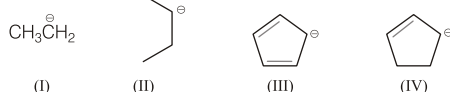- The unstable intermediate state

Smart Practice

Single Option Correct Type Questions

1. The correct stability order for the following species is
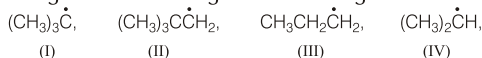

(I)   (II)   (III)   (IV)

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

2. The correct stability order for the following carbanions is

(I)   (II)   (III)   (IV)

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

3. Arrange the following in increasing order of stability.

$(CH_3)_3\overset{\bullet}{C}$, $(CH_3)_3C\overset{\bullet}{C}H_2$, $CH_3CH_2\overset{\bullet}{C}H_2$, $(CH_3)_2\overset{\bullet}{C}H$,
(I)   (II)   (III)   (IV)

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

4. The stability of carbonium ion depends upon
(a) the bond angle of the attached group
(b) the substrate with which it reacts
(c) the inductive and hyperconjugation effects with respect to attached group
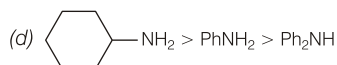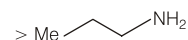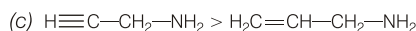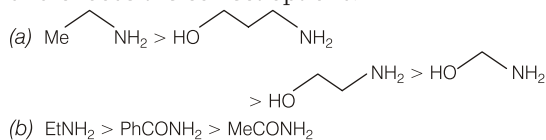(d) None of the above

More than One Correct Type Questions

5. The carbocation $CF_3 \!-\! C^\oplus$ is destabilised but carbocation $\overset{\oplus}{C}F_3$ is stabilised with the presence of three fluorine atoms because
(a) the highly electronegative fluorine atoms withdrawn shared pair of electrons between C—F bonds towards itself to a greater extent in $CF_3 \!-\! \overset{\oplus}{C}$ and intensifies positive charge on carbon
(b) in $\overset{+}{C}F_3$, the unshared pair of electron in the p-orbitals of each of the F-atoms can be shifted to positively charged carbon through the p-p overlap
(c) the highly electronegative fluorine atoms withdrawn shared pair of electrons between C—F bonds towards itself to greater extent in $\overset{+}{C}F_3$ and intensifies positive charge on carbon
(d) All of the above

6. Consider the following decreasing orders of basicity and choose the correct options.

(a)

(b) $EtNH_2 > PhCONH_2 > MeCONH_2$

(c) $HC\!\equiv\!C\!-\!CH_2\!-\!NH_2 > H_2C\!=\!CH\!-\!CH_2\!-\!NH_2$

(d) $-NH_2 > PhNH_2 > Ph_2NH$

7. Which of the following statements is/are correct for stability of carbanion?
(a) The stability of alkyl carbanions decreases as the number of alkyl groups attached to negatively charged carbon increases
(b) Greater the amount of s-character at the carbanionic carbon less will be its stability
(c) The electron withdrawing groups attached to negatively charged carbon increases its stability
(d) Carbanions are short lived species

Matching Type Question

8. Match the following Column I which represents species to the Column II representing corresponding factor on which their stability depends directly.
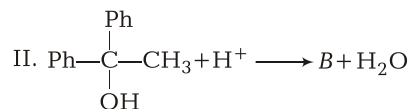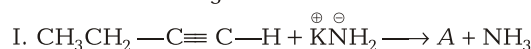
Column I	Column II
A. $Ph_3\overset{+}{C}$	p. Hyperconjugation
B. $HC \equiv \overset{\ominus}{C}$	q. Resonance
C.	r. Percentage of s-character

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

Passage Type Questions

Consider the following chemical reactions.

I. $CH_3CH_2 \!-\! C\!\equiv\! C\!-\!H + \overset{\oplus}{K}\overset{\ominus}{NH_2} \longrightarrow A + NH_3$

II. $Ph\!-\!\underset{\underset{OH}{|}}{\overset{\overset{Ph}{|}}{C}}\!-\!CH_3 + H^+ \longrightarrow B + H_2O$

III. $PhCH_2Cl + AlCl_3 \longrightarrow C + [AlCl_4]^-$

9. In which reaction(s), carbocations are formed?
(a) I and II   (b) II and III
(c) I and III   (d) III and IV

10. In which reaction(s), carbanion(s) is/are formed?
(a) Only I   (b) Only III
(c) I and II   (d) II and III

Answers

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

⬛ EXAM SPECTRUM

NEET 2016
(PHASE II)

PRACTICE PAPER
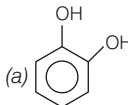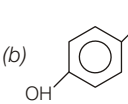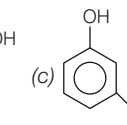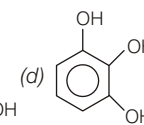### A COLLECTION OF ASSORTED SOLVED KNOCK OUTS

─ INSTRUCTIONS ─

- This test consists of 45 questions and each question is allotted 4 marks for correct response.
- Candidates will be awarded marks as stated above for correct response of each question. 1/4 mark will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
- There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted according as per instruction.

---

1. When benzene sulphonic acid and *p*-nitrophenol are treated with $NaHCO_3$ separately the gases released in each reaction respectively are

(a) SO_2, NO_2 (b) SO_2, NO (c) SO_2, CO_2 (d) CO_2, CO_2

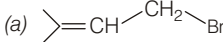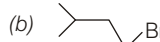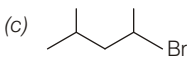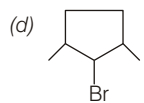**2.** $\dfrac{K_p}{K_C}$ for the following reaction will be,
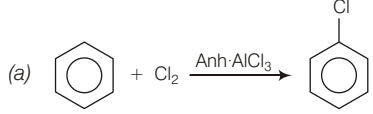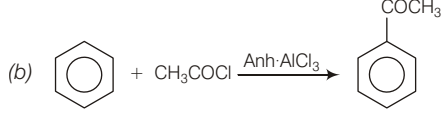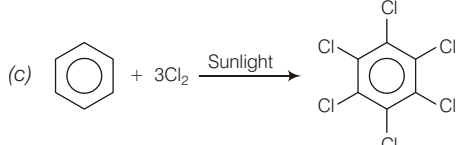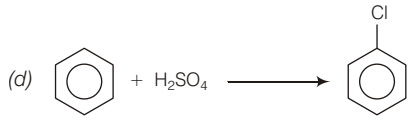
$$CO_2(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$$

(a) RT (b) $\dfrac{1}{RT}$ (c) $\dfrac{1}{\sqrt{RT}}$ (d) $\dfrac{RT}{2}$

3. How much amount of $CuSO_4 \times 5H_2O$ is required for the liberation of 2.54 g of I_2 when titrated with KI?

(a) 2.54 g   (b) 4.99 g   (c) 2.42 g   (d) 1.26 g

4. Which of the following has the smallest number of molecules?

(a) 0.1 mole of CO_2 gas   (b) 11.2 L of CO_2 gas at STP
(c) 22 g of CO_2 (d) 22.4×10^3 mL of CO_2 gas at STP

5. For the reversible reaction,

$$A(s) + B(g) \rightleftharpoons C(g) + D(g); \ \Delta G° = -350 \text{ kJ}$$

Which one of the following statement is true?
(a) The reaction is thermodynamically non-feasible
(b) The entropy change is negative.
(c) Equilibrium constant is greater than one
(d) The reaction should be instantaneous

6. If mole fraction of a solute in 1 kg benzene is 0.2, then molality of solute is

(a) 3.2   (b) 2   (c) 4   (d) 3.6

7. In the first order reaction, 75% of the reaction gets disappeared in 1.386 h. The rate constant of the reaction is

(a) $3.0 \times 10^{-3} \text{s}^{-1}$ (b) $2.8 \times 10^{-4} \text{ s}^{-1}$
(c) $1.5 \times 10^{-3} \text{ s}^{-1}$ (d) $1.8 \times 10^{-3} \text{ s}^{-1}$

8. Among the following species, identify the pair having same bond order CN^-, O_2^-, NO^+, CN^+

(a) CN^- and O_2^- (b) O_2^- and NO^+
(c) CN^- and NO^+ (d) CN^- and CN^+

9. Which of the following will produce only one product on reduction with $LiAlH_4$?

(a) $CH_3OCOCH_2CH_3$ (b) $CH_3CH_2OCOCH_2CH_3$
(c) $CH_3CH_2OCOCH_3$ (d) $CH_3CH_2OCOCH_2CH_2CH_3$

10. Which of the following compounds does not give a precipitate with excess of NaOH?

(a) $ZnSO_4$ (b) $FeSO_4$ (c) $AgNO_3$ (d) $HgCl_2$

11. Which of the following on thermal decomposition yields a basic as well as an acidic oxide?

(a) $KClO_3$ (b) Na_2CO_3 (c) $NaNO_3$ (d) $CaCO_3$

**12.** An excess of $AgNO_3$ is added to 100 mL of a 0.01 M solution of dichloridotetraaquachromium (III) chloride.

The number of moles of AgCl precipitated would be

(a) 0.0003   (b) 0.01
(c) 0.001   (d) 0.002

13. Which of the following statements regarding ozone, is not correct?

(a) The ozone molecule is angular in shape
(b) The ozone molecule is a resonance hybrid of two structures
(c) The oxygen-oxygen bond length in ozone is identical with that of molecular oxygen
(d) Ozone is used as germicide and disinfectant for the purification of air

14. The major product 'P' formed in the following reaction is $CH_3 - CH = CH_2 \xrightarrow[\text{peroxide}]{HI} P$

(a) $CH_3CH_2CH_2I$ (b) $CH_3 - \underset{|}{C}H - CH_3$

(c) $\underset{|}{C}H_2 - CH = CH_2$ (d) $\underset{|}{C}H_2 - \underset{|}{C}H_2$
       $\underset{|}{|}$ $\underset{|}{|}\ \ \underset{|}{|}$

                                            $\underset{|}{CH_3}$

15. The compound $CH_3 - C = CH - CH_3$ on reaction with $NaIO_4$ in the presence of $KMnO_4$ gives

(a) $CH_3COCH_3 + CH_3CHO$
(b) $CH_3CHO + CO_2$
(c) CH_3COCH_3
(d) $CH_3COCH_3 + CH_3COOH$

16. The reaction $2CH_3 - C - OC_2H_5 \xrightarrow{C_2H_5O^-Na^+}$
                        $\underset{O}{\|}$

$CH_3 - C - CH_2 - C - OC_2H_5 + C_2H_5OH$ is called
     $\underset{O}{\|}$ $\underset{O}{\|}$

(a) Etard reaction   (b) Perkin's reaction
(c) Claisen condensation (d) Claisen-Schmidt reaction

17. In the electrothermal process, for the production of phosphorus, the compound displaced by silica from calcium phosphate is

(a) calcium phosphide   (b) phosphine
(c) phosphorus   (d) phosphorus pentoxide

18. The mass of one molecule of a compound $C_{60}H_{122}$ is

(a) 1.3×10^{-20} g   (b) 5.01×10^{-21} g
(c) 3.72×10^{-30} g (d) 1.4×10^{-21} g

19. Which of the following statements is true?

(a) In aqueous medium, HF is a stronger acid than HCl
(b) $HClO_4$ is a weaker acid than $HClO_3$
(c) HNO_3 is a stronger acid than HNO_2
(d) H_3PO_3 is a stronger acid than H_2SO_3

20. Which of the following reactions does not yield an amine?

(a) $R - X + NH_3 \longrightarrow$
(b) $R - CH = NOH + [H] \xrightarrow{Na/C_2H_5OH}$
(c) $R - CN + H_2O \xrightarrow{H^+}$
(d) $R - CONH_2 \xrightarrow{LiAlH_4}$

21. According to IUPAC nomenclature sodium nitroprusside is named as

(a) sodium pentacyanonitrosylferrate (II)
(b) sodium pentacyanonitrosylferrate (III)
(c) sodium nitroferricyanide
(d) sodium nitroferrocyanide

22. When dil. H_2SO_4 is added to aqueous solution of potassium chromate, yellow colour of solution turns to orange colour. It indicates

(a) chromate ions are reduced
(b) chromate ions are oxidised
(c) monocentric complex is converted into dicentric complex
(d) oxygen gets removed from chromate ions

23. $SiCl_4$ on hydrolysis forms X and HCl, compound X loses water at 1000°C and gives Y. Compounds X and Y respectively are

(a) H_2SiCl_6, SiO_2 (b) H_2SiO_4, Si
(c) SiO_2, Si (d) H_4SiO_4, SiO_2

24. Bakelite is a product of the reaction between

(a) formaldehyde and NaOH (b) aniline and urea
(c) phenol and methanal   (d) phenol and chloroform

25. Which complex compound possesses sp^3d^2 hybridisation?

(a) $[Fe(NH_3)_6]^{3+}$ (b) $[Fe(CN)_6]^{4-}$
(c) $[Fe(CN)_6]^{3-}$ (d) $[Fe(Cl)_6]^{3-}$

26. The amount of H_2S required to precipitate 1.69 g of BaS from $BaCl_2$ solution is

(a) 3.4 g   (b) 0.24 g   (c) 0.34 g   (d) 0.17 g

27. The lanthanoid element that has the electronic configuration, $[Xe]\ 4f^7 5d^1 6s^2$ is

(a) Lutetium   (b) Terbium   (c) Ytterbium   (d) Gadolinium

28. Select the structural formula of resorcinol

29. For one mole of an ideal gas, increasing the temperature from 10°C to 20°C results

(a) Increase in the average kinetic energy by two times.
(b) Increase in the rms velocity by $\sqrt{2}$ times.
(c) Increase in the rms velocity by two times.
(d) Increase in both the average kinetic energy and rms velocity, but not significantly.

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30. Which one of the following statements is not correct?

(a) Al reacts with NaOH and liberates H_2
(b) $AlCl_3$ is a Lewis acid
(c) Al is used in the manufacture of electrical cables
(d) NaOH is used during Hall's process for the purification of bauxite

31. A solution contains 10mL of 0.1N NaOH and 10 mL of 0.05N H_2SO_4, pH of this solution is

(a) less than 7   (b) 7
(c) zero   (d) greater than 7

32. When nitric acid reacts with nitric oxide, a gas is released, which converts H_2S into

(a) SO_4^{2-} (b) S^{2-} (c) S   (d) $S_2O_5^{2-}$

33. The number of metamers of the compound with molecular formula $C_5H_{10}O$ is

(a) 1   (b) 3   (c) 8   (d 6

34. Which one of the following is least reactive in nucleophilic substitution reaction?

(a) $(CH_3)_3C$ ¾ Cl   (b) $CH_2 = CHCl$
(c) CH_3CH_2Cl (d) $CH_2 = CHCH_2Cl$

35. Facial and meridional isomerism will be exhibited by

(a) $[Co(NH_3)_3Cl_3]$ (b) $[Co(NH_3)_4Cl_2]$ Cl
(c) $[Co(en)_3]Cl_3$ (d) $[Co(NH_3)_5Cl]$ Cl_2

36. Which one of the elements with the following outer orbital configurations may exhibit the largest number of oxidation states?

(a) $3d^5 4s^1$ (b) $3d^5 4s^2$ (c) $3d^2 4s^2$ (d) $3d^3 4s^2$

37. Which one of the following alkyl bromides undergoes most rapid solvolysis in methanol solution to give corresponding methyl ether ?

(a) >=CH—CH₂—Br   (b) ⟩—Br
(c) (structure with Br)   (d) (cyclopentane with Br)

38. The percentages of free space in cubic closed packed structure and body centred packed structure are respectively?

(a) 30% and 26%   (b) 26 % and 32 %
(c) 32% and 48%   (d) 48% and 26%

39. The heat of combustion of C, S and CS_2 are

-393.3 kJ mol^{-1}, -293.7 kJ mol^{-1}
and -1108.76 kJ mol^{-1}.

What will be the heat of formation of CS_2.

(a) -128.06 kJ mol^{-1} (b) $+970$ kJ mol^{-1}
(c) $+1108.7$ kJ mol^{-1} (d) $+12$ kJ mol^{-1}

40. Inductive effect of which atom or group taken as zero to compare inductive effect of other atoms is

(a) Hydrogen (b) Chlorine   (c) Carbon   (d) Oxygen

41. Which of the following reactions is not an example of electrophilic substitution in benzene ring?

(a) benzene + Cl_2 $\xrightarrow{Anh\cdot AlCl_3}$ chlorobenzene

(b) benzene + CH_3COCl $\xrightarrow{Anh\cdot AlCl_3}$ acetophenone ($COCH_3$)

(c) benzene + $3Cl_2$ $\xrightarrow{Sunlight}$ hexachlorocyclohexane

(d) benzene + H_2SO_4 $\longrightarrow$ chlorobenzene

42. Which of the following compounds will be most reactive towards nucleophilic addition reaction?

(a) CH_3CO $CH_2CH_2CH_2CH_3$
(b) $CH_3CH_2COCH_2CH_2CH_3$
(c) $CH_3CH_2CH_2CH_2CH_2CHO$
(d) CH_3 ¾ CH_2 ¾ CO ¾ CH ¾ CH_3
          |
          CH_3

43. In which of the following reaction aniline does not liberate major product?

(a) $C_6H_5OH + NH_3$ ¾ $\overset{ZnCl_2}{\underset{300°C}{¾¾}}$ →
(b) $C_6H_5NO_2$ ¾¾¾ $\overset{Zn\ powder}{\underset{Alcoholic\ KOH}{¾¾}}$ →
(c) $C_6H_5Cl + NH_3$ ¾¾¾¾ $\overset{200°C\ high\ pressure}{\underset{Cu_2O}{¾¾¾}}$ →

(d) $C_6H_5NO_2 + 6[H]$ ¾ $\overset{Fe + H_2O}{\underset{HCl}{¾¾}}$ →

44. The reason for the loss of optical activity of lactic acid when ¾ OH group is changed by H is because

(a) chiral centre of the molecule is destroyed
(b) molecule accquires asymmetry
(c) due to change in configuration
(d) structural changes occur

45. Schottky defect in crystals is observed when

(a) unequal number of cations and anions are missing from the lattice sites
(b) equal number of cations and anions are missing from the lattice sites
(c) an ion leaves its normal site and occupies an interstitial site
(d) density of the crystals is increased

Answers with **Explanation**

1. **(d) Key Concept** *Benzene sulphonic acid and p-nitrophenol are strong acids, so these are capable to evolve* CO_2 *gas on reaction with* $NaHCO_3$

$$\underset{\text{Salt}}{HCO_3^-} + \underset{\text{Acid}}{H^+} \longrightarrow H_2O + CO_2\uparrow$$
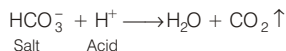
Benzene sulphonic acid and *p*-nitrophenol react with $NaHCO_3$ and evolve CO_2 gas
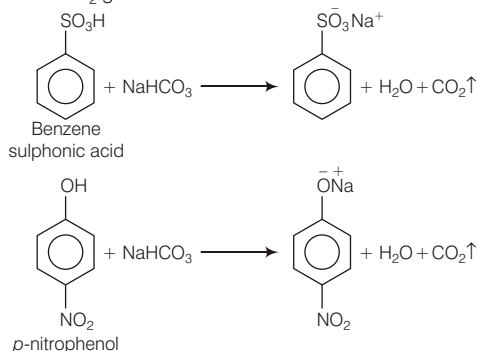
2. **(c)** $\Delta n_g = n_P - n_R = 1 - \dfrac{3}{2} = -\dfrac{1}{2}$

$$K_P = K_C (RT)^{\Delta n_g} = K_C (RT)^{-1/2}$$

$$\frac{K_p}{K_C} = \frac{1}{(RT)^{1/2}} = \frac{1}{\sqrt{RT}}$$

3. **(b)** $2CuSO_4.5H_2O + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + \underset{254\,g}{I_2} + 10H_2O$

Molecular mass of $2CuSO_4.5H_2O = [2(63.5 + 32 + 64) + 10(18)]$
$= 499\,g$

As 254 g of I_2 is liberated by 499 g $CuSO_4.5H_2O$

So, 2.54 g of I_2 will be liberated by x g $CuSO_4 \cdot 5H_2O$

$$x = \frac{499}{254} \times 2.54 = 4.99\,g$$

4. **(a)**

(a) 0.1 mole of CO_2 (b) $\dfrac{11.2}{22.4} = 0.5$ mole of CO_2

(c) $\dfrac{22}{44} = 0.5$ mole of CO_2 (d) $\dfrac{22.4 \times 10^3}{22400} = 1$ mole of CO_2

Equal number of moles have equal number of molecules

Hence, 0.1 mole of CO_2 gas has the smallest number of molecules.

5. **(c)** In the given reversible reaction, since the randomness increases (because solid is changing into gas), entropy will increase and thus, ΔS is positive. Reversible reaction never undergo to completion (i.e. never be instantaneous)

For the given reaction $\Delta G° = -350\,kJ$

$\because$ $\Delta G° = -2.303\,RT \log_{10} K$

          $-350 = -2.303\,RT \log_{10} K$

If K has value equal to 1, value of $\log K$ comes out to be zero and hence, $\Delta G°$ becomes zero. This is not possible, as the given value of $\Delta G°$ is -350 kJ. Thus, the value of K should be greater than zero. Moreover, the reaction is thermodynamically feasible.

6. **(a)** Let number of moles solute in solution $= x$

Moles of benzene in solution

$$= \frac{1000g}{78\,g\,mol^{-1}} = 12.82\,\text{moles}$$

Mole fraction of solute $= \dfrac{x}{x + 12.82} = 3.2$

$$0.2 = \frac{x}{x + 12.82}$$

$$0.2(x + 12.82) = x$$

$$x - 0.2\,x = 2.564$$

$$x = \frac{2.564}{0.8} = 3.205 = 3.2$$

$\therefore$ Molality $= \dfrac{\text{Number of moles of solute}}{\text{Mass of solvent (in kg)}} = \dfrac{3.2}{1} = 3.2$

7. **(b)** For the first order reaction

$$t = \frac{2.303}{K} \log \frac{[A]_0}{[A]}$$

$$K = \frac{2.303}{1.386 \times 60 \times 60} \log \frac{100}{25} \qquad \begin{bmatrix} [A] = [A]_0 - x \\ = 100 - 75 = 25 \end{bmatrix}$$

$$K = \frac{2.303 \times 0.6021}{1.386 \times 60 \times 60} = 2.77 \times 10^{-4}\,s^{-1}$$

$$\simeq 2.8 \times 10^{-4}\,s^{-1}$$

8. **(c) Key concept** *Species with the same number of electrons, will have same bond order.*

| Species	Number of electrons
CN^-	$6 + 7 + 1 = 14$
O_2^-	$8 + 8 + 1 = 17$
NO^+	$7 + 8 - 1 = 14$
CN^+	$6 + 7 - 1 = 12$

Since, CN^- and NO^+ have same number of electrons, they have same bond order i.e. 3
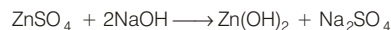
CN^- or $NO^+ = 14$

$$= \sigma s^2\, \overset{*}{\sigma}1s^2,\, \sigma 2s^2,\, \overset{*}{\sigma}2s^2,\, \sigma 2\,p_z^2,\, \pi 2\,p_x^2 = \pi 2\,p_y^2$$

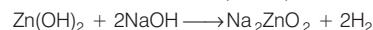Bond order $= \dfrac{N_b - N_a}{2} = \dfrac{10 - 4}{2} = 3$

9. **(a)** Only ethyl acetate undergoes reaction with $LiAlH_4$ to give ethyl alcohol, other esters given in options gives mixture of alcohols on reduction.

$$CH_3COOCH_2CH_3 + 2H_2 \xrightarrow{\text{LiAlH}_4} 2CH_3CH_2OH$$
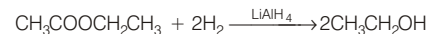
10. **(a)** On adding sodium hydroxide to the $ZnSO_4$ solution, first white precipitate of zinc hydroxide is obtained, which dissolves in excess of NaOH due to the formation of sodium zincate.

$$ZnSO_4 + 2NaOH \longrightarrow \underset{\substack{\text{White} \\ \text{(insoluble)}}}{Zn(OH)_2} + Na_2SO_4$$

$$Zn(OH)_2 + 2NaOH \longrightarrow \underset{\substack{\text{Sodium zincate} \\ \text{(soluble)}}}{Na_2ZnO_2} + 2H_2$$

11. **(d)** $\underset{\substack{\text{Basic oxide} \quad \text{Acidic oxide}}}{CaCO_3 \xrightarrow{\Delta} CaO + CO_2}$

CaO is a basic oxide as it is an oxide of alkaline earth metal (except BeO, all alkaline earth metal oxides are basic in nature).

12. **(c)** $[Cr(H_2O)_4Cl_2]Cl \rightleftharpoons [Cr(H_2O)_4Cl_2]^+ + Cl^-$

$$AgNO_3 + Cl^- \longrightarrow AgCl + NO_3^-$$

$[Cr(H_2O)_4Cl_2]Cl$ has one ionisable Cl^- ion
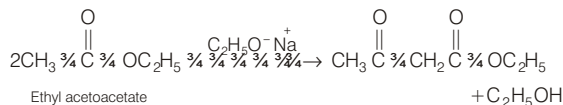
$\therefore$ Molarity of AgCl formed $= 0.01$ M

Moles of AgCl in 100 mL $= \dfrac{0.01}{1000} \times 100 = 0.001\,mol$

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13. *(c)* Due to resonance, the bond order in ozone is 1.5. Hence, O ¾ O bond length in O_3 is greater than O ¾ O bond length in O_2.

14. *(b)* The product of given reaction will be according to Markownikoff's rule. This is because peroxide effect is applicable only in case of HBr not in case of HI

$$CH_3 ¾ CH = CH_2 \xrightarrow[\text{peroxide}]{HI} CH_3 ¾ CH ¾ CH_3$$
$$|$$
$$I$$

15. *(d)*
$$\begin{array}{c} H_3C \\ \\ H_3C \end{array} C = CH—CH_3 + 3[O] \xrightarrow[\substack{\text{in the presence} \\ \text{of KMnO}_4}]{NaIO_4}$$

$$\begin{array}{c} H_3C \\ \\ H_3C \end{array} C = O + CH_3COOH$$
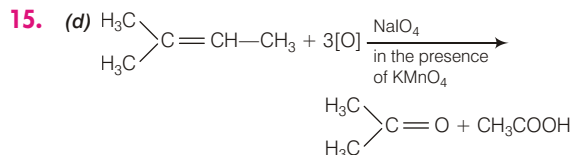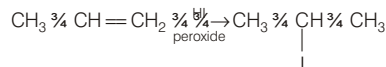
16. *(c)* Two molecules of ester condense to give β-keto ester in the presence of an alkali. This reaction is called Claisen condensation.

$$2CH_3 ¾ \overset{O}{\overset{||}{C}} ¾ OC_2H_5 \xrightarrow{C_2H_5O^- \overset{+}{Na}} CH_3 \overset{O}{\overset{||}{C}} ¾CH_2 \overset{O}{\overset{||}{C}} ¾ OC_2H_5$$

Ethyl acetoacetate $+C_2H_5OH$

17. *(d)* In electrothermal process, silica is heated with calcium phosphate, phosphorus pentoxide (P_4O_{10}) is obtained. P_4O_{10} is then reduced by coke in electric furnace to give white phosphorus.

$$2Ca_3(PO_4)_2 + 6SiO_2 \xrightarrow{} 6CaSiO_3 + P_4O_{10}$$
$$P_4O_{10} + 10\,C \xrightarrow{} P_4 + 10\,CO$$
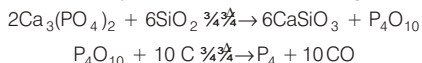
18. *(d)* The molecular mass of $C_{60}H_{122}$
$$= (60 \times 12 + 122)\,g$$
$$= (720 + 122)\,g = 842\,g$$

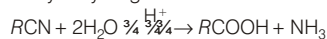The mass of one molecule of $C_{60}H_{122}$ = molecular mass of compound/Avogadro number
$$= \frac{842\,g}{6.023 \times 10^{23}} = 1.4 \times 10^{-21}\,g$$

19. *(c)* **Key Concept** HNO_3 *is more acidic than* HNO_2 *because* HNO_3 *contains more number of electronegative oxygen atoms which facilitate the easy removal of* H^+ *ion.*
The order of acidic strength is
$$HCl > HF$$
$$HClO_4 > HClO_3$$
$$HNO_3 > HNO_2$$
$$H_2SO_3 > H_2PO_3$$
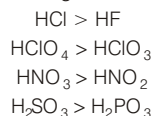
20. *(c)* Cyanides on hydrolysis give acids
$$RCN + 2H_2O \xrightarrow{H^+} RCOOH + NH_3$$
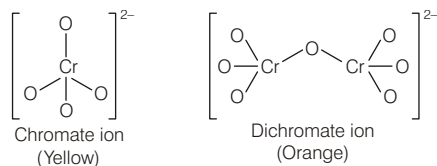While all other reactions give amines.

