

**Training of KRPs to Strengthen Numerical Problem solving Skills
in Chemistry at Senior Secondary School Level**

PAC 16.32

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**एन सी ई आर टी
NCERT**

Final Report

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Pedagogical Module for Solving Numerical Problems on the Mole concept and Tetremetric work

Problem: A drop of rain is held on the surface of a leaflet. This drop occupies 0.15 mL of volume. If the density of droplet water is 1g mL^{-1} , then how many water molecules are present in this drop of water?

Pedagogy Related to the Problem:

Re-reading the problem conveys the idea that the purpose of giving volume of the drop and density of droplet water, is to target mass of the drop of water. It is further implicit that once the mass of drop is ascertained it would be possible to calculate the number of moles of water present in the water by applying the relation:

$$n\text{H}_2\text{O} = \frac{\text{Mass of waterdrops}}{\text{Molar Mass of water}}$$

Where $n\text{H}_2\text{O}$ denotes moles of water present in drop of water. Lastly the number of water molecules can be worked out by multiplying the number of moles with the quantity 6.022×10^{23} , Avogadro's number. Let us now present the solution of the problem in various steps along with relevant calculations.

Solution:

Step 1: To calculate Mass of Water droplet

As we know the relation: Mass = volume x density

Therefore this mass would be = $0.15 \times 1 = 0.15\text{g}$

Step 2: To calculate numbers of moles of water present in 0.15g water.

$$n\text{H}_2\text{O} = \frac{0.15}{18} = \frac{15 \times 10^{-2}}{18} = 0.01\text{mol}$$

Where $n\text{H}_2\text{O}$ is numbers of moles of water

Step 3: To calculate numbers of small water molecules present in the drop

\therefore , Number of water molecules

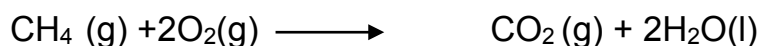
$$= 0.01 \times 6.022 \times 10^{23}$$

$$= 6.022 \times 10^{21}$$

Re-look into the accompanying problem suggests that this conveys a very relevant idea about central philosophy regarding mole concept which a correlation between. Macroscopic quantity (a drop) and Microscopic quantity, the huge numbers of water molecules, which is 6.022×10^{21} .

Practicing similar type of problems:

Problem 1: Consider the reaction:



If a cylinder containing methane weight 16 kg, then how many moles of O_2 and what numbers of oxygen molecules are needed for combustion of entire mass of methane contained in the cylinder.

[**Ans:** 2×10^3 moles of methane and 1.2044×10^{23} molecules of O_2]

Problem 2: If a drop of HCl issuing from the top of a burette occupies 0.1 mL of volume, further if the molarity of HCl is 0.1M, then how many H^+ ions issue from the drop? Assume HCl to fully ionize

(**Ans:** 6.022×10^{18})

Hint: To calculate numbers of moles of HCl present in the drop use the formulae

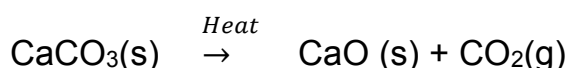
$$n_{\text{HCl}} = \frac{\text{Volume in (mL)} \times \text{Molarity}}{10^3}$$

Where, n_{HCl} , denotes moles of HCl present in the drop.

Problem: 10g of limestone (CaCO_3) is ignited carbon dioxide evolved in this ignition process occupies 1.12 litre of volume at STP. What is percentage of purity of this sample of limestone. (Given that the molar mass of $\text{CaCO}_3 = 100 \text{g mol}^{-1}$)

Pedagogy related to problem:

While dealing with the problem of mole concept many a times, the balanced equations involved becomes the guiding factors so here to effect appropriate calculations, one needs to produce balanced chemical equations, which is:



Re-reading of the problem in a meticulous way reflects that volume of the gas at STP is given to ascertain the number of moles of carbon dioxide using the relations that each mole of the gas at STP occupies a volume of the value of 22.4 litre. After this one may also apply the relationship $pV = nRT$ to calculate number of moles of the gas needed. Now a careful glance at the equation reflects 1:1 correspondence between moles of CO_2 produced and the moles of CaCO_3 ignited.

Having ascertained the moles of CaCO_3 present in the limestone, we calculate the actual amount of CaCO_3 present in the sample of limestone and finally the percentage purity of the sample. Let us now affect the calculations in a stepwise manner.

Step 1: To produce a balanced chemical reactions for the ignition of CaCO_3 ,



Step 2: To ascertain moles of CO₂ evolved

$$n_{CO_2(\text{evolved})} = \frac{1.12}{22.4} = \frac{1}{20} = 0.05 \text{ mol}$$

Step 3: To ascertain moles of CaCO₃ present in sample of limestone

As the correlations between the two quantities as per balanced equations is 1:1 therefore, moles of CaCO₃ present in limestone is also = 0.05 mL.

Step 4: To ascertain mass of CaCO₃ in the sample of limestone

$$\begin{aligned} \text{This would be} &= 0.05 \times \text{molar Mass of CaCO}_3 \\ &= 5 \times 10^{-2} \times 100 = 5 \text{ g} \end{aligned}$$

Step 5: To ascertain percentage purity of limestone sample.

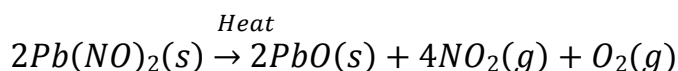
$$\text{This would be: } \frac{\text{Mass of CaCO}_3 \text{ actually present in sample}}{\text{Total mass of limestone taken}} \times 100$$

$$\text{and here it would be: } \frac{5}{10} \times 100 = 50\%$$

Relook into the entire process suggest that in these type of numerical problems, one has to keep focus on the target through appropriately using the given data and the chemical equations involved. Here it was the above said equations and the relations that each mole of a gas at STP only occupies a volume of the order of 22.4 litre.

Practising similar problem:

Problem 3: Lead nitrate decomposes according to the below listed manners:



If 6.64g of a sample of lead nitrate on heating produces 3.36g of residue of lead oxide then what is the percentage purity of the sample?

Ans: 75%

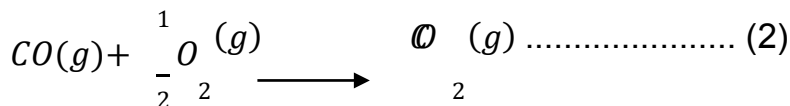
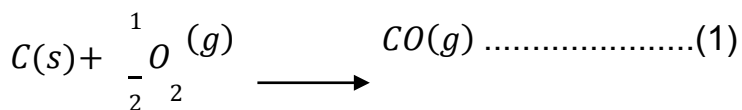
Problem: 12g of a sample of carbon is allowed to react with 24g of oxygen. Ascertain the ratio of carbon monoxide and carbon dioxide formed in this process.

Pedagogy related to problem:

Reading and re-reading of the problem incidentally brings into lime-light one very important aspect that whereas a reaction is carried out between one reducing agent and one oxidising agent then lower and higher oxidation state compounds come into the picture if the oxidising agent is as per need of the reaction. Here to convert 12g carbon directly into carbon dioxide we need one mole of oxygen as per the reaction:



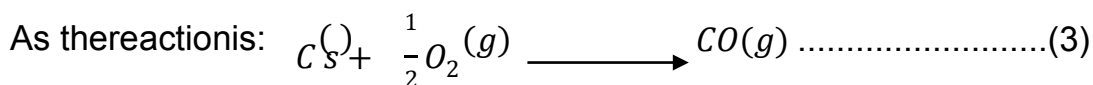
Since we do not have that much quantity of O₂, this incidentally brings into focus the following reactions:



Further in this problem another very important idea finds a mention, which is the idea of limiting reagent. How does it find a mention, it would be easy to understand, when solution to the problem is presented. At this stage, the idea of limiting reagent may be strengthened by taking the example of LPG in the kitchen. Here how much energy for cooking we get this is limited by LPG and not the oxygen of the air, which is always present in excess. So it can be safely said that a limiting reagent in the reaction is one that limits the use of amount of reacting substance as the amount of products produced.

Solution1:

Step 1: To ascertain the number of moles of CO formed and that of O₂ consumed



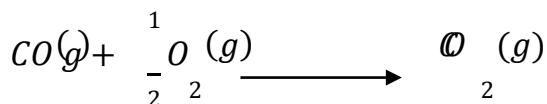
This suggests that to consume 1 mol of carbon which is, 12g of carbon, we need only half mole of O₂. Thus carbon here is the limiting reagent and oxygen present is in excess. Thus, moles of O₂ given is $\frac{24}{32} = 0.75$

Now as per the said equation marked (3), here from 0.75 mol of O₂, 0.50 is consumed to cause the reactions marked (3) here, it is, therefore, evident that moles of O₂ left out *unconsumed* = 0.75 – 0.50 = 0.25

Needless to say that moles of carbon monoxide formed is 1 mol

number. Step 2: To ascertain the number moles of carbon dioxide

formed We again consider the reactions marked (2) here, which is:



Analysis of the situation conveys to us that we have one mole CO and 0.25 moles of O₂. So this time if we have to fully consume one mole of CO, we need 0.50 mole of O₂ and we have only 0.25 mole of O₂. So O₂ is the limiting reagent this time. Since a careful glance on the equation of formations of CO₂, conveys to us that number of moles of CO consumed by O₂ is double its moles and same is the picture of moles of CO₂ formed. So it is simply clear that:

Moles of CO reacted = 2x0.25 = 0.5mol

Moles of CO_2 formed = $2 \times 0.25 = 0.5 \text{ mol}$

Step 3: To ascertain the moles of CO left out which is not converted into CO_2

This evidently would be $1.0 - 0.5 = 0.5 \text{ mol}$.

Step 4: To appropriately express the ratio of moles of CO and CO_2

Since CO left out is 0.5 mol and CO_2 formed is 0.5 mol

Therefore the ratio of CO: CO_2

= 0.5: 0.5

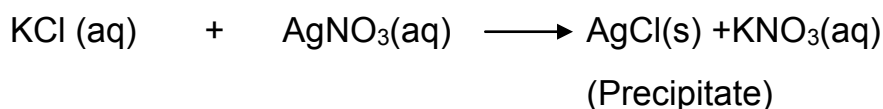
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Relook into the entire process and practising similar problems:

Here at each step relook is automatically done, so no need of further relook.

Practising similar problems:

Problem 4: Consider the reactions



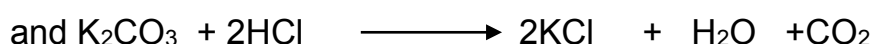
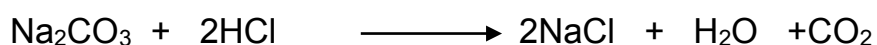
Given that the molar mass of KCl is 74.5 g mol^{-1} and that of AgNO_3 is 170 g mol^{-1} what shall be the mass of AgCl precipitate if to 1g (aq) KCl solution is mixed with 1g Aq. solution of AgNO_3 , When molar mass of AgCl is 143.5 g mol^{-1} . Which reacting substance is the limiting reagent?

(Ans: 0.844g, AgNO_3 is the limiting reagent)

Problem: 1.20g sample of Na_2CO_3 and K_2CO_3 was dissolved in water to form 100 mL of solutions. 20 mL of this solutions required 40 mL of 0.1M HCl for complete digestions of the solutions. Calculate the percentage of Na_2CO_3 is themixture.

Pedagogy Related the Problem:

Re-reading of the problem brings into picture that we have been given number of moles of HCl consumed. If we individually ascertain the moles of HCl consumed each by Na_2CO_3 and K_2CO_3 and summate this, it will be equal to the total number of moles of HCl consumed. From pedagogical point of view sometimes we refer to affect the solution, we should have one variable and one equation. How this would be possible it would be clear in various steps of the solution to this problem. Further the entire calculations work would centre on the following two chemical reactions.



These two equations suggest that HCl consumed in terms of number of moles would be twice the numbers of moles of individually present for Na_2CO_3 and K_2CO_3 .

Now if we suppose amount of Na_2CO_3 present in the mixture is xg . Then it is evident that K_2CO_3 amount would be $(1.20 - x) g$. Thus individual number of moles of two components would be:

$$n_{\text{Na}_2\text{CO}_3} = \frac{x}{106}$$

$$\text{and } n_{\text{K}_2\text{CO}_3} = \frac{(1.20-x)}{138}$$

As has been said earlier, the total number of moles of HCl consumed by the mixture would be $\frac{2x}{106} + \frac{2(1.20-x)}{138}$

Solution:

Step 1: To ascertain, the total numbers of moles of HCl consumed

As 20mL of the solutions requires 40 mL of HCl, therefore, the entire 100 mL of the solution would need, $5 \times 40 = 200\text{mL}$ of HCl.

$$\text{Thus } n_{\text{HCl consumed}} = \frac{200 \times 0.1}{10^3} = \frac{20}{10^3} = \frac{2}{10^2} = 0.02$$

Step 2: To Ascertain the individual moles of each component, i.e., Na_2CO_3 and K_2CO_3 .

Here if we assume $\text{Na}_2\text{CO}_3 = xg$ then $\text{K}_2\text{CO}_3 = (1.20 - x)g$ and their moles present are $\frac{x}{106}$ and $\frac{(1.20-x)}{138}$ respectively for Na_2CO_3 and K_2CO_3 .

Step 3: To ascertain the number of moles of HCl consumed collectively by these components

As said in the pedagogy part of this problem, it would be $\frac{2x}{106} + \frac{2(1.20-x)}{138}$

Step 4: To actually ascertain the value of x

Here we take advantage of the fact that one variable and one equations, therefore,

$$\text{here it is: } \frac{2x}{106} + \frac{2(1.2-x)}{138} = 0.02$$

This gives the value of $x = 0.569g$

Step 5: To calculate % of Na_2CO_3

$$\% \text{ of } \text{Na}_2\text{CO}_3 = \frac{0.569 \times 100}{1.2} = \frac{56.9}{1.2} = 47.42\%$$

Relook into the entire process and practising similar problems:

The relook of the process, conveys a working strategy of tackling numerical problems, which is that sometimes we come across with the situations, that if we

have variable component, we need one equation to solve and if we have two variable components we may need two equations to solve. These two variables situations we will come across on the module under head'solutions'.

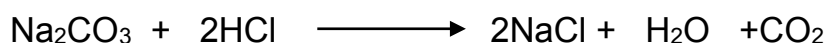
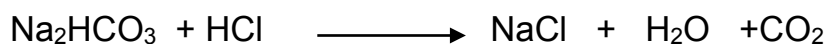
Practising similar problem:

1.90 g of an equimolar mixture of NaHCO_3 and Na_2CO_3 is digested in 0.1M HCl what volume of HCl is needed to digest the mixture fully.

(Ans: 300 mL)

Hint: Let volume of HCl consumed be $x \text{ mL}$ then, its moles will be equal to $\frac{x \times 0.1}{10^3}$
 $x \times 10^{-4}$.