21. *(b)* IUPAC name of sodium nitroprusside $Na_2[Fe(CN)_5NO]$ is sodium pentacyanonitrosylferrate (III) because in it NO is neutral ligand and the oxidation number of Fe is +3.
$$2 \times O \times N \text{ of Na} + O \times N \text{ of Fe} + 5 \times O \times N \text{ of C} \times N + 1 \times O \times N \text{ of NO} = 0$$
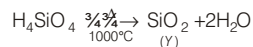$$2 \times (+1) + O \times N \text{ of Fe} + 5 \times (-1) + 1 \times 0 = 0$$
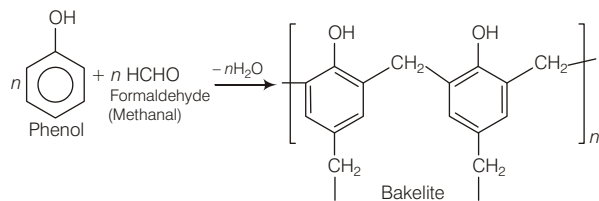$$O \times N \text{ of Fe} = 5 - 2 = +3$$

22. *(c)* $2K_2CrO_4 + H_2SO_4 \xrightarrow{} K_2Cr_2O_7 + K_2SO_4 + H_2O$

Chromate ion (Yellow)　　Dichromate ion (Orange)

23. *(d)* $SiCl_4 + 4H_2O \xrightarrow{} \underset{(X)}{H_4SiO_4} + 4HCl$

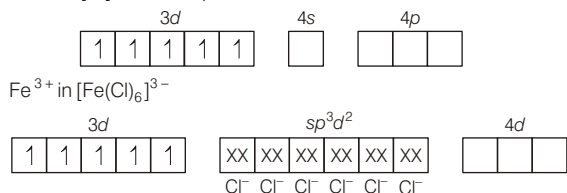$$H_4SiO_4 \xrightarrow{1000°C} \underset{(Y)}{SiO_2} + 2H_2O$$

24. *(c)*

25. *(d)* Cl^- being a weak field ligand, does not pair up with d-electrons of the metal atom and thus, forms an outer orbital complex.
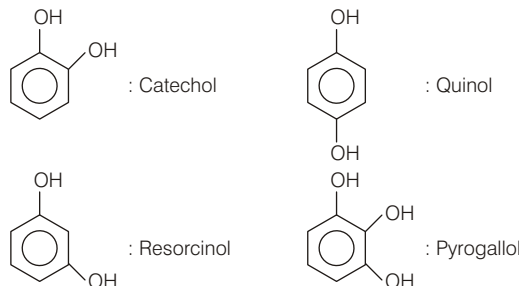In $[Fe(Cl)_6]^{3-}$, (Fe is present as Fe^{3+})
$$Fe^{3+} = [Ar]\, 3d^5\, 4s^0\, 4p^0$$

Fe^{3+} in $[Fe(Cl)_6]^{3-}$

26. *(c)* $\underset{\substack{(2g + 32\,g \\ = 34\,g)}}{BaCl_2 + H_2S} \xrightarrow{} \underset{\substack{(137g + 32\,g \\ = 169\,g)}}{BaS\downarrow} + 2HCl$

∵ 169 g of BaS is obtained by 34g of H_2S

∴ 1.69 g of BaS will be obtained by $H_2S = \dfrac{34 \times 1.69}{169} = 0.34\,g$

27. *(d)* The given electronic configuration corresponds to gadolinium $(Z = 64)$ which belongs of 4f-series.

28. *(c)*

29. *(d)* Given, $T_1 = 273 + 10 = 283\,K$
$$T_2 = 273 + 20 = 293\,K$$
Average Kinetic energy $(KE) = \frac{3}{2}KT$
$$\frac{(KE_1)}{(KE_2)} = \frac{283}{293} = 0.96$$
Root mean square (rms) velocity
$$v_{rms} = \sqrt{\frac{3RT}{M}}$$
$$\frac{v_{(rms)_1}}{v_{(rms)_2}} = \sqrt{\frac{T_1}{T_2}} = \sqrt{\frac{283}{293}} = 0.98$$
Thus, both average kinetic energy and root mean square velocity increases but not significantly when temperature is increased from 10°C to 20°C.

30. **(d)** NaOH is used in Baeyer's process for purification of bauxite ore. Hall's process involves extraction of aluminium metal from its oxide ore (alumina) by passing electric current through a solution of aluminium oxide in molten cryolite. This oxide ore is obtained from bauxite through Baeyer's process.

31. **(d)** 10 mL of 0.1M NaOH contains millimole

$$= 10 \times 0.1 = 1 \qquad (\because 0.1 \text{ N NaOH} = 0.1 \text{ M NaOH})$$

10 mL of 0.025 M H_2SO_4 contains millimole

$$= 10 \times 0.025 = 0.25 \qquad (\because 0.05 \text{ N } H_2SO_4 = 0.025 \text{ M } H_2SO_4)$$

$$\underset{1\,mol}{H_2SO_4} + \underset{2\,mol}{2NaOH} \xrightarrow{\quad} Na_2SO_4 + H_2O$$

0.25 millimole of H_2SO_4 will react with 0.5 millimole of NaOH.

$\therefore$ NaOH left $= 1 - 0.5 = 0.5$ millimole
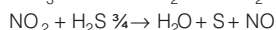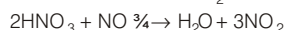
Volume of reaction mixture $= 20$ mL

Molarity of NaOH in mixture solution $= \dfrac{0.5}{20} = 2.5 \times 10^{-2}$ M

$$pOH = -\log [OH^-] = -\log (2.5 \times 10^{-2}) = 1.60$$
$$pH = 14 - pOH = 14 - 1.60$$
$$pH = 12.4$$

32. **(c)** When nitric acid (HNO_3) reacts with nitric oxide (NO), NO_2 gas is released which oxidises H_2S into sulphur.
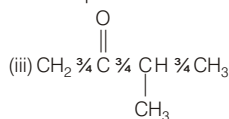
$$2HNO_3 + NO \xrightarrow{\quad} H_2O + 3NO_2$$
$$NO_2 + H_2S \xrightarrow{\quad} H_2O + S + NO$$

33. **(b)** Since the compound has $C_nH_{2n}O$ type general formula, it must be ketone (or aldehyde). It has the following metamers (the isomers having same functional group but different alkyl group attached with the same functional group)
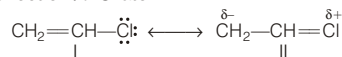
(i) $CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_2CH_2CH_3$ (ii) $CH_3CH_2 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_2CH_3$
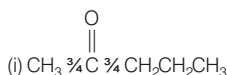
    2-pentanone   3-pentanone.

(iii) $CH_2 - \overset{\overset{\displaystyle O}{\|}}{C} - \underset{\underset{\displaystyle CH_3}{|}}{CH} - CH_3$
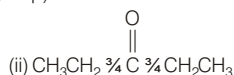
    3-methyl-2-butanone

Hence, it has three metamers.

34. **(b)** Chlorine of vinyl chloride ($CH_2{=}CHCl$) is non-reactive (less reactive) toward nucleophile in nucleophilic substitution reaction because it shows the following resonating structures due to $+M$ effect of $-$ Cl atom.

$$\underset{I}{CH_2{=}CH-\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:} \longleftrightarrow \underset{II}{\overset{\delta-}{CH_2}-CH{=}\overset{\delta+}{Cl}}$$

In structure II, Cl-atom has positive charge and partial double bond character with carbon of vinyl group, so it is more tightly attracted towards the nucleus and it does not get replaced by nucleophile in S_N reaction.

35. **(a)** Facial (*fac*) and meridional (*mer*) isomerism is a type of geometrical isomerism, that is shown by octahedral complexes having Ma_3b_3 general formula where, M is a central metal atom a and b are monodentate ligands. Hence, $[Co(NH_3)_3Cl_3]$ exhibits *fac-mer* isomerism as

   fac-form   *mer*-form
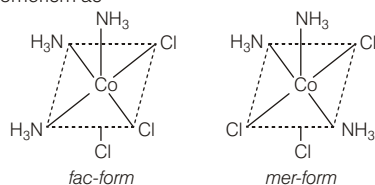
36. **(b)** Number of oxidation state = Number of valence electrons
Since, number of valence electrons is maximum in $3d^5 4s^2$, it shows maximum number of oxidation state.

37. **(a)** 1-bromo-3-methylbut-2-ene reacts most readily by S_N1 because the bromine is present on allylic carbon. Since, CH_3OH is a weak nucleophile and a weak nucleophile follows S_N1
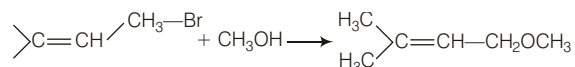
38. **(b)** Packing fraction of ccp $= \dfrac{\pi}{3\sqrt{2}} = 0.74 \rightarrow 74\%$

% free space in ccp $= (100 - 74)\% = 26\%$

Packing fraction of bcc $= \dfrac{\pi\sqrt{3}}{8} = 0.68 \rightarrow 68\%$

% free space in bcc $= (100 - 68)\% = 32\%$

**39.** **(a)** $C + 2S \xrightarrow{\quad} CS_2$

$$\Delta H = \Sigma \Delta H_p - \Sigma \Delta H_R = -1108.76 - (-393.3 + 2 \times (-293.7))$$
$$= -1108.76 + 393.3 + 587.4 = -128.06 \text{ kJ mol}^{-1}$$

40. **(a)** Hydrogen does not show I-effect. Its inductive effect is taken as zero. Electron releasing or electron withdrawing capabilities of other atoms are compared with respect to hydrogen atom.

41. **(c)** Cl_2 is added to benzene ring in the presence of sunlight to give benzene hexachloride
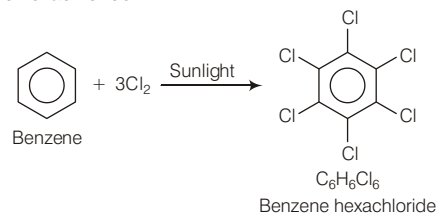
42. **(c)** The case in which a nucleophile attacks on the carbonyl group, depends upon the electron deficiency, i.e. magnitude of the positive charge on the carbonyl carbon. Since, an alkyl group has electron donating inductive effect (I-effect) therefore, greater the number of alkyl groups attached to the carbonyl group, greater is the electron density on the carbonyl carbon and hence, lower is its reactivity towards nucleophilic addition reactions.

$$\underset{H}{\overset{R}{>}}C{=}O \;>\; \underset{R}{\overset{R}{>}}C{=}O$$
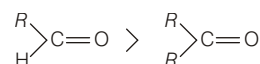
43. **(b)** Aniline is not obtained as a major product by the following reaction

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + \text{Zn powder} \xrightarrow[\;\;\;\;\;[H]\;\;\;\;\;]{\text{Alcoholic KOH}}$$
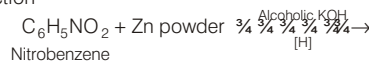
      Azobenzene
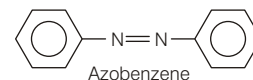
44. **(a)** When $-$ OH group of lactic acid is replaced by H, then chirality of carbon is lost.

$$CH_3 - \underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}} - COOH \xrightarrow{\quad} CH_3 - \underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}} - COOH$$
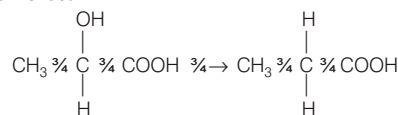
    Lactic acid

$\therefore$ Its optical activity is lost.

45. **(b)** When equal number of cations and anions are missing from the lattice sites then Schottky defect is observed in the crystal.

- A *solution* is a homogeneous mixture containing two or more components whose composition can be varied within certain limits.
- A *solvent* is the component present in large amount by mass and the other component(s) is/are termed as solute(s) that present in less amount by mass in solution.
- Solutions in which water acts as a solvent are called *aqueous solutions*, while in which water does not act as a solvent are called *non-aqueous solutions*.

❶ GENERALISED CONCENTRATION TERMS

(i) **Mass (m) percentage**

$$\frac{m_{solute}}{m_{solution}} \times 100 \text{ or } \frac{m_{solute}}{V_{solution} \times d_{solution}} \times 100$$

Here, d = density ; m alongwith subscript denotes mass of corresponding subscript.

(ii) **Volume (V) percentage**

$$\frac{V_{solute} \text{ (in mL)}}{V_{solution} \text{ (in mL)}} \times 100$$

(iii) **m/V percentage** $\dfrac{m_{solute}}{V_{solution}}$;

Here, volume is taken in litre (L).

(iv) **Parts per million** (ppm)

$$\frac{m_{solute} \text{ (in g)}}{V_{solution} \text{ (in L)}} \times 10^6$$

(v) **Mole fraction (χ)** $\chi_{solute} = \dfrac{n_{solute}}{n_{solute} + n_{solvent}}$;

$\chi_{solvent} = \dfrac{n_{solvent}}{n_{solute} + n_{solvent}}$;

$(\chi_{solute} + \chi_{solvent} = 1)$

Here, n = number of moles

(vi) **Molarity (M)** $\dfrac{n_{solute}}{V_{solution} \text{ (in L)}}$;

$$n_{solute} = \frac{m_{solute} \text{ (in g)}}{\text{Molar mass (g mol}^{-1})}$$

or $M = \dfrac{\text{Number of millimoles of solute}}{V_{solution} \text{ (in mL)}}$

$= \dfrac{\text{Per cent of solute} \times 10}{\text{Molecular mass of solute}}$

$= \dfrac{\text{Mass per cent of solute} \times \text{specific gravity of the solution} \times 10}{\text{Molecular mass of solute}}$

(vii) **Normality (N)**

$$\frac{\text{Number of gram-equivalents of solute}}{V_{solution} \text{ (in L)}}$$

$= \dfrac{m_{solute}}{E_{solute} \times V_{solution} \text{ (in L)}}$

or $N = \dfrac{m_{solute} \text{ (in g)}}{E_{solute} \times V_{solution} \text{ (in mL)}} \times 1000$

$= \dfrac{\text{Per cent of solute}}{E_{solute}} \times 10$

$= \dfrac{\text{Mass per cent of solute} \times \text{specific gravity of the solution} \times 10}{\text{Equivalent mass of the solute}}$

Here, E with subscript represents equivalent mass of corresponding subscript.

(viii) **Molality (m)**

$$m = \frac{n_{solute}}{m_{solvent} \text{(in g)}} \times 1000 = \frac{m_{solute} \text{(in g)} \times 1000}{M_{solute} \times m_{solvent} \text{(in g)}}$$

Here, M alongwith subscript denotes molecular mass, m alongwith subscript denotes mass, while single m denotes molality.

(ix) **Formality (F)** $= \dfrac{\text{Moles of substance added to the solution}}{\text{Volume of solution (in L)}}$

Note Formality describes the solute which is mixed in a liquid rather than the solute present in the solution after the dissolution process.

(x) **Demal (D)** It is equal to molar concentration at 0°C, i.e. 1 D represents, one mole of solute present in one litre of the solution at 0°C.

Remember Normality and molarity, change with temperature because they involve volumes while molality, mole fraction and mass fraction do not change with temperature because they involve mass.

(xi) **Strength** Strength of solution

$$= \frac{m_{solute} \text{ (in g)}}{V_{solution} \text{(in L)}}$$

❷ SOME SPECIAL FORMULAE

Concentration terms	Relation
Molarity (M) and strength	$M = \dfrac{\text{Strength (in g L}^{-1})}{M_{solute}}$
Molarity (M) and mole fraction of solute (χ_{solute})	$\chi_{solute} = \dfrac{M_{solvent}}{M(M_{solvent} - M_{solute}) + d}$
Molality (m) and mass per cent of solute (x)	$m = \dfrac{1000 \times x}{(100 - x) \times M_{solute}}$
Molality (m) and mole fraction of solute (χ_{solute})	$\chi_{solute} = \dfrac{m M_{solvent}}{1 + m M_{solvent}}$
Normality (N) and strength	$N = \dfrac{\text{Strength (in g L}^{-1})}{E_{solute}}$
Normality (N) and molarity (M)	Normality $\times$ equivalent mass = Molarity $\times$ molecular mass
Normality (N) and mass percentage of solute (x)	$N = \dfrac{x \times d \times 10}{E}$
Molality (m) and molarity (M)	$M = \dfrac{m \times d}{1 + \dfrac{m M_{solute}}{1000}}$

❸ CONCENTRATION TERMS WITH MIXING OF SOLUTIONS

(i) **In case of dilution** If molarity and volume of solution are changed from M_1, V_1 to M_2, V_2 then $M_1 V_1 = M_2 V_2$
- Volume of water added;

$$V_2 - V_1 = \left(\frac{M_1 - M_2}{M_2}\right) V_1$$

- If n_1 moles of reactant 1 react with n_2 moles of reactant 2 then, $\dfrac{M_1 V_1}{n_1} = \dfrac{M_2 V_2}{n_2}$

(ii) **In case of mixing** Let four samples of solution (with same solvent and solute) with molarities M_1, M_2, M_3, M_4 and volumes V_1, V_2, V_3, V_4 are mixed. The molarity (M) of resultant solution is given as

$$M_1 V_1 + M_2 V_2 + M_3 V_3 + M_4 V_4 = M(V_1 + V_2 + V_3 + V_4)$$

CONCE...
your Rev...
SOLU...

COLLIGATIVE

The properties of a dilute solution which depend only on number of solute particles are called colligative properties

① **Factors affecting colligative properties**
- Fraction of solute and solvent particles
- Nature of solvent
- Dissociation and association of solute particles

② **Types of Colligative Properties**

Ⓐ **Relative lowering of vapour pressure** When a non-volatile solute is added to a solvent, the vapour pressure of the solution (p_s) is always less than the vapour pressure of pure solvent ($p°$). Relative lowering of vapour pressure,

$$\frac{p° - p_s}{p°} \approx \frac{n}{N} \approx \frac{W_{solute} \times M_{solvent}}{W_{solvent} \times M_{solute}}$$

where, n and N are number of moles of solute and solvent respectively.

Effect of lowering of vapour pressure on other Two colligative properties

Ⓑ Elevation in boiling point (ΔT_b)	Ⓒ Depression in freezing point (ΔT_f)
The boiling point of the solution increases.	The freezing point of the solution decreases.
$\Delta T_b = (T_b - T_b°) = K_b m$ $= \dfrac{K_b \times W_{solute} \times 1000}{M_{solute} \times W_{solvent}}$ $= \dfrac{M_{solvent} R(T_b°)^2}{\Delta H_{vap} \times 1000}$ $= \dfrac{0.002 (T°)^2}{l_v}$	$\Delta T_f = (T_f° - T_f) = K_f m$ $= \dfrac{K_f \times W_{solute} \times 1000}{M_{solute} \times W_{solvent}}$ $= \dfrac{M_{solvent} R(T_f°)^2}{\Delta H_{fusion} \times 1000}$ $= \dfrac{0.002 (T°)^2}{l_f}$
where, $T_b°$ = boiling point of pure solvent	where, $T_f°$ = freezing point of pure solvent
T_b = boiling point of solution.	T_f = freezing point of solution.
$T°$ = normal boiling point of solvent	$T°$ = normal freezing point of solvent
ΔH_{vap} = enthalpy change for vaporisation	ΔH_{fusion} = enthalpy change for fusion
l_v = latent heat of vaporisation	l_f = latent heat of fusion

Ⓓ **Osmosis and osmotic pressure** Osmosis is the spontaneous flow of the solvent molecules through semipermeable membrane from a pure solvent to a solution or from a dilute to a concentrated solution. The external pressure which must be applied on the solution in order to stop the flow of the solvent molecules into the solution through semipermeable membrane is termed as osmotic pressure (π).

For a dilute solution, $\pi = \dfrac{n_{solute} \times ST}{V_{solution}}$

PT MAP
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TION

PROPERTIES

- If two solutions having different osmotic pressures, the one having lower pressure is called *hypotonic* and the other with higher pressure is called *hypertonic solution*.

ADVANTAGES OF OSMOTIC PRESSURE
- The molar masses of non-volatile solutes can be measured by using van't Hoff equation of solution.
- Osmotic pressure of a dilute solution is measured more accurately as compared to ΔT_b and ΔT_f, which are very small in these conditions.
- It is measured at room temperature, hence, the method is particularly useful for biomolecules which are generally unstable at high temperatures.
- People taking a lot of salt or salty food experience water osmosis. The resulting puffiness or swelling is called edema.
- The use of salt and sugar as preservatives in pickle and jams has its basis in preventing growth of fungi and bacteria by osmosis.

③ **Reverse Osmosis**
When a pressure more than the osmotic pressure, is applied to the solution, the solvent may pass from solution into the solvent through the semipermeable membrane. This type of osmosis is known as *reverse osmosis*. It is used for the desalination of sea water.

④ **Abnormal Colligative Properties**
Ⓐ **van't Hoff Factor** Any change in the number of particles of solute leads to a change in colligative properties.
  (i) **In case of dissociation** If one molecule of solute dissociates into 'n' ions and 'α' is the degree of dissociation, then, total number of moles of solute (i) in solution after dissociation, $i = 1 + (n-1)\alpha$ $i > 1$ if $n \geq 2$. Here, i = van't Hoff factor.
  (ii) **In case of association** If n molecules associate to form one giant molecule.

$$i = 1 + \left(\frac{1}{n} - 1\right)\alpha$$

$i < 1$ if $n \leq 2$.

$$i = \frac{\text{Observed value of colligative property}}{\text{Normal value of colligative property}}$$

Ⓑ **Molar Mass**

$$i = \frac{\text{Calculated molar mass of solute } (M_c)}{\text{Observed molar mass of solute } (M_o)}$$

$$\frac{p° - p_s}{p°} = i\,\chi_B, \quad \Delta T_f = iK_f m$$

$$\Delta T_b = iK_b m$$

$$\pi = i\,\frac{n_{\text{solute}} \times ST}{V_{\text{solution}}}$$

❹ SOLUBILITY
It is defined as the maximum amount of a solute that can be dissolved in given amount of solvent (usually 100 g) at a given temperature.

(A) SOLUBILITY OF A SOLID IN A LIQUID
- Two substances with intermolecular forces of about the same type and magnitude are likely to be very soluble in one another (i.e. like dissolves like).
- At a certain temperature,
  Amount of solute is less than its solubility, then solution is called *unsaturated solution*.
  Amount of solute equals to its solubility, then solution is called *saturated solution*.
  Amount of solute is greater than its solubility, then solution is called *super saturated solution*.

(B) SOLUBILITY OF GAS IN LIQUID
All gases are soluble in water or in other liquids upto a certain extent.

(C) FACTORS AFFECTING SOLUBILITY
  (i) **Nature of the gas** Easily liquefiable gases are more soluble in common solvent such as water. The gases which react with solvent possess high solubility.
  (ii) **Nature of the solvent** Polar solvents dissolve polar gases while non-polar solvents dissolve non-polar gases.
  (iii) **Temperature** Solubility decreases with increase in temperature.
  (iv) **Pressure** Solubility increases and decreases with increase and decrease in pressure respectively.

❺ HENRY'S LAW
At a definite temperature, the solubility of a gas in the liquid is directly proportional to the partial pressure of the gas over the solution.

$$p \propto \chi \Rightarrow (1/K), \quad \chi = K_H \chi$$

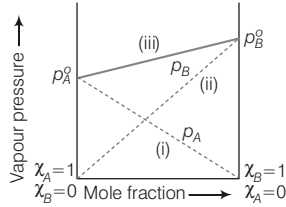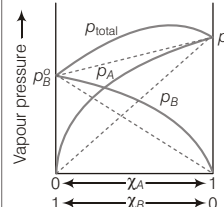Here, χ = Mole fraction of gas
  p = Partial pressure of gas
  K_H = Henry's law constant

APPLICATIONS OF HENRY'S LAW
- In avoiding toxic effects of high concentration of nitrogen in blood under water.
- In packing of soda cans.
- In avoiding anoxia.
- In removing dissolved gases from boiler feedwater.

LIMITATIONS OF HENRY'S LAW
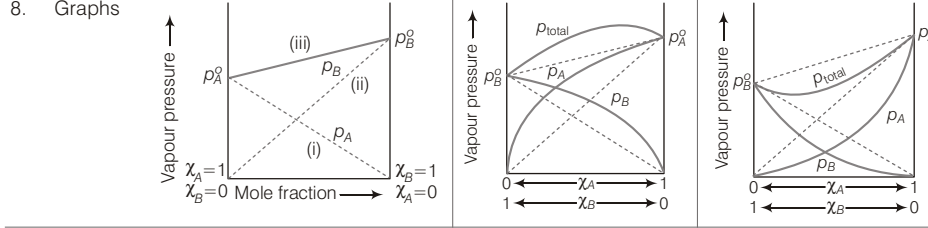It does not hold good:
- at very low temperature.
- at very high pressure.
- when gas reacts with solvent.
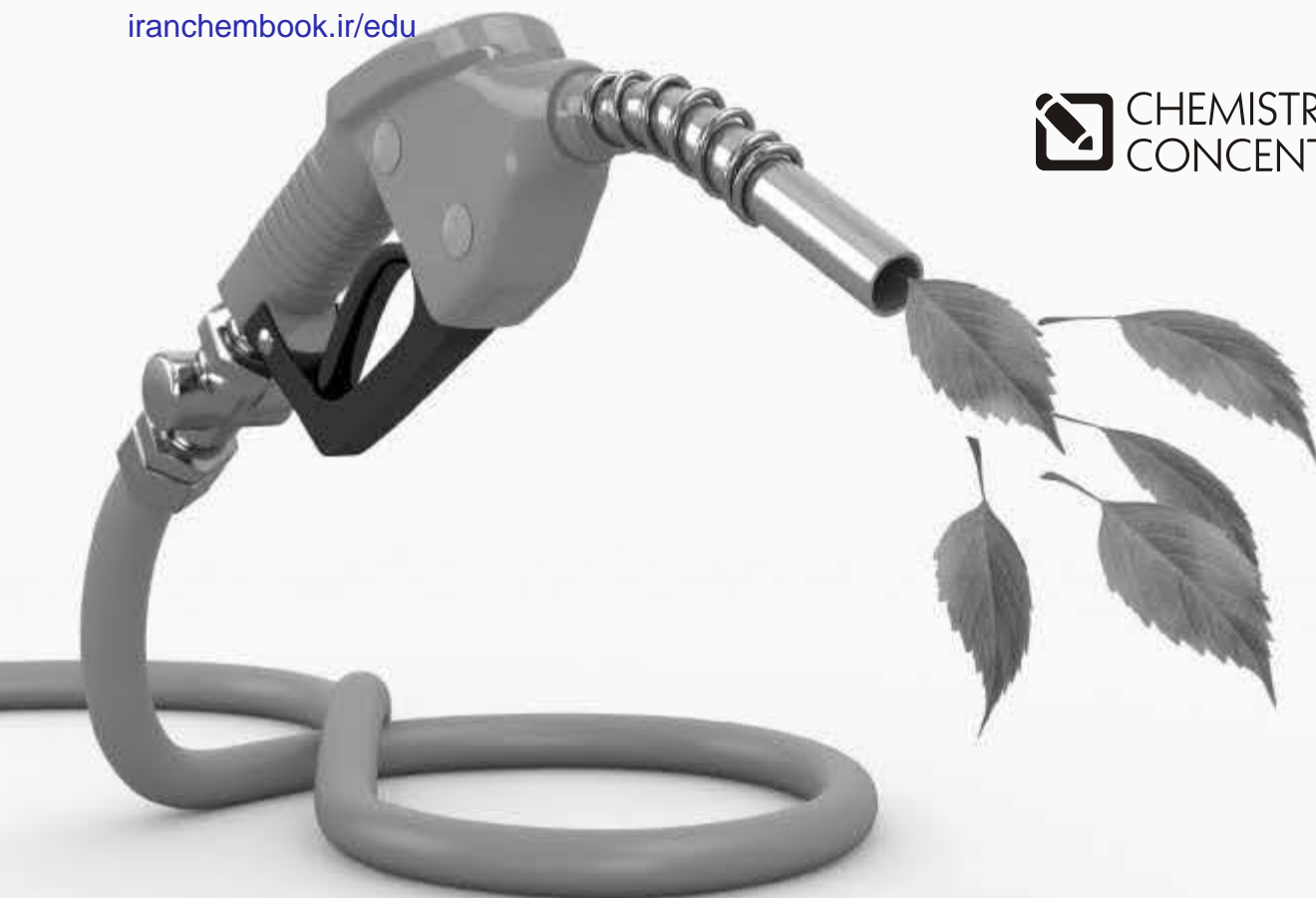- when gas associates or dissociates in solvent.

❻ VAPOUR PRESSURE OF LIQUID SOLUTIONS
The pressure exerted by the vapours of a solvent while in equilibrium with pure solvent at a given temperature.

Vapour pressure of liquid-liquid solutions (Raoult's law)	Vapour pressure of gas in liquid solutions	Vapour pressure of solid in liquid solutions
• According to Raoult's law, the partial vapour pressure of any volatile constituent of a solution is directly proportional to its mole fraction in solution. $p_i = p_i° \chi_i$. Here, p_i, $p_i°$ and χ_i are partial pressure, vapour pressure of pure liquid and mole fraction of a component in a solution respectively. • For more than two components in a solution, p_{total} = sum of partial pressures of all components.	• For a solution of a gas in a liquid, one of the components is so volatile that it can exist as a gas. • If we compare the equations of Raoult's law and Henry's law, it can be seen that the partial pressure of the volatile component or gas is directly proportional to its mole fraction. • The proportionality constant K_H, differs from $p_i°$. • Thus, Raoult's law becomes a special case of Henry's law.	• When a non-volatile solute is added to a solvent, the vapour pressure of solvent gets lowered. • The vapour pressure of pure solvent ($p°$) is always greater than the vapour pressure of solution (p). • According to Raoult's law, the relative lowering in vapour pressure of a dilute solution is equal to the mole fraction of the solute present in the solution, i.e. $\frac{p° - p}{p°} = \chi_B$ • Here, χ_B = mole fraction of solute

❼ IDEAL AND NON-IDEAL SOLUTIONS

|	Ideal solution		Non-ideal solution	
			Positive deviation from Raoult's law	Negative deviation from Raoult's law
1.	Raoult's law	Obey	Do not obey	Do not obey
2.	Enthalpy change after mixing	$\Delta H_{\text{mix}} = 0$	$\Delta H_{\text{mix}} > 0$	$\Delta H_{\text{mix}} < 0$
3.	Total pressure for two components	$p_T = p_A + p_B$	$p_T > p_A + p_B$	$p_T < p_A + p_B$
4.	Volume change after mixing	$\Delta V_{\text{mix}} = 0$	$\Delta V_{\text{mix}} > 0$	$\Delta V_{\text{mix}} < 0$
5.	Intermolecular force	$A-A$, $A-B$ and $B-B$ interactions are same.	$A-B$ interactions are weaker than $A-A$ and $B-B$.	$A-B$ interactions are stronger than $A-A$ and $B-B$.
6.	Escaping tendency	Same before and after mixing.	Increases after mixing.	Decreases after mixing.
7.	Examples	n-hexane + n-heptane	Acetone + ethanol	Acetone + aniline
8.	Graphs			

CHEMISTRY CONCENTRATE

CRYOSCOPY

Temperature is a Measure of Energy involved in Molecular Motions. When solvent molecules are cold enough, they don't have much Heat Energy so, they do not show much Molecular Motions or their molecular motions are restricted. Consequently, they can pack in a more organised structure, called solid structure. At high temperatures, they have so much Heat Energy that they can escape the attraction of their neighbours. In this article, we shall study how we can speed up Molecular Motions of solvent molecules by adding non-volatile molecules rather than by increasing temperature.

Depression in Freezing point (Cryoscopy)

- The temperature at which the liquid and solid states of a substance have the same vapour pressure is called freezing point.
- The addition of non-volatile solute to the pure solvent, results decrease in vapour pressure of solvent. Thus, there will exist an equilibrium between solvent molecules and non-volatile solute molecules at a lower pressure and hence at a lower temperature.

- The freezing point of a pure solvent decreases when a non-volatile solute is added to it. (The freezing point of pure solvent is always higher than the solution of pure solvent and non-volatile solute).
- The difference between the freezing points of the pure solvent and its solution with non-volatile solute is called depression in freezing point.
- It is a colligative property i.e. depends only on the number of particles of solute in the solution and independent of composition of solute particles.

⬛ CHEMISTRY CONCENTRATE

- This can be clarified from vapour pressure *versus* temperature graph in case of water, which is shown below.
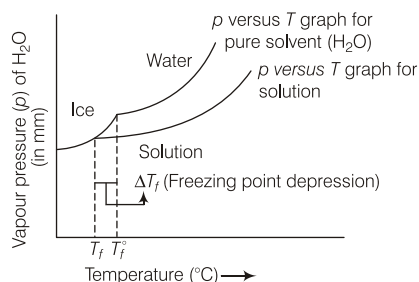
- The decrease in the freezing point from T_f° to T_f is called depression in freezing point (ΔT_f). Hence, $\Delta T_f = T_f^\circ - T_f$.

- It has been experimentally found that for a dilute solution, the depression in freezing point (ΔT_f) is directly proportional to molality (m) of the solution.

  Hence, $\Delta T_f \propto m$ or $\Delta T_f = K_f \, m$

  where K_f is called *molal depression constant* or *freezing point depression constant or cryoscopic constant.*

- Unit of K_f = K kg mol^{-1} or °C kg mol^{-1}.

- The value of K_f depends only on nature of the solvent like its molecular mass ($M_{Solvent}$), freezing point (T_f°) and ethalpy of fusion (ΔH_{fusion}) and it is given by

$$K_f = \frac{MR\,(T_f^\circ)^2}{\Delta H_{fusion} \times 1000} \text{ or } K_f = \frac{R \cdot T_f^{0^2}}{1000 \times L_f}; \ L_f = \frac{\Delta H_{fusion}}{M_{solvent}}$$

  where, L_f = Latent heat of fusion

- We can use different formulae for molality to find different terms related to the solute like its molecular mass (M_{Solute}) mole fraction, etc. Hence,

$$\Delta T_f = \frac{K_f \times W_{Solute} \times 1000}{M_{Solute} \times W_{Solvent}} \text{ or } \Delta T_f = K_f \, \frac{\chi_{Solute} \times 1000}{M_{Solvent} \times \chi_{Solvent}}$$

$$\left\{ \begin{array}{c} \chi_{Solute} = \dfrac{n_{Solute}}{n_{Solute} + n_{Solvent}} \\ n = \text{ Number of moles corresponding} \\ \text{to subscript} \end{array} \right\}$$

Thermometer used in the Measurement of Freezing Point Depression

Beckmann thermometer was invented by Ernst Beckmann, a German chemist to measure colligative properties like elevation in boiling point and depression in freezing point.

- Beckmann thermometer is only able to measure small difference in temperature but not absolute temperature.
- It is of around 40-50 cm length covering about 5°C with each degree is divided into 100 equal parts with each part equals to one-hundredths of a degree. This thermometer is capable of measuring a small temperature change of 0.001°C.
- This thermometer was popularly used to measure colligative properties during 20th century and is now replaced by electronic thermometers.

Derivation for the Expression of K_f

Let us consider a very dilute solution. For a very dilute solution, the mole fraction of solvent varies with temperature, T as

$$\ln(\chi_{Solvent}) = -\frac{\Delta_{Fus}H}{R}\left(\frac{1}{T} - \frac{1}{T_{mp}}\right) \quad \ldots\text{(i)}$$

where, $\Delta_{fus}H$ and T_{mp} are enthalpy of fusion and melting point of solvent respectively or

$$\ln(1 - \chi_{Solute}) = -\frac{\Delta_{Fus}H}{R}\left(\frac{1}{T} - \frac{1}{T_{mp}}\right) \quad \ldots\text{(ii)}$$

Since, we have considered a very dilute solution therefore

$$\chi_{Solvent} \approx 1$$

Now, applying Taylor's single-term series expansion, which give

$$\ln(1 - \chi_{Solute}) \approx -\chi_{Solute}$$

Now, the expression in Eq. (ii) becomes

$$-\chi_{Solute} \approx -\frac{\Delta_{Fus}H}{R}\left(\frac{1}{T} - \frac{1}{T_{mp}}\right)$$

or $\quad \chi_{Solute} \approx \dfrac{\Delta_{Fus}H}{R}\left(\dfrac{T_{mp} - T}{T \cdot T_{mp}}\right) \quad \ldots\text{(iii)}$

For a very dilute solution, the equilibrium temperature, $T \approx T_{mp}$. Thus, we can use either melting point or freezing point. Hence, the expression in Eq. (iii) becomes

$$\chi_{Solute} = \frac{\Delta_{Fus}H}{R} \times \left(\frac{T_{mp} - T}{T_{mp}^2}\right)$$

or $\quad \chi_{Solute} \approx \dfrac{\Delta_{Fus}H}{R} \times \dfrac{\Delta T_f}{T_{mp}^2} \quad \ldots\text{(iv)}$

Again mole fraction and molality are related as

$$m = \frac{\chi_{Solute} \times 1000}{M_{Solvent} \times \chi_{Solvent}} \quad \ldots\text{(v)}$$

where, m and $M_{Solvent}$ are molality and molecular mass of solvent respectively

From Eqs. (iii) and (v), we get

$$\Delta T_f = \left(\frac{M_{Solvent} \cdot RT_{mp}^2}{1000 \cdot \Delta_{Fus}H}\right)m$$

or $\quad \Delta T_f = K_f \cdot m$

where, K_f = cryoscopic constant or freezing point depression constant.

Example 2 Calculate the molal depression constant (in K kg mol^{-1}) of a solvent which has freezing point 16.6°C and latent heat of fusion 180.75 Jg^{-1}.

(a) 1.87   (b) 3.86
(c) 1.80   (d) 3.05

Sol. **(b)** $K_f = \dfrac{RT_f^{\circ 2}}{1000 \times L_f}$

Given, $R = 8.314 \, \text{JK}^{-1}\text{mol}^{-1}$

$T_f^{\circ} = 16.6°C = 273 + 16.6 = 289.6 \, \text{K}$

$L_f = 180.75 \, \text{Jg}^{-1}$

∴ $K_f = \dfrac{8.314 \times (289.6)^2}{1000 \times 180.75} = 3.86 \, \text{K kg mol}^{-1}$

Abnormal Colligative Properties

Since, colligative properties depend upon the total number of solute particles, therefore, any change in the number of particles of solute, will lead to a change in colligative properties.

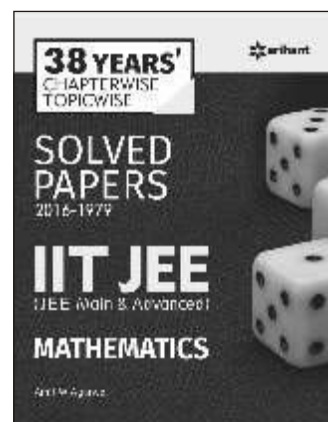| Case I (When solute molecules dissociate into *n* ions)	Case II (When solute molecules/ions associate into a big giant molecule)
For strong electrolytes Strong electrolytes dissociate completely in the solvent, the value of van't Hoff factor (*i*) is equal to the sum of different types of ions produced after dissociation e.g. For NaCl solution $i = 1 + 1 = 2$	Electrolytes like CH$_3$COOH, C$_6$H$_5$COOH, C$_6$H$_5$OH etc, when dissolved in water, associated to form a large molecule due to hydrogen bonding. This results a decrease in the effective number of particles present in the solution and hence, a decrease in the value of observed colligative property.
For weak electrolytes $A_xB_y(s) \rightleftharpoons xA^{y+}(aq)$ $+ yB^{x-}(aq)$ $\begin{array}{ccc} 1 & 0 & 0 \\ 1-\alpha & x\alpha & y\alpha \end{array}$ Total particles before dissociation = 1 Total particles after dissociation $= (1 - \alpha + x\alpha + y\alpha)$ van't Hoff factor (*i*) can be calculated as, $i = \dfrac{\text{Total particles after dissociation}}{\text{Total particles before dissociation}}$ where, α = degree of dissociation if $x + y = n, \alpha = \dfrac{i-1}{n-1}$	$nA \rightleftharpoons A_n$ $\begin{array}{cc} 1 & 0 \\ 1-\alpha & \alpha/n \end{array}$ Total particles before association = 1 Total particles after association $= 1 - \alpha + \dfrac{\alpha}{n}$ van't Hoff's factor (*i*) can be calculated as $i = \dfrac{\text{Total particles after association}}{\text{Total particles before association}}$ $i = 1 - \alpha + \dfrac{\alpha}{n}$ or $\alpha = \dfrac{(i-1)n}{(1-n)}$ where, n = Number of molecules of solute *A* present in the associated structure

Example 3 The molecular mass of NaCl determined by studying freezing point depression of its 0.5% aqueous solution is 30. The apparent degree of dissociation of NaCl is

(a) 0.60   (b) 0.50
(c) 0.30   (d) 0.95

Sol. **(d)** NaCl $\longrightarrow$ Na$^+$ + Cl$^-$

$i = \dfrac{\text{Calculated molecular mass}}{\text{Experimental molecular mass}} = \dfrac{58.5}{30}$

$= 1.95$

$\alpha = \dfrac{i-1}{n-1}$ {In case of dissociation}

Here, $n = 2$

∴ $\alpha = \dfrac{1.95 - 1}{2 - 1}$

$= 0.95$

Cryotherapy

A new hope for prostate cancer patients

- Cryotherapy is the controlled freezing of the prostate gland. The freezing destroys cancer cells.
- Cryotherapy is done under general or spinal anesthesia. The prostate is imaged and measured. An aiming program projects images on a screen.
- Cryoprobes (special needles) are placed in the prostate under the skin, guided by ultrasound. Argon gas creates an ice balls that kills cells in that area.
- Monitoring lowers the risk of injury to the nearby normal tissues. The procedure is usually done in 2 hours.
- Once, cancer cells are killed by cryotherapy, the immune system becomes again able to fight cancer cells.
- Cryotherapy is not cancer specific. The treatment affects all cells in the targeted area. Freezing can damage molecular, cellular or whole tissue.
- Cryotherapy can cause immediate cell death, delayed death due to lack of oxygen, and programmed cell death.

Effect of Abnormal Colligative Property on Freezing Point Depression

- When a solute is an electrolyte and it is dissolved in the solvent leading to an increase in the number of solute particles results, an increase in the magnitude of the observed colligative property.
- When the solute is capable to associate in the solution due to intermolecular hydrogen bonding, the number of solute particles decreases. This leads to a decrease in the magnitude of the observed colligative property.
- Hence, in order to account for association or dissociation of solutes, a new factor called van't Hoff factor was introduced to the formulae for freezing point depression. These are given as, $\Delta T_f = iK_f m$

where, $i = \dfrac{\text{observed colligative property}}{\text{expected colligative property}}$

CHEMISTRY CONCENTRATE

$$= \frac{\text{measured } \Delta T_f}{\text{expected } \Delta T_f} = \frac{\text{normal molar mass}}{\text{abnormal molar mass}}$$

For association, $i < 1$ (solute particles decrease in solution) For dissociation, $i > 1$ (solute particles increase in solution)

Example 4 List the following aqueous solutions in the order of their increasing expected freezing point value.

A	0.050 m $CaCl_2$
B	0.15 m NaCl
C	0.10 m HCl
D	0.050 m CH_3COOH
E	0.10 m $C_{12}H_{22}O_{11}$

(a) B < C < A < E < D
(b) E < D < C < B < A
(c) B < A < C < E < D
(d) E < C < D < B < A

Sol. (a) **Key Concept**
- The lowest freezing point will correspond to the solution with the greatest concentration of solute particles.
- To determine the total concentration of solute particles in each case, we must determine whether the substance is a non-electrolyte or an electrolyte and consider the number of ions formed when an electrolyte ionises.

$CaCl_2$, NaCl and HCl are strong electrolytes, CH_3COOH is a weak electrolyte and $C_{12}H_{22}O_{11}$ is a non-electrolyte. The molality of each solution in total particles is as follows

0.050 m $CaCl_2 \Rightarrow$ 0.050 m in Ca^{2+} and 0.10 m in Cl^-
$$\Rightarrow \text{0.15 m in both particles}$$
0.15 m NaCl $\Rightarrow$ 0.15 m Na^+ and 0.15 m in Cl^-
$$\Rightarrow \text{0.30 m in both particles}$$
0.10 m HCl $\Rightarrow$ 0.10 m H^+ and 0.10 m in Cl^-
$$\Rightarrow \text{0.20 m in both particles}$$
0.050 m CH_3COOH, is a weak electrolyte
Hence, it furnishes very low amount of ions. Therefore, it will possess lowest value of molality for its constituent ions.
0.10 m $C_{12}H_{22}O_{11} \Rightarrow$ Non-electrolyte 0.10 m in particles.
As, freezing point depends on the total molality of solute particles in the solution. Hence, order for freezing point is
$$B < C < A < E < D$$

Practical Applications of Cryoscopy

Cryoscopy (depression in freezing point) has many practical uses
- The radiator fluid (water + ethylene glycol), in an automobile engine does not freeze in winter (unless it is extremely cold – 30 to – 40℃), due to freezing point depression.
- The depression in freezing point in road salting allows the street ice to melt at lower temperature, preventing the accumulation of dangerous, slippery ice.
- The depression in freezing point is used by some organisms lived in extreme cold. Such creatures produce high concentration of various compounds such as sorbital and glycerol. This elevated concentration of solute decreases the freezing point of the water inside them, preventing the organisms from freezing solid even as the water around them freezes.
- The depression in freezing point has an application in the making of home made ice-cream. The ice-cream is put in the metal container which is surrounded by crushed ice. Then salt is put on the ice to lower its melting point. The melting of the solution tends to lower the equilibrium temperature of the ice/water solution to the melting point of the solution. This gives a temperature gradient across the metal container into the salt water ice solution which is lower than 0°C. This solution allows ice-cream to freeze by the transfer of heat from ice-cream mixture.

Example 5 An automobile antifreeze consists of ethylene glycol, $CH_2(OH)CH_2(OH)$, a non-volatile non-electrolyte. Calculate the freezing point of 25.0 mass percentage of solution of ethylene glycol in water ($K_f = 1.86℃$ molal^{-1})

(a) 10.0°C   (b) – 10.0°C   (c) 15.5°C   (d) – 15.5°C

Sol. (b) **Strategy** *Let assume for convenience that we have 1 kg i.e. 1000 g of solution. As solution is 25.0 mass % ethylene glycol, therefore the masses of ethylene glycol and water in the solution are 250 g and 750 g respectively. Using these quantities we can calculate molality of the solution.*

$$\text{Molality} = \frac{\text{Moles of } C_2H_6O_2}{\text{Mass of } H_2O \text{ (in kg)}}; \quad \left(\text{Mole} = \frac{\text{Mass (in g)}}{\text{Molar mass}}\right)$$

$$= \frac{250 \text{ g} / 62.1 \text{ g mol}^{-1}}{0.75 \text{ kg}} = 5.37 \text{ m}$$

Now, as we know, $\Delta T_f = K_f m = (1.85°\text{Cm}^{-1}) \cdot (5.37 \text{ m})$
$$\simeq 10.0°\text{C}$$
Hence, the freezing point of the solution is
$$= \text{Normal freezing point of solution} - \Delta T_f$$
$$= 0.0°\text{C} - 10.0°\text{C} = -10.0°\text{C}$$

AMAZING REALITIES Researchers in France have developed two new cobalt-based materials that may be used to replace platinum, a rare and expensive metal, in producing hydrogen from water (electrolysis).

Smart Practice

1. A solution contains 1.25 g of a certain non-volatile substance in 20 g of water, it freezes at 271.94 K. Calculate the molecular mass of the solute.
$(K_f = 1.86 \text{ K kg mol}^{-1})$

   (a) 324.00 g mol^{-1} (b) 40.37 g mol^{-1}
   (c) 109.66 g mol^{-1} (d) 206.34 g mol^{-1}

2. In a cold climate, water gets frozen causing damage to radiator of a car. Ethylene glycol is used as an antifreezing agent. Calculate the amount of ethylene glycol to be added to 4 kg of water to prevent it from freezing at $-6°C$
$(K_f$ for water $= 1.85 \text{ K kg mol}^{-1})$

   (a) 944.23 g   (b) 234.23 g   (c) 747.78 g   (d) 804.32 g

3. In a 0.2 molal aqueous solution of a weak acid HX the degree of ionisation is 0.3. Taking K_f for water as 1.85, the freezing point of the solution will be nearest to

   (a) $-0.481°C$ (b) $-0.360°C$ (c) $-0.260°C$ (d) $+0.481°C$

4. A certain substance 'A' tetramerises in water to the extent of 80%. A solution of 2.5g of A in 100 g of water lowers the freezing point by 0.3°C. The molar mass (in g mol^{-1}) of A is

   (a) 31   (b) 62   (c) 122   (d) 244

5. What is the freezing point of a solution containing 8.1g HBr in 100g water assuming the acid to be 90% ionised?
$(K_f$ for water $= 1.86 \text{ K kg mol}^{-1})$

   (a) $-0.350°C$ (b) $-1.35°C$ (c) $-2.35°C$ (d) $-3.53°C$

6. The freezing point depression of 0.001m, $K_x[Fe(CN)_6]$ is 7.10×10^{-3} K. If for water, K_f is 1.86 K kg mol^{-1}, value of x will be

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

7. If the freezing point of a 0.01 molal aqueous solution of a cobalt (III) chloride-ammonia complex (which behaves as a strong electrolyte) is $-0.0558°C$, the number of chloride(s) in the coordination sphere of the complex is

   $[K_f$ of water $= 1.86 \text{ K kg mol}^{-1}]$ **[IIT JEE 2015]**
   (a) 1   (b) 2   (c) 3   (d) 4

8. 1 kg of 1 molal sucrose solution in water is cooled to $-3.534°C$. What mass of ice would be separated out at this temperature?

   $[K_f$ of water $= 1.86 \text{ K mol}^{-1} \text{ kg}]$
   (a) 352.98 g   (b) 482.47 g
   (c) 407.78 g   (d) 957.20 g

9. An aqueous solution contains 5% by mass of urea and 10% by mass of glucose. What will be its freezing point? $[K_f (H_2O) = 1.86 \text{ K mol}^{-1} \text{ kg}]$

   (a) $-4.78°C$ (b) $-2.78°C$ (c) $-1.08°C$ (d) $-3.04°C$

10. 1 g of monobasic acid in 100g of water lowers the freezing point of water by 0.168°C. If 0.2 g of same acid requires 15.1mL of $N/10$ alkali for complete neutralisation, calculate degree of dissociation of acid $[K_f'$ for H_2O is 1.86K mol^{-1}kg]

    (a) 18.3 %   (b) 15.0%   (c) 19.6 %   (d) 27.7%

CHEMISTRY IN action

2 New Xenon oxides

2 New xenon oxides may helpful in providing clues to the "missing Xenon paradox". Compared to its fellow noble gases, argon and krypton, there is relatively little xenon in the Earth's atmosphere. This goes against predictions based on the relative abundance of xenon in carbonaceous chondrites, meteorites that are thought to be made of the same materials as the early Earth. This difference between expected and actual abundance of xenon is known as the "missing xenon paradox." In an effort to understand why the Earth's crust and atmosphere lacks the expected amount of xenon, researchers have made two new xenon compounds under high pressure conditions.

One theory to account for the missing xenon is that it is located within the Earth's lower mantle or the core. The Earth's core would have a very different reaction conditions from the crust. One difference would be the extremely high pressures. Xenon chemistry changes at high pressure. At pressures above 80 GPa xenon takes on a hexagonal close-packed morphology. At around 135 GPa, xenon has a metallic character. Xenon may be trapped within the mantle as an inorganic compound. Among the new oxides one Xe3O2 was predicted to be stable at pressures above 75GPa. Xe3O2 was made with an oxygen concentration of less than 25mol% and has a three-dimensional morphology that consists of planar chains of XeO4 squares. Xenon atoms within the chains likely have a Xe4+ oxidation state while between the planar chains are unoxidized xenon atoms.

Xe3O2 was stable to about 38 GPa. Additionally using the same methods but in a high-O2 environment (O2 levels above 50mol%), Xe2O5, a new xenon compound was also isolated. It was stable at pressures above 77 GPa. Both compounds were characterized using powder x-ray diffraction, x-ray absorption spectroscopy, and Raman spectroscopy. The experimental data on crystal structure of Xe2O5 were used to constrain theoretical stretches of a stable xenon oxide. This was how a Xe2O5 formula and structure with a minimal enthalpy were identified. In this structure, each xenon atom is connected to an oxygen atom with square planar corners, and every other xenon bonds with a fifth oxygen atom to form a square pyramid. Notably these two xenon atom types are different oxidation states, Xe4+ and Xe6+, and the Xe-O bond remains intact as the pressure is lowered.

Additional studies looking at the highest occupied molecular orbitals at pressure around 83 GPa showed that Xe2O5 would likely be an insulator, while Xe3O2 has properties indicative of a small bandgap semiconductor. This research provides experimental and theoretical justification for two new xenon oxide compounds whose minimal pressure at which they are stable is lower than previously thought, indicating that these xenon oxides are more stable than predicted.

Answers with Explanation

1. **(c)** Given, Freezing point of solution $= 271.94\,K$

Freezing point of water $= 273\,K$

$$\Delta T_f = (273 - 271.94)\,K = 1.06\,K$$

Now, $\quad M_{Solute} = \dfrac{1000 \times K_f \times W_{Solute}}{\Delta T_f \times W_{Solvent}} = \dfrac{1000 \times 1.86 \times 1.25}{1.06 \times 20}$

$$= 109.66\,g\,mol^{-1}$$

2. **(d)** Given, $\Delta T_f = 6°C$,

$$W_{Solvent} = 4\,kg = 4000\,g$$

$$M_{Solute} = 62\,g\,mol^{-1},\ K_f = 1.85\,K\,kg\,mol^{-1}$$

$\therefore \qquad m = \dfrac{\Delta T_f}{K_f} = \dfrac{W_{Solute} \times 1000}{M_{Solute} \times W_{Solvent}}$

$\therefore \quad W_{Solute} = \dfrac{\Delta T_f \times M_{Solute} \times W_{Solvent}}{K_f \times 1000} = \dfrac{6 \times 62 \times 4000}{1.85 \times 1000} = 804.32\,g$

3. **(a)** $HX \rightleftharpoons H^+ + X^-$

$$\alpha = 0.3$$

$$i = 1 + \alpha(n - 1)$$

or $\qquad i = 1 + 0.3(2 - 1) = 1 + 0.3 \qquad (n = 2\ for\ HX)$

$$i = 1.3$$

$\therefore \qquad \Delta T_f = mK_f i = 0.2 \times 1.85 \times 1.3 = 0.481°C$

$\therefore$ Freezing point of solution = freezing point of water $- \Delta T_f$

$$= (0 - 0.481)°C = -0.481°C$$

4. **(b)** $4A \rightarrow A_4$, As substance tetramerises, so $n = 4$

Degree of association

$$\alpha = \dfrac{1 - i}{1 - \dfrac{1}{n}} \quad or \quad 0.8 = \dfrac{1 - i}{1 - \dfrac{1}{4}} \quad or \quad i = 0.4$$

$\because \qquad \Delta T_f = iK_f m$

$$0.3 = 0.4 \times 1.86 \times \dfrac{W_{Solute} \times 1000}{M_{Solute} \times W_{Solvent}}$$

$$0.3 = 0.4 \times 1.86 \times \dfrac{2.5 \times 1000}{M_{Solute} \times 100}$$

or $\qquad M_{Solute} = 62\,g\,mol^{-1}$

5. **(d)** $\underset{1-\alpha}{HBr} \rightleftharpoons \underset{\alpha}{H^+} + \underset{\alpha}{Br^-}$

$$i = 1 + \alpha\,(n - 1) = 1 + 0.9\,(2 - 1) = 1.9$$

$\therefore \qquad \Delta T_f = iK_f m = 1.9 \times 1.86 \times \dfrac{8.1}{81} \times \dfrac{1000}{100} = 3.53°C$

$\therefore \qquad T_f = T_f^\circ - \Delta T_f = 0 - 3.53°C = -3.53°C$

6. **(b)** $\because \Delta T_f = iK_f m$

or $\quad 7.10 \times 10^{-3} = i \times 1.86 \times 0.001 \quad or \quad i = 3.817$

Now, $\quad \alpha = \dfrac{i - 1}{n - 1} \quad or \quad 1 = \dfrac{3.817 - 1}{(x + 1) - 1} \quad or \quad x = 2.817 \approx 3$

7. **(a)** Given, $T_f = -0.0558°C$,

$$\Delta T_f = 0 - (-0.558°C) = 0.0558°C$$

$m = $ molality $= 0.01$, $\quad \Delta T_f = iK_f m$

or $\qquad i = \dfrac{\Delta T_f}{K_f \times m} = \dfrac{0.0558}{1.86 \times 0.01}, \quad i = 3$

$i = 3$, indicates there are three ions in the given complex. Also, given complex behaves as a strong electrolyte, hence, $\alpha = 100\%$

Finally, complex is $[Co(NH_3)_5Cl]Cl_2$

Coordination sphere of above complex is $[Co(NH_3)Cl]^{2+}$

Therefore, number of Cl^- ions in the coordination sphere of the complex $= 1$

8. **(a)** $\Delta T_f = K_f \times$ molality $= \dfrac{1000 \times K_f \times W_{Solute}}{M_{Solute} \times W_{Solvent}}$ ...(i)

$$\Delta T_f = K_f \qquad [\because\ m = 1]$$

$\therefore \qquad 1.86 = \dfrac{1000 \times 1.86 \times W_{Solute}}{342 \times W_{Solvent}}$

or $\qquad \dfrac{W_{Solute}}{W_{Solvent}} = \dfrac{1.86 \times 342}{1000 \times 1.86} = 0.342$ ...(ii)

$$W_{Solute} + W_{Solvent} = 1000\,g \qquad ...(iii)\ [Given]$$

or $\qquad W_{Solvent}\left(\dfrac{W_{Solute}}{W_{Solvent}} + 1\right) = 1000\,g$