From equimolar point of view, we can ascertain the actual moles of each component and with the aid of following two equations, we can target the number of moles of HCl needed and equate to $x \times 10^{-4}$, thereupon, calculate the value of x . The two said equations would be:



Atomic Structure

1. Sample problem:

A photon of wavelength $4 \times 10^{-7} \text{m}$ strikes on metal surface, the work function of the metal being 2.13 eV. calculate.

- i. The energy of photon(eV)
- ii. The kinetic energy of the emission
- iii. The velocity of the photoelectron

1. Read and re-read the problem:

Re-read the problem with a reasoning about the photoelectric effect, frequency, wavelength and energy of electromagnetic radiation.

2. Correlate the problem with the related theory:

Photoelectric effect:

When radiation with certain minimum frequency (ν_0) strike the surface of a metal, the electrons are ejected from the surface of the metal. This phenomenon is called photo-electric effect. The three important facts observed are:

- i. If the frequency of the radiation is less than ν_0 , no electrons are ejected. The value ν_0 is called Threshold Frequency. The minimum energy required to eject the electron ($h\nu_0$) is called work function(W_0).
- ii. The velocity and hence the kinetic energy of the electron ejected depends upon the frequency of the incident radiation and is independent of its intensity.
- iii. The no. of photoelectrons ejected is proportional to the intensity of incident radiation.

What happens is when light of some particular frequency falls on the surface of metal, the photon gives its entire energy to the electron which will be dislodged only if this energy is sufficient to overcome the force of attraction of the electron by the nucleus. This certain minimum frequency is called threshold frequency ν_0 .

If the frequency of the incident light (ν) is more than ν_0 , the excess energy ($h\nu - h\nu_0$) is imparted to the electron. Hence, greater is the frequency of the incident light, greater is the kinetic energy of the emitted electron.

$$\frac{1}{2}mv^2 = h\nu - h\nu_0$$

$$\text{or } h\nu = h\nu_0 + \frac{1}{2}mv^2$$

$$= w_0 + \frac{1}{2}mv^2$$

Increasing the intensity of light of a given frequency increases the number of photons but does not increase the energy of photons.

3. Break down the given numerical problems in relevant steps:

a) What is given?

λ and therefore Energy in J

$$E = hv = \frac{hc}{\lambda}$$

Work function $W_0 = hv_0$.

What is expected?

Energy in eV?

Kinetic energy, $\frac{1}{2}mv^2$ in eV

Velocity in ms^{-1} ?

Steps to be followed:

- i) Since wave-length is given, energy of photon hv can be calculated.
- ii) The energy calculated will be in J, convert it into eV ($1eV = 1.602 \times 10^{-19}J$)
- iii) Work function ($h\nu_0$) is given, hence K.E. can be calculated as $\frac{1}{2}mv^2 = hv - hv_0$.
- iv) From K.E., velocity of the photoelectron can be found.

4. Apply relevant formulae and making precise calculations:

$$\text{Energy of the photon, } E = hv = \frac{hc}{\lambda}$$

$$= \frac{(6.62 \times 10^{-34} \text{ J s}) \times (3 \times 10^8 \text{ ms}^{-1})}{4 \times 10^{-7} \text{ m}}$$

$$= 4.97 \times 10^{-19} \text{ J}$$

$$= \frac{4.97 \times 10^{-19}}{1.602 \times 10^{-19}} \text{ eV} = 3.10 \text{ eV}$$

$$\text{Kinetic energy of emission, } \frac{1}{2}mv^2 = hv - hv_0$$

$$= 3.10 - 2.13$$

$$= 0.97 \text{ eV}$$

Velocity of the photoelectron

$$\frac{1}{2}mv^2 = 0.97 \text{ eV} = 0.97 \times 1.602 \times 10^{-19} \text{ J}$$

$$\text{or } \frac{1}{2} \times (9.11 \times 10^{-31} \text{ kg}) \times v^2 = 0.97 \times 1.602 \times 10^{-19} \text{ J}$$

$$\text{or } v^2 = 0.341 \times 10^{12}$$

$$\text{or } v = 5.84 \times 10^5 \text{ ms}^{-1}$$

5. Relook:

- i) Check all the relations and equations.
- ii) Are the units used correct?
- iii) Are the values of Planck's constant, velocity of light etc. taken correct?

6. Practice:

i) Calculate the kinetic energy of the electron ejected when yellow light of frequency $5.2 \times 10^{14} \text{ sec}^{-1}$ falls on the surface of potassium metal. Threshold frequency of potassium is $5 \times 10^{14} \text{ sec}^{-1}$.

[Ans. $1.325 \times 10^{-20} \text{ joules}$]

ii) The threshold energy for photoelectric emission of electrons from a metal is $3.056 \times 10^{-15} \text{ joule}$. If light of 4000 \AA wavelength is used, will the electrons be ejected or not? Justify.

[Ans: No]

II. Sampleproblem:

What is the energy in joules required to shift the electron of the hydrogen atom from the first Bohr orbit to the fifth Bohr orbit and what is the wavelength of the light emitted when the electron returns to the ground state? The ground state electron energy is -2.18×10^{-11} ergs.

1. Read and re-read the problem:

Bohr's Model for Hydrogen Atom and Line spectrum of Hydrogen.

2. Correlate the problem with the relevant theory:

According to Bohr's model, the energy associated with the electron is given by:

$$E_n = -R_H \left[\frac{1}{n^2} \right] \text{ where } n = 1, 2, 3 \text{ [(i)]}$$

Where R_H is called Rydberg constant having value 2.18×10^{-18} g.

Energy is absorbed if the electron moved from the orbit of smaller Principal quantum number to the orbit of higher Principal quantum number. The energy gap between the two orbits is given by the equation.

$$\Delta E = E_f - E_i \text{ [(ii)]}$$

Combining equations (i) & (ii)

$$\Delta E = \left[-\frac{R_h}{n_f^2} \right] - \left[-\frac{R_h}{n_i^2} \right] \text{ [Where } n_i, n_f \text{ stand for the initial orbit and final orbits]}$$

$$\Delta E = R_h \left[\frac{1}{n_i^2} \right] - \left[\frac{1}{n_f^2} \right]$$

In case of absorption, $n_f > n_i$, ΔE positive and in case of emission spectrum, $n_i > n_f$, and ΔE is negative.

3. Break down the given numerical problems in relevant steps:

a) What is given?

n_i

n_f

Ground state electron energy

What you are asked to find out?

$\Delta E?$

$\lambda?$

4. Apply relevant formulae and making precise calculations:

$$\Delta E = R_H \left[\frac{1}{n_i^2} \right] - \left[\frac{1}{n_f^2} \right]$$

$$\begin{aligned}
&= 2.18 \times 10^{-18} \left[\frac{1}{1^2} \right] - \left[\frac{1}{5^2} \right] \\
&= 2.18 \times 10^{-18} \times \frac{24}{25} \\
&= 2.18 \times 10^{-18} J
\end{aligned}$$

When electron returns to ground state (i.e. $n=1$), energy emitted is 2.09×10^{-11} ergs.

$$\text{As } E = h\nu = \frac{hc}{\lambda} = \frac{(6.62 \times 10^{-27} \text{ erg sec})(3 \times 10^{10} \text{ cm s}^{-1})}{\lambda}$$

$$\text{or } \lambda = \frac{(6.62 \times 10^{-27} \text{ erg sec})(3 \times 10^{10} \text{ cm sec}^{-1})}{2.09 \times 10^{-11} \text{ ergs}}$$

$$= 9.51 \times 10^{-6} \text{ cm} = 951 \text{ \AA}$$

5. Relook:

- i) Check all the formula and relations.
- ii) Check the units used.

6. Practice:

i) Calculate two wave number for the longest wavelength transition in the Balmer series of atomic hydrogen.

[Ans. $1.523 \times 10^6 \text{ m}^{-1}$]

ii) Calculate the wavelength of the radiations emitted when an electron in a hydrogen atom undergoes a transition from 4th Energy level to the 2nd energy level. In which part of the electromagnetic spectrum does this line lie?

[Ans: 486.3 nm, visible region]

III. Sample problem:

A tennis ball of mass 6.0×10^{-2} kg is moving with a speed of 62 ms^{-1} . Calculate the wavelength associated with this moving tennis ball. Will the movement of this ball exhibit a wave character?

1. Read and re-read the problem:

2. Correlate the problem with the related theory:

de Broglie proposed that matter, like radiation, should also exhibit dual behaviour, i.e., both particle and wave-like properties. He gave the following relation between wavelength (λ) and momentum (p) of a material particle.

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

Where m is the mass of the particle, v its velocity and p its momentum.

3. Break down the given numerical problems in relevant steps:

a) What is given?

mass

velocity

h is known

What you are asked to find out?

λ ?

4. Apply relevant formula and making precise calculations:

$$\lambda = \frac{h}{mv} = \frac{6.6 \times 10^{-34}}{6.0 \times 10^{-2} \times 62}$$

$$= 1.77 \times 10^{-34} \text{ m}$$

Since the wavelength is too small to be observed, hence we do not observe any wave character.

5. Relook:

Check the formula and the units.

6. Practice:

i) Two particles A and B are in motion. If the wavelength associated with particle A is 5×10^{-8} m, calculate the wavelength associated with particle B if its momentum is half of A.

[Ans. 10^{-7} m]

IV. Sample problem:

A golf ball has a mass of 40g and a speed of 45 m/s. If the speed can be measured within accuracy of 2%, calculate the uncertainty in position.

1. Read and re-read the problem visualizing Heisenberg's uncertainty Principle:

2. Correlate the problem with the theoretical concepts:

Heisenberg's uncertainty Principle states that it is impossible to determine simultaneously, exact position and exact momentum (or velocity) of an electron.

Mathematically,

$$\Delta\lambda \times \Delta p \geq \frac{h}{4\pi}$$

$$\text{or } \Delta\lambda \times \Delta(mv_x) \geq \frac{h}{4\pi}$$

$$\text{or } \Delta\lambda \times \Delta v_x \geq \frac{h}{4\pi M}$$

3. Break down the given numerical problems in relevant steps:

a) What is given?

Δv

mass m

h is constant

What is required?

$\Delta\lambda$?

4. Apply relevant formula and making precise calculations:

Uncertainty in speed, $\Delta v_x = 2\%$ of 45 m s^{-1}

$$\text{or } \Delta v = \frac{2}{100} \times 45 = 0.49 \text{ m s}^{-1}$$

Applying uncertainty principle

$$\begin{aligned} \Delta\lambda &= \frac{h}{4\pi m \Delta v} \\ &= \frac{6.62 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{4 \times 3.14 \times (40 \times 10^{-3} \text{ kg})(0.9 \text{ m s}^{-1})} \end{aligned}$$

$$= 1.46 \times 10^{-33} \text{ m}$$

5. Relook:

- i) Check the formula and give values
- ii) Check the units used
- iii) Revise the calculations.

6. Practice:

i) Calculate the minimum uncertainty in Velocity of a particle of mass 1.1×10^{-27} kg if uncertainty in its position is 3×10^{-10} cm ($\hbar = 6.6 \times 10^{-34}$ kg m²S⁻¹).

[Ans. 1.59×10^4 m s⁻¹]

ii) Calculate the uncertainty in the Velocity of an electron if the uncertainty in its position is 1 \AA .

[Ans. 5.77×10^5 m s⁻¹]

Solid State

I. Sample Problem:

An element A crystallises in FCC structure. 200g of this element has 4.12×10^{24} atoms. The density of A is 7.2 g cm^{-3} . Calculate the edge length of the unit cell.

1. Read and re-read the problem:

Recalling different types of unit cells and close packing.

2. Correlate the problem with the related theoretical concepts:

A face centred cubic (FCC) unit cell contains atoms at all the corners and at the centre of all the faces of the cube. Here, the total no. of atoms per unit cell is 4.

In case of cubic crystal:

Volume of a unit cell $= a^3$

Mass of the unit cell = No. of atoms in unit cell \times mass of each atom
 $= z \times m$

Mass of an atom present in the unit cell

$$m = \frac{M}{N_A} \text{ (where } M \text{ is the molar mass)}$$

Therefore, density of the unit cell:

$$= \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

$$= \frac{Zm}{a^3} = \frac{ZM}{a^3 N_A}$$

$$\text{or } d = \frac{ZM}{a^3 N_A}$$

Out of the five parameters (d , z , M , a and N_A) if any four are known, we can determine the fifth.

3. Break down the given numerical problems in relevant steps:

a) What is given?

fcc arrangement

no. of atoms per unit cell = 4

density

Mass of each atom

What are required to find out?

a ?

4. Apply relevant formula and make precise calculations:

Let length of each edge = a cm.

Volume of unit cell = $a^3 \text{ cm}^3$

$$\text{Mass of each atom} = \frac{200}{48.12 \times 10^{24}}$$

$$= 48.54 \times 10^{-24}$$

No. of atoms per unit cell = 4

Mass of unit cell = $4 \times 48.54 \times 10^{-24}$

$$= 1.94.16 \times 10^{-24} \text{g}$$

$$\text{Now, density} = \frac{\text{Mass}}{\text{Volume}}$$

$$\text{or } 7.2 = \frac{194.16 \times 10^{-24}}{a^3}$$

$$\text{or } a^3 = \frac{194.16 \times 10^{-24}}{7.2}$$

$$= 26.97 \times 10^{-24} \text{Cm}^3$$

$$\text{or } a = 2.999 \times 10^{-8} \text{ Cm}$$

$$= 299.9 \text{ pm}$$

5. Relook:

Check the formula and calculation part

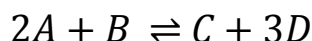
6. Practice:

i) An element having bcc geometry has atomic mass 50. Calculate the density of the unit cell, if its edge length is 290pm

[Ans. 6. 81g Cm^{-3}]

Pedagogical Module for Solving Numerical Problems on Equilibrium

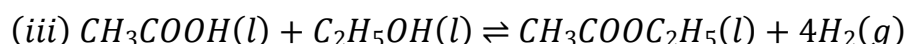
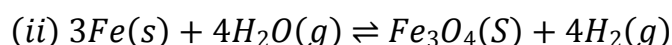
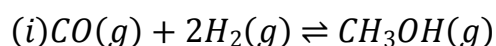
Problem: 1 Consider the reaction



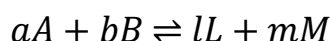
The reaction is carried out in a closed vessel of capacity one litre by taking 4 moles of each of the reactants A and B. At a certain temperature when the equilibrium is established, only one mole of C is formed. Calculate the value of equilibrium constant.

Pedagogy related with the problem:

It would be worthwhile here to consider the pedagogy associated with equilibrium "as a concept". Precisely equilibrium is a stage that we encounter in reversible changes of the type given below:



The Sign \rightleftharpoons is symbolic of the reversibility of the changes listed here. Here it is also said that equilibrium is always recognised by the constancy in macroscopic properties of the system, whereas microscopic properties do change at the equilibrium. This means that the properties that we are able to observe and which are bulk properties in nature become constant at the equilibrium but still changes continue to occur at the atomic or molecular level. This continuous change at the atomic or molecular level in fact is the representation of dynamic nature of equilibrium. As concentration of various species involved in the equilibrium stage is also a microscopic property, this reflects that at equilibrium, concentration of various species involved in the change are held constant. Now for the general reactions of the type



Where [A], [B], [C] and [M] are the concentrations of species A, B, L and M (here A, B are reactants and L, M are products) and a, b, l and m are their number of moles participating in the reaction, the equilibrium position in terms of equilibrium constant K_c is follows:

$$K_c = \frac{[L]^l \times [M]^m \dots \dots \dots}{[A]^a \times [B]^b} \quad (i)$$

Where these all the concentrations of species A, B, L and M are constant at equilibrium.

Kc here simply is notation of equilibrium constant in terms of concentration of the species. Needless to say that if equilibrium concentration of A, B, L and M are constant then the value of Kc too would constant and this would change with change in temperature through the equation.

$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \dots \dots \dots (2)$$

Wherein, K₂ is equilibrium constant value at temperature T₂ Kelvin and K₁ is the equilibrium constant value at temperature T₁ Kelvin. Further R is a universal gas constant and ΔH is the enthalpy change of the reaction.

Rereading of problem suggests us that the concentration of D is to be ascertained from the relationship between C and D. Thus if at equilibrium One mole of C is formed, and then the ratio 1:3 between C and D as conveyed by the equation reflects that the number of moles of D formed are three moles. Further, One mole of C is formed by the consumption of two moles of A and One mole of B. Therefore at equilibrium the moles of reactions and products present is as follows:

A.....2moles, C..... 1mole
 B.....6moles, D..... 3moles

As value of vessel is one litre, evidently molar concentration at equilibrium of various species now would be:

[A]=2, [B] =1
 [C]=1, [D] =3

Connecting the problem with related theories:

Here the problem relates to not any theory but with law of equilibrium and according to that

$$K_c = \frac{[C] \times [D]^3}{[A]^2 \times [B]} \dots \dots \dots (3)$$

Steps 3, 4, and 5 would automatically find the mention, once we attempt the solution of the problem.

Solution:

Step 1: To ascertain the number of moles of various species (involved) at the equilibrium of the change

These are already indicated here as A, B, C and D as 2, 3, 1 and 3.

Step 2: To ascertain the molar concentrations of each species involved in the change.

These too here been indicated,

Step 3: To write the value of K which is K_c here appropriately

$$\text{This is } K_c = \frac{[C] \times [D]^3}{[A]^2 \times [B]}$$

Step 4: To calculate the value of the

$$\text{Thus } K_c = \frac{1 \times 3^3}{2^2 \times 3} = \frac{1 \times 9}{4 \times 3} = \frac{3}{4} = 0.75$$

∴ K_c for the reaction is 0.75 mole L⁻¹

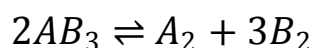
Rolook into the entire process:

Relook or re-examination brings following points for consideration while attempting such problems and these are:

- i) We must focus on balanced chemical equation
- ii) Balanced chemical equation only will give appropriate relationship between various species
- iii) Certain unknown quantities we sometimes ascertain from the given data and this may not be given.
- iv) K, equilibrium constant is function of temperature

Practicing similar problems:

Problem 1: Consider the reactions:



If the reaction is carried out by taking 8 moles of AB₃ in a closed vessel of capacity 1 litre and at equilibrium 2 moles of A₂ are formed at a certain temperature, then what is the value of K_c for the reactions.

Ans: 27(mol L⁻¹)²

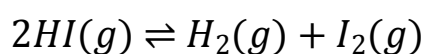
(**Hint:** if two moles of A₂ are formed then B₂ present at equilibrium must be 6 moles and 2 moles of A₂ are formed from 4 moles of AB₃).

Problem 2: The degree of dissociations of N₂O₄ into NO₂ at one atmosphere and 40°C is 0.310. Calculate the value of K_p. What shall be the value of degree of dissociations at 10 atmospheric pressure?

Pedagogy related with the problems:

Here K_p designates in terms of the partial pressure of the species. So it is worthwhile here to consider the pedagogy itself related to the concept of partial pressure.

As the name itself suggests, partial pressure is the part of the total pressure of the system, wherein the system would involve in any components. Through the equations $pV = nRT$, we know pressure at a given volume and temperature is a function of numbers of moles of the gas. Evidently if in a system various components are involved, then the total pressure of the system shall be the pressure occupied by total number of moles of all gaseous components present in the system. To get further clarification, let us consider a reversible change:



Carried out in a closed vessel of some stipulated volume and at a certain fixed temperature. Let at equilibrium the following position is ensured:

Total Pressure, at equilibrium = P moles

Number of moles of $HI = a$ moles

Number of moles of $H_2 = b$ moles

Number of moles of $I_2 = c$ moles

This total number of moles of all the gases present in the flask is $(a + b + c)$ moles and their total pressure is ' P ' atmosphere. Thus for $(a + b + c)$ moles, pressure is p atmosphere and for a moles, the pressure will be $\frac{p}{(a+b+c)} a$

This is the partial pressure of H_2 in the flask (which is system also) and is denoted as p_{H_2} . Needless to say in an analogous)

manner $p_{H_2} = \frac{p \times b}{(a+b+c)}$, and

$$p_{I_2} = \frac{p \times c}{(a+b+c)}$$

We may now generalize that:

Partial pressure of any component = $\frac{\text{Total Pressure} \times \text{moles of that component}}{\text{Total moles}}$

and the term $\frac{\text{moles of any component}}{\text{Total number of moles of all components the system}}$

is called mole fractions of the component in question. We now say that

Partial Pressure = Total Pressure \times mole fraction of the component

Rereading of the problems brings into focus the following aspects:

- i) Producing a balanced chemical equation
- ii) Ascertaining the expression for K_p
- iii) Calculating the value of K_p
- iv) As temperature remains the same, using the calculated value of K_p for affecting the new degree of dissociations. The problem centres around two parts:
 - a) Calculation of K_p
 - b) Using the value of K_p to calculate the demanded degree of dissociations.

Step 4 and 5 automatically get their mentions once solution to the problem is carried out.

Solution:

Step 1: To Produce Balanced Chemical Reactions

This is $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Step 2: To check out appropriate moles of the component at equilibrium let us again consider the reaction which is $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ let α be the degree of dissociation of N_2O_4 at the given pressure and temperature. Further let P be the total pressure at equilibrium, therefore, at equilibrium we will have $(1-\alpha)$ moles of N_2O_4 and against that we will have 2α moles of NO_2 at equilibrium

$[N_2O_4 \quad \alpha - \text{produces } 2\alpha \text{ moles of } NO_2]$

Therefore total moles of N_2O_4 and NO_2 at equilibrium = $(1 - \alpha) + 2\alpha = (1 + \alpha)$

Step 3: To calculate partial pressure of each component at equilibriums.

This is: $p_{N_2O_4} = \frac{P(1-\alpha)}{(1+\alpha)}$

and $p_{NO_2} = \frac{2P\alpha}{(1+\alpha)}$

Step 4: To check out Appropriate Formula for K_p , we have already applied law of Equilibrium, according to that $K_p = \left[\frac{2P\alpha}{(1+\alpha)} \right]^2 / \frac{P(1-\alpha)}{(1+\alpha)}$

Simplifying we get; $K_p = \left[\frac{4P\alpha^2}{(1-\alpha)^2} \right]$

Further if α is very small, then $(1-\alpha^2)$, may be replaced by unity, therefore this gives $K_p = 4P\alpha^2$

Step 5: To calculate K_p value

Since α here is 0.31, which is not a small value, therefore, we use the expressions:

$$\begin{aligned}
 K_p &= \frac{4P\alpha^2}{(1-\alpha^2)} \\
 &= \frac{4P\alpha^2}{0.904} \\
 &= \frac{0.384}{0.904} \\
 &= 0.425
 \end{aligned}$$

Step 1: To calculate the desired λ value at 10 atmospheric pressure

$$\text{Since } K_p = 0.556 \frac{4Px^2}{(1-\lambda)}$$

(As temperature is same therefore, K_p is same)

$$\text{Therefore, } 0.425 = \frac{4 \times 10 \times \alpha^2}{(1-\alpha)}$$

To make the calculation simple, we may here assume $(1 - \alpha^2)$ equal to unity, doing so gives us $\alpha^2 = \frac{0.425}{40}$

$$\begin{aligned}
 &= \frac{425}{4} \times 10^{-4} \\
 &= 106.25 \times 10^{-4}
 \end{aligned}$$

$$\begin{aligned}
 \text{Thus } \alpha &= 10.25 \times 10^{-2} \\
 &= 0.1025 \\
 &= 10.25\%
 \end{aligned}$$

Relook into the entire process

It suggests that if α is very-very small then $(1 - \alpha)$ may be replaced by unity and this gives

$$K_p = 4Px^2$$

$$\text{Thus, } \alpha^2 = \frac{K_p}{4P}$$

$$\text{Or } \alpha = \left(\frac{K_p}{4P}\right)^{1/2}$$

In other words α is inversely proportioned to P , means that at higher pressure α is less, thus what this problem conveys that at 1 atm, $\alpha = 0.31 = 31\%$ and at 10 atm, $\alpha = 11.5\%$.

Practising similar problems:

Problem 2: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$.

At same temperature and 4 atm pressure the degree of dissociations of PCl_5 is 10 atm. What shall be its degree of dissociations at 1 atm.

Ans: 20%

[Hint: $K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}}$]

Proper applications of law of chemical equilibrium suggests that factors 2, and its square 4 do not appear in the expression of K_p .

Problem 3: Calculate the pH of 0.005M H_2SO_4

Pedagogy related to the processes

Rereading of the problem conveys the fact that the acid given is not a monobasic acid and it is a dibasic acid, whose one mole on ionization would give two moles of H^+ ions.

Correlation of the problem with related theory:

The concept of pH is related to the ionic product of water. This ionic product of water is denoted as K_w and K_w is a kind of equilibrium constant, whose value at 298K is 1.0×10^{-14} (g ion mol^{-1})². As water ionizes in the manner: $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$. This K_w is multiple of the ionic concentration of the two ions that water produces on ionizations. Since for neutral water $[H^+] = [OH^-]$ and each is 1.0×10^{-7} g ion mol^{-1} . This is how for neutral water $p_H = -\log 10^{-7} = -(-7) \log 10 = 7$, One should always keep in mind that for neutral water pH is 7. so long ionic product of water is 1×10^{-14} g ion. If the value of K_w changes, then frame of reference of pH for neutral water should change. Thus if we suppose that at some elevated temperatures $K_w = 1.0 \times 10^{-12}$, then now each of the ion i.e., H^+ and OH^- would have concentration 1.0×10^{-6} g ion mol^{-1} . Therefore this time pH of neutral waters $pH = \log 10^{-6} = -(-6) \log 10 = 6$

In conclusion we may remark that pK_w always is multiple of $[H^+]$ $[OH^-]$ but its value is a functions of temperature and is 1.0×10^{-14} only so long temperature is 298K (25°C).

Steps 3, 4 and 5 are self reflected in the solution of the problem.

Solution:

Step 1: To write expression for ionization of H_2SO_4 . This is $H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$.

Step 2: To ascertain the concentration of H⁺ ions

Since volume of solution we are not changing therefore, whatever is the concentration of H₂SO₄, twice will be the concentration of H⁺ ions, so [H⁺ = 0.005 × 2 = 0.01] = 1 × 10⁻².

Step 3: To calculate the pH of desired solutions.

As pH = log[H⁺] = -log 10⁻² = -(-2) log 10 = 2

Relook into the entire process

Four aspects need consideration here and these are:

- i) Proper ionizations, equations for the target electrolyte needs to be produced.
- ii) Truly speaking pH = -log [H₃O⁺], as in water [H⁺] is aquated and better represented as [H₃O⁺], but for simplicity we take [H₃O⁺] = [H⁺].
- iii) Actually the total [H⁺] ion would be 1.0 × 10⁻² + 1.0 × 10⁻⁷ (From H₂SO₄ ionization) (From water ionization)

= 1.0000 × 10⁻², which is as good as 1.0 × 10⁻²

Thus if contribution from target electrolyte is close to 10⁻⁷, we may not neglect water contribution. For example pH = 10⁻⁵ M b⁺⁺ would not be 5, it may be 4.98, as total [H⁺] ion is 1.0 × 10⁻⁵ because 0.01 × 10⁻⁵ is the contributions from water.

- iv) If the electrolyte is weak then we either need α or K value to do calculations. Because for strong electrolytes we take α = 1.

Practicing similar type of problems:

Calculate the pH of 0.005 M Ba(OH)₂ solution assuming Ba(OH)₂ to be fully ionized.

Ans: 12

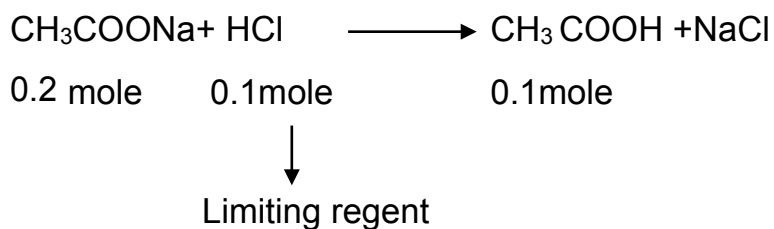
Hint: we would have [OH⁻] = 10 × 10⁻² and we would take help of the relations [H⁺] [OH⁻] = 1.0 × 10⁻¹⁴, and therefore ascertain [H⁺] concentration and calculate pH of the solution.

Problem 4: To 0.2 moles of CH₃COONa present in one litre of its aqueous solution 0.1 mole of HCl is added, if pK_a of CH₃COOH is 4.74 then what shall be the pH of the resulting solution?

Pedagogy related to the problem:

Relooking of the problem, throws light on the aspect that buffer is designed by the structural combination of weak acid and its salt. We have been given salt of weak acid that instead of the weak acid, the strong acid moles are given. Could it be that

strong acid leads to the formations of weak acid? This indeed is the answer as here the following reactions occur:



Correlation of problem with related theory:

Here we have to follow the following Henderson Equation to calculate the desired result

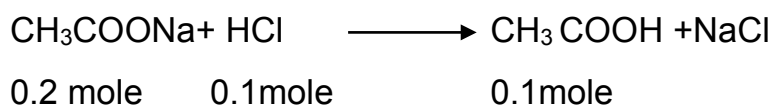
$$\text{pH} = \text{pKa} + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

Steps 3,4 and 5 themselves find reactions in the following solution to the problem.