From Eq. (ii), $W_{Solvent}\,(0.342 + 1) = 1000\,g$

or $\qquad W_{Solvent} = 745.16\,g$

and $W_{solute} = (1000 - 745.16)\,g = 254.84\,g$ (from Eq. (iii))

When solution is cooled to $-3.534°C$, mass of sucrose remains same. Therefore, from Eq. (i),

$$3.534 = \dfrac{1.86 \times 1000 \times 254.84}{342 \times W_{Solvent}}$$

or $W_{solvent} = 392.18\,g$ (new mass of water)

Thus, ice separated out $= (745.16 - 392.18)\,g = 352.98\,g$

9. **(d)** $\because$ % by mass $= \dfrac{\text{mass of solute}}{\text{mass of solvent}} \times 100$

Let mass solution is $100\,g$

Mass of water $= 100 -$ (mass of urea $+$ mass of glucose)

$$= 100 - (5 + 10) = 85\,g$$

$\therefore \qquad \Delta T_f = \Delta T_{Urea} + \Delta T_{Glucose}$

$$= \left(\dfrac{1000 \times 1.86 \times 5}{60 \times 85}\right)K + \left(\dfrac{1000 \times 1.86 \times 10}{180 \times 85}\right)K$$

$$= (1.824 + 1.216)K = 3.04\,K = 3.04°C$$

$\therefore$ Freezing point of aqueous solution $= (0 - 3.04)°C = -3.04°C$

10. **(c)** $\Delta T_f = \dfrac{1000 \times K_f \times W_{Solute}}{W_{Solvent} \times (M_{Solute})_{exp}}$

Given, $\qquad \Delta T_f = 0.168°C = 0.168\,K, W_{Solute} = 1\,g,$

$$W_{Solvent} = 100\,g \quad and \quad K_f = 1.86\,K\,mol^{-1}\,kg$$

$$0.168 = \dfrac{1000 \times 1.86 \times 1}{100 \times (M_{Solute})_{exp}}$$

$(M_{Solute})_{exp} = 110.71\,g\,mol^{-1}$

But, at neutralisation point, milliequivalents of acid = milliequivalents of alkali

$$\dfrac{0.2}{E_{Acid}} \times 1000 = 15.1 \times \dfrac{1}{10}, \qquad E_{Acid} = 132.45\,g\,mol^{-1}$$

and $(M_{Solute})_{cal} = (132.45 \times 1)g\,mol^{-1}$ (since acid is monobasic)

$$HA \rightleftharpoons H^+ + A^-$$

at $t = 0$ $\qquad\qquad 1 \qquad\quad 0 \qquad\quad 0$
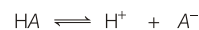
after dissociation $\quad\ 1 - \alpha \qquad \alpha \qquad\ \alpha$

Now, $i = \dfrac{\text{observed molecular mass}}{\text{expected molecular mass}} = \dfrac{132.45\,g\,mol^{-1}}{110.71\,g\,mol^{-1}} = 1.196$

$\therefore\ \alpha = \dfrac{i - 1}{n - 1}$ or $\alpha = \dfrac{1.196 - 1}{2 - 1} = 0.196$ or $\alpha = 19.6\%$

&arihant

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▣ IUPAC IDOLISER

NOMENCLATURE OF
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⌄
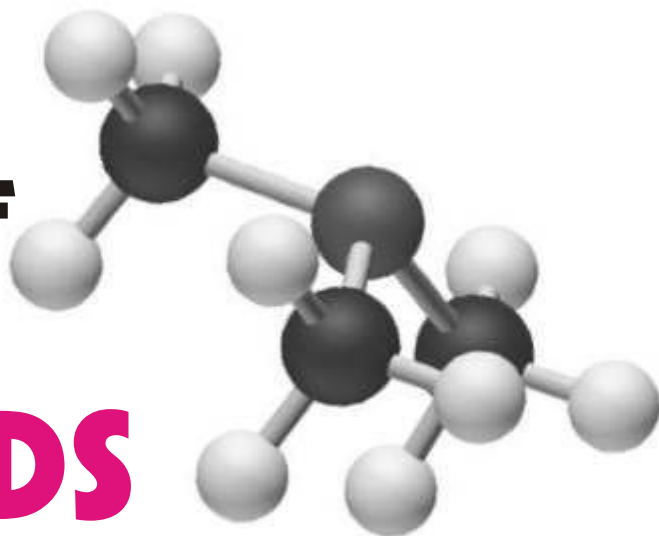
This section is targetted to provide an insight of IUPAC nomenclature of organic and inorganic compounds through questions as every year at least 1-2 questions are asked on IUPAC nomenclature in all the competitive exams and boards.

Numbering of Longest Carbon Chain

In the last issue, we studied about the selection of longest carbon chains of organic molecules. In this issue, we will study about the numbering of longest carbon chain through examples. Numbering of car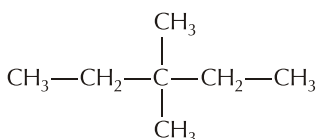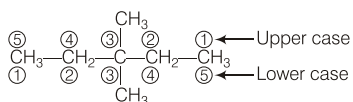bon chain has a very important role in IUPAC nomenclature. The IUPAC names of organic molecules tell us about the position of various functional groups, substituents, or unsaturation etc.

Lets start with some examples which are given below.
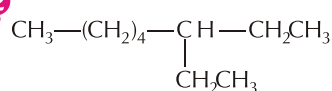
Example ❶

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

Sol. **Rule** *Numbering can be done from either of the ends for a symmetrical compound.*

$$\underset{①\quad②\quad③|\quad④\quad⑤}{\overset{⑤\quad④\quad③|\quad②\quad①}{\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{CH_3-CH_2-C-CH_2-CH_3}}}}$$ ← Upper case
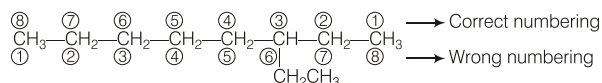← Lower case

- As compound is symmetrical, so numbering can be done by either of the ends, i.e. either by upper case or lower case.

Example ❷

$$CH_3-(CH_2)_4-\underset{\underset{CH_2CH_3}{|}}{CH}-CH_2CH_3$$

Sol. **Rule** *If a single branch or 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.*

$$\underset{①\quad②\quad③\quad④\quad⑤\quad⑥|\quad⑦\quad⑧}{\overset{⑧\quad⑦\quad⑥\quad⑤\quad④\quad③\quad②\quad①}{\underset{\underset{CH_2CH_3}{|}}{CH_3-CH_2-CH_2-CH_2-CH_2-CH-CH_2-CH_3}}}$$ ⟶ Correct numbering
⟶ Wrong numbering

Example ❸

$$H_3C-\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3$$
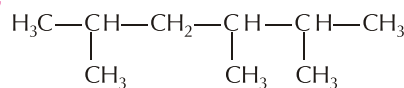
Sol. **Rule** *If all the side chains attached to longest possible carbon chain, are of same length, then numbering must be done in accordance with the lowest sum rule i.e. numbering should be done in such a way that the sum of numbers of side chains will be the least.*

$$\underset{⑥\quad⑤|\quad④\quad③|\quad②|\quad①}{\overset{①\quad②\quad③\quad④\quad⑤\quad⑥}{\underset{\underset{CH_3\quad\quad CH_3\ CH_3}{|\quad\quad\quad |\ \ |}}{H_3C-CH-CH_2-CH-CH-CH_3}}}$$
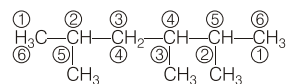
For upper case; 2 + 4 + 5 = 11
For lower case; 2 + 3 + 5 = 10
Hence, lower case numbering is correct.

IUPAC IDOLISER

Example 4

$$CH_3-CH-CH_2-CH_2-CH-CH-CH_2-CH_3$$

with branches: CH_3 below first CH; CH_2 and CH_3 below; CH_3 below CH_2.
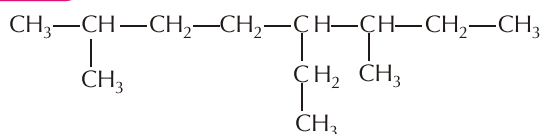
Sol. **Rule** *In case of branches of different lengths, the numbering must be done in accordance with the lowest set of locant rule. (The word locant is used by IUPAC for those carbon atoms in a chain, which bears a branch or a multiple bond or a functional group). According to this rule, "While comparing two or more different sets of locant containing, the same number of terms, the set of locant is lowest, which when compared term by term, has the lowest term at the first point of difference."*

① ② ③ ④ ⑤ ⑥ ⑦ ⑧ (2, 5, 6)→set-1
$$CH_3-CH-CH_2-CH_2-CH-CH-CH_2-CH_3$$
⑧ ⑦ ⑥ ⑤ ④ ③ ② ① (3, 4, 7)→set-2

with CH_3, CH_2, CH_3 branches and CH_3.
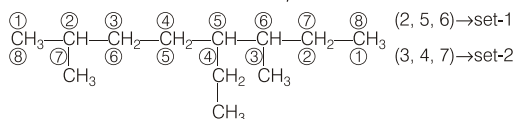
- As in a chain two sets of locants come as (2, 5, 6) and (3, 4, 7) then the first set will be preferred because the first term i.e. 2 in the first set is lower than the first term in the second set i.e. 3.

Example 5

$$CH_3-CH-CH-CH_2-CH-CH_3$$

with CH_3, CH_2, CH_2, CH_3 branches.
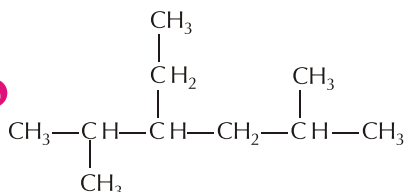
Sol. **Rule** *If for two sets of locants, first term is same, then check the second term and prefer the set of locants in which second term is lowest.*

① ② ③ ④ ⑤ ⑥ (2, 3, 5)→set-1
$$CH_3-CH-CH-CH_2-CH-CH_3$$
⑥ ⑤ ④ ③ ② ① (2, 4, 5)→set-2

with CH_3, CH_2, CH_3, CH_3 branches.

In the above case, set 1 is preferred over set 2.

Example 6

$$CH_3-CH_2-CH-CH_2-CH_2-CH_2-CH-CH_2-CH_3$$

with CH_3 and CH_2-CH_3 branches.

Sol. **Rule** *If the side chains of different lengths are present at the same distance from both of the ends, then the chain with lesser number of carbon atoms must get the least possible number.*

① ② ③ ④ ⑤ ⑥ ⑦ ⑧ ⑨
$$CH_3-CH_2-CH-CH_2-CH_2-CH_2-CH-CH_2-CH_3$$
⑨ ⑧ ⑦ ⑥ ⑤ ④ ③ ② ①

with CH_3 and CH_2CH_3 branches.

In the above compound, upper case numbering is correct.

Example 7

$$H_3C-CH=CH-CH-CH_2-CH_3$$

with CH_3 branch.

Sol. **Rule** *If multiple bond is present along with the side chain then numbering must be done in such a manner that multiple bond will get the lowest possible number.*

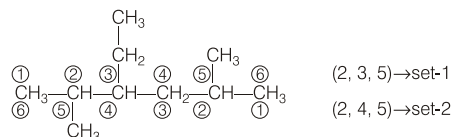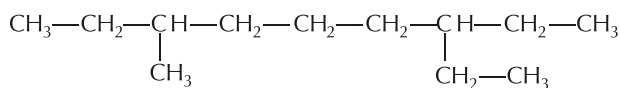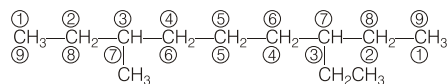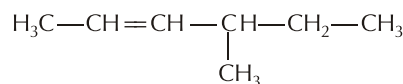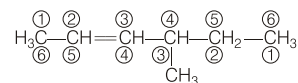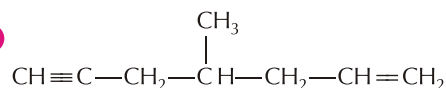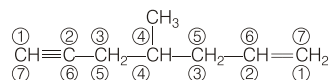① ② ③ ④ ⑤ ⑥
$$H_3C-CH=CH-CH-CH_2-CH_3$$
⑥ ⑤ ④ ③ ② ①

with CH_3 branch.

In the above compound, upper case numbering is correct.

Example 8

$$CH\equiv C-CH_2-CH-CH_2-CH=CH_2$$

with CH_3 branch above.

Sol. **Rule** *If double bond and triple bond are present in the compound at the same position, then the double bond must be preferred over the triple bond.*

① ② ③ ④ ⑤ ⑥ ⑦
$$CH\equiv C-CH_2-CH-CH_2-CH=CH_2$$
⑦ ⑥ ⑤ ④ ③ ② ①

with CH_3 branch.

For the above compound, lower case numbering is correct.

Example 9

$$CH_3-CH=CH-CH_2-C\equiv CH$$
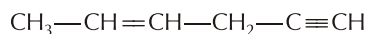
Sol. **Rule** *If triple bond and double bond, are not present at the same footing, then the bond with least number is preferred.*

⑥ ⑤ ④ ③ ② ① → Correct numbering
$$CH_3-CH=CH-CH_2-C\equiv CH$$
① ② ③ ④ ⑤ ⑥ → Wrong numbering

Example 10

$$CH_3-CH=CH-CH_2-COOH$$
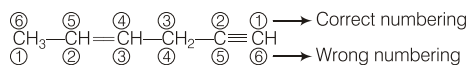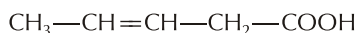
Sol. **Rule** *If any other functional group is present in the compound other than multiple bond, then numbering must be done in such a manner that the functional group will get the lowest possible number.*

⑤ ④ ③ ② ① → Correct numbering
$$CH_3-CH=CH-CH_2-COOH$$
① ② ③ ④ ⑤ → Wrong numbering

Example 11

$$CH_3-CH-CH_2-CH_3$$

with OH branch.
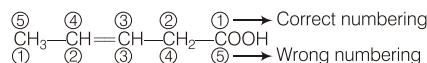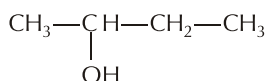
Sol. **Rule** *The functional groups, which do not contain carbon in them, then the carbon, which is attached to the functional group, will get the least possible number.*

① ② ③ ④ → Correct numbering
$$CH_3-CH-CH_2-CH_3$$
④ ③ ② ① → Wrong numbering

with OH branch.

IUPAC IDOLISER

Practice Problems

Give the correct numbering to the longest carbon chains of the following.

(i) $H_2C=CH-CH_2-CH_2-\underset{\underset{CH_3}{|}}{C}H-C\equiv CH$

(ii) $CH_3CH_2-\underset{\underset{CH_2CH_3}{|}}{C}H-CH_2-CH_2-CH_3$

(iii) $CH_3-CH_2-CH_2-\underset{\underset{\underset{CH_3}{|}}{C}H-CH_3}{|}}{C}H-CH_2-\underset{\underset{CH_3}{|}}{C}H-CH_3$

(iv) $CH_3-CH=\underset{\underset{CH=CH_2}{|}}{C}-CH_2-CH_2-CH_3$

(v) $CH_3-CH_2-CH_2-\underset{\underset{CH_2OH}{|}}{C}H-CH_3$

(vi) $CH_3-CH_2-CH_2-CN$

Practice Problem Answers (June 2016 Issue)

(i) $CH_3-\underset{\underset{CH_2-CH_2-CH_3}{|}}{C}H-\overset{\overset{CH_2-CH_3}{|}}{C}H-CH_2-CH_3$

(ii) $CH_3-\underset{\underset{CH_2CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}H-C\equiv CH$

(iii) $H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH=CH_2$

(iv) $H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}H-\overset{\overset{OH}{|}}{C}-CH=CH_2$

(v) $CH_3-\underset{\underset{CH_3}{|}}{C}H-CH_2-CH_2-\underset{\underset{\underset{H_3C~~CH_3}{CH}}{CH_2}}{C}H-CH_2-CH_2-\overset{\overset{CH_3}{}}{C}H{}_{CH_3}$

(vi) $HC\equiv C-\underset{\underset{CH_2CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH=CH_2$

इंजीनियरिंग प्रवेश परीक्षाओं की तैयारी के लिए पुस्तकें...

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हिन्दी माध्यम की एकमात्र पुस्तकें जिसकी अध्ययन सामग्री व प्रश्नों का कठिनता स्तर इंजीनियरिंग प्रवेश परीक्षाओं के अनुरूप है

PERSONALITIES SPECTRUM

"THERE IS NO LESS INVENTION IN APTLY APPLYING A THOUGHT FOUND IN A BOOK THAN IN BEING THE FIRST AUOTHER OF THE THOUGHT."

SIR ROBERT BOYLE
(THE FATHER OF MODERN CHEMISTRY)
(25/01/1627-31/12/1691)

Robert Boyle was a leading intellectual figure of the 17th century and one of the founders of Modern Chemistry. He was a natural philosopher, Chemist, physicist and inventor, born in Lismore, County Waterford, Ireland. He belonged to the privileged social class (Anglo-Irish) in Ireland, whose members were mostly the descendants and successors of the Protestant Ascendancy. He was one of the pioneers of modern experimental scientific method. Today, he is best known for Boyle's law which states, "*in a closed system at constant temperature, volume and pressure are inversely proportional to each other.*

LIFE HISTORY

Robert Boyle was born into an aristocratic family on January 25, 1672 in Lismore Castle, in the small town of Lismore, Ireland.

He was educated at Eton and then travelled and studied in Europe. He returned from the continent in 1644 and was extremely interested in science and settled in Dorset where he built a laboratory. In 1655 or 1666, Boyle moved to Oxford. It was here that he engaged Robert Hooke as an assistant and together they devised the most famous piece of experimental equipment associated with Boyle, the vacuum chamber of air-pump. He was the first prominent scientist to perform controlled experiments and publish his work with details concerning procedure, apparatus and observations. He began to publish in 1659 and continued to do so for the rest of his life on subjects as diverse as philosophy, medicine and religion.

It is Boyle's law for which he remains most famous. In 1668, Boyle moved permanently to London, living with his sister. In 1680 he refused the presidency of the Royal Society because the oath required to violate his strongly held religious principles. Boyle died in London on 31 December 1691.

CONTRIBUTION TO CHEMISTRY

Boyle's chief scientific interest was Chemistry, his first published scientific work, *New Experiments Physico-Mechanical, Touching the spring of the Air and Its Effects* (1660), concerned the physical nature of air, as displayed in a brilliant series of experiments in which he used an air pump to create vacuum. The second edition of this work, published in 1662, delineated the quantitative relationship that Boyle derived from experimental values, later known as "**Boyle's law**".

In his experiments Boyle made many important observations, including that of the weight gain by metals when they are heated to become crumbly residue. He interpreted this phenomenon as caused by fiery particles that were able to pass through the walls of glass vessels. Robert Boyle put Chemistry on a firm scientific footing, transforming it from a field bogged down in alchemy and mysticism into one based on measurement. He defined elements, compounds and mixtures and he coined the new term 'chemical analysis', a field in which he made several powerful contributions.

JOHN DALTON (06/07/1766-27/06/1844)
"If I have succeeded better than many who surround me, it has been chiefly may I say almost solely from universal assiduity."

Ever since he was a child, John Dalton wanted to learn as much as possible, yet he was the son of a poor Quaker weaver. So from a young age, he had to help his family. But he didn't let this stop him from learning; he just found a way to do both. At the young age of twelve, he taught the local school. His eagerness to learn and his great understanding of math and science quickly moved him up in the ranks.

Dalton's first experiment had to do with meteorology. Throughout his entire life, he would watch the weather and track what was happening in order to better predict the weather. Dalton also early on. He also discovered what is known as Dalton's Law of partial pressure. This law is simply that the total pressure of a system is going to be equal to sum of the partial pressures of each individual gas. This discovery led to one of his greatest discoveries: all matter is made up of individual particles called atoms. He developed this discovery into his atomic theory.

LIFE HISTORY

John Dalton (1766-1844) was born into a modest Quaker family in Cumberland, England and earned his living for most of his life as a teacher and public lecturer, beginning in his village school at the age of 12. After teaching 10 years at a Quaker boarding school in Kendal, he moved on to a teaching Philosophical Society, which provided him with a stimulating intellectual environment and laboratory facilities. The first paper he delivered before the society, was on colour blindness, which afflicted him and is sometimes still called 'Daltonism.'

Dalton arrived at his view of atomism by way of meteorology, in which he was seriously interested for a long period : he kept daily weather records from 1787 until his death, his first book was *Meteorological Observations* (1793), and he read a series of papers on meteorological topics before the Literary and Philosophical Society between 1799 and 1801. John Dalton got a small pension from the government that helped him live a normal life. He had a minor stroke in 1837 and yet another one in the next year that affected his speech. In 1844, he had another stroke and died in the same year.

CONTRIBUTION TO CHEMISTRY

The great interest in meteorology and the atmosphere led him to the study of gases and forming the atomic theory. He published a paper explaining that when two different gases were mixed together, they acted independently as if the other one is not present. Dalton, also postulated the law of thermal expansion.

In the year 1803, Dalton was able to submit another paper, 'The law of multiple proportions,' which states that elements always combine in whole number ratios. He created the first table of atomic weights, hydrogen being the first one having a mass of 1 amu.

In a way to expand his theory, Dalton published, 'A new system of chemical philosophy' in the year 1808, which states that atoms of different elements can be distinguished from one another by their varying atomic weights. Thus he became the first scientist to describe atomic behaviour in terms of the measurement of weight. He also explained that atoms cannot be created or destroyed. Though Dalton's work was welcomed by some people, it received much debate and hype among scientists. However, people began accepting Dalton's work, when more experiments were made on the subject matter in the later years.

CONCEPT
MISCONCEPT

General Perception Atomic Mass and Mass Number are Same Quantities

Reality These two quantities are totally different.

Explanation Atomic mass is the average relative mass of atoms as compared to the mass of an atom of C-12 isotope taken as 12, whereas mass number is the sum of protons and neutrons.

General Perception Carbon is the Element that Forms Maximum Number of Compounds

Reality It is hydrogen that forms maximum number of compounds.

Explanation The compounds formed by carbon are less than that of hydrogen. Hydrogen forms maximum compounds because it can share as well as transfer its valence electron.

General Perception Lime Water and Milk of Lime are Two Different Compounds of Calcium

Reality Chemically both of these are calcium hydroxides.

Explanation Lime water is a clear solution of $Ca(OH)_2$ and milk of lime is the suspension of $Ca(OH)_2$ in water.

General Perception Dry Ice is a Variety of Ice

Reality Dry ice is actually solid CO_2.

Explanation The dry ice sublimes if it is kept under 1 atm pressure. It does not melt and hence, does not wet the surface on which it is kept. That is why it is termed as dry ice.

General Perception Matter Exists in Three States Named as Solid, Liquid and Gas

Reality Actually, six states of matter have been reported yet.

Explanation The six states of matter are given as :

   (i) Solid   (ii) Liquid   (iii) Gas

  (iv) Plasma   (v) Fermionic condensate

  (vi) Bose-Einstein Condensate

Among these six states of matter, first three states are observed in our daily routine and constitute almost whole of our earth. Fourth state of matter, plasma, is composed of ionic matrix, which exists only at very high temperatures ($\approx 10^7$ K).

Such a high temperature may be attained during nuclear fusion reactions or thermonuclear reactions. The source of energy of stars is supposed to be thermonuclear reaction, so plasma state is known to exist naturally in the core of stars (e.g., sun).

On earth, some phenomena, such as thundering of clouds, explosion of hydrogen bomb etc., are supposed to involve plasma. Two other states, fermionic condensate and Bose-Einstein's condensate have also been observed during the nuclear fusion reactions.

General Perception Uncertainty Principle Applies only on Calculation of Position and Momentum of Very Small or Subatomic Particles

Reality Uncertainty principle applies on all conjugate pairs of variables whose product has dimensions of action.

Explanation Conjugate pairs of two variables are those pairs, which include two variables, whose product has dimensions of action or work, e.g. $\Delta p \cdot \Delta x$ (momentum and position), $\Delta E \cdot \Delta t$ (energy and time), $\Delta \omega \cdot \Delta \theta$ (angular momentum and angle) are conjugate pairs.

Thus, all of these pairs show uncertainty principle.

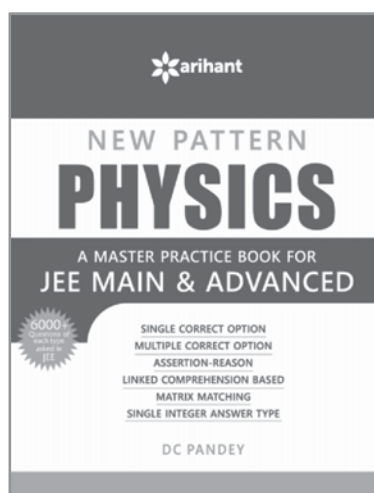**General Perception** Osmosis and Diffusion are Same Processes

Reality Osmosis is entirely different process from diffusion process.

Explanation Diffusion involves the movement of solute particles, when a solute is dissolved in solvent, solute particles move from region of high solute concentration to lower concentration till concentration of solute becomes uniform throughout the solution. Osmosis involves spontaneous net flow of solvent molecules from dilute solution to concentrated solution.