Solutions

Step 1: To ascertain the moles of weak acid

The reactions:



Using the idea of limiting reagent this is 0.1 moles. Remember that we universally follow the idea that the stronger one produces the weaker one may it be acid/oxidant/nucleophile.

Step 2: To ascertain the concentrations of left out salt and the formed weak acid, this is:

$$[\text{CH}_3\text{COOH}] = 0.1, [\text{CH}_3\text{COONa}] = 0.1$$

Step 3: To ascertain pH of the system using appropriate relation

For relation $\text{pH} = \text{pKa} + \log \frac{[\text{Salt}]}{[\text{Acid}]}$

Now $[\text{Salt}] = [\text{Acid}]$ each is 0.1 and $\text{pKa} = 4.74$

$$\text{Thus, pH} = 4.74 + \log \frac{0.1}{0.1} = 4.74 + \log 1$$

$$= 4.74 + 0$$

$$= 4.74$$

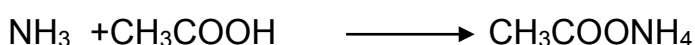
Relook into the entire process:

Sometimes the data is not directly given but it is indirectly cited, so is the case here, through which we have generated the concentrations of weak acid, which was not given

Practisizing similar type of problems:

Problem 4: To 100 mL of 0.1M aqueous NH₃ solution (wherein NH₄OH) is added 50 mL of 0.1M CH₃COOH. If pK_a of the base is 4.76, then what shall be the pH of the solution?

[Hint: The reactions:



Would be the source of salt. Further moles of NH₃ are in excess this, is 0.1 mole, idea of limiting reagent needs to be used and use of equations.

$\text{pOH} = \text{pK}_b + \log \frac{[\text{Salt}]}{[\text{base}]}$ need to be done to affect calculations. Finally, use the reactions. $\text{pH} + \text{pOH} = 14$

Problem:

0.1 M NH₄Cl aqueous solution at 298 K undergoes hydrolysis: given that at this temperature, the value from pK_b of NH₄OH is 4.74 then calculate.

Equilibrium constant when NH₄OH gets neutralised by a strong acid.

Pedagogy related to the problem:

Hydrolysis involves interactions of the ions of the given salt with water. This interaction process causes cleavage of the H-OH bond of water causing the aqueous system either to be acidic or basic. Experiences tell us that here we come across with four different situations, which are being presented along with certain desired expressions and suitable examples of hydrolysis of salts for each situation.

Situation 1: cation of the salt undergoes hydrolysis but anion does not.

Examples Expressions for K_w Expression for pH



CuSO₄

FeCl₃

Here K_w is the common expression for the hydrolysis constant followed by common expression for pH of the examples of salts chosen. Terms K_w, and C have their

used meaning in the name of ionic product, dissociation constant of weak base and concentration of the salt respectively.

Situation 2: Anion of the salt undergoes hydrolysis but cation does not.

Examples	Expressions for K_w	Expression for pH
NaF	$K_h = \frac{K_w}{K_a}$	$pH = \frac{1}{2} [pK_w + pK_a + \log c]$

KCNHCO

ONa

Now the terms K_a and C stand for the ionization constant of weak acid and concentration of the salt chosen.

Situation 3: Cation as well as anion both hydrolysis.

Examples	Expressions for K_w	Expression for pH
NH_4F	$K_h = \frac{K_w}{K_a \times K_b}$	$pH = \frac{1}{2} [pK_w + pK_a - pK_b]$

HCOONH₄

NH₄CN

Here all the terms that find mentions have their usual meaning.

Situation 4: Neither cation nor anion hydrolysis

Examples of the salts falling in this category are NaCl, KCl, KBr, KI, NaBr, NaI etc. As no hydrolysis of the said salts is experienced, so no mention this time for K_h and resultant pH of the system has been cited. Students need to be made acquainted with the facts that:

- i) Such cations hydrolyse which on hydrolysis form weak base and consequently media is always acidic here.
- ii) Such anions undergo hydrolysis, which on hydrolysis produce weak acid and media is always basic here.
- iii) In case of the salts where cation and anions of the salt both face hydrolysis, weak acid and weak base are formed and the media is acidic or basic depends on the aspect among the weak acid and weak base which one is comparatively stronger. If the weak acid formed is stronger compared to the weak base formed then the media would be acidic and vice-versa.

Rereading of the problem conveys the following points:

- i) The concentration of the salts is given, this could probably be needed for ascertaining pH of the system.

- ii) Equilibrium constant for the reactions between NH_4OH and strong acid may be calculated from K_h value itself.

Correlating the Problem with Related Theory:

As has been stated in the pedagogical issues related with hydrolysis, here NH_4^+ ion would undergo hydrolysis but Cl^- will not as HCl forms strong acid. Steps 3, 4 and 5 find mention on the solutions of the problem. The solution of the problem is now as follows:

Solution:

Step 1: To write appropriate equation for the hydrolysis of NH_4^+ ion:

The reaction involved is: $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{OH} + \text{H}^+$

Step 2: To ensure the appropriate expressions to be used for calculations of K_w and to insert relevant values:

This is: $K_h = \frac{K_w}{K_b}$

Since pK_b is 4.74, from here we make $4.74 = -\log K_b$

This will give the value of K_b as 1.80×10^{-5}

$$\therefore K_h = \frac{1.0 \times 10^{-14}}{1.80 \times 10^{-5}} = \frac{10 \times 10^{-10}}{1.8} = 5.55 \times 10^{-10}$$

Because at the given temperature K_w is 1.0×10^{-14}

Step 3: To ensure the appropriate expression to be used for calculating pH and to insert relevant values.

This is $\text{pH} = \frac{1}{2} [pK_w - pK_b - \log c]$

$$= \frac{1}{2} [14 - 4.74 - \log 10^{-1}]$$

(As from K_w value 1.0×10^{-14} , we get $pK_w = 14$ and $C = 10^{-1}$)

$$\text{Thus, pH} = \frac{1}{2} [14 - 4.74 - (-1) \log 10]$$

$$\text{pH} = \frac{1}{2} [14 - 4.74 + 1]$$

as, $\log 10 = 1$

$$= \frac{1}{2} (15 - 4.74)$$

$$= \frac{1}{2} (10.26)$$

$$= 5.13$$

Step 4: To calculate equilibrium constant for Reverse Reactions

$$K_h = \frac{1}{K_a}$$

Since $K_h = 5.5 \times 10^{-10}$

$$K_h = \frac{1}{5.5 \times 10^{-10}} = 1.8 \times 10^{-9}$$

Relook into the entire process:

The reasonable cause for the medium to acidic seems to that as products we have two substances. One is free H^+ ions and the other is weak base NH_4OH . This weak base will not ionize fully, therefore, system will always have more number of moles of H^+ ions compared to OH^- , which in turn will make the media acidic. Further neutralization of NH_4OH by strong acid and is the reverse of hydrolysis.

Practising Similar Topic of Problem:

Problem 5: 0.1 M $NaHCO_3$ aqueous solutions at 298K undergo hydrolysis. If pK_a and K_a values for the $HCOOH$ acid are 3.74 and 1.80×10^{-4} at this temperature, then what shall he:

(i) K_h (ii) pH and (iii) Reciprocal of the equilibrium constant value for hydrolysis change.

Ans. $K_h = 5.55 \times 10^{-11}$, pH = 8.37

$$K'_h = 1.8 \times 10^{10}$$

Problem: Given that at a certain temperature K_{sp} for $AgCl$ is 1.0×10^{-10} . If Ag^+ ion of the concentration value 1.0×10^{-4} M is added to the following three test tubes containing three different concentrations of Cl^- ion. In which case would precipitate of $AgCl$ would appear.

Serial Number of Test Tube	Conc. of Cl^- ion
I	1.0×10^{-7}
II	1.0×10^{-8}
III	1.0×10^{-5}

Pedagogy related to problem:

Rereading of the problem reveals that some condition for the precipitations needs to be ensured.

Correlation of the problem with related theory:

The theory associated with solubility product constant of the salt suggests that each salt at a certain temperature has a stipulated value of K_{sp} .

The multiple of two ionic concentrations of ions given by the salt as per the law of equilibrium must exceed K_{sp} value of the salt, and the salt then only would precipitated.

This now needs to be worked out in three steps for each test tube.

Step 1: Ascertaining the Multiple of ionic concentrations for test tube I.

As $\text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$ is the equilibrium under examination, therefore, for test-tube-I

$$[\text{Ag}^+][\text{Cl}^-] = 1.0 \times 10^{-4} \times 1.0 \times 10^{-7}$$

$$= 1.0 \times 10^{-11}$$

[Remember that as the equation reveals coefficient for Ag^+ and Cl^- each is unity only]

Step 2: To calculate the Multiple of ionic concentrations for test-tube-II.

$$\text{This time it is } 1.0 \times 10^{-4} \times 1.0 \times 10^{-8} = 10 \times 10^{-12}$$

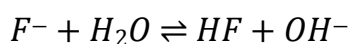
Step 3: To calculate the Multiple of ionic concentrations for test-tube-III.

$$\text{For test tube marked III, it is } 10 \times 10^{-4} \times 1.0 \times 10^{-5} = 1.0 \times 10^{-9}$$

In conclusion, we see that only in test-tube-III the product $[\text{Ag}^+][\text{Cl}^-]$ exceeds K_{sp} , therefore, here only AgCl would precipitate.

This now needs to be worked out in three steps for each test tube.

Hint: We have to work out data for the change



Relook into the entire problem:

The essence of the problem brings into picture the following points:

- i) The nature of the salt, needs to be carefully taken into considerations. For example for PbCl_2 , the equation is:
 $\text{PbCl}_2 \rightleftharpoons \text{Pb}^{2+} + 2\text{Cl}^-$, therefore, the multiple would require $[\text{Pb}^{2+}][\text{Cl}^-]^2$, to judge whether precipitations would occur or not.
- ii) This is a problem related to the laboratory practices and thus reveals that out of Zn^{2+} ions and Cd^{2+} ions, since K_{sp} for CdS is low. This is the precise reason that CdS is preferably precipitated under low S^{2-} ion concentration in acidic media in II group compared to Zn^{2+} ion which precipitate as ZnS in basic media in IV group.

Since this K_{sp} concept encountered and practised so oftenly in the laboratory, therefore, no similar additional problems are mentioned. Instead to strengthen the use of K_{sp} , we take a new challenging problem.

Problem 3: Given that at a certain temperature, the value of K_{sp} for PbI_2 is 4.0×10^{-12} , then what shall be the concentrations of iodide ions in the solution?

Solution for problem:

Step 1: To produce the relevant equations, it is



Step 2: To produce, relevant, relationship between K_{sp} of the salt and its solubility. If 'S' is the solubility then we shall []^S as the molar concentration of Pb^{2+} and 2S as the molar concentration of iodide ions as it is twice of Pb^{2+} .

Step 3: To produce appropriate relation between K_{sp} and S

$$\text{This is } K_{sp} = [Pb^{2+}] [I^-]^2$$

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

$$= 4S^3$$

Step 4: To ascertain value of 'S' since given $K_{sp} = 4.0 \times 10^{-12}$

$$\text{Therefore } 4.0 \times 10^{-12} = 4S^3$$

$$\therefore S^3 = \frac{4.0 \times 10^{-12}}{4} = 1.0 \times 10^{-12}$$

$$\therefore S = 1.0 \times 10^{-4}$$

Remember solubility is concentrations here of the target species.

Therefore, solubility is: PbI_2 is $1.0 \times 10^{-4} \text{ mol L}^{-1}$.

Step 5: To ascertain solubility of iodide ions.

As the concentrations of iodide ions is twice that of Pb^{2+} ions and concentration of Pb^{2+} is the same as that of PbI_2 dissolved. Therefore, if Solubility of PbI_2 is $1.0 \times 10^{-4} \text{ mol L}^{-1}$, then the concentrations of iodide ions is:

$$2 \times 1.0 \times 10^{-4} \text{ mol L}^{-1} = 2.0 \times 10^{-4} \text{ mol L}^{-1}$$

Pedagogical Module for Solving Numerical Problems on Solution Chemistry

Problem: A solution of sodium nitrate (NaNO_3) is designated as 1M solution. If the density of the solution is 1.25g mL^{-1} , then what shall be the molality of this nitrate solution, given that molar mass of NaNO_3 is 85gmol^{-1} .

Pedagogy Related with Problem:

Re-reading the problem once helps us to recall that it is related to change in mode of concentrations from molarity to molality. This we know is possible only through density data and we ensure ourselves that for this purpose only the density data is given.

Correlating the Problem with Related Theories:

Here the theory part is rather very simple and it is that 1 mole of NaNO_3 (i.e., 85g of NaNO_3) is present in 1000 mL of the solution. This mass-volume relationship needs to be translated into mass-mass relationship, as molality is defined as the number of moles of solute present in kg of the solvent.

To bring into focus other steps of the pedagogical model, let us affect its solutions.

Solution:

Step 1: To calculate Mass of the solution

As Mass = volume x density

Therefore, on multiplying the factors 1000 by 1.25, we get the factors 1250g, which is mass of the solution.

Step 2: To ascertain the Mass of the solvent

As mass of solution = Mass of solute + Mass of solvent

Therefore, $1250 = \text{Mass of solvent} + 85$

$\therefore \text{Mass of solvent} = 1250 - 85 = 1165\text{g}$

Step 3: To calculate Molality of the solution, as 1165g of the solvent contains 85g of NaNO_3

Therefore amount of NaNO_3 present per kg of solvent on 1000g of solvent is:

$$= \frac{85}{1165} \times 1000$$

To convert this amount into molality we need to divide the factors $\frac{85}{1165} \times 1000$ further by 85, to ascertain the moles of NaNO₃ present is 1000g of solvent. Thus $m = \frac{85 \times 1000}{1165 \times 85} = \frac{1000}{1165} = 0.858$

where m is the molality of the solvent.

The solution of the problem automatically brings into highlights steps 3, 4 and 5 of our pedagogy model.

Relook into the entire process

A careful glance at the solution of the problem suggests that mole fraction also is mass-mass relationship, therefore, we can interconvert molality and mole fraction into each others, find out the support of density data. However converting each of the above molar of concentrations into and molarity and molality and mole fraction into other molality and mole fractions, the support of density data is always desired.

Practicing similar type of problems:

Problem 1: A given solution of H₂SO₄ is 95% mass-volume sample of its aqueous solution. If the density of such a sample of H₂SO₄ is 1.98g mL⁻¹, then determine the molality of such a sample of H₂SO₄

Ans. 9.41

Problem 2: Two liquid components A and B at certain temperature TK, form a pairs of ideal liquid solution. If vapour pressure of A at TK is 300 torr and that of B at this temperature is 100 torr, then what shall be the total pressure above the liquid mixture if it is an equilibrium mixture of two components?

Pedagogy related to the problem:

Re-reading of the problem suggests that if it is an equimolar mixture of two components then mole fractions of each component is 0.5 [To get clarity to this point, suppose moles of each component is x then total moles is 2x, therefore, mole

fractions of each component is $\frac{x}{2x} = 0.5$]. Further pondering over the problem it reflects that here Raoult' law needs to be applied.

Correlating the problem with related theories:

As stated above, from the point view of new of theory we take the help of Raoult' law which is: $P_{Total} = P^oA \times x_A + P^oB \times x_B$

Where P_{Total} stands for total pressure of the system above the liquid solutions and P^oA is the vapor pressure of the liquid component A and P^oB is the vapor pressure of the component.

Again steps 3, 4 and 5 of pedagogical model would themselves find mentions, once solutions to the problem is affected.

Solution:

Step 1: To ascertain mole fractions of each component

As it is equimolar mixture, therefore, as stated earlier, the mole fractions of each component would be 0.5.

Step 2: To calculate total pressure above the liquid mixture, we would the formula $P_{Total} = P^{\circ}A \times x_A + P^{\circ}B \times x_B$ as $P^{\circ}A = 300$ and $P^{\circ}B = 100$ then and $x_A = x_B$ and each is 0.5.

$$\begin{aligned} \text{Therefore } P_{Total} &= 300 \times 0.5 + 100 \times 0.5 \\ &= 150 + 50 = 200 \text{ torr} \end{aligned}$$

Relook into the entire process:

The relook, into the problem brings into focus, two very important ideas and these are:

- i) To ascertain mole fractions, we need, no. of moles of the component, whose mole fractions needs to be calculated and the total number of all the component is in the liquidmixture.
- ii) Vapours pressure of the liquid is a functions of temperature that is for this aspect that whereas vapour pressure is given, the temperature is also mentioned.

Practising similar problems:

Problem 2: In the above stated problem if the vapours of the liquid mixture are condensed and the liquid mixture is again vaporized at the same temperature, then what shall be the new total pressure of the liquid mixture.

Ans: 250 toss

[Hint: In the vapour formed, when the total pressure above the liquid mixture was 200 torr, the contributions of component A was 150 torr and that of B was 50 torr. In the liquid formed by condensing the vapours mole fractions of component A asliquid would be pressuredueto $\frac{\text{Component}}{\text{Total Pressure}}$ and evidently this is $\frac{150 \text{ torr}}{200 \text{ torr}} = 0.75$

Similarly as liquid mole component fraction of B $= \frac{50 \text{ torr}}{200 \text{ torr}} = 0.25$.

Now temperature remains the same, it is possible toss you to work out the solution to theproblem]

Problem 2: At 300K, the pressure of an ideal solution containing one mole A and three moles of B is 550 torr. At the same temperature if one mole of B is added then

new pressure of the liquid mixture becomes 560 torr. What are the vapour pressures of the components A and B at 300K.

Ans: Vapour pressure A is 480

torr Vapour pressure B is 600

torr

[**Hint:** This problem centres around, a very fundamental principal and this is that if we come across with two variables then to ascertain their value we must have two equations. Suppose the two vapour pressure at 300K are x and y respectively then we would generate two equations from the given data and these are:

$$0.25x + 0.75y = 550 \dots\dots\dots (i)$$

$$\text{and } 0.20x + 0.80y = 560 \dots\dots\dots (ii)$$

$$\text{or } +3y = 2200 \dots\dots\dots (iii)$$

$$\text{and } +4y = 2800 \dots\dots\dots (iv)$$

As in the first case mole fraction of A is 0.25, that of B is 0.75 afterwards A is 0.20 and B is 0.80, as one mole of B is additionally added]

Problem: An aqueous solutions of a non-volatile non-electrolyte solute which is 2 percent mass by mass exerts a pressure of 755 torr, at the boiling point of the liquid. Find out the molar mass of the solute.

Pedagogy related to problem:

This problem really needs to be read and reread. This exercise should reveal certain aspects and these are:

- i) Aqueous solution could have meaning.
- ii) The composition of the solution is that 2g of non-volatile non-electrolyte solute is present in 98g of waters.
(Because 2g solute is present in 100g of solutions)
- iii) As water boils at 100 torr, therefore this is the vapour pressure of the pure solvent.

Correlating the problem with Relation theory:

For non-volatile solute, the form of the Raoult's law that would be applicable would

$$\text{be: } \frac{P^0 - P}{P} = \frac{w}{\frac{W}{M}}$$

Where P^0 is the vapour pressure of the pure solvent, P is the vapour pressure of the solutions. w and W are the masses of solutes and solvent respectively. Further m and M are the molecular masses of the solute and the solvent.

Once again steps 3, 4 and 5 would automatically come in the picture, once we start working out the problem. It is as follows:

Step 1: To Ascertain the value of P^0

As a mention of the boiling point of the solvent has been made, therefore, this value is 760 torr.

Step 2: To ascertain the value of w , M and W : These are 2, 18 and 98 respectively.

Step 3: To assess what is more given

This is the value of P , which is 755 torr.

Step 4: Application of the above stated data into an appropriate relations, which is

$$\frac{P^0 - P}{P} = \frac{\frac{w}{W}}{\frac{m}{M}}$$

Where m is the molar mass of the solute, which needs to be calculated.

Step 5: To calculate m value, thus

$$\frac{760 - 755}{755} = \frac{\frac{2}{98}}{\frac{m}{18}} = \frac{2 \times 18}{98m}$$

$$\text{Therefore, } \frac{5}{755} = \frac{1}{151} = \frac{36}{98m}$$

$$\text{Therefore, } m = \frac{31 \times 151}{98} = 55.47 \text{ g mol}^{-1}$$

Relook into the entire process:

Here, the usual form of the Raoult's law which is appropriate is: $\frac{P^0 - P}{P^0} = \frac{n}{N+n}$ (i)

Where quantities n , and N stand for number of moles of solute and the solvent.

However the form: $\frac{P^0 - P}{P} = \frac{n}{N+n}$ (ii) which is derived from relations (i) is more

convenient to apply in affecting calculations, therefore, this should be applied.

Further the number of moles of the solute n , which $2/m$, where m is the molar mass of the solute, remains $2/m$, as solute is non-electrolyte. We know from our knowledge of colligative properties that the effective number of moles of particles responsible for lowering of vapour pressure of the solvent depends upon the nature of electrolyte substance, for example for same moles of KCl and BaCl_2 , this value would differ if these are fully dissociated.

Practising similar type of problem:

Compare the relative lowering of Vapour pressure of water, under identical conditions for 1 mol of sugar, 1 mole of KCl and 1 mol of BaCl_2 , assume that KCl and BaCl_2 are fully ionized.

Ans: x , $2x$ and $3x$ where x is the lowering in vapour pressure produced by sugar)

Hint: Sugar will remain 1 not only that KCl one mole on fully ionizations produces 2 moles of practical's and similarly $BaCl_2$, one mole, would produce three moles of practical's as per the following equations:



Problem: Calculate the osmotic pressure exerted by $0.1M K_4[Fe(CN)_6]$ solution, at $27^\circ C$; which is $0.1M$ and in its concentrations and which is 50% only ionized at this concentrations and temperature given that the value of $S = 0.082 atm lit mol^{-1} K^{-1}$.

Pedagogy related with the problem:

Rereading of the problem brings into lime-light the following points:

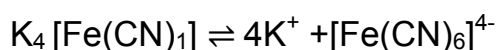
- (i) The temperature needs to be converted into Kelvin, because on all process. This finds mention in the Kelvin state inrelations.
- (ii) Number of moles given is 0.1
- (iii) Volume through $0.1M$ is 1litre
- (iv) Somewhere the idea of equilibrium needs to be applied.

Correlate the problems both related themes:

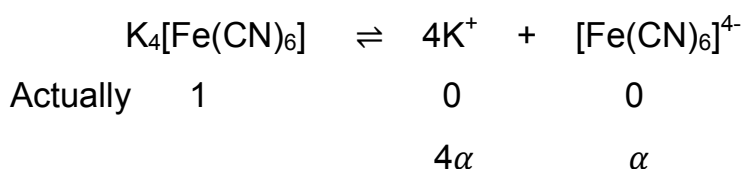
Here, the suitable relation that needs to be applied is

$$\Pi V = nST$$

Where Π is Osmotic pressure that needs to be calculated, V is the volume of the solution, S the solution constant, which is universal constant like gas constant. Finally T is the temperature of the solution in Kelvin. Another very important thing that needs consideration is to ascertain the effective moles of particles of all particles present at equilibrium responsible for Osmoses. Thus if $K_4[Fe(CN)_6]$ ionizes in the manner:



and α is the degree of ionizations at equilibrium then we would have the picture.



Solution $(1 - \alpha)$

Thus the total numbers of moles of all particles of equilibrium would be

$$(1 - \alpha) + 4\alpha + \alpha = (1 + 4\alpha)$$

Once again steps 3, 4 and 5 would be when actual solution to the problem is presented. Which is as follows:

Step 1: To ascertain the effective value of n

As stated above, here n is $(1 + 4\alpha)$ as $\alpha = 0.5$, so it is $(1 + 4 \times 0.5) = 3$. Remember it is for 1 mole, therefore for 0.1 it is 0.3.

Step 2: To properly assess, what is given here,

$$V = 1 \text{ litre}$$

$$S = 82 \times 10^{-3}$$

$$T = 300$$

$n = 0.3$ (By applying the idea of colligative property and equilibrium)

Step 3: To assess what is to be ascertained. Here Π needs to be ascertained.

Step 4: To calculate Π as $\Pi = \frac{n \times S \times T}{V} = \frac{0.3 \times 82 \times 10^{-3} \times 300}{1} \text{ atm}$

$$= 9 \times 82 \times 10^{-2}$$

$$= 7.38 \text{ atm}$$

Relook into the Entire Process: Relook conveys the important points. These are:

- i) Affect calculations at equilibrium whereas dissociations or associations is encountered
- ii) Effective number of moles responsible for colligative properties are functions of the nature of solute.

Practising similar problems:

Given that the volume of solutions constant S , is $0.082 \text{ atm litremol}^{-1} \text{ K}^{-1}$ calculate the osmotic pressure at 300k for the following systems.

- i) 0.1M Urea solutions (urea is non-electrolyte)
- ii) 0.1M NaCl solutions
- iii) 0.1M BaCl_2

Assume α value to be unity n cose of NaCl and BaCl_2

Ans. (i) 2.46 atm (ii) 4.92 atm (iii) 7.38 atm

Chemical Kinetics

The entire chemistry is governed by three important chemical regulations. The feasibility of a chemical reactions is ascertained by the principles of thermodynamics. The change in free energy, entropy and enthalpy are helpful in deciding the spontaneity of any chemical reaction. Secondly, the extent of any chemical reaction is known by its equilibrium study. The study is helpful in knowing the extent of product formation and in turn helpful in controlling the reaction for higher utility. Lastly, the kinetic study helps to know the time to reach equilibrium. This kinetic study also traces the entire path of a chemical reaction and in turn helps to decide the mechanism of chemical reactions.

Since chemical reactions are enumerable and each reaction may have a specific path, hence kinetic study has got much wider dimension. However, based on molecular interactions they are grouped into generalized categories like first order, second order, third order, etc. The time dependence or rate of reaction depends on concentration of reactant, nature of reactants, catalyst, pressure and temperature. Since chemical reactions involve breaking and making of bonds, the collision among molecular species must be energetic. In other words they should collide with minimum threshold energy. Since kinetic energy of molecules are governed by temperature, hence temperature plays vital role in the kinetic study of chemical reaction.

Numerical problems are basically application part of any theory and unfortunately many a times students do not try to make a proper link between the numerical problems and the related theories. Hence, an appropriate pedagogy is needed to connect numerical problems with appropriate scientific principles. The suggested pedagogy is given below to understand all dimension of chemical kinetics.

Problem 1:

In a reaction between A and B, the initial rate of reaction was measured for different initial concentrations of A and B as given below:

A/mol L ⁻¹	0.20	0.20	0.40
B/mol L ⁻¹	0.30	0.10	0.05
ro/mol L ⁻¹ S ⁻¹	5.07x10 ⁻⁵	5.07x10 ⁻⁵	1.43x10 ⁻⁴

What is the order of reaction w.r.t. A and B.

In the solution of this problem following pedagogy have been adapted.

1. Read and reread with reasoning:

At a first glance it is seen that rate of reaction is same for two sets of initial concentrations but varies for last set of initial concentrations. By careful examination of reaction it is seen that concentration of A remains same in two sets but becomes double in last set. On the other hand concentration of B is varying in all three sets.

2. Correlate the problem with related theory:

Since rate of reaction involve molecular interaction hence it depends on concentration of molecular species. The order of reaction is basically number of species whose concentration changes during rate determining step. Mathematically it is the sum of the power of concentration terms in the rate expression. In the detailed mechanism of the reaction it is sum of the powers of concentration terms in slowest or rate determining step.

3. Break down the problem of numerical in various steps:

The problem given above can be broken down in three steps corresponding to three sets of initial concentrations and determined rates.

Step 1: In first case simply rate of reaction is given for 0.20 and 0.30 mol L⁻¹ concentration of A and B respectively. This is simply a data having no specific information regarding the solution.

Step 2: In the second set the concentration of B is reduced to 0.1 keeping concentration of A constant. It is observed that rate of reaction remains unaltered by varying the concentration of B. Hence, one can tell that rate of reaction does not depend on the concentration of B.

Step 3: In third case concentration of A is doubled from 0.20 to 0.40 mol L⁻¹ while concentration of B is changed from 0.30 to 0.05 mol L⁻¹. By this change it is observed that rate changes from 5.07 × 10⁻⁵ to 1.43 × 10⁻⁴. This increase is $\frac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}} = 2.8$

2.8, this shows rate of reaction is sensitive towards the concentration of A and increases by approx 1.8 time for doubling the concentration. Now we can write $[A]^x = 2.8$ and $[A]^x = 2^{1.5}$. Hence $x = 1.5$. This shows that order of reaction is 1.5.

Step 4: Apply relevant Formulae/Equation:

Taking above data we can write the equation as $r_o = k [A]^{1.5} [B]^0$

Step 5: Make precise and meticulous calculation:

At this stage we have to write complete rate expression and calculate order

$$\begin{aligned} r_o &= k [A]^{3/2} [B]^0 \\ &= k [A]^{1.5} \end{aligned}$$

$Order = 1.5$

Hence, we can tell that rate is 1.5 order w.r.t. concentration of A and Zero order w.r.t. concentration of B.

Step 6: Relook into the entire process and practicing similar problems:

When we relook into the entire process following observations are made:

- (i) The order of the reaction may be fractional whereas molecularity of any elementary step cannot be fractional.
- (ii) Though we mix more than one reactants during reactions but rate of reaction may not depend on the concentration of all reactants.
- (iii) Order of the reaction is experimentally determinable quantity. It cannot be ascertained only by looking into the reaction.