Another difference is that osmosis requires a semi-permeable membrane while no such membrane is required in diffusion.
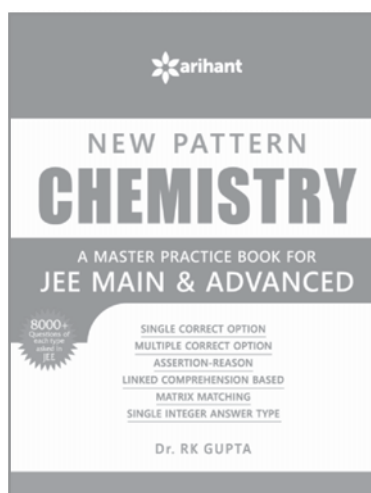
SUPERB PRACTICE BOOKS FOR
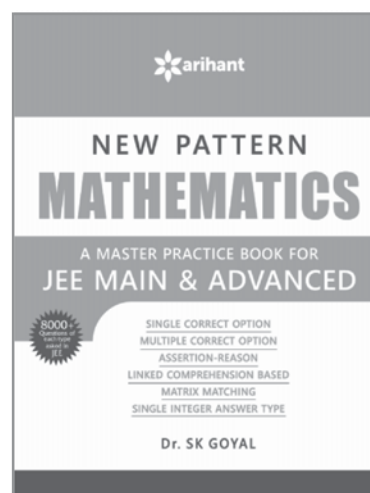## JEE MAIN & ADVANCED

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- **SINGLE INTEGER**
- **ANSWER TYPE**

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BRAiN TEASERS

To boost up your ranks in JEE Main and Advanced

1. A solution of polystyrene in benzene contains 10 g/L polystyrene. The equilibrium height of the column of solution (density = 0.88 g cm^{-3}) in the osmometer corrected for the capillary rise is 11.6 cm at 25°C. What is the number average molar mass of the polystyrene? [Assuming the solution is ideal]
(a) 24.8×10^3 g mol^{-1}
(b) 12.6×10^2 g mol^{-1}
(c) 6.023×10^3 g mol^{-1}
(d) 21.6×10^2 g mol^{-1}

2. The most appropriate reason for larger number of oxidation states exhibited by the actinoids than the corresponding lanthanoids is
(a) more energy difference between 5*f* and 6*d*-orbitals than between 4*f* and 5*d*-orbitals
(b) lesser energy difference between 5*f* and 6*d*-orbitals than between 4*f* and 5*d*-orbitals
(c) larger atomic size of actinoids than the lanthanoids
(d) greater reactive nature of the actinoids than the lanthanoids

3. Rank the following in the order of increasing value of the equilibrium constant for hydration.

I   II   III

(a) I < II < III
(b) III < I < II
(c) II < I < III
(d) II < III < I

4.
$$A \xrightarrow{H_2O_2/\overline{O}H} B$$
with B_2H_6/THF forming A, and $A \xrightarrow{CH_3COOH} C$
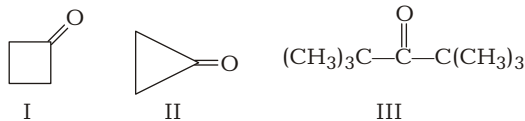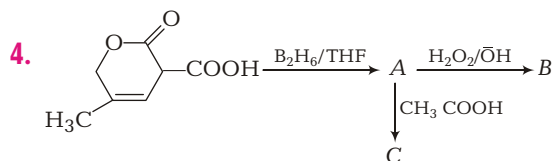
Three compounds I, II and III are given as,

I   II

III
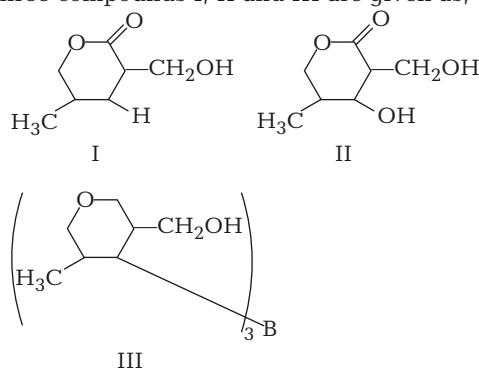
The compounds *A*, *B* and *C* respectively, are
(a) I, II and III   (b) I, III and II   (c) III, II and I   (d) III, I and II

5. One gas bleaches the coloured matter by reduction temporary while the other one by oxidation permanently. The gases respectively are
(a) SO_2 and Cl_2 (b) O_3 and Cl_2
(c) H_2S and CO_2 (d) Cl_2 and SO_2

6. For a hypothetical H-like atom, the potential energy of the system is given by $U(r) = - ke^2 /r^3$, where, *r* is the distance between the two particles. If Bohr's model of quantisation of angular momentum is applicable, then velocity of particle is given by
(a) $v = \dfrac{n^2 h^3}{ke^2 8\pi^3 m^2}$ (b) $v = \dfrac{n^3 h^3}{8ke^2 \pi^3 m^2}$
(c) $v = \dfrac{n^3 h^3}{24ke^2 \pi^3 m^2}$ (d) $v = \dfrac{n^2 h^3}{24ke^2 \pi^3 m^2}$

7. If mono-molecular adsorption takes place, how much ammonia in mL at STP, would be adsorbed on the surface of 25 g charcoal?
[Diameter of ammonia molecule is 0.3 nm]
(a) 13148.8 mL   (b) 15258.5 mL
(c) 15879.6 mL   (d) 15234.6 mL

8. The solubilities of carbonates decrease downward in magnesium group due to a decrease in
   (a) hydration energies of cations
   (b) interionic attraction
   (c) entropy of solution formation
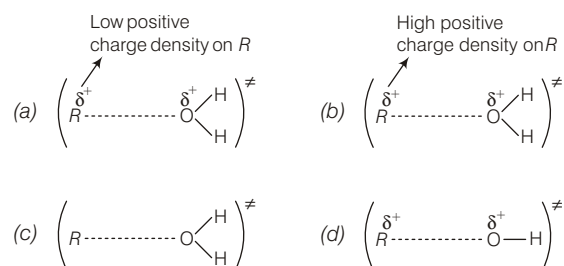   (d) lattice energies of the solids

9. The half-cell reactions for rusting of iron are

$$2H^+ + \frac{1}{2}O_2 + 2e^- \longrightarrow H_2O; \quad E° = +1.23V$$

$$Fe^{2+} + 2e^- \longrightarrow Fe\ (s); \quad E° = -0.44V$$
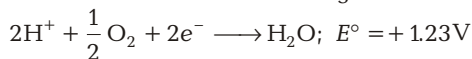
$\Delta G°$ (in kJ) for the reaction is
   (a) − 76   (b) − 322   (c) − 176   (d) − 122

10. Most appropriate transition state in dehydration of alcohol is (in acidic medium)

Answers with Explanation

1. **(a)** We know that,

$$p = h\rho g = (0.116\ m)\ (0.88 \times 10^3\ kg\,m^{-3})\cdot(9.8\ ms^{-2})$$

$$= 1000\ Pa$$

$$\pi = \frac{mST}{MV},\ M = \frac{mST}{\pi V}$$

$$M = \frac{(10\ g)\cdot(8.314\ JK^{-1}mol^{-1})\ (298\ K)}{(10^3\ Pa)\cdot(10^{-3}\ m^3)}$$

$$= 24.8 \times 10^3\,g\ mol^{-1}$$

2. **(b)** Due to the energy differences, lanthanoids have lesser energy difference between $5f$ and $6d$-orbitals than between $4f$ and $5d$-orbitals. The presence of either half-filled or completely filled or empty 4 f-subshells.

3. **(b)** Structure II is highly unstable due to high angular strain. Hence, it will have highest value of equilibrium constant for hydration.
   Structure III is unstable due to crowdness.
   Structure I is unstable due to angular strain, but this strain is less than that of strain in structure II.
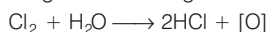   Hence, increasing value order of the equilibrium constant for hydration is III < I < II.

4. **(c)** B_2H_6/THF besides reacting at (C═C) also selectively reduces only (—COOH) group to (—CH_2OH) group in cyclic ester.
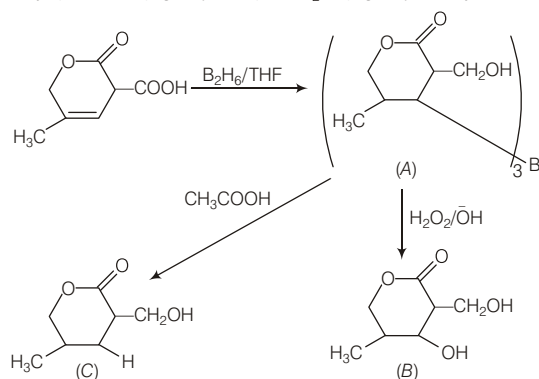
5. **(a)** $SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2\,[H]$
   Hence, temporary bleaching is done through reduction and permanent bleaching is done through oxidation.

$$Cl_2 + H_2O \longrightarrow 2HCl + [O]$$

6. **(c)** Magnitude of the force,

$$\frac{d\,[U(r)]}{dr} = \frac{3ke^2}{r^4}$$

$$\therefore \quad \frac{3ke^2}{r^4} = \frac{mv^2}{r}$$

We know that $mvr = \dfrac{nh}{2\pi}$

$$r = \frac{nh}{2\pi\,m\cdot v}$$

$$3ke^2 \times \frac{8\pi^3 m^3 v^3}{n^3 h^3} = mv^2$$

$$v = \frac{n^3 h^3}{24ke^2\pi^3 m^2}$$

7. **(a)** Total Area, $A = 25000\ m^2 = 25 \times 10^7\,cm^2$

$$r = 1.5 \times 10^{-8}\ cm$$

Area of one NH_3 molecule $= \pi r^2 = 7.068 \times 10^{-16}\ cm^2$

Number of NH_3 molecules persent on 25 g charcoal

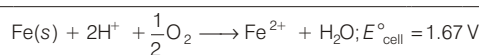$$= \frac{25 \times 10^7}{7.068 \times 10^{-16}} = 3.53 \times 10^{23}$$

Moles of $NH_3 = \left(\dfrac{3.53 \times 10^{23}}{6.023 \times 10^3}\right) = 0.587$

$\Rightarrow$ Volume of NH_3 at STP required

$$= (22400 \times 0.587)\,mL = 13148.8\ mL$$

8. **(a)** With increase in size of M^{2+} ions from Mg^{2+} to Ba^{2+}, the hydration energy decreases significantly, while there is only a small change in lattice energy. This decreases the solubility significantly.

9. **(b)** $2H^+ + \dfrac{1}{2}O_2 + 2e^- \longrightarrow H_2O; E° = +1.23\,V$ ...(i)

$\underline{Fe^{2+} + 2e^- \longrightarrow Fe(s); E° = -0.44\ V}$ ...(ii)

$$Fe(s) + 2H^+ + \frac{1}{2}O_2 \longrightarrow Fe^{2+} + H_2O; E°_{cell} = 1.67\ V$$

[substracting Eq. (ii) from Eq. (i)]

$$\Delta G° = -nFE°_{cell} = -2 \times 96500 \times 1.67$$

$$= -322310\ J \approx -322\ kJ$$

10. **(b)** In highly acidic medium, —OH gets protonated and H_2O is good leaving group and majority of bond is broken in the reaction.

![] EXTRA DOSE

EXEMPLAR SIMPL!FiED

EXTRACT OF EXTRAORDINARY EXEMPLAR PROBLEMS

Only One Correct Option Type Questions

1. The empirical formula and molecular mass of a compound are CH_2O and 180 g respectively. What will be the molecular formula of the compound?
(a) $C_9H_{18}O_9$ (b) CH_2O
(c) $C_6H_{12}O_6$ (d) $C_2H_4O_2$

2. If the density of a solution is 3.12 g mL^{-1}, the mass of 1.5 mL solution in significant figures is
(a) 4.7 g   (b) 4680×10^{-3} g
(c) 4.680 g   (d) 46.80 g

3. If 500 mL of a 5 M solution is diluted to 1500 mL, what will be the molarity of the solution obtained?
(a) 1.5 M   (b) 1.66 M
(c) 0.017 M   (d) 1.59 M

4. One mole of any substance contains 6.022×10^{23} atoms/molecules. Number of molecules of H_2SO_4 present in 100 mL of 0.02 M H_2SO_4 solution is
(a) 12.044×10^{20} molecules
(b) 6.022×10^{23} molecules
(c) 1×10^{23} molecules
(d) 12.044×10^{23} molecules

5. Which of the following reactions is not correct according to the law of conservation of mass?
(a) $2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$
(b) $C_3H_8(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(g)$
(c) $P_4(s) + 5O_2(g) \longrightarrow P_4O_{10}(s)$
(d) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$

6. The number of atoms present in one mole of an element is equal to Avogadro's number. Which of the following element contains the greatest number of atoms?
(a) 4 g He   (b) 46 g Na   (c) 0.40 g Ca   (d) 12 g He

Short Answer Type Questions

7. What is the difference between molality and molarity?

8. The reactant which is entirely consumed in reaction is known as limiting reagent. In the reaction, $2A + 4B \longrightarrow 3C + 4D$, when 5 moles of A react with 6 moles of B, then
(a) which is the limiting reagent?
(b) calculate the amount of C formed.

9. What will be the mass of one atom of C-12 in grams?

10. The density of 3 molal solution of NaOH is 1.110 g mL^{-1}. Calculate the molarity of the solution.

11. Calculate the mass per cent of calcium, phosphorus and oxygen in calcium phosphate $Ca_3(PO_4)_2$.

12. A vessel contains 1.6 g of dioxygen at STP (273.15 K, 1 atm pressure). The gas is now transferred to another vessel at constant temperature, where pressure becomes half of the original pressure. Calculate the volume of the new vessel.

13. Volume of a solution changes with change in temperature, then what will be the molality of the solution be affected by temperature? Give reason for your answer.

14. Hydrogen gas is prepared in the laboratory by reacting dilute HCl with granulated zinc. Following reaction takes place

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

Calculate the volume of hydrogen gas liberated at STP when 32.65 g of zinc reacts with HCl. (1 mole of a gas occupies 22.7 L volume at STP; atomic mass of Zn = 65.3 u)

15. Calculate the average atomic mass of hydrogen using the following data

Isotope	% natural abundance	Molar mass (u)
^1H	99.985	1
^2H	0.015	2

16. If 4 g of NaOH dissolves in 36 g of H_2O, calculate the mole fraction of each component in the solution. Also, determine the molarity of solution. (specific gravity of solution is $1 g\ mL^{-1}$)

Matching Type Questions

17. Match the following physical quantities with units.

	Physical quantity		Unit
A.	Molarity	1.	$g\ mL^{-1}$
B.	Mole fraction	2.	mol
C.	Mole	3.	Pascal
D.	Molality	4.	Unitless
E.	Pressure	5.	$mol\ L^{-1}$
F.	Luminous intensity	6.	Candela
G.	Density	7.	$mol\ kg^{-1}$
H.	Mass	8.	Nm^{-1}
		9.	kg

18. Match the following.

A.	88 g of CO_2	1.	0.2 mol
B.	6.022×10^{23} molecules of H_2O	2.	2 mol
C.	5.6 L of O_2 at STP	3.	1 mol
D.	96 g of O_2	4.	6.022×10^{23} molecules
E.	1 mole of any gas	5.	3 mol

Assertion and Reason

Directions (Q.Nos. 19-21) 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) Both A and R are true and R is the correct explanation of A
(b) Both A and R are true but R is not the correct explanation of A
(c) A is true but R is false
(d) A is false but R is true

19. **Assertion** (A) The empirical mass of ethene is half of its molecular mass.

Reason (R) The empirical formula represents the simplest whole number ratio of various atoms present in a compound.

20. **Assertion** (A) Combustion of 16 g of methane gives 18 g of water.

Reason (R) In the combustion of methane, water is one of the products.
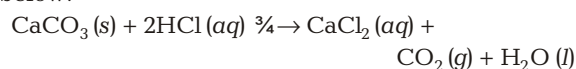
21. **Assertion** (A) One atomic mass unit is defined as one twelfth of the mass of one carbon-12 atom.

Reason (R) Carbon-12 isotope is the most abundant isotope of carbon and has been chosen as standard.

Long Answer Type Questions

22. Define the law of multiple proportions. Explain it with two examples. How does this law point to the existence of atoms?

23. Calcium carbonate reacts with aqueous HCl to give $CaCl_2$ and CO_2 according to the reaction given below:
$$CaCO_3\ (s) + 2HCl\ (aq) \longrightarrow CaCl_2\ (aq) + CO_2\ (g) + H_2O\ (l)$$
What mass of $CaCl_2$ will be formed when 250 mL of 0.76 M HCl reacts with 1000 g of $CaCO_3$? Name the limiting reagent. Calculate the number of moles of $CaCl_2$ formed in the reaction.

Answers with Explanation

1. *(c)*

> **STRATEGY**
> (i) *Empirical formula shows the simplest whole number ratio of different elements present in a molecule, so find the number of moles by dividing molecular mass with empirical formula mass.*
> (ii) *To calculate the molecular formula of the compound, multiply the number of moles to the subscript of the elements present in the empirical formula.*

Empirical formula mass of $CH_2O = 12 + 2 \times 1 + 16 = 30\ g\ mol^{-1}$

Molecular mass $= 180\ g\ mol^{-1}$

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{180}{30} = 6$$

$\therefore$ Molecular formula $= (\text{Empirical formula})_n$
$$= (CH_2O)_n = C_6H_{12}O_6$$

2. *(a)* **Key Concept** When measured quantities are multiplied or divided, the number of significant figures in the result is same as that in the quantity having smallest number of significant figures.

Given that, density of solution $= 3.12\ g\ mL^{-1}$

Volume of solution $= 1.5\ mL$

For a solution, Mass $=$ volume $\times$ density
$$= 1.5\ mL \times 3.12\ g\ mL^{-1} = 4.68\ g$$

The digit 1.5 has only two significant figures, so the answer must also be limited to two significant figures. So, it is rounded off to reduce the number of significant figures.

Hence, the answer is reported as 4.7 g.

⬛ EXTRA DOSE

3. **(b)**

> **STRATEGY**
> *In case of dilution, molarity is calculated by using dilution equation for molarity, $M_1V_1 = M_2V_2$, we have, V_1 (before dilution) and V_2 (after dilution), so calculate molarity of the given solution from this equation.*

Given that, $M_1 = 5\,M$

$V_1 = 500\,mL$

$V_2 = 1500\,mL$

$M_2 = ?$

For dilution, a general formula is

$$\underset{\text{(Before dilution)}}{M_1V_1} = \underset{\text{(After dilution)}}{M_2V_2}$$

$$5 \times 500 = M_2 \times 1500$$

or $M_2 = 1.66\,M$

4. **(a)**

> **STRATEGY**
> - To find number of molecules, first find out number of millimoles of given solution:
> - Millimoles of H_2SO_4 = Molarity × Volume (in mL)
> - Convert millimoles to moles.
> - Finally, find out number of molecules from the given formula :
>   Number of molecules = Number of moles × Avogadro number

One mole of any substance contains 6.022×10^{23} molecules.

Hence, Number of millimoles of H_2SO_4

$$= \text{molarity} \times \text{volume in mL}$$

$$= 0.02 \times 100 = 2\ \text{millimoles}$$

$$= 2 \times 10^{-3}\ \text{mol}$$

Number of molecules = number of moles × N_A

$$= 2 \times 10^{-3} \times 6.022 \times 10^{23}$$

$$= 12.044 \times 10^{20}\ \text{molecules}$$

5. **(b) Key concept** Law of conservation of mass states that,

"During a chemical reaction, total mass of reactants equal to total mass of products or total mass remains constant during a chemical change".

In the following equation,

$$\underset{44g}{C_3H_8(g)} + \underset{32g}{O_2(g)} \longrightarrow \underset{44g}{CO_2(g)} + \underset{18\,g}{H_2O(g)}$$

$$44 + 32 \neq 44 + 18$$
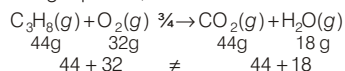
i.e. mass of reactants ≠ mass of products.

Hence, law of conservation of mass is not followed.

6. **(d)**

> **STRATEGY**
> The number of atoms is related to Avogadro's number (N_A) by
> Number of atoms = moles × N_A
> The number of atoms of elements can be compared easily on the basis of their moles only because N_A is a constant value. Thus, element with large number of moles will possess greatest number of atoms.

For comparing number of atoms, first we calculate the moles as all are monoatomic

Number of moles of atom × N_A = Number of atoms.

Number of Moles for 4 g He $= \dfrac{4g}{4\,g\,mol^{-1}} = 1\ mol$;

$$46\ g\ Na = \dfrac{46g}{23g\,mol^{-1}} = 2\ mol$$

$$0.40\ g\ Ca = \dfrac{0.40g}{40g\,mol^{-1}} = 0.01\ mol$$

$$12\ g\ He = \dfrac{12\,g}{4g\,mol^{-1}} = 3\ mol$$

Hence, 12 g He contains greatest number of atoms as it possesses maximum number of moles.

7.

Molality	Molarity
It is defined as the number of moles of solute dissolved in 1 kg of solvent.	It is defined as the number of moles of solute dissolved in 1L of solution.
It is independent of temperature.	It depends upon temperature (because, volume of solution µ temperature).

8. **Key concept** Limiting reagent limits the amount of product formed because it is present in lesser amount and gets consumed first.

$$2A + 4B \longrightarrow 3C + 4D$$
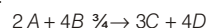
According to the given reaction, 2 moles of A react with 4 moles of B.

Hence, 5 moles of A will react with 10 moles of B

(a) It indicates that reactant B is limiting reagent as it will consume first in the reaction because we have only 6 moles of B.

(b) Limiting reagent decides the amount of product produced. According to the reaction,

4 moles of B produces 3 moles of C.

$\therefore$ 6 moles of B will produce $\dfrac{3 \times 6}{4} = 4.5$ moles of C

9. The mass of a carbon-12 atom was determined by a mass spectrometer and found to be equal to 1.992648×10^{-23} g. It is known that 1 mole of C-12 atom weighing 12 g and contains N_A number of atoms. Thus,

1 mole of C-12 atoms = 12 g = 6.022×10^{23} atoms

Þ 6.022×10^{23} atoms of C-12 have mass equal to 12 g

$\therefore$ 1 atom of C-12 will have mass

$$= \dfrac{12}{6.022 \times 10^{23}}\ g$$

$$= 1.992648 \times 10^{-23}g$$

$$\approx 1.99 \times 10^{-23}g$$

10.

> **STRATEGY**
> - Determine the mass of solution from the given molality and that of volume of solution by relating mass and density to each other, i.e.
> $$\text{Volume} = \dfrac{\text{Mass}}{\text{Density}}$$
> - Then, calculate the molarity of solution as
> $$\text{Molarity} = \dfrac{\text{Number of moles}}{\text{Volume (in litre)}}$$

3 molal solution of NaOH means 3 moles of NaOH are dissolved in 1 kg solvent. So, the mass of solution = 1000 g solvent + 120 g NaOH = 1120 g solution

(Molar mass of NaOH = 23 + 16 + 1 = 40 g and 3 moles of NaOH = 3 × 40 = 120 g)

$$\text{Volume of solution} = \frac{\text{Mass of solution}}{\text{Density of solution}} \qquad \left(\because d = \frac{m}{V}\right)$$

$$V = \frac{1120 \text{ g}}{1.110 \text{ g mL}^{-1}}$$

$$= 1009 \text{ mL}$$

$$\text{Molarity} = \frac{\text{Moles of solute} \times 1000}{\text{Volume of solution (mL)}}$$

$$= \frac{3 \times 1000}{1009} = 2.973 \text{ M}$$

$$\approx 3 \text{ M}$$

11.

> **STRATEGY**
>
> To calculate the mass per cent of atom, use the following formula
>
> Mass per cent of an element
>
> $= \dfrac{\text{Atomic mass of the element present in the compound}}{\text{Molar mass of the compound}} \times 100$

Mass per cent of calcium

$$= \frac{3 \times (\text{atomic mass of calcium})}{\text{molecular mass of Ca}_3(\text{PO}_4)_2} \times 100$$

$$= \frac{3 \times 40 \text{ u}}{310 \text{ u}} \times 100$$

$$= 38.71\%$$

Mass per cent of phosphorus

$$= \frac{2 \times (\text{atomic mass of phosphorus})}{\text{molecular mass of Ca}_3(\text{PO}_4)_2} \times 100$$

$$= \frac{2 \times 31 \text{ u}}{310 \text{ u}} \times 100$$

$$= 20\%$$

Mass per cent of oxygen

$$= \frac{8 \times (\text{atomic mass of oxygen})}{\text{molecular mass of Ca}_3(\text{PO}_4)_2} \times 100$$

$$= \frac{8 \times 16 \text{ u}}{310 \text{ u}} \times 100$$

$$= 41.29\%$$

12. $p_1 = 1 \text{ atm}, p_2 = \dfrac{1}{2} = 0.5 \text{ atm}, T_1 = 273.15, V_2 = ?, V_1 = ?$

32 g dioxygen occupies = 22.4 L volume at STP

∴ 1.6 g dioxygen will occupy volume

$$= \frac{22.4 \text{ L} \times 1.6 \text{ g}}{32 \text{ g}} = 1.12 \text{ L}$$

$$V_1 = 1.12 \text{ L}$$

From Boyle's law (as temperature is constant),

$$p_1 V_1 = p_2 V_2$$

$$V_2 = \frac{p_1 V_1}{p_2}$$

$$= \frac{1 \text{ atm} \times 1.12 \text{ L}}{0.5 \text{ atm}} = 2.24 \text{ L}$$

13. No, molality of the solution does not change with temperature since, mass remains unaffected with temperature.

$$\text{Molality}, m = \frac{\text{Moles of solute}}{\text{Mass of solvent (in g)}} \times 1000$$

14. Given that, mass of Zn = 32.65 g

1 mole of gas occupies = 22.7 L volume at STP

Atomic mass of Zn = 65.3 u

The given equation is

$$\underset{65.3 \text{ g}}{\text{Zn}} + 2\text{HCl} \longrightarrow \text{ZnCl}_2 + \underset{1 \text{ mol} = 22.7 \text{ L at STP}}{\text{H}_2}$$
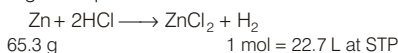
From the above equation, it is clear that 65.3 g Zn when reacts with HCl, produces = 22.7 L of H_2 at STP

∴ 32.65 g Zn when reacts with HCl, will produce

$$= \frac{22.7 \times 32.65}{65.3}$$

$$= 11.35 \text{ L of } H_2 \text{ at STP}$$

15. Many naturally occurring elements exist as more than one isotopes. When we take into account the existence of these isotopes and their relative abundance (per cent occurrence), the average atomic mass of the element can be calculated as

Average atomic mass

$$= \frac{\{(\text{Natural abundance of } {}^1\text{H} \times \text{molar mass}) + (\text{Natural abundance of } {}^2\text{H} \times \text{molar mass of } {}^2\text{H})\}}{100}$$

$$= \frac{99.985 \times 1 + 0.015 \times 2}{100}$$

$$= \frac{99.985 + 0.030}{100} = \frac{100.015}{100} = 1.00015 \text{ u}$$

16.

> **STRATEGY**
>
> (i) To proceed the calculation, first calculate the number of moles of NaOH and H_2O.
>
> (ii) Then, find mole fraction of NaOH and H_2O by using the formula, $\chi_{\text{NaOH}} = \dfrac{n_{\text{NaOH}}}{n_{\text{NaOH}} + n_{\text{H}_2\text{O}}}$ and $\chi_{\text{H}_2\text{O}} = \dfrac{n_{\text{H}_2\text{O}}}{n_{\text{NaOH}} + n_{\text{H}_2\text{O}}}$
>
> (iii) Then, calculate molarity $= \dfrac{W \times 1000}{m \times V}$, so in order to calculate molarity, we require volume of solution which is given by, $V = \dfrac{m}{\text{specific gravity}}$

Number of moles of NaOH,

$$n_{\text{NaOH}} = \frac{4}{40} = 0.1 \text{ mol} \qquad \left\{\because n = \frac{\text{Mass (g)}}{\text{Molar mass (g mol}^{-1})}\right\}$$

Similarly, $n_{\text{H}_2\text{O}} = \dfrac{36}{18} = 2 \text{ mol}$

Mole fraction of NaOH,

$$\chi_{\text{NaOH}} = \frac{\text{moles of NaOH}}{\text{moles of NaOH} + \text{moles of H}_2\text{O}}$$

$$\chi_{\text{NaOH}} = \frac{0.1}{0.1 + 2} = 0.0476$$

Similarly, $\chi_{\text{H}_2\text{O}} = \dfrac{n_{\text{H}_2\text{O}}}{n_{\text{NaOH}} + n_{\text{H}_2\text{O}}} = \dfrac{2}{0.1 + 2} = 0.9524$

Total mass of solution = mass of solute + mass of solvent

$$= (4 + 36)\text{g} = 40 \text{ g}$$

$$\text{Volume of solution} = \frac{\text{Mass of solution}}{\text{specific gravity}} = \frac{40 \text{ g}}{1 \text{ g mL}^{-1}} = 40 \text{ mL}$$
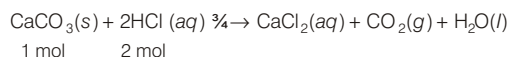
$$\text{Molarity} = \frac{\text{Moles of solute} \times 1000}{\text{Volume of solution (mL)}} = \frac{0.1 \times 1000}{40} = 2.5 \text{ M}$$

📓 EXTRA DOSE

17. $A \rightarrow (5), B \rightarrow (4), C \rightarrow (2), D \rightarrow (7), E \rightarrow (3), F \rightarrow (6), G \rightarrow (1), H \rightarrow (9)$

A. Molarity = concentration in $mol\ L^{-1}$

$$Molarity = \frac{Number\ of\ moles}{Volume\ (in\ litre)}$$

B. Mole fraction = Unitless

C. $Mole = \dfrac{Mass\ (g)}{Molar\ mass\ (g\ mol^{-1})} = mol$

D. Molality = concentration of solute in mol per kg of solvent

$$Molality = \frac{Number\ of\ moles}{Mass\ of\ solvent\ (in\ kg)}$$

E. The SI unit of pressure is pascal (Pa), equal to one newton per metre square (N/m^2 or $kg\ m^{-1}\ s^{-2}$). This special name for the unit was added in 1971; before that, pressure in SI was expressed simply as N/m^2.

F. Unit of luminous intensity = Candela

The candela is the luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency 540×10^{12} hertz and that has a radiant intensity in that direction of 1/683 watt per steradian.

G. $Density = \dfrac{Mass}{Volume} = g\ mL^{-1}$

H. Unit of mass = kilogram

The kilogram is the unit of mass; it is equal to the mass of the international prototype of the kilogram.

18. $A \rightarrow (2), B \rightarrow (3), C \rightarrow (1), D \rightarrow (5), E \rightarrow (4)$

A. Number of moles of CO_2 molecule

$$= \frac{Weight\ in\ gram\ of\ CO_2}{Molecular\ weight\ of\ CO_2}$$

$$= \frac{88}{44} = 2\ mol$$

B. 1 mole of a substance

$$= N_A\ molecules = 6.022 \times 10^{23}\ molecules$$

$$= Avogadro\ number$$

$$= 6.022 \times 10^{23}\ molecules\ of\ H_2O = 1\ mol$$

C. 22.4 L of O_2 at STP = 1 mol

$$5.6\ L\ of\ O_2\ at\ STP = \frac{5.6}{22.4}\ mol = 0.25\ mol$$

D. Number of moles of 96 g of $O_2 = \dfrac{96}{32}\ mol = 3\ mol$

E. 1 mole of any gas

$$= Avogadro\ number$$

$$= 6.022 \times 10^{23}\ molecules$$

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

The molecular formula of ethene is C_2H_4 and its empirical formula is CH_2.

Thus, molecular formula = (Empirical formula)$_2$

20. *(d)* Assertion is false but Reason is true.

Combustion of 16 g of methane gives 36 g of water.

$$CH_4 + 2O_2 \xrightarrow{} CO_2 + 2H_2O$$
$$\text{1 mol} \qquad\qquad\qquad\quad \text{2 mol}$$
$$\text{= 16 g} \qquad\qquad\qquad\quad \text{= 36 g}$$
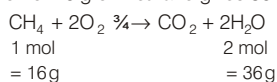
21. *(b)* Both Assertion and Reason are true but Reason is not the correct explanation of Assertion.

Atomic masses of the elements obtained by scientists by comparing with the mass of carbon comes out to be close to the whole number value.