Problem 2:

The half life for radioactive decay of ^{14}C is 5730 years. An archaeological artefact containing wood had only 80% of the ^{14}C found in a living tree. Estimate the age of the sample.

1. Read and reread the problem:

By careful reading the problem we see that one has to know the order or kinetics of radioactive disintegration reactions. Secondly concentrations must be related with presence of radioactive ^{14}C at the time of age determination. Thirdly the rate constant should be expressed in terms of half life period of ^{14}C .

2. Correlate the problem with related theory:

Radioactive disintegration obeys first order kinetics where completion of any fraction of reaction does not depend on initial concentration. The half life of the reaction is correlated with rate constant by the expression as:

$$t_{1/2} = \frac{0.693}{k}$$
$$k = \frac{0.693}{t_{1/2}}$$

For the first order reaction the expression for rate constant is derived to be $k = \frac{2.303}{t} \log \frac{C_0}{C}$

Where C_0 is initial concentration and C is the concentration after time t .

3. Break down the problem of numerical in various steps:

The present problem can be broken down in following steps:

Step 1: Write the expression for rate constant involving time, which is to be calculated.

$$k = \frac{2.303}{t} \log \frac{C_0}{C}$$

Step 2: Identifying the values of unknown. Here concentration is expressed in terms of C^{14} percentage. Hence $C_0=100$ and $C=80$. K is expressed in terms of half lifeperiod of carbon.

Step 3: Apply relevant formulae. Now we write the working formula for the problem.

$$t = \frac{2.303}{k} \log \frac{C_0}{C}$$

$$\text{Since } t_{1/2} = \frac{0.693}{k}$$

$$k = \frac{0.693}{t^{1/2}}$$

$$\text{Hence, we can write } t = \frac{2.303}{0.693/t^{1/2}} \log \frac{C_0}{C}$$

$$t = \frac{0.693 \times t^{1/2}}{0.693} \log \frac{C_0}{C}$$

Step 4: Make precise and meticulous calculations: Now substitute the values of all unknowns and make precise calculations.

$$t = \frac{2.303 \times 5730}{0.693} \log \frac{100}{80}$$

$$= 1845 \text{ years}$$

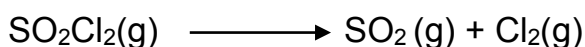
5. Relook the problems:

When we relook into the entire process it becomes evident that follow of first order kinetics by radioactive disintegration serves the very purpose of determining the age of rocks, monuments, trees. It has become the basis of carbon dating technology where no. of counts are measured for the monuments under examination and the corresponding fresh material applying similar procedure another problem can be solved as given below:

During nuclear explosion, one of the products is ^{90}Sr with half life of 28.1 years. If 1 μg of ^{90}Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically.

Problem 3:

The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume



Experiment	Time/s ⁻¹	Total Pressure atm
1	0	0.5
2	100	0.6

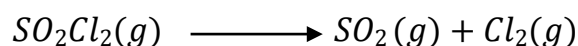
Calculate the rate of the reaction when total pressure is 0.65 atm.

Step 1: While rereading the problem it is seen that concentration terms are not given in the problem. Hence, it has to be expressed in terms of pressure. Since it follows first order kinetics the corresponding equation is applied to find the rate.

Step 2: For gases we can utilize $pV = nRT$ equation. Hence, $p = n/V RT = CRT$. So we use pressure in place of concentration in all our calculation. Secondly, by the help of given data we have to calculate rate constant, there after that rate constant should be utilized to determinerate.

Step 3: This problem should be broken into two parts. In first part rate constant is determined utilizing expression for first order rate constant. In the second part rate of reaction is determined once we know the first order rate constant.

Step 4: The given equation is:



Initial stage $a \equiv (P_0)$	0	0
--------------------------------	---	---

after time $(a - x)$		
----------------------	--	--

$t \equiv (P_0 - x)$	x	x
----------------------	-----	-----

$$P_t = P_0 - x + x + x = P_0 + x$$

$$x = (P_t - P_0)$$

The equation for first order is:

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

In this problem $a \equiv P_0$

$$\text{and } a - x \equiv P_0 - (P_t - P_0) = 2P_0 - P_t$$

$$\text{Hence, we can write } k = \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_t}$$

The data supplied can be substituted in the equation as:

$$k = \frac{2.303}{t} \log \frac{0.5}{2 \times 0.5 - 0.5}$$

$$k = 2.23 \times 10^{-3}$$

In the second step we have to determine rate of reaction utilizing this rate constant. The expression for the rate is written as:

$$\text{rate} = k[SO_2Cl_2] = k(a - x)$$

At the final pressure of 0.65 atm we have to find the value of $(a - x)$.

$$P_t = P_0 + x$$

$$0.65 = 0.5 + x$$

$$x = 0.65 - 0.5 = 0.15$$

$$a - x = 0.5 - 0.15 = 0.35$$

Hence, the rate = $k(a - x)$

$$= 2.23 \times 10^{-3} \times 0.35$$

$$= 7.805 \times 10^{-4} \text{ atm s}^{-1}$$

Step 5: By relooking into problem it reflects the importance of pressure data in investigating the rate equation. Secondly rate of reaction at a particular time depends on the concentration of reactant at that time.

Problem 4:

The time required for 10% completion of a first order reaction at 298K is equal to that required for its 25% completion at 308K. If the value of A is $4 \times 10^{10} \text{ s}^{-1}$ calculate k at 318K and Ea.

Step 1: If we reread this problem it seems to be an application of Arrhenius equation. Here data for two reactions are supplied. By comparing the two kinetic data ratio of rate constants can be evaluated.

Step 2: This problem reflects the effect of temperature on reaction kinetics and application of Arrhenius equation and integrated form of Arrhenius equation.

Step 3: The numerical problem can be broken down in two parts. In first part ratio of rate constants at 298K and 308K can be calculated. In the second part by employing Arrhenius equation in its simple form rate constant at 318K can be calculated.

Step 4: The expression for first order rate constant is given by:

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

$$\text{at } 298 \text{ } k_{298} = \frac{2.303}{t_1} \log \frac{100}{75}$$

$$\text{at } 308 \text{ } k_{308} = \frac{2.303}{t_2} \log \frac{100}{90}$$

$$\text{Hence } t_1 = \frac{0.1055}{k_{298}} \text{ \& } t_2 = \frac{0.2879}{k_{308}}$$

Now at above completion time take n for reaction is same. Hence

$$\begin{aligned} \frac{0.1055}{k_{298}} &= \frac{0.2879}{k_{308}} \\ &= \frac{k_{298}}{k_{308}} = 2.7289 \end{aligned}$$

This is in accordance with the general observation that rate constant of rate doubles or sometimes triples by every 10°C rise of temperature. Now applying integrated Arrhenius equation we get:

$$\begin{aligned} \log \frac{k_2}{k_1} &= \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \\ \log 2.7289 &= \frac{E_a}{2.303 \times 8.314} \left(\frac{1}{298} - \frac{1}{308} \right) \end{aligned}$$

$$E_a = 76.623 \text{ kJ mol}^{-1}$$

Now we can employ the Arrhenius equation $k = A e^{E_a/RT}$

$$\text{or } \log k = \log A - \frac{E_a}{RT}$$

Substitute the values

$$\log k = \log(4 \times 10^4) - \frac{76623}{8.314 \times 318}$$

$$\log k = -1.9822$$

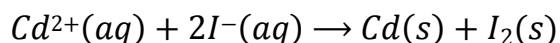
$$\text{or } k = 1.042 \times 10^{-2} \text{ sec}^{-1}$$

By relooking into the problem we realize that Arrhenius theory serves as an important tool to determine several parameters like activation energy rate constant and even temperature if other known required parameters are known. It can be applied to solve similar problems.

Electrochemistry

1. Sample Problem:

Calculate the cell potential to determine whether the following reaction is spontaneous in the given direction:



1. Read and re-read the problem:

Re-read the given problem visualizing the concept of oxidation and reduction.

2. Correlate the problem with the related theory:

The potential difference between the two electrodes of a galvanic cell is called the cell potential and is measured in volts. The cell potential is the difference between the electrode potentials (reduction potentials) of the cathode and the anode. By convention, we keep the, anode on the left and the cathode on the right while representing the galvanic cell. Under this convention

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

A spontaneous reaction is that which occurs by itself. The redox reaction will proceed in the direction for which the difference between the two half reaction potentials is positive.

3. Break down the given numerical problems in relevant steps:

a) What is given?

Reactants $\rightarrow \text{Cd}^{2+}(\text{aq}) + 2\text{I}^{-}(\text{aq})$

Products $\rightarrow \text{Cd}(\text{s}) + \text{I}_2(\text{s})$

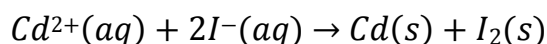
What are you asked to find out?

E° cathode in V?

E° anode in V?

E° cell

b) Step to be followed:



i) Write the individual half reactions:



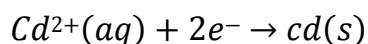
ii) Look for the reduction potentials for the two half reactions from the Table.

E° cathode

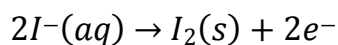
E° anode

iii) $E^\circ \text{ cell} = E^\circ \text{ cathode} - E^\circ \text{ anode}$.

4. Apply relevant formulae:



The oxidation no. of cadmium decreases, it is reduced



The oxidation no. of iodine increases, it is oxidized

Cadmium is the cathode and iodine is the anode

$E^\circ \text{ cathode} = -0.40 \text{ V}$ (from Table)

$E^\circ \text{ anode} = +0.54 \text{ V}$ (from Table)

$E^\circ \text{ cell} = E^\circ \text{ cathode} - E^\circ \text{ anode}$

If the cell potential is positive, the reaction is spontaneous.

5. Make precise and meticulous calculations

$$E^\circ \text{ cell} = -0.40 \text{ V} - 0.54 \text{ V} = -0.94 \text{ V}$$

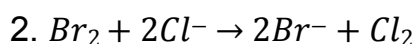
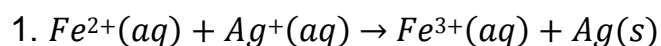
As the cell potential is negative, the reaction is not spontaneous.

6. Relook:

- i. Are the units correct?
- ii. Are the calculations according to convention?
- iii. Are the number of significant figures correct?
- iv. Is the answer reasonable?

As the reduction potential for the half reaction for iodine was more positive, I_2 is more likely to be reduced than Cd^{2+} .

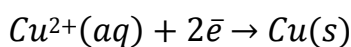
7. Practice:



[Ans. -0.29 V , non-spontaneous]

II. Sample problems:

When an aqueous solution of CuSO_4 is electrolyzed, copper is deposited at the cathode as:



If a constant current was passed for 5 hours and 404mg of Cu was deposited, calculate the current passed through CuSO_4 .

1. Read and re-read the problems:

Re-read the given problem visualizing the concept of electrolysis and reading Faraday's laws.

2. Correlate the problem with the theoretical concepts:

The quantitative aspects of electrolysis were first described by Michael Faraday in the form of the well known Faraday's two laws of electrolysis:

i) First Law: During electrolysis, the amount of chemical reaction occurring at any electrode is proportional to the quantity of electricity passed through the electrolyte.

ii) Second Law: The amounts of different substances liberated by the same quantity of electricity passing through the electrolyte solution are proportional to their chemical equivalent weight (Atomic mass of metal \div No. of electrons required to reduce the cation).

3. Break down the given numerical problems in relevant steps:

a) What is given?

Amount of Cu deposited
= 0.404g

What to find out?

Quantity of electricity passed to deposit
0.404g of Cu?

Gain of 2 electrons means $2F$ electric charge

Atomic mass of Cu = 63.5 a.m.u.

Time for which electrolysis was carried out = 5 hrs.

4. Apply relevant formula and making calculations:

$$63.5\text{g of Cu deposited by } 2F \text{ electric charge } 0.404\text{g} \quad " \quad " \quad " \quad " = \frac{2}{63.5} \times 0.404$$
$$= 0.0127F$$

It is known,

$$1F = 96,500 \text{ columns}$$

$$0.0127F = 0.0127 \times 96,500 = 1225.6 C$$

$$\begin{aligned} \text{Current passed} &= \frac{1225.6}{5 \times 60 \times 60} \\ &= 0.0680 \text{ ampere} \\ &= 6.8 \times 10^{-2} \text{ ampere} \end{aligned}$$

5. Relook:

- i. Are the units correct?
- ii. Are all the conversions taken into account?
- iii. Are the correlations correct?

6. Practice:

i) An electric current of 100 ampere is passed through a molten liquid of sodium chloride for 5 hours. Calculate the volume of chlorine gas liberated at the electrode at NTP.

[Ans. 208.91 L]

ii) Exactly 0.4 Faraday electric charge is passed through three electrolyte cells in series, first containing AgNO_3 , second CuSO_4 and third FeCl_3 solution. How many grams of each metal will be deposited assuming only cathodic reactions in each cell?

[Ans: Ag=43.2g, Cu=12.7g, Fe=7.47g]

III. Sample problems:

The conductivity of a 0.01M solution of acetic acid at 298K is $1.65 \times 10^{-4} \text{ S cm}^{-1}$.

Calculate:

- i. Molar conductivity of the solution
- ii. Degree of dissociation of CH_3COOH
- iii. Dissociation constant for acetic acid

Given that:

$$\lambda(\text{H}^+) = 349.1 \text{ and } \lambda^\circ(\text{CH}_3\text{COO}^-) = 40.9 \text{ S m}^2\text{mol}^{-1}$$

1. Read and re-read the problems:

According to the concept of conductivity, Kohlrausch's Law, degree of dissociation of weak electrolyte etc.

2. Correlate the problem with the theoretical concepts:

Conductivity:

The inverse of resistivity is called conductivity or specific conductance, represented by the symbol, κ . It may be defined as the conductance of one centimetre cube of a solution of an electrolyte. Thus, $K = \frac{1}{f}$

Units of conductivity are $\text{ohm}^{-1}\text{cm}^{-1}$ or Sm^{-1}

Molar Conductivity, Λ_m – defined as the conducting power of all the ions produced by dissolving one mole of an electrolyte in solution. It is related to specific conductance as:

$$\Lambda = K \times V$$

The degree of dissociation can be calculated at any concentration as:

$$\alpha = \frac{\lambda_m}{\lambda_m^\circ}$$

Where α is the degree of dissociation, λ_m is the molar conductance at concentration c and λ_m° is the molar conductance at infinite dilution.