22. 'Law of multiple proportions' was first studied by Dalton in 1803 which may be defined as follows :

When two elements combine to form two or more chemical compounds, then the masses of one of the elements which combine with a fixed mass of the other, bear a simple ratio to one another.

e.g. Hydrogen combines with oxygen to form two compounds, namely, water and hydrogen peroxide, respectively.

$$\text{Hydrogen + Oxygen} \xrightarrow{} \text{Water}$$
$$\text{2 g} \qquad\quad \text{16 g} \qquad\quad \text{18 g}$$

$$\text{Hydrogen + Oxygen} \xrightarrow{} \text{Hydrogen peroxide}$$
$$\text{2 g} \qquad\quad \text{32 g} \qquad\quad \text{34 g}$$
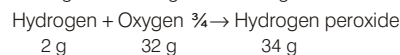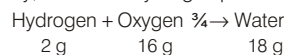
Here, the masses of oxygen (i.e. 16 g and 32 g) which combine with a fixed mass of hydrogen (2 g) bear a simple ratio, i.e. 16 : 32 or 1 : 2.

As we know that, when compounds mixed in different proportions. Then they form different compounds. In the above examples, when hydrogen is mixed with different proportion of oxygen, then they form water or hydrogen peroxide.

It shows that there are constituents which combine in a definite proportion. These constituents may be atoms. Thus, the law of multiple proportions shows the existence of atoms which combine to form molecules.

23. Molar mass of $CaCO_3 = 40 + 12 + 3 \times 16 = 100\ g\ mol^{-1}$

Moles of $CaCO_3$ in 1000 g,

$$n_{CaCO_3} = \frac{Mass\ (g)}{Molar\ mass\ (g\ mol^{-1})}$$

$$n_{CaCO_3} = \frac{1000\ g}{100\ g\ mol^{-1}} = 10\ mol$$

$$Molarity = \frac{Moles\ of\ solute\ (HCl) \times 100}{Volume\ of\ solution}$$

(It is given that moles of HCl in 250 mL of 0.76 M HCl $= n_{HCl}$)

$$0.76 = \frac{n_{HCl} \times 100}{250}$$

$$n_{HCl} = \frac{0.76 \times 250}{1000} = 0.19\ mol$$

$$CaCO_3(s) + 2HCl\ (aq) \xrightarrow{} CaCl_2(aq) + CO_2(g) + H_2O(l)$$
$$\text{1 mol} \qquad\quad \text{2 mol}$$

According to the equation,

1 mole of $CaCO_3$ reacts with 2 moles of HCl

$\therefore$ 10 moles of $CaCO_3$ will react with $\left(\dfrac{10 \times 2}{1} \right) = 20$ moles of HCl

But we have only 0.19 moles of HCl, so HCl is limiting reagent and it limits the yield of $CaCl_2$.

Since, 2 moles of HCl produce 1 mole of $CaCl_2$.

0.19 mole of HCl will produce $= \dfrac{1 \times 0.19}{2} = 0.095\ mol\ CaCl_2$

Molar mass of $CaCl_2 = 40 + (2 \times 35.5) = 111\ g\ mol^{-1}$

$\therefore$ 0.095 mole of $CaCl_2 = 0.095 \times 111 = 10.54\ g$

EXPLICATION SERIES

[Elements : How They were Discovered?]

In the last issue, we have read about sulphur, its discovery, abundance on Earth, recognisation, properties and allotropic forms etc. In this issue, we will read about gold (Au) and silver (Ag). Often we hear about the varying prices of gold and silver in newspapers and newschannels etc. But have you ever imagined, when these two elements were recognised first in the past. We shall discuss about these two elements one by one. Lets start with gold.

Gold

- Karl Marx wrote, "Gold is infact the first metal that man has discovered". It mostly occurs in a native state in nature. The word gold is an Anglo-Saxon word, similar to the Anglo-Saxon word for yellow, 'geolo'. It is believed to come from Sanskrit jval meaning to shine.

- Gold articles were found in excavations together with stone tools dating from the Neolithic Age. But in that time, people found gold by chance. Only after the emergence of classes in society, first attempt was made to mine gold.

- During excavations of pyramids of all dynasties in Egypt, archaeologists found in great numbers not only gold jewellery but also household articles. Gold was known not only in Egypt, as early as in the 10th century, it was used in China, India, states of Mesopotamia etc. Thus, gold was known to the peoples of ancient states in Europe and Asia. The oldest gold mines were found in India and Nubia (The region along the Nile river located in Northern Sudan and Southern Egypt).

- The processes of gold purification known in antiquity did not yield the pure metal but usually alloys consisting of gold and silver which were named as azem. A natural gold-silver alloy, electrum was also known.

- Wars were waged, nations and states were innihilated, monstrous crimes were committed for the sake of gold. But possession of gold did not bring peace to man. On the contrary, sorrow and fear of loosing treasure filled his soul.

- The alchemic period between 4th and the 16th centuries was a gloomy one in the history of the search for gold. The efforts of alchemists were directed towards the search for the *philosophers stone*, which they held and possessed the property of transforming base metals into gold.

- All the attempts to find the philosophers stone turned out to be unsuccessful, although many alchemists gave their lives for this idea. All reports about the discoveries of methods of preparing gold from other metals were pure fake tricks to get money.

- Most gold is ancient or comes from Central American Aztecs and South American Incas brought to Europe by the Spanish an Portuguese in the 16th century and which have been recycled over and over again. In 1830, world output was no more than 12 tonnes per annum. But around that time, new gold discoveries were being made. Finds were discovered in Siberia, California, New South Wales and Victoria, Australia, Transvaal, South Africa, the Klondike and Alaska and they all produced gold rushes. World production was then around 150 tonnes per year. *It is now around* 2300 *tonnes per annum.*

- Gold is the most malleable metal among all metals and it is soft enough to be cut with a knife. Stone age peoples hammered gold into plates for ornamental purposes. Today 1 g can be beaten into a square metre sheet and just 230 atoms thick one cubic centimeter would make a sheet of 18 m^2.

- The largest modern stock of gold is the 30,000 tonnes in the US Federal Reserve Bank in New York, which belongs to 18 different nations. It is estimated that all the world's gold gathered together would only make a cube around 18 metres per side i.e. about 6000 cm^3. And that's gold.

Silver

- The mining of silver began some 5000 yr ago. The name *silver* seems to stem from the Assyrian *serpu* or Gothic *silbur*. The latin *argentum* originates most likely from the Sanskrit arganta, which means *light* and *white*.

- Silver is a more active metal than gold but its abundance in Earth's crust is about fifteen times higher than gold. It occurs much less frequently in a native state. It is not surprising that in antiquity silver was valued higher that gold.

- In ancient Egypt, for instance, the ratio between the costs of these metals was 2.5 : 1. Gold was used mainly for coins and jewellery; silver had other uses: for example for making water vessels.

- In the 4th century, the army of Alexander the Great conquered Persia and Phoenicia, entered India. Here, the Greek army was struck by an outbreak of a mysterious gastrointestinal disease and the men demanded to be sent home.

- Interestingly, the Greek military commanders fell victim to the disease far less frequently than their men. More than two thousand years had passed before scientists found an explanation of it. The soldiers drank from tin cups and their superiors from silver ones.

- It was proved that silver dissolves in water forming a colloid solution that kills pathogenic bacteria. Although, the solubility of silver in water is low but that is quite enough for disinfection.

- Silver mines have been known from the ancient times. The largest deposits of silver were found in Greece, Spain and Germany. After the discovery of America silver deposits were also found in Peru and Mexico.

- Ancient people even figured out how to refine silver. They heated the silver arc and blew air over it, this process is called cupellation.

- Like gold, silver was used in coins but the cost of silver compared to that of gold was gradually decreases.

- Russian word *rubl* (rouble) and *kopeika* (kopeck) owe their origin to silver. Rouble came into being in Kievan Russia in the 13th century a silver bar weighing about 200 g. The word *kopeika* appeared later in 1534, when coins with an image of a horse man holding a speak were first minted.

- Silver forms in star explosions called supernovae, as does gold. A study published in September 2012 in the journal Astronomy and Astrophysics found that smaller stars that explode, produce silver, while larger stars produce gold.

- Silver played a big role in making early photography possible. Silver nitrate was used on photographic plates in the first, clunky cameras.

- Silver has been used to prevent the infection of injuries for hundreds of years. Silver does not kill microbes in its metallic form, which is unreactive. The metal works against bacteria in its ionic form. The metal must lose an electron to become positively charged. The positively charged silver ion interferes with bacterial cell walls and disrupts other microbial processes.

- Silver is stable in oxygen and water but tarnishes when exposed to sulphur compounds in air or water to form a black sulphide layer. That is why, silver is coated with transparent lacquers. Researchers are working to create nanometer-thick coatings that can replace the current hand-painted lacquers with something thinner, completely invisible and long lasting.

▣ JEE ADVANCED DRILL

[30 BEST INTEGER
TYPE PROBLEMS ON SOLUTIONS]

A collection of chapterwise best problems of their types

1. If the freezing point of a 0.01 molal aqueous solution of a cobalt (III) chloride-ammonia complex (which behaves as a strong electrolyte) is $-0.0558°$ C, the number of chloride(s) in the coordination sphere of the complex is [K_f of water $= 1.86$ K kg mol^{-1}] **[JEE adv. 2015]**

2. MX_2 dissociates into M^{2+} and X^- ions in an aqueous solution, with a degree of dissociation (α) of 0.5. The ratio of the observed depression of freezing point of the aqueous solution to the value of the depression of freezing point in the absence of ionic dissociation is **[JEE adv. 2014]**

3. 2.5 g of a monobasic acid when dissolved in 100 g of water, elevates the boiling point of the solution by 0.15°C. If 2.5g of acid requires 20.40 milliequivalents of NaOH for the complete neutralisation, then the degree of dissociation of acid is, $x - 1.564$, find the value of x. [K_b of water $= 0.512$K kg mol^{-1}]

4. If a substance when dissolved in 100g of water lowers the freezing point by 1.40°C and if same solute is dissolved in 100 g of benzene lowers the freezing point by 1.28°C. If the substance has normal molecular mass in benzene and is completely dissociated in water. Calculate into how many ions do it dissociate in water? (K_f for water and C_6H_6 are 1.86 and 5.12 K mol^{-1}kg, respectively)

5. 2.55 g of a non-electrolytic solute with empirical formula, $C_{10}H_{10}Fe$ was added to 112.2 g of benzene and a homogeneous solution was prepared. The boiling point of the solution was found to be 80.26°C. Find the ratio of molecular formula mass to empirical formula mass of non-electrolyte. (The boiling point and K_b values for benzene are 80.10°C and 2.53° K kg mol^{-1} respectively)

6. 23% of acetic acid is dissociated when 3.0×10^{-3} kg of acetic acid is added to 500 cm^3 of water. If the depression in freezing point is $x \times 10^{-1°}$ C, find the value of x. Given, K_f and density of water are 1.86 K kg mol^{-1} and 0.997 g cm^{-3}, respectively.

7. An organic compound ($C_xH_{2y}O_y$) was burnt with twice the amount of oxygen needed for complete combustion to CO_2 and H_2O. The hot gases when cooled to 0°C and 1 atm pressure, its volume becomes 2.24 L. The water collected during cooling weigh 0.9 g. The vapour pressure of pure water at 20°C is 17.5 mm Hg and is lowered by 0.104 mm when 50g of the organic compound is dissolved in 1000 g of water. Find the value of x.

8. Find the osmotic pressure (in atm), if 0.85% aqueous solution of $NaNO_3$ is approximately 90% dissociated at 27°C (Round off to the nearest integer).

9. The number of moles of benzene which can freeze out on addition of 7.32 g triphenyl methane to 1000 g of benzene at a temperature of 0.2°C less than the normal freezing point of benzene. ($K_f(C_6H_6) = 5.12$ K kg mol^{-1})

10. A $M/10$ solution of potassium ferrocyanide is 46% dissociated at 18°C. Calculate its osmotic pressure in atm.

11. 25.6 g of sulphur in 100 g benzene undergoes depression in freezing point of 5.12°C. If K_f (benzene) is 5.12°C kg mol^{-1} and molecular formula of sulphur in benzene is S_x then find the value of x.

12. K_a (ionisation constant) for tartaric acid is $x \times 10^{-3}$. If a 0.100 molal solution freezes at $-0.205°C$, find the value of x. Assume that only the first ionisation is important and 0.100 molal $= 0.100$ molar, $K_f = 1.86$ kg mol^{-1}K.

13. If the apparent degree of ionisation of KCl (Mol. mass $=74.5\,g\,mol^{-1}$) in water at 290 K is 0.86, calculate the mass of KCl which must be made upto $1dm^3$ (1L) of aqueous solution to have the same osmotic pressure as the 40% solution of glucose at that temperature ?

14. A 0.001 molal solution of $[Pt(NH_3)_4\,Cl_n]Cl_{4-n}$ in water had a freezing point depression of 0.0054°C. Assuming 100% ionisation of the complex. Find the value of n. [$K_f(H_2O) = 1.86\,kg\,mol^{-1}K$].

15. Air contains N_2 and O_2 in the ratio of 4 : 1. Calculate the ratio of solubilities in terms of mole fraction of N_2 and O_2 dissolved in water at atmospheric pressure and room temperature at which Henry's constants for N_2 and O_2 are 6.60×10^7 and 3.30×10^7 torr, respectively.

16. Calculate the osmotic pressure (in atm) of solution obtained by mixing 100 mL of 3.4% solution of urea (molecular mass $= 60$) and 100 mL of 1.6% solution of cane sugar (molecular mass $= 342$) at 20°C (Round off to the nearest integer).

17. 1.4 g of acetone dissolved in 100 g of benzene gave a solution which freezes at 277.12 K and pure benzene freezes at 278.4 K. 2.8 g of solid (A) dissolved in 100 g of benzene gave a solution which freezes at 277.76 K. If molecular mass of A is $n \times 58$, find the value of n.

18. 29.2% (w/w) HCl stock solution has a density of 1.25 gmL^{-1}. The molecular weight of HCl is $36.5\,gmol^{-1}$. Find the volume (mL) of stock solution required to prepare a 200 mL solution of 0.4 MHCl.

19. The vapour pressure of water at 293 K is 2338 Pa and the vapour pressure of an aqueous solution is 2295.8 Pa. If solution density is $1010\,kg\,m^{-3}$ at 313 K and osmotic pressure at 313 K is 2.53×10^x Pa. Find the value of x. (Molecular mass of solute $= 60$)

20. A mixture of two immiscible liquids, nitrobenzene and water, boils at 99°C. It has a partial vapour pressure of water 733 mm and that of nitrobenzene 27 mm. Calculate the ratio of the masses of nitrobenzene to the water in distillate.

21. The osmotic pressure of an aqueous solution of sucrose is 2.47 atm at 373 K and the molar volume of the water present in the solution is $18.10\,cm^3$. If elevation in boiling point of this solution is $(x \times 10^{-2})$ K find the value of x ($\Delta H_{vap} = 540\,cal\,g^{-1}$, assume volume of the solution equal to volume of solvent).

22. At 37°C and 0.80 atm partial pressure, the solubility of N_2 was found to be $5.6 \times 10^{-4}\,molL^{-1}$. A deep sea diver breathes compressed air with the partial pressure of N_2 equals to 4.0 atm. The total volume of blood in his body is 5.0 L. After sometime he comes back on the water surface where total pressure of N_2 is 0.80 atm. If volume of N_2 escaped during his return from depth to surface, at 37°C and 1 atm, is $(x - 1.715)$, find the value of x.

23. At 20°C, the osmotic pressure of a urea solution is found to be 400 mm. This solution is diluted and temperature is raised to 35°C, when the osmotic pressure is found to be 105.3 mm. How many times is this solution diluted?

24. An aqueous solution of glucose boils at 100.01°C. Molal elevation constant of water is 0.5 K molality^{-1}. If the number of molecules of glucose present in 100 g water are $x \times 10^{21}$, find the value of x.

25. Pure benzene boiled at 80°C. The boiling point of a solution containing 1g of substance dissolved in 83.4g of benzene is 80.175°C. If latent heat of vaporisation of benzene is 90 cal g^{-1} and molecular mass of solute is $\dfrac{569.16}{n}$, find the value of n.

26. If osmotic pressure of the aqueous solution of a given solute at 27°C is $(10.315 + x)$, find the value of x. (At 27°C, $\Delta T_f = 0.93$°C, $K_f = 1.86\,K\,mol^{-1}\,kg$, Assume molality as molarity).

27. 17.4% (m/V) K_2SO_4 solution at 27°C is isotonic to 5.85% (m/V) NaCl solution at 27°C. If NaCl is 100% ionised, and % ionisation of K_2SO_4 in aqueous solution is $(10 \times x)$%, find the value of x.

28. A decimolar solution of potassium ferrocyanide is 50% dissociated at 300 K. If osmotic pressure of the solution is 7.483×10^x, find the value of x.

$(R = 8.314\,JK^{-1}mol^{-1})$

29. 0.85% aqueous solution of $NaNO_3$ in 0.1 L volume is apparently 90% dissociated at 27°C. Calculate its osmotic pressure in atm to the nearest integer value.

30. 75.2g of C_6H_5OH is dissolved in 1 kg of solvent of $K_f = 14$ K molality^{-1}. If depression in freezing point is 7K and % of phenol that dimerises is $(15 \times x)$%, find the value of x.

Answers with Explanation

1. *(1)* **Strategy**

- *Number of chloride ions can be calculated by van't Hoff factor(i).*
- *As molality (m), molal depression constant (K_f) and depression in freezing point (ΔT_f) are given. van't Hoff factor (i) can be calculated by the following formula*

$$\Delta T_f = iK_f m$$

Given, ΔT_f = depression in freezing point = $0 - (-0.0558)$

$$= 0.0558°C$$

$$m = \text{molality} = 0.01$$

According to the formula,

$$\Delta T_f = K_f \times i \times m$$

$$\Rightarrow \qquad i = \frac{\Delta T_f}{K_f \times m}$$

$$= \frac{0.0558}{1.86 \times 0.01}, i = 3$$

$i = 3$, indicates that there are three ions in the given complex. Also, given complex behaves as a strong electrolyte, hence $\alpha = 100\%$

Finally, the complex becomes

$$\underset{\text{Coordination sphere}}{[\text{Co(NH}_3)_5\text{Cl}]} \qquad \underset{\text{Ionisation sphere}}{\text{Cl}_2}$$

Therefore, number of Cl^- ions in the coordination sphere of the complex = 1.

2. *(2)* **Strategy**

- *Degree of dissociation (α) is given and $\dfrac{(\Delta T_f)_{\text{observed}}}{(\Delta T_f)_{\text{calculated}}}$ is asked to find out.*

- $\dfrac{(\Delta T_f)_{\text{observed}}}{(\Delta T_f)_{\text{theoretical}}} = i$ *(van't Hoff factor)*

- *We can calculate i with the following formula*

$$i = 1 + \alpha(n-1)$$

n = number of dissociated ions

$$MX_2 \longrightarrow M^{2+} + 2X^-$$

$$i = 1 + \alpha(n-1)$$
$$i = 1 + \alpha(3-1) \qquad (\because n = 3)$$

or, $\qquad\qquad i = 1 + 2\alpha = 1 + 2(0.5) = 2$

$$\therefore \quad \frac{(\Delta T_f)_{\text{observed}}}{(\Delta T_f)_{\text{calculated}}} = 2$$

3. *(2)* **Strategy** *This problem can be solved by calculating the molecular mass of the acid from milliequivalents of NaOH. After finding molecular mass we can easily find the value of α*

For neutralisation,

Milliequivalents of HA = Milliequivalents of NaOH

$$\Rightarrow \qquad \frac{2.5}{E} \times 1000 = 20.40 \qquad (E = \text{Equivalent mass of H}A)$$

or $\qquad E = \dfrac{2500}{20.40} = 122.5\,\text{g mol}^{-1}$

Since, HA is a monobasic acid, therefore,

Equivalent mass (E) = Molecular mass (M) = 122.5 g mol^{-1}

$$HA \rightleftharpoons H^+ + A^-$$
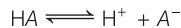
Before dissociation $\quad 1 \qquad\qquad 0 \qquad 0$
After dissociation $\quad 1-\alpha \qquad\qquad \alpha \qquad \alpha$

$$i = 1 + \alpha(n-1)$$
$$= 1 + \alpha(2-1)$$
$$= 1 + \alpha$$

Now, molality (m) is given as,

$$m = \frac{W_{\text{solute}} \times 1000}{M_{\text{solute}} \times W_{\text{solvent}}} = \frac{2.5 \times 1000}{122.5 \times 100} = 0.204\,\text{molal}$$

$$\Delta T_b = i \times K_b \times m \Rightarrow 0.15 = (1+\alpha) \times 0.512 \times 0.204$$

or $\qquad 1 + \alpha = 1.436$ or $\alpha = 0.436$

Now, $\qquad\qquad x - 1.564 = 0.436 \qquad\qquad$ [Given]

$\therefore \qquad\qquad\qquad x = 2$

4. *(3)* The given problem can be solved by going through the following steps:

Step 1 Apply the following formula separately for both cases, i.e. when mass of substance dissolves in C_6H_6 and H_2O

$$\Delta T_f = \frac{1000 \times K_f \times W_{\text{solute}}}{100 \times (M_{\text{solute}})_{\text{normal}}}$$

Case I For C_6H_6, $1.28 = \dfrac{1000 \times 5.12 \times W_{\text{solute}}}{100 \times (M_{\text{solute}})_{\text{normal}}} \qquad$ ...(i)

Case II For H_2O, $1.40 = \dfrac{1000 \times 1.86 \times W_{\text{solute}}}{100 \times (M_{\text{solute}})_{\text{abnormal}}} \qquad$ ...(ii)

Dividing Eq. (ii) by (i) we get,

$$\frac{(M_{\text{solute}})_{\text{normal}}}{(M_{\text{solute}})_{\text{abnormal}}} \approx 3.0$$

or $\qquad i = 3 \left[\dfrac{(M_{\text{solute}})_{\text{normal}}}{(M_{\text{solute}})_{\text{abnormal}}} = i \right]$

Let solute be A_xB_y.

$$A_xB_y \rightleftharpoons xA^+ + yB^-$$
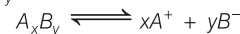
Before dissociation $\quad 1 \qquad\qquad 0 \qquad 0$
After dissociation $\quad 1-\alpha \qquad\qquad x\alpha \qquad y\alpha$

$$i = 1 - \alpha + x\alpha + y\alpha$$

$\therefore \qquad\qquad i = 3$ and $\alpha = 1$

From $\qquad\qquad i = 1 + \alpha(n-1)$

$$3 = 1 + 1(n-1)$$
$$3 - 1 = n - 1$$
$$2 = n - 1$$
$$n = 3$$

5. *(2)* Given, the elevation in boiling point,

$$\Delta T_b = (80.26 - 80.10) = 0.16°C$$
$$W_{\text{solute}} = 2.55\,\text{g}; W_{\text{solvent}} = 112.2\,\text{g}$$

Let the molecular mass of the solute be M_{solute}.

Now, from $\Delta T_b = i \times K_b \times m$

$$= i \times K_b \times \frac{W_{\text{solute}} \times 1000}{M_{\text{solute}} \times W_{\text{solvent}}}$$

[For non-electrolytic solute $i = 1$]

or $\qquad 0.16 = \dfrac{1 \times 2.53 \times 2.55 \times 1000}{M_{\text{solute}} \times 112.2}$

$\Rightarrow \qquad M_{\text{solute}} = 360\,\text{g mol}^{-1}$

Given, empirical formula of the solute = $C_{10}H_{10}Fe$

$\therefore$ Empirical formula mass = $12 \times 10 + 10 + 56$

$$= 186 \, g \, mol^{-1}$$

$\therefore \quad \dfrac{\text{Molecular mass}}{\text{Empirical formula mass}} = \dfrac{360}{186} \approx 2$

6. *(2)* **Strategy**

- *The formula for asked quantity is given as*

$$\Delta T_f = iK_f m$$

- *Find out i with the help of* α

- *Find out molality (m);* $m = \dfrac{\text{Moles of acetic acid}}{\text{Mass of water}} \times 1000$

  Where, moles of acetic acid

  $$= \dfrac{\text{Mass of acetic acid (in g)}}{\text{Molecular mass of acetic acid (g mol}^{-1})}$$

  and Mass of water = Volume × Density

- *Put the value of i, K_f and m in the formula mentioned in first step.*

Given,

Volume of water = $500 \, cm^3$

Density of water = $0.997 \, g/cm^3$

$\therefore$ Mass of water = $500 \times 0.997 = 498.5 \, g$

Now, Moles of acetic acid = $\dfrac{3 \times 10^{-3} \times 1000}{60} = 0.05$

and Molality = $\dfrac{0.05 \times 1000}{498.5} = 0.1003$

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$
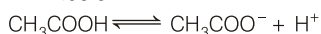
Initial moles	1	0	0
After dissociation	$1-\alpha$	α	α

$\therefore$ Total number of moles after dissociation

$$= 1 - \alpha + \alpha + \alpha = 1 + \alpha$$

van't Hoff factor, $i = \dfrac{\text{Moles after dissociation}}{\text{Initial moles}} = \dfrac{1 + \alpha}{1}$

$$\alpha = 23\% = 0.23$$

$\therefore \qquad\qquad i = 1 + 0.23 = 1.23$

$\therefore$ Depression in freezing point $(\Delta T_f) = iK_f m$

$$= 1.23 \times 1.86 \times 0.1003 = 0.229°C$$

$$= 2.29 \times 10^{-1}°C \simeq 2 \times 10^{-1}°C$$

$\therefore$ The value of x is 2.

7. *(2)* **Strategy**

- *Apply Raoult's law of lowering in vapour pressure*

$$\dfrac{p° - p_{total}}{p°} = \dfrac{n}{n + N}$$

  n = Number of moles of solute

  N = Number of moles of solvent

  p° = Partial pressure of volatile solvent

  p_{total} = Total vapour pressure of solution

- *Find molecular mass of organic compound.*

- *With the help of unitary method find out relation between x and y*

- *Compare the calculated molecular mass with observed molecular mass*

- *Find the value of x*

Given, $p° - p_{total} = 0.104 \, mm \, Hg$

$\qquad\qquad p° = 17.5 \, mm \, Hg$

$\therefore$ From Raoult's law,

$$\dfrac{0.104}{17.5} = \dfrac{n}{n + N} \quad \text{or} \quad \dfrac{N}{n} + 1 = 168.27$$

$$\Rightarrow \qquad\qquad \dfrac{N}{n} = 167.27$$

or $\qquad\qquad \dfrac{N}{n} = \dfrac{1000/18}{50/M} \Rightarrow M \simeq 150 \, g \, mol^{-1}$

$$(M = \text{Molecular mass of solute})$$

$$C_xH_{2y}O_y + (2x + y)O_2 \longrightarrow xCO_2 + yH_2O$$
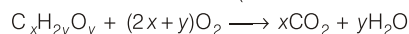
$\because 18y \, g$ of H_2O produced from 1.0 mole of compound

$\therefore 0.9 \, g$ of H_2O will be produced from $\dfrac{0.9}{18y} = \dfrac{1}{20y}$ mol of compound

At the end, moles of O_2 left $= \dfrac{(2x + y)}{20y}$

Moles of CO_2 formed $= \dfrac{x}{20y}$

$\Rightarrow$ Total moles of gases at STP $= \dfrac{2x + y}{20y} + \dfrac{x}{20y} = \dfrac{2.24}{22.4}$

or $\qquad\qquad \dfrac{3x + y}{20y} = \dfrac{2.24}{22.4}$

or $\qquad\qquad\qquad y = 3x$

Molar mass of organic compound; $150 = 12x + 2y + 16y$

or $\qquad 150 = 12x + 2(3x) + 16(3x)$

or $\qquad x = 2.27 \simeq 2$

8. *(5)* Given, $\qquad \alpha = 90\% = 0.90$

The dissociation of $NaNO_3$ takes place as,

$$NaNO_3 \rightleftharpoons Na^+ + NO_3^-$$
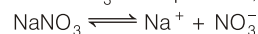
Initial moles	1	0	0
Final moles	$1-\alpha$	α	α

$$i = \dfrac{1 - \alpha + \alpha + \alpha}{1} = 1 + \alpha$$

$$i = 1 + 0.90 = 1.90$$

Concentration $(C) = \dfrac{0.85}{85} \times \dfrac{1000}{100} = 0.1$

Osmotic pressure, $\pi = iCST$

$$= 1.90 \times 0.1 \times 0.082 \times 300$$

$$= 4.674 \, atm \simeq 5 \, atm$$

9. *(3)* Molar mass of triphenylmethane

$$(C_6H_5)_3CH = 224 \, g \, mol^{-1}$$

Let the solution contains $x \, g$ of benzene (solvent)

$$\Delta T_f = iK_f m = iK_f \times \dfrac{W_{solute} \times 1000}{M_{solute} \times W_{solvent}}$$

$$0.2 = 5.12 \times \dfrac{7.32}{244} \times \dfrac{1000}{x}; \ (i = 1)$$

$$x = 768 \, g$$

Mass of C_6H_6 that freezed out = $1000 - 768 = 232 \, g$

$\because$ Mass of 1 mole of $C_6H_6 = 78 \, g$

$\therefore$ Number of moles of C_6H_6 freezed out $= \dfrac{232}{78} = 2.97 \simeq 3$.