According to Kohlrausch law, at infinite dilution when the dissociation is complete, the molar conductivity for a given salt can be expressed as the sum of the individual contributions from the ions of the electrolyte. Thus

$$\Lambda^\circ = \nu_+ \lambda_+^\circ + \nu_- \lambda_-^\circ$$

Where ν_+ and ν_- are the number of cations and anions per formula unit of electrolyte.

from Kohlrausch law, the calculations of dissociation constant of weak electrolyte can be done.

$$K = \frac{C \alpha^2}{1 - \alpha}$$

$$\text{or } K = \frac{C(\frac{\Lambda}{\Lambda^\circ})^2}{\frac{(1-\frac{\Lambda}{\Lambda^\circ})}{\Lambda}} = \frac{C \Lambda}{\Lambda^\circ(\Lambda^\circ - \Lambda)}$$

3. Break down the given numerical problems in relevant steps:

a) **What is given?**

What to find out?

K

Λ^c ?

C

α ?

$\lambda^\circ(H^+), \lambda^\circ(CH_3COO^-)$

Steps involved:

- i) Calculation of molar conductivity of solution
- ii) Calculation of Λ^c with the help of Kohlrausch's law
- iii) Calculation of α
- iv) Calculation of dissociation constant, K

4. Apply relevant formula and making precise calculations:

i) Calculation of molar conductivity of solution

$$\begin{aligned} \Lambda &= \frac{K \times 1000}{C} \\ &= \frac{1.65 \times 10^{-4} \times 1000}{0.01} \\ &= 16.5 \text{ S cm}^2 \text{ mol}^{-1} \end{aligned}$$

ii) Calculation of $\Lambda^\circ(CH_3COOH)$

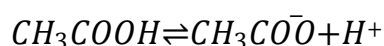
$$\begin{aligned} \Lambda^\circ(CH_3COOH) &= \lambda^\circ(H^+) + \lambda^\circ(CH_3COO^-) \\ &= 349.1 + 40.9 \\ &= 390 \text{ S cm}^2 \text{ mol}^{-1} \end{aligned}$$

iii) Calculation of α

$$\alpha = \frac{16.5}{390} = 0.0423$$

iv) Calculation of K

Acetic acid dissociates as:



Initial conc. C 0 0

Equilib. conc. $C(1-\alpha)$ $C\alpha$ $C\alpha$

$$\text{Now, } K = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$= \frac{C\alpha \times C\alpha}{C(1-\alpha)}$$

$$\text{or } K = \frac{C\alpha^2}{1-\alpha}$$

$$= \frac{0.01 \times (0.0423)^2}{1 - 0.0423}$$

$$= 1.87 \times 10^{-5}$$

5. Relook:

- i. Revise the various formulae & steps.
- ii. Check the units involved.
- iii. Check the calculations done.

6. Practice:

i) Conductivity of 0.00241 M acetic acid is $7.896 \times 10^{-5} \text{ S cm}^{-1}$ calculate its molar conductivity and if Λ° for acetic acid is $309.5 \text{ S cm}^{-2} \text{ mol}^{-1}$, what is its dissociation constant?

[Ans. 1.85×10^{-5}]

ii) The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and length 50 cm is $5.55 \times 10^3 \text{ ohm}$. Calculate its:

- a. Resistivity
- b. Conductivity, and
- c. Molar conductivity

[Ans: 87.135 ohm cm , $1.148 \times 10^{-2} \text{ S cm}^{-1}$, $229.6 \text{ S cm}^2 \text{ mol}^{-1}$]

Pedagogical Model for solving Numerical Problems

Organic Chemistry – I

Some basic Principals and Techniques for Nitrogen compounds

Quantitative Analysis of C, H by Liebig method and N by Dumas method:

1. 2.0g of an organic compound on complete combustion gave 1.47g of CO₂ gas and 1.2g of water. 1.0g of the same compound gave 432.66 mL of N₂ gas collected at 300k and 735 mm pressure in Dumas method (Aqueous tension at 300k was 15 mm). Find percentage composition of carbon, hydrogen and nitrogen in the organic compound.

The following steps will help us to solve this numerical problem.

Read and reread the numerical with reasoning:

Read the numerical with ease. Reread the language of the above numerical and start thinking of theory involved to help you to solve this problem. Make up your mind to attack the problem with the theory involved.

Correlate the problem with related theories:

Organic compounds on complete combustion with dry oxygen give CO₂ gas and most of the compounds give H₂O also on complete combustion. 12g of carbon on complete combustion gives 44g of CO₂ and 2g of hydrogen on complete combustion forms 18g of water vapours. By applying unitary method, percentage of C & H, can be calculated. In Dumas method of nitrogen estimation, the organic compound on heating with reduced copper oxide (CuO) in the atmosphere of CO₂ gas liberates N₂ gas collected over KOH solution in the nitrometer. Applying the pressure, volume and temperature relationship and knowing the volume of N₂ gas collected at the given temperature and pressure corresponding volume of N₂ gas at S.T.P. can be calculated after taking care of the aqueous tension. We also know that 22400 mL of N₂ at STP weighs 28g. Thus by unitary method, we can find the amount of Nitrogen present in 1g of organic compound and hence, percentage of nitrogen can be calculated.

Breakdown the numerical problem in various steps:

Percentage of carbon, hydrogen and nitrogen can be calculated by applying the formulae given in the next step.

Apply relevant formulae & making calculations:

Following percentage of C, H and N can be calculated by applying formula.

$$(a) \text{ Percentage of carbon} = \frac{12 \times \text{Mass of CO}_2 \text{ formed} \times 100}{44 \times \text{mass of organic compound}}$$

$$= \frac{12 \times 1.47 \times 100}{44 \times 2} = 20.04$$

$$(b) \text{ Percentage of hydrogen} = \frac{2}{18} \times \frac{\text{Mass of H}_2 \text{ liberated} \times 100}{\text{Mass of organic compound}}$$

$$= \frac{2 \times 1.2 \times 100}{18 \times 2} = 6.69$$

(c) Percentage of Nitrogen:

We will have to calculate volume of N₂ liberated at STP by applying pressure, volume and temperature relationship equation as given below:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \text{ (combined gas law equation)}$$

As per numerical problem, 432.66 mL (V₁) of N₂ gas is liberated at 300K (T₁) and 735-15=720 mm pressure (P₁). V₂ can be found out by putting standard values of P₂ as 1 atm or 760 mm and T₂ as 273K.

$$\frac{720 \times 432.66}{300} = \frac{760 \times V_2}{273}$$

$$\text{or } V_2 \text{ (Vol. of N}_2 \text{ gas at S.T.P.)} = \frac{720 \times 432.66 \times 273}{300 \times 760} = 372.998 = 373 \text{ mL}$$

Knowing that 22400 mL of any gas at S.T.P. corresponds to the molar mass of the gas. Thus 22400 mL of N₂ gas at S.T.P. weighs 28g. Mass of 373 mL of N₂ gas at S.T.P. can be found out by unitary method. 22400 mL of N₂ gas S.T.P. = 28g of N₂

$$\text{Mass of 373 mL of N}_2 \text{ gas at STP} = \frac{28 \times 373}{22400} = 0.4662 \text{ g}$$

The above mass is present in 1g, then how much in 100g i.e. percentage of nitrogen

$$= \frac{\text{Mass of N}_2 \times 100}{\text{Mass of organic compound}}$$

$$\text{Thus percentage of C, H and N in the given organic compound are:} = \frac{.4662 \times 100}{1} =$$

46.62

C = 20.04

H = 6.67

N = 46.62

Relook into the entire process:

(a) After solving the numerical problem, you are advised to relook into usage of correct formulae and a relook on calculations to ensure correct results.

Sum of the above three percentages (20.04 + 6.67 + 46.62) comes out to be 73.33. Sum of all the percentages should be 100. Here is the point of rethinking for you. Why is it so? In such a case, if percentage sum does not come out to be 100, it is presumed that rest of the percentage is due to oxygen unless and otherwise stated. This will be helpful to you in determining as given in empirical & molecular formula portion of some basic concepts in Organic Chemistry.

Thus, the percentage composition of different elements in the given organic compound is:

$$C = 20.04$$

$$H = 6.67$$

$$N = 46.62$$

$$O = 26.67$$

(b) Can you think of some alternative equation for determining volume of N_2 gas liberated at S.T.P.

Practice for similar problems:

Numerical problem no. 2: Extension of No. 1

The organic compound in above numerical problem is water soluble, does not give shooty flame on burning but with aqueous NaOH solution. Molar mass of the compound is 60_u . What is name and structure of the organic compound is numerical Number 1?

Procedure:

(a) Determination of Empirical Formula of component:

Empirical formula of the compound can be found out after getting percentage composition of all elements (sum should be 100) by adopting the procedure as given in the Table below:

Element	Percentage	Divided by At. mass of element	Dividend	Divide by the least value	Whole Number
<i>C</i>	20.04	12	1.67	1.67	1
<i>H</i>	6.67	1	6.67	1.67	4
<i>N</i>	46.62	14	3.33	1.67	2
<i>O</i>	26.67	16	1.67	1.67	1

Thus empirical formula i.e. $C_1H_4N_2O_1$ or CH_4N_2O with empirical formula mass as $12 \times 1 + 1 \times 4 + 14 \times 2 + 16 \times 1 = 12 + 4 + 28 + 16 = 60$ a.m.u.

(b) Molecular formulae:

Molar mass of the compound is 60 a.m.u. value of n (multiplication factor) can be found by dividing molar mass by empirical formula mass.

$$n = \frac{\text{Molar Mass}}{\text{Empirical formula mass}} = \frac{60}{60} = 1$$

Hence molecular formula of the compound is $(CH_4N_2O) \times 1 = CH_4N_2O$

(c) Application of Laboratory knowledge:

Applying your laboratory knowledge and the characteristics of the compound like solubility of the compound in water and burning of the compound without smoky flame indicate aliphatic nature of the compound. Liberation of ammoniac gas on heating with aqueous solution of NaOH indicates presence of amide group in compound.

(d) Now derive structure of the compound and write chemical name of the compound.

Numerical Problem No. 3: (Practice Problem)

An organic compound contains 74.0% carbon, 8.65% hydrogen and 17.3% nitrogen. The organic compound is insoluble in water and burns with a sooty flame. The acidic solution of the compound on treatment with sodium nitrite solution at 273-278 forms diazonium salt which on treatment with alkaline solution of phenol at 278-283K gives an orange, red dye. Molar mass of the organic compound is 81u. Derive structure of the compound and write its IUPAC name. Write IUPAC name of the compound.

Numerical problem no. 4 (C_5H_7N) (practice problem)

The low boiling organic liquid (b.p. $17^\circ C$) 'A' is highly soluble in water liberates nitrogen and a compound 'B' which forms yellow ppt with NaOH and I_2 on heating. The compound 'A' on analysis is found to contain 53.3% carbon, 15.6% hydrogen and 31.1% nitrogen. Derive structures of organic compounds 'A' and 'B'. (C_2H_7N and C_2H_6O)

Numerical Problem no. 5 (practice problem)

121g of organic compound is found to contain 84g of carbon, 7g of hydrogen, 14g of nitrogen and rest oxygen, the compound on burning gives a sooty flame and liberates a gas on heating with aqueous NaOH solution. Which forms white dense fumes with HCl rod. The compound is insoluble in water. Derive structure of the organic compound (Empirical Formula C_7H_7NO)

Quantitative Analysis of C, H by Liebig method and N by Kjeldahl's method:

1. Numerical Problem:

5.9g of an organic compound contains 2.4g of carbon, and 0.5g of hydrogen. Ammonia gas liberated after kjeldahlisation of 2.59g of the same compound was absorbed in 52mL of 1 M H_2SO_4 . The residual acid after titration with NaOH solution required 60mL of 1MNaOH solution. The organic compound is soluble in water and does not give smoke on burning but gives ammonical smell on heating with NaOH solution. Molar mass of the organic compound is 59U. Derive structure of the organic compound.

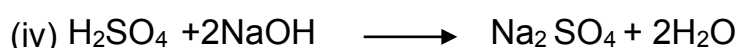
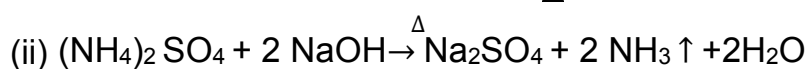
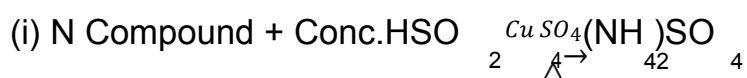
The following steps will help you to solve this numerical problem.

Read and reread the numerical problem with reasoning:

Give a simple but thorough reading to the numerical with ease. Reread language of the above numerical and think about the theory involved to help you to solve the problem. Make up your mind to attack the problem with theory involved.

Correlate the problem with related theories:

Knowing mass of the organic compound and mass of carbon and hydrogen present in the compound, percentages of carbon and hydrogen can be calculated by applying unitary method. For percentage determination. We recall the principle of kjeldahl's method when the nitrogenous organic compound is first digested with conc. H_2SO_4 to convert nitrogen compound into $(NH_4)_2SO_4$ which on further digestion with hot NaOH solution liberates ammonia gas which is absorbed in a known volume of conc. H_2SO_4 of the known molarity. The residual sulphuric acid left in the flask is determined by titration against standard NaOH solution. Knowing the volume of H_2SO_4 left unused by ammonia gas, the volume of standard H_2SO_4 used by absorption of NH_3 gas is determined by subtracting the unused volume of H_2SO_4 from the volume of standard H_2SO_4 taken initially. In this way, volume of NH_3 gas solution of given molarity corresponding to the amount of nitrogen in organic compound is determined as given in class XI book in unit 12. Applying the basic principle that 1000 mL of 1M NH_3 solution corresponds to 14g of nitrogen, the amount of nitrogen can be determined in given mass of organic compound and percentage of nitrogen can be found out by unitary method. Following basic reactions involved may be helpful to us to better understand theoryinvolved:



Break down the numerical problem in various steps:

First of all, you are to find the percentage of carbon, hydrogen and nitrogen by applying various formulae as given in next step. You must find sum of all the three percentages. If the total percentage comes out to be 100, well and good, otherwise difference corresponds to oxygen. This point, we must remember.

Apply relevant formulae & making calculations:

Percentage of C, H and N can be calculated by applying formulae as given below:

(a) Percentage of carbon: 5.9g of organic compound contains 2.4g of carbon.

Hence, percentage of carbon = $\frac{2.4 \times 100}{5.9} = 40.67$

(b) 5.9 g of the same organic compound contains 0.5g of hydrogen. Hence,

percentage of hydrogen = $\frac{0.5 \times 100}{5.9} = 8.47$

(c) Percentage of N by kjeldahl's method:

Mass of organic compound taken =

2.59g Initial volume of 1M H₂SO₄ taken =

52mL

Vol. of 1M NaOH used to neutralise the residual 1M H₂SO₄ = 60 mL or 60 mL of 1M NaOH solution \equiv 30 mL of 1M H₂SO₄ (residual)

\therefore Volume of 1M H₂SO₄ used for absorption of liberated NH₃ gas = 52-30 = 22 mL

or 22 mL of 1M H₂SO₄ = 44 mL of 1M NH₃ liberated

We know that 1000 mL of 1M NH₃ \equiv 17g of NH₃ or 14g of N

\therefore 1mL of 1M NH₃ solution = $\frac{14}{1000}$ g of N and 44 mL of 1M NH₃ solution = $\frac{14 \times 44}{1000}$ g of N.