17. *(4)* We know that, $\Delta T_f = K_f \times \dfrac{W_{solute} \times 1000}{M_{solute} \times W_{solvent}}$

Case I $(278.4 - 277.12)K = K_f \times \dfrac{1.4\,g \times 1000}{58\,gmol^{-1} \times 100\,g}$

$1.28 = K_f \times \dfrac{14}{58}$ ...(i)

Case II $(278.4 - 277.76)K = K_f \times \dfrac{2.8 \times 1000}{m(A) \times 100}$

$0.64 = K_f \dfrac{28}{m(A)}$ ...(ii)

Dividing Eq. (ii) by Eq. (i), we get,

$M(A) = 232$ or $n \times 58 = 232$ or $n = 4$

18. *(8)* Molarity (M_1) of stock concentrated solution can be calculated using following relation

$$M_1 = \frac{x \times d \times 10}{m_B} = \frac{29.2 \times 1.25 \times 10}{36.5} = 10$$

($x = w/w\%$, d = density, m_B = molecular weight of HCl)
Now, from dilution law,

$M_1 V_1(\text{concentrated}) = M_2 V_2$ (Diluted)

$10 \times V_1 = 0.4 \times 200$

$V_1 = 8\,mL$

19. *(6)* At 293 K, $\dfrac{p^\circ - p_T}{p_T} = \dfrac{n}{N} = \dfrac{n \times 18}{W}$

Using the given data, $\dfrac{2338 - 2295.8}{2295.8} = \dfrac{n \times 18}{W} \times \dfrac{1000}{1000}$

$\dfrac{n}{W} = \dfrac{42.2}{2295.8} \times \dfrac{1}{18}$ $\Rightarrow$ $W = 979.25 \times n$

∴ Mass of solution = $979.25n$ + Mass of solute

$= 979.25n + n \times 60 = 1039.25ng$

$= 1.0393n\,Kg$

∴ $V_{solution} = \dfrac{\text{Mass of solution}}{\text{density}} = \dfrac{1.0393n\,kg}{1010\,kgm^{-3}}$

Now, $pV = nRT$

$p \times \dfrac{1.0393n}{1010} = n \times 8.314 \times 313$ or $p = 2.53 \times 10^6 Pa$

∴ $x = 6$

20. *(4)* $p' = \chi_A p_T$

p' = Partial pressure of the component,
χ_A = Mole fraction of the component,
p_T = Total pressure of solution

For nitrobenzene, $27 = 760 \times \dfrac{\dfrac{W_2}{123}}{\dfrac{W_1}{18} + \dfrac{W_2}{123}}$ ...(i)

For water, $733 = 760 \times \dfrac{\dfrac{W_1}{18}}{\dfrac{W_1}{18} + \dfrac{W_2}{123}}$ ...(ii)

∴ Dividing Eq. (ii) by Eq. (i), we get

$$\frac{W_1}{W_2} = 4$$

21. *(5)* Osmotic pressure,

$\pi = CST$ ...(i)

C = Concentration of solution
S = Solution constant
T = Temperature in Kelvin

Given, $\pi = 2.47$ atm, $T = 373$ K
From Eq. (i), $2.47 = C \times 0.0821 \times 373$

or $C = 9.93 \times 10^{-2} M$

Thus, 1000 mL solution contains 9.93×10^{-2} moles

or $(9.93 \times 10^{-2} \times 342)$ g of sucrose.

∵ Volume of solution ≈ Volume of solvent

∴ Volume of solvent = 1000 mL

Moles of water = $\dfrac{1000}{18.10}$

or, Mass of water = $\dfrac{1000}{18.10} \times 18 = 994.475$ g

Therefore, molality of solution = $\dfrac{\text{Moles of solute}}{\text{Mass of solvent (in kg)}}$

$= \dfrac{9.93 \times 10^{-2}}{994.475 \times 10^{-3}} = 9.985 \times 10^{-2}$ mol Kg^{-1}

$\Delta T_b = K_b \times \text{molality} = \dfrac{RT_b^2}{1000\Delta H_{vap}} \times \text{molality}$

or $\Delta T_b = \dfrac{2 \times (373)^2}{1000 \times 540} \times 9.985 \times 10^{-2} = 5.145 \times 10^{-2} K$

22. *(2)* According to Henry's law, $\chi = K_H \cdot p$

(χ = Solubility, p = Total pressure of N$_2$)

or $5.6 \times 10^{-4} = K_H \times 0.80$

$K_H = 7.0 \times 10^{-4}$ molL^{-1}atm^{-1}

Let at 4 atm, solubility of N$_2$ in 5 L blood is S, then

$S = 7.0 \times 10^{-4} \times 4.0 \times 5 = 140.0 \times 10^{-4}$ mol/5L

At surface, when $p = 0.80$ atm solubility S' is

$S' = 7.0 \times 10^{-4} \times 0.80 \times 5 = 28 \times 10^{-4}$ mol/5L

Moles escaped = $S - S' = (140 - 28) \times 10^{-4}$

$= 0.0112$ mol/5L   (At 0.80 atm pressure)

Now from, $pV = nRT$

$V = \dfrac{nRT}{p} = \dfrac{0.0112 \times 0.0821 \times 310}{1} = 0.285$ L

or $x - 1.715 = 0.285$ or $x = 2$

23. *(4)* Given, initially $\pi = \dfrac{400}{760}$ atm,   T = 293 K

Now from, $\pi V = nST$

$\dfrac{400}{760} \times V_1 = n \times S \times 293$ ...(i)

After dilution, let volume becomes V_2 and temperature is raised to 35°C, i.e. 308 K, and osmotic pressure increases to $\pi' = \dfrac{105.3}{760}$ atm, then

$\dfrac{105.3}{760} \times V_2 = n \times S \times 308$ ...(ii)

Dividing Eq. (i) by Eq. (ii)

$\dfrac{V_1}{V_2} = \dfrac{293}{308} \times \dfrac{105.3}{400}$ or $V_2 = 4V_1$

Thus, solution is diluted to 4 times.

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24. *(1)* Since, $\Delta T_b = \dfrac{1000\,K_b' \times w}{m \times W} = \dfrac{1000\,K_b' \times n}{W}$

$$\left(n = \text{Number of moles of solute} = \dfrac{w}{m}\right).$$

Given, $\Delta T_b = 100.01 - 100 = 0.01, W = 100\,g$

$\qquad K_b' = 0.5\,K\,\text{molality}^{-1}$

$\therefore \qquad 0.01 = \dfrac{1000 \times 0.5 \times n}{100} \quad \Rightarrow \quad n = 2 \times 10^{-3}\,\text{mole}$

$\therefore$ Number of molecules in 2×10^{-3} mole of glucose.

$\qquad = 2 \times 10^{-3} \times 6.023 \times 10^{23} = 1.2 \times 10^{21}\,\text{molecules}$

$\qquad \simeq 1.0 \times 10^{21}\,\text{molecules}$

$\therefore \qquad\qquad\qquad x = 1$

25. *(3)* Boiling point of benzene $= (80 + 273)\,K = 353\,K$

Latent heat $(l_v) = 90\,\text{cal g}^{-1}$

$\qquad \Delta T_b = 80.175 - 80 = 0.175\,K,$

$\qquad w = 1g, W = 83.4g.$

$\qquad K_b' = \dfrac{RT^2}{100\,lv} \quad \text{or } K_b' = \dfrac{2 \times (353)^2}{1000 \times 90} = 2.769\,\text{mol}^{-1}\,kg$

$\qquad \Delta T_b = \dfrac{K_b' \times 1000 \times w}{mW}$

Using the given data,

$\qquad 0.175 = \dfrac{2.769 \times 1000 \times 1}{m \times 83.4} \quad \Rightarrow \quad m = 189.72\,\text{g mol}^{-1}$

Now, $\qquad \dfrac{569.16}{n} = 189.72 \quad \text{or} \quad n = 3$

26. *(2)* $\Delta T_f = K_f m$ (i)

and $\qquad\qquad \pi = \text{Molarity} \times R \times T \qquad\qquad\qquad …\text{(ii)}$

On dividing (i) by (ii)

or $\qquad\qquad\qquad \dfrac{\Delta T_f}{\pi} = \dfrac{K_f}{RT} \qquad\quad (\because \text{Molarity} = \text{Molality})$

$\qquad\qquad\qquad \dfrac{0.93}{\pi} = \dfrac{1.86}{0.0821 \times 300}$

or $\qquad\qquad\qquad \pi = 12.315\,\text{atm}$

or $\qquad\qquad 10.315 + x = 12.315$

or $\qquad\qquad\qquad x = 2$

27. *(5)* For dissociation of K_2SO_4

$$K_2SO_4 \rightleftharpoons 2K^+ + SO_4^{2-}$$
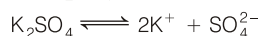
Initially	1	0	0
After dissociation	$1- \alpha$	2α	α

Now, $\pi_1 = iCST = (1 + 2\alpha)\dfrac{w}{mV}ST$

$\qquad = (1 + 2\alpha)\dfrac{17.4 \times 1000}{174 \times 100} \times ST$

Similarly, for dissociation of NaCl,

$$NaCl \rightleftharpoons Na^+ + Cl^-$$
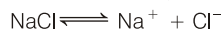
$\qquad\qquad\quad 1 \qquad\quad 0 \qquad\quad 0$

$\qquad\qquad (1 - \alpha_1) \quad\; \alpha_1 \qquad\; \alpha_1$

$\qquad \pi_2 = (1 + \alpha_1)\dfrac{5.85 \times 1000}{58.5 \times 100}ST$

$\qquad \pi_2 = ST \times 2 \qquad\qquad\qquad\qquad [\because \alpha_1 = 1]$

Given, $\pi_1 = \pi_2$ (isotonic solution)

$\therefore \; ST \times 2 = ST \times (1 + 2\alpha) \quad \text{or} \quad \alpha = 0.5 \text{ or } 50\% \text{ ionisation}$

or $\qquad (x \times 10)\% = 50\%$

$\qquad\qquad\qquad x = 5$
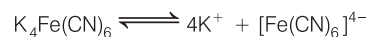
28. *(5)* Using the equation,

$$\pi \times V = nST \quad \text{or} \quad \pi = \dfrac{n}{V}ST$$

Given, molarity $= \dfrac{n}{V} = 0.1\,\text{mol L}^{-1}$

or molarity $= \dfrac{0.1}{10^{-3}}\,\text{mol m}^{-3} = 10^2\,\text{mol m}^{-3}$

$\therefore \qquad\qquad \pi = (10^2 \times 8.314 \times 300)\,\text{Nm}^{-2}$

Now,

$$K_4Fe(CN)_6 \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$$

Before dissociation	1	0	0
After dissociation	$1- \alpha$	4α	α

$\qquad \alpha = \text{degree of dissociation} = 0.5$

According to van't Hoff equation,

$\qquad (i) = \dfrac{\pi_{\text{experimental}}}{\pi_{\text{calculated}}} = 1 + 4\alpha$

$\therefore \; \pi_{\text{exp}} = \pi_{\text{cal}}\,(1 + 4\alpha) = 10^2 \times 8.314 \times 300 \times (1 + (4 \times 0.5))$

$\qquad = 7.483 \times 10^5$

i.e. $\; x = 5$

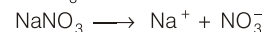**29.** *(5)* Using the equation, $\pi = \dfrac{n}{V}ST = \dfrac{w_{NaNO_3}}{M_{NaNO_3}} \times \dfrac{RT}{V}$

Given, $\; w_{NaNO_3} = 0.85\,g, M_{NaNO_3} = 85,$

$\qquad\qquad S = 0.0821\,L\,\text{atm K}^{-1}$

$\qquad\qquad T = 27°C = 300\,K, V = 0.1\,L$

$\qquad \pi_{\text{calc}} = \dfrac{0.85 \times 0.0821 \times 300}{85 \times 0.1} = 2.463\,\text{atm}$

But in solution, $NaNO_3$ ionises as

$$NaNO_3 \longrightarrow Na^+ + NO_3^-$$

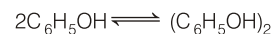|			
Initially	1	0	0
At equilibrium	$1- \alpha$	α	α

Thus, total moles $= 1 - \alpha + \alpha + \alpha = 1 + \alpha$

or $\qquad \dfrac{\pi_{\text{exp}}}{\pi_{\text{cal}}} = 1 + \alpha$

or $\qquad \pi_{\text{exp}} = 2.463 \times 1.9 = 4.67\,\text{atm} \qquad (\alpha = 90\%, \text{i.e. } 0.9)$

$\qquad\qquad \simeq 5\,\text{atm}$

30. *(5)* Phenol dimerises as follow

$$2C_6H_5OH \rightleftharpoons (C_6H_5OH)_2$$

Initially	1	0
After dissociation	$1- \alpha$	$\dfrac{\alpha}{2}$

$\qquad\qquad \Delta T_f = i\,K_f \times \text{Molality}$

Given $\qquad\qquad w = 75.2\,g, W = 1\,Kg, K_f = 14\,K\,\text{molality}^{-1}$

$\qquad\qquad \Delta T_f = 7\,K$

$\therefore \; 7 = \dfrac{14 \times 75.2}{94}\left(1 - \dfrac{\alpha}{2}\right) \quad \text{or} \quad \alpha = 0.75 \text{ i.e. } 75\%$

or $\qquad\qquad 15 \times x = 75\%$

$\qquad\qquad\qquad x = 5$

DO YOU KNOW?

- **Hybrid cars are much more energy efficient, environmental friendly and gives excellent mileage than non-hybrid cars.**
  - A vehicle is a hybrid if it utilises more than one form of onboard energy to achieve propulsion. In practice, a hybrid have a traditional internal combustion engine and a fuel tank, as well as one or more electric motors and a battery pack.
  - Hybrid cars are sometimes mistakenly confused with electric vehicles.
  - Hybrid cars have two propulsion systems : an electric motor and a gasoline engine. The energy to power such a car comes from gasoline. The electricity comes ultimately from its gasoline engine, which charges the battery that is used to run the electric motor. However, the gasoline engine in a hybrid car is smaller than that in a normal car and the gasoline engine switches off when the hybrid car is stopped at low speed. Therefore, fuel efficiency is high and hybrid cars get upto 60 mpg in city driving, twice as much as the gasoline mileage of non-hybrid, conventional cars overall, the hybrid car is much more energy efficient than a conventional car.
  - A number of hybrid cars, such as Toyota Prius, Honda Insight, Honda Civic, Ford Escape, etc; are examples of hybrid cars. When the Toyota Prius starts up, the electric motor is used, but when the car is accelerating and the demand for power is high, both the electric motor and the gasoline engine are used. At speeds of less than about 20 mph, the electric motor alone provides the propulsion, so hybrid cars get their best gasoline mileage in city traffic.
  - The Prius cruises using both propulsion systems, although some of the energy from the engine is used to charge the batteries using the motor generator. When going downhill, the Prius turns off the gasoline engine. Furthermore, when the brakes are applied, the motor generator converts some of the kinetic energy of the car into electricity, charging the batteries, and saving energy wasted in a conventional car.
  - The batteries that power the motor are nickel-metal hydride (NMH) batteries that are charged by the gasoline engine during normal driving or as the car goes downhill so the car never need to be plugged in to be recharged. Eventually, the batteries need to be replaced.
  - Because a hybrid car does not use the gasoline engine all the time, it produces much less exhaust, containing both polluting gases and carbon dioxide, than a conventional car. e.g. the Toyota Prius has such low tailpipe emissions that it qualifies the California Air Resources Board's stringent Super-Ultra Low Emission Vehicle class due to its environmentally friendly nature.
  - In addition of their excellent gas mileage, demand for hybrid cars is projected to rise as emission standards grow stricter.

- **Some hydrated metal ions also behave as weak acids.**
  - Some hydrated metal ions, especially those of the transition metals, are also weak acids. When a salt containing a metal ion dissolves in water, the metal ion becomes hydrated, often with six water molecules around it. $[M(H_2O)_6]^{n+}$, where M represents a metal ion, whose charge is $n+$. There are $M{-}O{-}H$ bonds in the hydrated ion, as shown by the structure in the margin. Metal ions other than those in Groups IA and 2A have large enough charges and small enough sizes to attract the shared electron pairs in the $M{-}O$ bond to themselves.
  - The weakens the $O{-}H$ bond, making the hydrogen in a $M{-}O{-}H$ bond more acidic than it would be in the $O{-}H$ bond of a water molecule that is not bonded to metal ion. Thus, the $[M(H_2O)_6]^{n+}$ ion can donate H^+, the solution becomes acidic and the positive charge of the remaining hydrated metal ion has been decreased by one.
  - The ionisation reaction and acid ionisation constant expression for a hydrated metal ion, such as Fe^{3+} can be written as

$$[Fe(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Fe(H_2O)_5OH]^{2+}(aq) + H_3O^+(aq)$$

$$K_a = \frac{[Fe(H_2O)_5OH]^{2+}\ [H_3O^+]}{[[Fe(H_2O)_6]^{3+}]} = 6.3 \times 10^{-3}$$

  - The K_a value shows that a solution of $FeCl_3$, will have about the same pH as a solution of phosphoric acid ($K_a = 7.5 \times 10^{-3}$) of equal concentration. Many metal ions form weakly acidic aqueous solutions, and this property is important in the chemistry of such ions in the environment. i.e. Al^{3+} ions in soils react with water to produce an acidic environment that can be detrimental to tree growth.

- **How are stones formed hanging from the ceilings of underground cave?**
  - Stalactites are natural stone formations hanging from the ceilings of underground caves. They are formed by the interaction of water and limestone (calcite), which is largely $CaCO_3$. The water is weakly acidic due to dissolved carbon dioxide and it dissolves $CaCO_3$. When the solution is exposed once again to the air, the CO_2 escapes and the solid calcite deposited. Over long time period, fantastic shapes of solid stone are formed.

- **When someone dives in water, the temperature of water becomes slightly higher.**
  - Potential and kinetic energy are interconverted when someone dives into water. These interconversions are governed by the law of conservation of energy. The diver has great gravitational potential energy on the diving board at the surface of the water, because the platform is higher above the earth, some of the potential energy has been converted into kinetic energy on the diver's altitude above the water, decreases and velocity increases, maximum kinetic energy occurs just prior to impact with the water. Upon impact, the diver works on the water, splashing it aside; eventually the initial potential energy difference is converted into motion on the nanoscale–the temperature of the water has become slightly higher.

CHEMISTRY @ SPECTRUM FOR YOU

In this section, we invite our readers to send their problems and we will try to provide the best possible solutions given by our expert panel.

[01] Dear Sir, I have solved many numericals related to entropy change with the help of formula, but I am really confused about qualitative aspect of entropy. Please explain. **[Deepak Kumar, Nainital]**

● Deepak, for simplicity you can understand entropy in terms of energy. Entropy is the dispersal of energy in a sample of matter. Hence, the matter with highly energised species, has more entropy than the matter with low energised species. You may follow the guidelines given below for more clarity:

The order of entropy for different states of matter is

Gas > Liquid > Solid

In a solid, the particles can vibrate only around their lattice positions. When a solid melts, its particles can move around more freely and molar entropy increases. When a liquid vaporises, the position of restrictions due to forces between the particles nearly disappear, and large increase in entropy occurs. e.g. the entropies (in $JK^{-1}mol^{-1}$) of the halogens $I_2(s)$, $Br_2(l)$ and $Cl_2(g)$ are 116.1, 152.2 and 223.1, respectively.

Entropies of more complex molecules are larger than those of simpler molecules Especially in a series of closely related compounds. In a more complicated molecule, there are more ways for the atoms to move in three dimensional space and hence, there is greater entropy. e.g. the entropies (in $JK^{-1}\ mol^{-1}$) of the gases: methane, ethane and propane are 186.26, 229.6 and 269.9 respectively. For atoms or molecules of similar molar mass, such as: Ar, CO_2 and $CH_3CH_2CH_3$ entropies (in $JK^{-1}\ mol^{-1}$) are 154.7, 213.74 and 269.9 respectively.

Entropies of ionic solids that have similar formulae are larger when the attractions among the ions are weaker The weaker such forces are, the easier for ions is to vibrate about their lattice positions and hence, the greater is the entropy. e.g. the entropy of NaF(s) is 51.5 JK^{-1} mol^{-1} and that of MgO(s) is 26.94 $JK^{-1}mol^{-1}$; Na^+ and F^- with unit positive and negative charges respectively attract each other less than Mg^{2+} and O^{2-}, each of which has two units of opposite charges, therefore, NaF(s) has higher entropy than MgO. NaF(s) and NaCl(s) have entropies (in $JK^{-1}mol^{-1}$) of 51.5 and 72.13. Chloride ions, Cl^-, are larger than fluoride ions, F^- and attractions are smaller when the ions are farther apart.

Entropy usually increases when a pure liquid or solid dissolves in a solvent Energy usually becomes more dispersed when different kind of molecules mix together and occupy a larger volume.

An example is $NH_4NO_3(s)$ and $NH_4NO_3(aq)$ with standard molar entropies of 151.08 $JK^{-1}mol^{-1}$ and 259.8 $JK^{-1}mol^{-1}$, respectively. Some ionic compounds that dissolve in water, are exceptions to this generalisation because the ions are strongly hydrated.

**Entropy decreases when a gas dissolves in a liquid**

Although gas molecules are dispersed among solvent molecules in a solution, the very large entropy of the gas phase is lost when the widely separated gas particles become crowded together with solvent particles in the liquid solution.

[02] Dear Sir, how does acidic strength of oxoacids vary ? **[Archana Gupta, Meerut]**

● Acids in which the acidic hydrogen is bonded directly to oxygen (H—O bond) are called oxoacids. Three of the strong acids: nitric acid (HNO_3), perchloric acid ($HClO_4$) and sulphuric acid (H_2SO_4) are oxoacids.

Nitric acid   Perchloric acid   Sulphuric acid
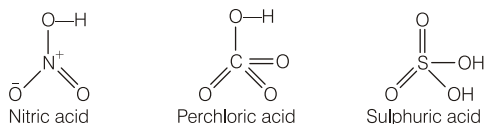
Like other oxoacids, they have at least one hydrogen atom bonded to an oxygen and have the general formula.
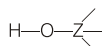
The nature of Z and other atoms that may be attached to it are important in determining the strength of the H—O bond and thus, the strength of an oxoacid. In general, acidic strength decreases with decreasing electronegativity of Z. This is reflected in the differences among the K_a values of HOCl, HOBr and HOI, as the electronegativity of the halogen decreases from chlorine (3.0) to bromine (2.8) to iodine (2.5).

Acid	HOCl	HOBr	HOI
K_a value	3.5×10^{-8}	2.5×10^{-11}	2.3×10^{-11}

The number of oxygen atoms attached to Z also significantly affects the strength of the H—O bond and oxoacid strength.

The acidic strength increases as the number of oxygen atoms attached to Z increases. The terminal oxygen atoms (those not in an H—O bond) are sufficiently electronegative, alongwith Z, to withdraw electron density from the H—O bond. This weakens the bond, promoting the transfer of an H^+ ion to water. The more terminal oxygen atoms present, the greater the electron density shift and the greater the acidic strength. A particularly striking example of this trend is seen with the oxoacids of chlorine from the weakest, hypochlorous acid (HOCl), to the strongest, perchloric acid ($HClO_4$).

Acid	HOCl	$HClO_2$	$HClO_3$	$HClO_4$
	Hypochlorous acid	Chlorous acid	Chloric acid	Perchloric acid
K_a value	3.5×10^{-8}	1.1×10^{-2}	$\simeq 10^3$	$\approx 10^8$

To be a strong acid, an inorganic oxoacid must have at least two more oxygen atoms than acidic hydrogen atoms in the molecule. Thus, sulphuric acid is a strong acid. In contrast the inorganic oxoacid phosphoric acid (H_3PO_4) has only four oxygen atoms for three hydrogen atoms and is a weak acid.

[03]

Dear Sir, what is the difference between equivalent mass and molecular mass and how can I calculate equivalent mass for various species?   [Neha Singh, Delhi]

● You put a very good question, Neha. many students solve different kind of problems related to equivalent mass with the help of formulae without knowing the exact difference between molecular mass and equivalent mass.

The concept of molecular mass express the amount of matter, i.e. sum of total masses of atomic entities present in a molecule. On the other hand, concept of equivalent mass gives the amounts of substances that react with each other. By definition, equivalent mass of a substance is the mass of it which reacts with 1.008 g of hydrogen, 8.0 g of oxygen or 35.5 g of chlorine. Generally, for numericals we use masses in grams. You can go through the following chart for calculation of equivalent mass for various species.
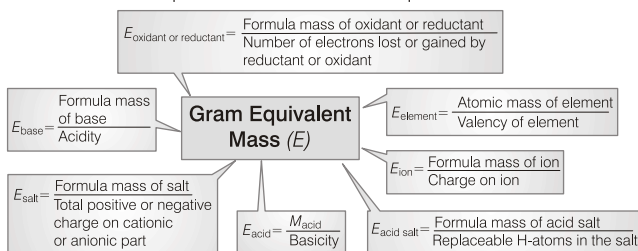

Note : Basicity is number of replaceable hydrogen atoms present in acid and Acidity is number of $\overline{O}H$ furnished by one mole of base.

[04]

Dear Sir, as book says, —COOH group has lower —R-effect than —CHO, how?   [Abhay, Pithoragarh]

● — COOH and — CHO groups both show —R-effect when these are attached to benzene ring. But there are two types of conjugation occured, in the case of —COOH group :

(i) Within —COOH group.

(ii) Within benzene ring due to electron withdrawing nature of —COOH group

These conjugations in case of — CHO and —COOH groups with benzene ring are given below:
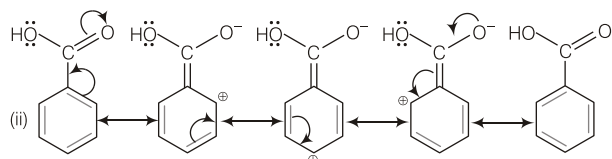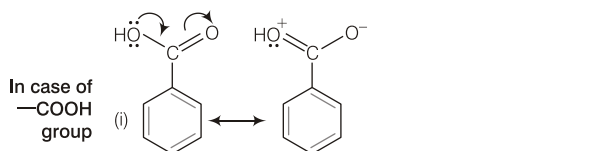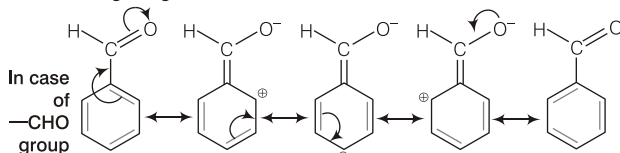
The conjugation within —COOH group decreases the extent of —R-effect within the aromatic ring. This type of conjugation, which decreases the extent of other conjugation, is known as cross conjugation.

Hence, due to cross conjugation —COOH group shows lower —R-effect than —CHO group.

[05]

Dear Sir, how do medicines control high blood pressure problems?   [Suraj Kumar, Lucknow]

● Suraj, many high blood pressure (hypertension) medications come under the heading of ACE inhibitors. ACE (Angiotensin converting enzyme) plays a key role in controlling blood pressure. It catalyses the activation of Angiotensin, a vasoconstrictive hormone, from its inactive zymogen, Angiotensinogen.

$$\text{Angiotensinogen} \xrightarrow{\text{ACE}} \text{Angiotensin}$$
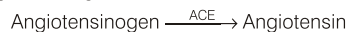
This process involves the cleaving of the last two amino acids from the carboxyl terminal of the decapeptide.

Asp —Arg — Val — Tyr — Ile — His — Pro — Phe — His — Leu. The octapeptide, Angiotensin, is a potent constrictor of the blood vessels and, therefore, increases blood pressure. When a competitive inhibitor occupies the active site of ACE, however, the hormone stays in its inactive zymogen state. As a consequence, blood pressure is lowered.

A large number of ACE inhibitors are currently in the market. Some are sulphur containing compounds, such as Captopril; others are non-sulphur containing compounds, such as Accupril and Altace.

The active site of the enzyme, ACE, contains several key chemical entities: arginyl, aspartyl residues and a Zn^{2+} ion.

Each of these interacts with the group on the inhibitor. The arginyl residue attracts the —COO^- group; the aspartyl amide attracts the — $C = O$ group, and the Zn^{2+} forms a salt with the negatively charged sulphide ion or —COO^- group. The key element is the proper separation of these functional groups on the inhibitor molecule.

☒ TOUCH UP

[COLLIGATIVE PROPERTIES]
FOR CLASS XII

Topicwise Collection of Best Subjective Problems
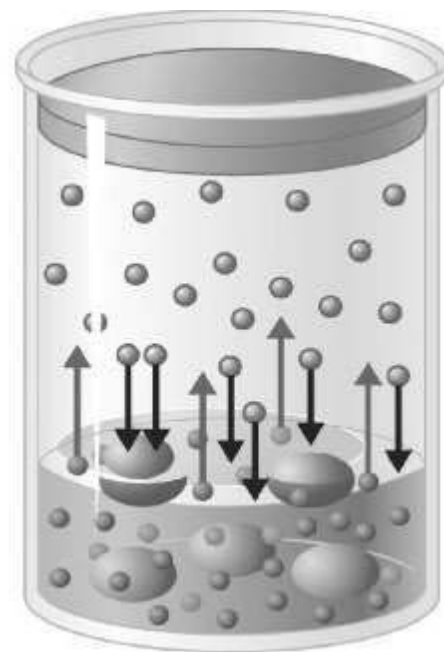
Very Short Answer Type [1 Mark]

1. What happen to the process of osmosis if pressure more than the osmotic pressure is applied on solution?

2. Why the molecular mass of benzoic acid yields abnormally higher value when determined by colligative properties?

3. State the condition for reverse osmosis.

4. What is the effect on boiling point when acetone is dissolved in water?

5. Why ordinary thermometer is not used when molecular weight of solute is determined by elevation in boiling point or depression in freezing point method?

6. Write the general equation of osmotic pressure for dilute solutions.

7. What is the value of van't Hoff factor for sodium phosphate?

8. Write any two factors which affect the colligative properties.

9. What is the relation between elevation in boiling point and molality of the solution?

10. Define van't Hoff factor.

Very Short Answer Type [2 Marks]

11. What is the advantage of using osmotic pressure instead of other colligative properties for the determination of molar masses of solute in solutions?

12. Why freezing point depression of 0.1 M sodium chloride is nearly twice to that of 0.1 M glucose solution?

13. Explain how the molecular mass of solute can be determined by a method based on measurement of osmotic pressure?

14. What do you mean by boiling point elevation constant for a solvent?

15. An aqueous solution freezes at $-0.186°$ C $(K_f = 1.86°C \text{ kgmol}^{-1}$ and $K_b = 0.512°$ C $\text{kgmol}^{-1})$. What is the elevation in boiling point?

Short Answer Type [3 Marks]

16. The vapour pressure of benzene at 30°C is 164.88 mm Hg. In 3 mol of benzene, when 6g of acetic acid was dissolved, the vapour pressure of the solution becomes 162.04 mm Hg. Calculate the degree of association of acetic acid in benzene at 30°C.

17. A 0.561 m solution of unknown electrolyte depresses the freezing point of water by 2.93°C. What is van't Hoff factor for this electrolyte? $[K_f$ for water $= 1.86°$ C kg mol^{-1}]

18. The vapour pressure of a solution containing 2 g of NaCl in 100 g water, which dissociated in one Na$^+$ and one Cl$^-$ ion in water is 751 mm at 100°C. Calculate the degree of ionisation of NaCl.

Long Answer Type [5 Marks]

19. At 300 K, 36 g of glucose present in a litre of its solution has an osmotic pressure of 4.98 bar. If the osmotic pressure of the solution is 1.52 bar at the same temperature, what would be its concentration?

20. The degree of dissociation of $Ca(NO_3)_2$ in a dilute aqueous solution containing 7g of the salt per 100 g of water at 100°C is 70 per cent. If the vapour pressure of water at 100°C is 760 mm, calculate the vapour pressure of the solution.

Solutions

1. A phenomenon opposite to osmosis, i.e. reverse osmosis takes place.

2. Benzoic acid yields abnormally higher value of molecular mass when determined by colligative properties because it dimerises in water due to intermolecular hydrogen bonding.

3. Pressure applied on the solution should be larger than osmotic pressure for reverse osmosis.

4. Acetone is a volatile liquid and form non-ideal solution with water hence, the boiling point of resulting solution increases.

5. Since, very small elevation in boiling point and depression in freezing point occur, hence, a thermometer having a least count of 0.001°C is required. Therefore, Beckmann thermometer which can read upto 0.001°C is used.

6. Osmotic pressure is proportional to the molarity (C) of the solution at a given temperature (T).
$$\pi \propto C, \ \pi = CST \ \text{or} \ \pi V = nST$$

7. van't Hoff factor is the number of ions produced.
$$Na_3PO_4 \longrightarrow 3Na^+ + PO_4^{3-}$$
So, van't Hoff factor $= 3 + 1 = 4$

8. Factors affecting colligative properties are
   (i) Fraction of solute and solvent particles in solution.
   (ii) Nature of solvent.

9. The elevation in boiling point is directly proportional to the molality of the solution, i.e. $\Delta T_b \propto m$ or $\Delta T_b = K_b m$

10. van't Hoff factor is defined as the ratio of the experimental value of the colligative property to the calculated value of the colligative property.
$$i = \frac{\text{Abnormal colligative property}}{\text{Normal colligative property}}$$
or
$$i = \frac{\text{Normal (calculated) molecular mass}}{\text{Abnormal (Observed) molecular mass}}$$

11. The osmotic pressure method has the advantage over other methods as
    (i) pressure measurement is done around at the room temperature and molarity of the solution is used instead of molality.
    (ii) Its magnitude is large even for very dilute solutions as compared to other colligative properties.

12. Colligative properties are directly proportional to the number of particles present in the solution.
    NaCl being a strong electrolyte, completely dissociates into its ions. One molecule of NaCl gives two ions on dissociation, but glucose being a non-electrolyte does not dissociate and hence present as a single molecule.

13. It can be determined by the relation between osmotic pressure and molar mass.
$$\pi V = n_2 SRT \ \text{or} \ \pi V = \frac{W_2 SRT}{M_2}, M_2 = \frac{W_2 SRT}{\pi V}$$
where, π = osmotic pressure, M_2 = molar mass of the solute

14. Boiling point elevation constant is equal to the elevation in boiling point when 1 mole of a solute is dissolved in 1kg of solvent. It is also called as ebullioscopic constant.
We know that, $\Delta T_b = K_b m$
When $m = 1$, then $\Delta T_b = K_b$, where, K_b = ebullioscopic constant

15. $\Delta T_f = K_f \times$ molality
$$\text{Molality} = \frac{0.186}{1.86} = 0.1 \ \text{mol kg}^{-1}$$
From, $\Delta T_b = K_b \times m = 0.512 \times 0.1 = 0.0512°C$

16. Using the relation for lowering in vapour pressure and considering the van't Hoff factor (i), we get
$$\frac{\Delta P}{P_A^\circ} = i\chi_B \Rightarrow \frac{164.88 - 162.04}{164.88} = i\left[\frac{0.1}{0.1 + 3}\right].$$
$$i = 0.533$$
Hence, acetic acid associates in benzene as
$$2(CH_3COOH) \rightleftharpoons (CH_3COOH)_2$$
$$1 - \alpha \qquad\qquad \alpha/2$$
$$\Rightarrow \quad i = 1 - \alpha/2 \Rightarrow \quad \alpha = 2(1 - 0.533) = 0.934$$

17. Given, $m = 0.561$ m, $\Delta T_f = 2.93°C$ and $K_f = 1.86°C$ kg mol^{-1}
$$\Delta T_f = iK_f m$$
$$i = \frac{\Delta T_f}{K_f m} = \frac{2.93°C}{1.86°C \ \text{kg mol}^{-1} \times 0.561 \ \text{m}} = 2.807$$

18. According to Raoult's law,
$$\therefore \quad \frac{p^\circ - p_s}{p_s} = \frac{w \times M}{m \times W} \Rightarrow \frac{760 - 751}{751} = \frac{2 \times 18}{m \times 100} \Rightarrow m_{\text{exp}} = 30.04 \ \text{g}$$
For the dissociation of NaCl,
$$NaCl \rightleftharpoons Na^+ + Cl^-$$
Initially $\qquad 1 \qquad\quad 0 \qquad 0$
At $t = 0 \quad 1 - \alpha \qquad \alpha \qquad \alpha$
$$\frac{m_N}{m_{\text{exp}}} = 1 + \alpha \quad \text{(i.e. total moles in solution)}$$
$$\frac{58.5}{30.04} = 1 + \alpha \Rightarrow \alpha = 0.9474 \ \text{or} \ 94.74\%$$

19. We know that,
$$\pi = CST = \frac{W_B \times S \times T}{M_B \times V}$$
For both solutions, S, T and V are constant.
For first solution.
$$4.98 \ \text{bar} = \frac{(36 \ \text{g}) \times S \times T}{(180 \ \text{g mol}^{-1}) \times V} \qquad\qquad \dots(i)$$
For second solution,
$$1.52 \ \text{bar} = \frac{W_B \times S \times T}{M_B \times V} \qquad\qquad \dots(ii)$$
On dividing Eq. (ii) by Eq. (i), we get,
$$\frac{1.52 \ \text{bar}}{4.98 \ \text{bar}} = \frac{W_B \times R \times T}{M_B \times V} \times \frac{180 \times V}{36 \times R \times T}$$
$$\frac{W_B}{M_B} = \frac{1.52}{4.98 \times 5} = 0.0610 \ \text{mol L}^{-1}$$

20. $$\underset{1-x}{Ca(NO_3)_2} \longrightarrow \underset{x}{Ca^{2+}} + \underset{2x}{2NO_3^-}$$
van't Hoff factor, $i = \frac{1 - x + x + 2x}{1} = \frac{1 + 2x}{1} = 1 + 2 \times 0.7 = 2.4$
Now, $i = \frac{\text{Observed lowering of vapour pressure}}{\text{Normal lowering of vapour pressure}}$
Observed lowering of vapour pressure
$$= i \times \text{normal lowering of vapour pressure}$$
$$p^\circ - p_{\text{obs}} = i \times \left\{\frac{n}{n + N} \cdot p^\circ\right\}$$
$$760 - p_{\text{obs}} = 2.4 \times \frac{\frac{7}{164}}{\frac{7}{164} + \frac{100}{18}} \times 760 = 13.90$$
[Molar mass : $Ca(NO_3)_2 = 164 \ \text{g mol}^{-1}$, $H_2O = 18 \ \text{g mol}^{-1}$]
$$p_{\text{obs}} = 760 - 13.90 = 746.10 \ \text{mm}$$

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TOUCH UP

BOHR'S MODEL

FOR CLASS XI

Topicwise Collection of best subjective problems

Very Short Answer Type [1 Mark]

1. Why hydrogen gas kept in a flask at room temperature does not emit radiations?

2. What does the negative sign mean for energy of an electron in hydrogen atom?

3. Write down the formulae for calculating the ionisation enthalpy (from $n=1$ to $n=\infty$) of hydrogen and H-like species.

4. Which spectral lines are associated with IR region in H-spectrum?

5. Write the expression for angular momentum of an electron in a given stationary state.

6. Which spectral line of H-atom is sensitive to human eye?

7. Which series of line spectrum is obtained when electrons fall from higher energy level to second energy level?

8. Why the atoms show spectra only when they are heated or given energy in some other form?

9. Why Bohr's orbit is known as energy level?

10. Write the equation for the frequency (ν) associated with the absorption or emission of the photon also write in terms of wave number ($\bar{\nu}$).

Short Answer type (2 Marks)

11. Write down the expression for the velocity of electron in the nth orbit for H-like species.

12. What do you understand by 'ground state' and 'excited state'? What is the value of energy of electron in a hydrogen atom in the ground state?

13. Write the expression for Bohr's frequency.

14. Calculate the radius of Bohr's third orbit for hydrogen atom.

15. Calculate the energy of a He$^+$ ion in its first excited state.

Short Answer Type (3 Marks)

16. Calculate the frequency of the spectral line emitted when the electron in $n=3$ in H-atom de-excites to ground state. [Given, $R_H =109677 cm^{-1}$]

17. What is the ratio of differences between 2nd and 3rd Bohr's orbit energy to that of between 3rd and 4th orbit energy?

18. Find the value of n corresponding to the excited state of He$^+$ ion, if on transition to the ground state the ion emits photons in succession with wavelength of 108.5 nm and 30.4 nm.

Long Answer Type (5 Marks)

19. Determine the frequency of revolution of an electron in the second Bohr's orbit of hydrogen atom.

20. For H-atom, the Bohr's radius for first orbit is 0.529 Å and the radius of maximum probability according to wave mechanical model is also 0.529 Å. How do the two approaches differ?

Solutions

1. This is because almost all the atoms are in the ground state and there are no energy levels of lower energy to which an electron can jump. Hence, the atoms cannot emit any radiations.

2. The negative sign means that the energy of electron in the atom is lower than the energy of a free electron at rest.

3. For hydrogen, $E_n = -\dfrac{2.18 \times 10^{-18}}{n^2}$ J atom^{-1}

   For H-like species, $E_n = -\dfrac{2.18 \times 10^{-18} Z^2}{n^2}$ J atom^{-1}

4. Paschen, Brackett, Pfund and Humphery series are associated with IR region in H-spectrum.

5. The angular momentum of an electron in a given stationary state can be expressed as $m_e vr = \dfrac{n \cdot h}{2\pi}$, where $n = 1, 2, 3, \ldots$

6. Balmer series is sensitive to human eye.

7. The series of line spectrum obtained is Balmer series.

8. When energy is given in the form of heat or by some other means, some of the electrons jump to the higher energy levels, i.e. $n = 2$, $n = 3$, etc. These electrons then come back to lower energy levels. and the atom radiates energy in this process.

9. The orbits are named according to the energy levels or electrons present in it. Hence, orbits (shells) are called energy levels.

10. The frequency (ν) associated with the absorption or emission of the photon is $\nu = \dfrac{\Delta E}{h} = \dfrac{R_H}{h}\left[\dfrac{1}{n_i^2} - \dfrac{1}{n_f^2}\right] = 3.29 \times 10^{15}\left[\dfrac{1}{n_i^2} - \dfrac{1}{n_f^2}\right]$

    In terms of wave number ($\bar{\nu}$)

    $\bar{\nu} = \dfrac{\nu}{c} = \dfrac{R_H}{hc}\left[\dfrac{1}{n_i^2} - \dfrac{1}{n_f^2}\right] = 1.09677 \times 10^7\left[\dfrac{1}{n_i^2} - \dfrac{1}{n_f^2}\right]$ m^{-1}

11. The velocity of electron in nth orbit can be calculated as

    $v_n = \dfrac{2\pi k Z e^2}{nh} = \dfrac{Z e^2}{2\varepsilon_0 nh} = \left(\dfrac{c}{137}\right) \cdot \dfrac{Z}{n} = 2.2 \times 10^6 \dfrac{Z}{n}$ m/s

    where, c (speed of light) $= 3 \times 10^8$ m/s

12. The state of an electron in the atom with the lowest energy is called its ground state while the states with higher energy than ground state are called excited states. The energy of a hydrogen atom in the ground state is -13.6 eV.

13. The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by ΔE is given by, $\nu = \dfrac{\Delta E}{h} = \dfrac{E_2 - E_1}{h}$ where, E_1 and E_2 are the energies of lower and higher allowed energy states, respectively. This expression is called Bohr's frequency.

14. Since, Bohr radius is given by $r_n = n^2 (0.529 \text{ Å})$
    $\therefore$ Radius for third orbit ($n = 3$), $r_3 = (3)^2 (0.529 \text{ Å}) = 4.761 \text{Å}$

15. The energy is $E_n = -\dfrac{R_H hc\, Z^2}{n^2} = -\dfrac{(13.6 \text{ eV}) Z^2}{n^2}$

    For a He$^+$ ion, $Z = 2$ and for the first excited state, $n = 2$ so that the energy of He$^+$ ion in the first excited state is -13.6 eV.

16. Using Rydberg's equation,

    $\dfrac{1}{\lambda} = R_H\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]$, $\dfrac{c}{\lambda} = \nu = R_H \cdot c\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]$

    Given, $R_H = 109677$ cm^{-1}, $c = 3 \times 10^{10}$ cm/s, $n_1 = 1$; $n_2 = 3$

    $\nu = 109677 \times 3 \times 10^{10}\left[\dfrac{1}{1^2} - \dfrac{1}{3^2}\right] = 2.92 \times 10^{15} \text{s}^{-1}$

17. As, $E_n = -1312\, n^2$ kJ/mol

    $\Delta E_{3\text{-}2} = -1312\left[\left(\dfrac{1}{n_2^2}\right) - \left(\dfrac{1}{n_1^2}\right)\right] = -1312\left[\left(\dfrac{1}{9}\right) - \left(\dfrac{1}{4}\right)\right] = -\dfrac{1312 \times (-5)}{36}$

18. Given, $\lambda_1 = 30.4 \times 10^{-7}$ cm, $\lambda_2 = 108.5 \times 10^{-7}$ cm
    Let the excited state of He$^+$ be n_2

    For first transition, $\dfrac{1}{\lambda_1} = R_H Z^2\left(\dfrac{1}{1^2} - \dfrac{1}{n_2^2}\right)$

    $\therefore \quad \dfrac{1}{30.4 \times 10^{-7}} = 109677 \times 2^2\left[\dfrac{1}{1^2} - \dfrac{1}{n_1^2}\right]$

    $\therefore \qquad\qquad n_1 = 2$
    Now, for λ_2, $n_1 = 2$, $n_1 = ?$

    $\therefore \quad \dfrac{1}{108.5 \times 10^{-7}} = 109677 \times 2^2\left[\dfrac{1}{2^2} - \dfrac{1}{n_2^2}\right]$

    $\therefore \qquad\qquad n_2 = 5$

    Hence, the excited state of He$^+$ is fifth orbit.

19. The frequency of revolution of an electron is

    Frequency $(\nu) = \dfrac{1}{\text{Time period } (T)}$

    Time period $(T) = \dfrac{\text{Total distance covered in one revolution}}{\text{Velocity } (v)} = \dfrac{2\pi r}{v}$

    $\therefore$ Frequency $(\nu) = \dfrac{v}{2\pi r}$

    $\because$ Radius of the electron, $r_n = 0.529\dfrac{n^2}{Z}$ Å

    ($Z = 1$ for H-atom)

    $\therefore$ Radius of the electron in the second Bohr's orbit of H-atom will be

    $r_2 = 0.529 \times 10^{-10}\dfrac{(2)^2}{1}$ m $= 2.116 \times 10^{-10}$ m

   Velocity of the electron,

    $v_n = 2.18 \times 10^6\left(\dfrac{1}{n}\right)$ ms^{-1}, $v_2 = 2.18 \times 10^6\left(\dfrac{1}{2}\right) = 1.09 \times 10^6$ ms^{-1}

    $\therefore$ Frequency $(\nu) = \dfrac{v_2}{2\pi r_2} = \dfrac{1.09 \times 10^6}{2\pi \times (2.116 \times 10^{-10})}$

    $\nu = 8.20 \times 10^{14}$ Hz

    Similarly, $\Delta E_{4\text{-}3} = -1312\left(\dfrac{1}{16} - \dfrac{1}{9}\right) = -\dfrac{1312 \times (-7)}{16 \times 9}$

    Ratio of their difference $\dfrac{\Delta E_{3\text{-}2}}{\Delta E_{4\text{-}3}} = \dfrac{1312 \times 5}{36} \times \dfrac{16 \times 9}{1312 \times 7}$

    $\therefore \qquad\qquad \dfrac{\Delta E_{3\text{-}2}}{\Delta E_{4\text{-}3}} = \dfrac{20}{7}$

20. Bohr found that the electron will always moving around the nucleus in a circular path of radius 0.529 Å. He also suggested that electron cannot be found at distance less than or more than 0.529 Å. However, wave mechanical model suggests that electron is likely to be found at this distance but there is definite radius shorter and larger than 0.529 Å.
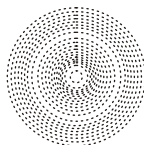
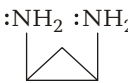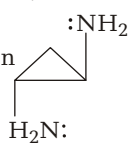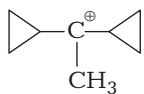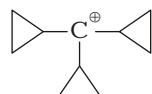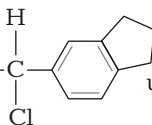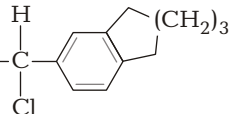The electron cloud picture of 1s orbital having radius of maximum probability (0.529 Å)
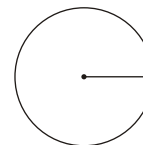
The Bohr picture of orbital in which electron is found only at this distance. i.e. Bohr radius 0.529 Å

In other words, according to wave mechanical model, the electron keeps moving towards or away from the nucleus and the maximum probability of locating it is at radius of 0.529 Å from the nucleus.

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QUIZZER (NO. 20)

1. When the Baeyer process is used for recovering aluminium from ores, some aluminium is always lost because of the formation of an unworkable mud having the following average formula: $3Na_2O \cdot 3Al_2O_3 \cdot 5SiO_2 \cdot 5H_2O$. Since, the aluminium and sodium ions are always in excess in the solution from which this precipitate if formed, the precipitation of silicon in the mud is complete. A certain ore contains 13% (by mass) Kaolin $(Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O)$ and 87% Gibbsite $(Al_2O_3 \cdot 3H_2O)$. What per cent of the aluminium in this ore is recoverable in the Baeyer process?

(a) 10%   *(b)* 90%   *(c)* 15%   *(d)* 85%

2. Helium can be excited to higher energy state by absorption of 58.44 nm wavelength. The lowest excited singlet state, with the configuration $1s^1 2s^1$, lies below the $1s^1 2p^1$ state with 4875 cm^{-1} wavelength. What would be the average He—H bond energy have to be in order that HeH_2 could form non-endothermically from He and H_2? Assume that the compound would form the lowest excited singlet state of helium for any difference between ΔE and $\Delta H [\Delta H_f = 218.0$ kJ mol$^{-1}]$.

(a) 990 kJmol^{-1} *(b)* 880 kJmol^{-1}
(c) 790 kJmol^{-1} *(d)* 1215 kJmol^{-1}

3. Two students use same stock solution of $ZnSO_4$ and a solution of $CuSO_4$. The emf of one cell is 0.03V higher than that of other. The concentration of $CuSO_4$ in the cell with higher emf value is 0.5M. Find out the concentration of $CuSO_4$ in the other cell. $\left(\dfrac{2.303RT}{F} = 0.06 \right)$

(a) 0.01 M   *(b)* 0.03 M   *(c)* 0.02 M   *(d)* 0.05 M

4. At 20°C and total pressure of 760 torr, 1L of water dissolves 0.043 g pure oxygen or 0.019 g of pure nitrogen. Assuming that dry air is composed of 20% oxygen and 80% nitrogen (by volume), determine the masses of oxygen and nitrogen dissolved by 1L of water at 20°C exposed to air at a total pressure of 760 torr.

(a) 0.0086 g L^{-1} and 0.015 g L^{-1}
(b) 0.015 g L^{-1} and 0.0086 g L^{-1}
(c) 0.0025 g L^{-1} and 0.015 g L^{-1}
(d) 0.0025 g L^{-1} and 0.008 g L^{-1}

5. A lead bullet weighing 18.0 g travelling with 500 m/s is embedded in a wooden block weighing 1.00 kg. If both the block and the bullet were initially at 25.0°C, what is the final temperature of the block containing the bullet? Assume no heat loss to the surrounding.

(Heat capacity of wood = 0.500 kcal kg^{-1}K^{-1},

Heat capacity of lead = 0.030 kcal kg^{-1}K^{-1}).

(a) 62.2°C   *(b)* 26.1°C   *(c)* 72.3°C   *(d)* 50.3°C

6. Consider the following statements,

I. is more basic than

II. is more stable than

III. undergoes hydrolysis more easily than

Choose the correct option regarding correct statements.

(a) II and III   *(b)* Only I
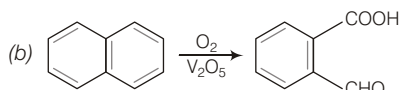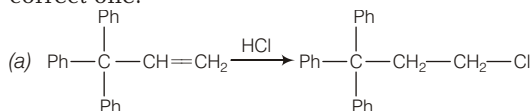*(c)* Only III   *(d)* I and III

📷 QUIZZER

7. Identify the product D in the following reaction sequence.

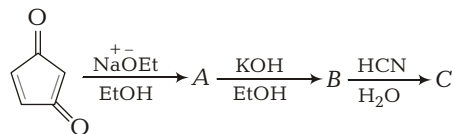$$CH_3CH_2CH{=}O \xrightarrow[H_3O^+]{SeO_2/HCOOH} A \xrightarrow{NaOH} B$$
$$\xrightarrow{Heat} C + D$$
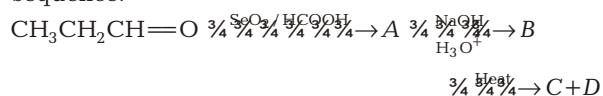
(a) cis-lactide
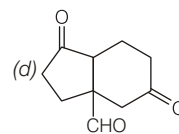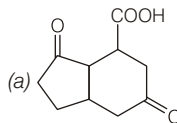(b) trans-lactide
(c) Either cis or trans - lactide
(d) lactic acid

8. Consider the following reactions and choose the correct one.

9. Consider the following reaction sequence,

$$\xrightarrow[EtOH]{NaOEt} A \xrightarrow[EtOH]{KOH} B \xrightarrow[H_2O]{HCN} C$$
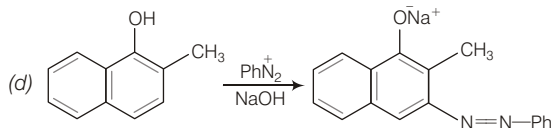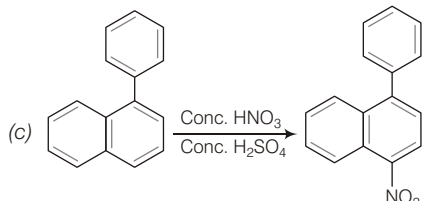
Identify the compound C.
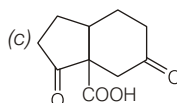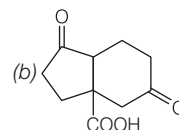
10. 0.5g sample containing MnO_2 is treated with HCl, liberates Cl_2. The Cl_2 passed into a solution of KI and 30.0 cm^3 of 0.1M $Na_2S_2O_3$ to titrate the liberated iodine. Calculate the percentage of MnO_2 in sample. (Atomic weight of Mn = 55 u)
(a) 26.1
(b) 30.9
(c) 20.2
(d) 40.3

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Quizzer (No. 20)

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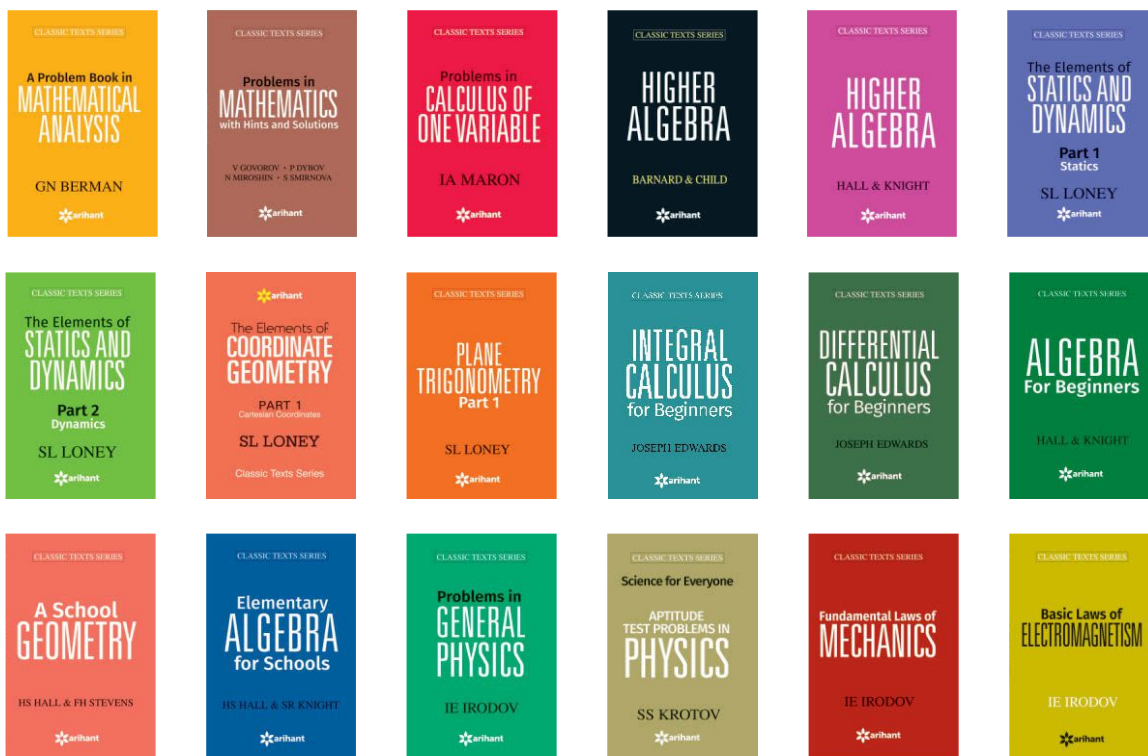
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