This much nitrogen is present in 2.59g of organic compound

\therefore Percentage of nitrogen = $\frac{14 \times 44 \times 100}{1000 \times 2.59} = 23.78$

Sum of all percentages of C, H & N = 40.67 + 8.47 + 23.78 = 72.92

(d) Percentage of oxygen:

Since percentage sum of C, H and N is not 100, \therefore Oxygen is also present & % of oxygen = 100 - 72.92 = 27.08.

(e) Determination of Empirical formula:

Knowing all the four percentages, empirical formula of the organic compound can be determined by following the procedure as given earlier 12.1 and as given below:

<i>Element</i>	<i>Percentage</i>	<i>Divided by Atomic mass</i>	<i>Dividend</i>	<i>Divide by the lowest value</i>	<i>Whole Number</i>
<i>C</i>	40.67	12	3.39	1.70	2
<i>H</i>	8.47	1	8.47	1.70	5
<i>N</i>	23.78	14	1.70	1.70	1
<i>O</i>	27.08	16	1.70	1.70	1

∴ Empirical formula of the given organic compound = C₂H₅NO.

(f) Determination of molecular formula of organic compound.

Molar mass of the given organic compound is 59u. Dividing molar mass by empirical formula mass, value of n can be found out. Multiplying empirical formula by n, molecular formula of the organic compound can be determined.

$$n = \frac{\text{Molar mass}}{\text{Empirical formula mass}} = \frac{59}{12 \times 2 + 1 \times 5 + 14 \times 1 + 16 \times 1} = \frac{59}{59} = 1$$

∴ Molecular formula of the organic compound is C₂H₅NO × 1 = C₂H₅NO

(g) Application of laboratory knowledge and determination of structure of the organic compound.

Laboratory knowledge and characteristics of the compound like solubility in water and burning of the compound without smoky flame indicate aliphatic nature of the compound. Liberation of ammonia gas on heating with aqueous solution of NaOH indicate the presence of $\text{-}\overset{\text{H}}{\text{C}}\text{-NH}_2$ group in the compound.

Let us try to write structure of the compound after taking out $\text{-}\overset{\text{H}}{\text{C}}\text{-NH}_2$. We are left with (C₂H₅NO – CONH₂) – CH₃ group.

∴ Compound can be $\overset{\text{H}}{\text{H}}\text{C} \cdot \overset{\text{H}}{\text{C}}\text{-NH}_2$

Molar mass of this compound is:

$$3 + 12 + 12 + 16 + 14 + 2 = 59u$$

Molar mass of the given organic compound is also 59u.

Hence, the given organic compound is: $\overset{\text{H}}{\text{H}}\text{C} \cdot \overset{\text{H}}{\text{C}}\text{-NH}_2$

Name of the organic compound is: Acetamide or Ethnamide

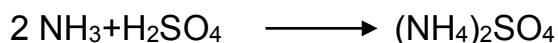
12.2.5. Relook into the entire process:

(a) After solving the numerical problem, you are advised to relook into the usage of the correct formula along with calculations to reach correct result.

(b) Physical and chemical tests help you in distinguishing and discriminating between soluble and insoluble compounds, aliphatic and aromatic nature and

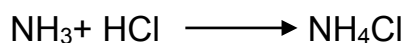
presence of the functional group. Molar mass of the compound helps us in arriving at the molecular formula of the compound and ultimately taking us to the correct structural formula of the organic compound.

(c) In kjeldahl's method of estimation of nitrogen, the mole concept studied in unit 1 in class XI helps us to understand the proper stoichiometry of ammonia and dibasic sulphuric acid. While calculating the volume of ammonia released & absorbed by conc. H_2SO_4 this may be remembered that 2 moles of ammonia are completely absorbed by 1 mole of conc. H_2SO_4 as given in the following equation:



2 mole: 1 mole

If numerical involves monobasic acid like HCl, the stoichiometry will be 1:1



12.2.6. Practice for similar problem:

Numerical No. 2: 9.3g of organic liquid of 1.02g/cm^3 density is found to contain 7.2g carbon and 0.7g of hydrogen. 4.65g of the compound after kjeldilisation was absorbed in 50mL of 1M H_2SO_4 . The residual acid on titration with 1M NaOH solution was found to consume 54mL of 1M NaOH solution. The liquid is immiscible with water and the acidic solution forms diazonium salt with NaNO_2 solution with HCl and gives orange and red dye with alkaline solution of phenol at 273-278K.

Derive structure yourself

Ans: $\text{C}_6\text{H}_7\text{N}$

Numerical No. 3: 1.07g of the organic compound on analysis gives 0.84g of carbon and 0.09g of hydrogen. The same amount of the organic compound on heating with reduced copper oxide at 573K in an atmosphere of CO_2 evolved 846 mL of N_2 at 335 mm pressure (aqueous tension at 573K = 15 mm). The organic compound is insoluble in water, gives sooty flame on heating and forms diazonium salt on treating with NaNO_2 & HCl at 273-275K. Write the probable structure of the organic compound of the organic compound melts at 43°C what is the structure of the organic compound?

Ans: $\text{C}_7\text{H}_9\text{N}$

Organic Chemistry – II

Some Basic Principles and Techniques and Haloalkanes and Haloarenes

Quantitative Analysis of Halogens Problem:

1. Numerical Problem:

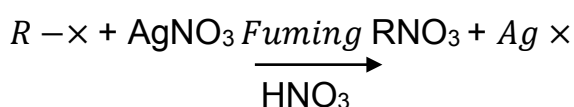
1.47g of organic compound contains 0.72g of carbon and 0.04g of hydrogen. Same amount of organic compounds on heating with AgNO_3 and fuming HNO_3 in carius tube gave 2.87g of AgCl . The organic compounds is insoluble in water and does not get hydrolysed with aqueous NaOH . Molar mass of the compound is 147. What is the molecular formula of compound. Write the probable structures of various compounds. If m.p. of the organic compounds is 53°C , what is the compound. Write IUPAC name of the organic compound

12.3.1 Read and read with reasoning:

Read statement of the problem carefully and read it again logically to solve the problem.

12.3.2 Correlate the problem with related theories:

After reading the problem with care, you can find percentage of carbon and hydrogen by using unitary method. For quantitative estimation of chlorine in the present numerical on halogens in general, recall the carius tube method wherein halogen containing compound is heated with fuming HNO_3 and AgNO_3 in the carius tube. In this way, halogen present in the organic compound is converted into halide.



($x = \text{Cl, Br, I}$) Δ

$\text{Ag}x$ is filtered, heated and dried.

Knowing mass of organic compound taken and dry $\text{Ag}x$ thus obtained, percentage of halogen can be calculated by using the stoichiometry of 1:1; that is one mole of x will produce one mole of $\text{Ag}x$ let mass of organic compound taken = m g

Mass of $\text{Ag}x$ obtained = m_1 g

$$\begin{aligned} \text{(i) Percentage of Cl} &= \frac{35.5 \times m_1 \times 100}{\text{Molar mass of AgCl} \times \text{Mass of organic compound taken}} \\ &= \frac{35.5 \times m_1 \times 100}{143.5 \times \text{Mass of organic compound taken}(m)} \end{aligned}$$

$$(ii) \text{Percentage of Br} = \frac{80 \times m_1 g(\text{Mass of AgBr formed}) \times 100}{188 \times \text{Mass of organic compound taken}(m)}$$

$$(iii) \text{Percentage of I} = \frac{127 \times m_1 g(\text{Mass of AgI formed}) \times 100}{235 \times \text{Mass of organic compound taken}}$$

Break down numerical problem in various steps:

- Determination of percentage of C, H and Cl.
- Determination of empirical formula.
- Determination of molecular formula.
- Derivation of the probable organic compounds.
- Derivation of probable structures.
- Identification of the probable structures.

12.3.4 Apply relevant formulae:

$$(a) \text{Percentage of C} = \frac{\text{Mass of carbon} \times 100}{\text{Mass of organic compounds}}$$

$$(b) \text{Percentage of H} = \frac{\text{Mass of hydrogen} \times 100}{\text{Mass of organic compounds}}$$

$$(c) \text{Percentage of Cl} = \frac{35.5 \times \text{Mass of AgCl} \times 100}{143.5 \times \text{Mass of organic compounds taken}}$$

Make precise and meticulous calculations:

(a) Percentage determination of Elements:

$$\text{Percentage of C} = \frac{\text{Mass of carbon} \times 100}{\text{Mass of organic compounds taken}} = \frac{0.72 \times 100}{1.47} = 48.98$$

$$\text{Percentage of H} = \frac{\text{Mass of hydrogen} \times 100}{\text{Mass of organic compounds taken}} = \frac{0.04 \times 100}{1.47} = 2.72$$

$$\text{Percentage of Cl} = \frac{\text{Mass of AgCl formed} \times 35.5 \times 100}{\text{Mass of organic compound taken} \times \text{Molar mass of AgCl}} = \frac{2.87 \times 35.5 \times 100}{1.47 \times 143.5} = 48.30$$

(b) Percentage determination of Elements:

Empirical formula of organic compounds can be determined as per details given in Table below:

Name of Element	Percentage	Atomic Mass	Dividend by lowest number	Divide by whole number
C	48.98	12	4.08 ÷ 0.68	6
H	2.72	1	2.72 ÷ 0.68	4
Cl	48.30	35.5	1.36 ÷ 0.68	2

Empirical formulae of organic compound is C₆H₄Cl₂

Empirical formulae mass = 12 × 6 + 1 × 4 + 35.5 × 2

$$= 72 + 4 + 71 = 147.4$$

Molar mass of organic compound = 147

$$\therefore n = \frac{\text{Molar mass}}{\text{Empirical formula mass}} = \frac{147}{147} = 1$$

\therefore Molecular formula is $C_6H_4Cl_2$

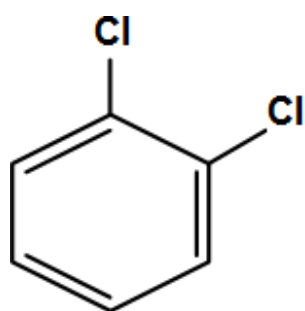
d) Derivation of probable organic compounds:

Physical properties like insoluble nature of the dichloro compound and non-hydrolysis nature with aqueous NaOH and the molecular formula, $C_6H_4Cl_2$ indicate that organic compound is not aliphatic in nature. The compound may be aromatic.

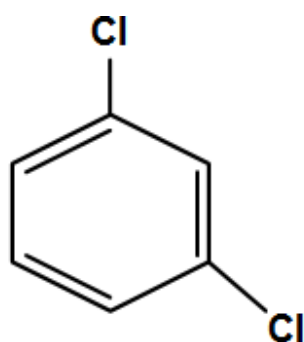
\therefore the organic compounds can be dichlorobenzene

e) Probable structures:

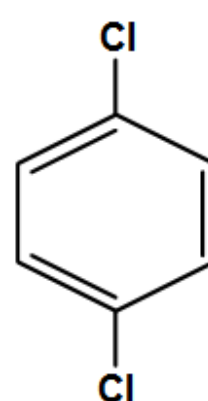
Following can be the probable structures of the given organic compounds in which two chlorine atoms are attached to the benzene ring at ortho, meta and para positions.



o-dichlorobenzene
($C_6H_4Cl_2$)

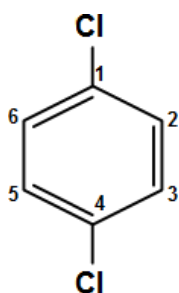


m-dichlorobenzene
($C_6H_4Cl_2$)



p-dichlorobenzene
($C_6H_4Cl_2$)

(f) m.p. of the given organic compounds is $53^\circ C$. Literature survey reveals that $53^\circ C$ is the m.p. of p – dichlorobenzene. The other two isomers have lower melting points. Hence the organic compounds is:



1, 4- dichlorobenzene

12.3.6. Relook into the entire process:

After solving the numerical problem you are advised to have a relook into the whole process starting from theory involved, formulae applied and the calculations done by you. This always helps you in reconfirming your result. Similarly you can solve numerical problems related to bromo and iodo compounds changing the atomic & molar masses.

12.3.7. Practice the following similar problems:

Numerical No. 2:

0.246g of an organic compound on complete combination with hot reduced CuO gives 0.198g of CO₂ and 0.1014g of H₂O. 0.37g of the same compound on treatment with fuming HNO₃ and AgNO₃ gives 0.638g of AgBr. What is the molecular formula of the organic compound.

(C₂H₅Br)

Numerical No. 3:

197g of organic compound is found to contain 6g of carbon, 0.5g of hydrogen. 3.94g of the same compound on heating with fuming HNO₃ and AgNO₃ formed 7.05g of AgI. The compound is insoluble in water and can be prepared in laboratory by heating propanone with I₂ and NaOH solution. Find the empirical and molecular formula of the organic compound.

(CHI₃)

12.3.8. Extension of the Module:

This module can further be extended to calculate percentage of sulphur making use of the Principle of conversion of sulphur as BaSO₄ on heating organic compound with conc. HNO₃ and BaCl₂. Similarly phosphorus present with H₃PO₄ can be precipitated as ammonium phosphomolybdate, (NH₄)₃ PO₄.12 MoO₃ on heating with conc HNO₃ and ammonium molybdate. Phosphoric acid obtained by heating organic compound containing phosphorus with conc. HNO₃ can also be precipitated Mg(NH₄) PO₄ on treatment with magnesia mix (Mg Cl₂+NH₄Cl+NH₃ solution). Mg(NH₄) PO₄ on ignition is converted into Mg₂P₂O₇.

Percentage of sulphur and phosphorus can be calculated by the following formulae as given in NCERT book (Class XI).

$$(a) \text{ Percentage of Sulphur} = \frac{32 \times \text{Mass of BaSO}_4 \times 100}{233 \times \text{Mass of organic compound taken}}$$

(b) (i) Percentage of Phosphorus = if precipitated & liquid as (NH₄)₃ PO₄.12MoO₃

$$= \frac{31 \times \text{Mass of ammonium phosphomolybdate} \times 100}{187 \times m}$$

(c) Percentage of *Phosphorus* = if precipitated as MgNH_4PO_4 and Ignited as $\text{Mg}_2\text{P}_2\text{O}_7$)

$$= \frac{62 \times \text{Mass of } \text{Mg}_2\text{P}_2\text{O}_7 \times 100}{222 \times m}$$