

Quantitative Methods in Chemistry
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Lecture-03
Defining Other Parameters for Concentration (% , ppm/ppb, p-value)

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The slide contains handwritten notes on a white background with a black border. At the top left is the NPTEL logo. At the top right is the logo of the Indian Institute of Science Education and Research, Bhopal. The text is written in blue and red ink. The title 'Quantitative methods in Chemistry' is in red, followed by 'Week 1 Lecture 3' also in red. The main definition is:
$$\text{Normality} = \frac{\text{no. of moles}}{\text{Vol. of soln (L)}} \times \text{neg.} \rightarrow \begin{matrix} 1 \text{ mol} \\ \text{H}^+ \\ \text{e}^- \\ 1 \text{ eq.} \end{matrix}$$
 A bracket under 'no. of moles' is labeled 'Molarity'. Below this, three definitions are given:
$$\text{Weight percent / mass percent} \Rightarrow \frac{\text{mass of solute (g)}}{\text{mass of solution (g)}} \times 100\%$$

$$\text{Volume percent} \Rightarrow \frac{\text{Volume of solute (ml)}}{\text{Volume of solution (ml)}} \times 100\%$$

$$\text{Weight/volume percent} \Rightarrow \frac{\text{mass of solute (g)}}{\text{Volume of soln. (ml)}} \times 100\%$$

Today, we are going to the third lecture of the first week in quantitative methods in chemistry. In the last 2 classes we defined what is the definition of molarity, molality and normality, briefly overview in what I did with normality last class is that normality is defined by number of moles present in a given volume of solution in liters times the number of equivalents where the number of equivalence is defined as that amount of substance of a chemical that furnishes 1 mole of H⁺ electrons are 1 for univalent 1 by 2 for a divalent, 1 by 3 for a trivalent and so on.

So, now that we see this basically this is nothing but molarity. So, normality will be given by the product of molarity to the number of equivalence okay. So, now let us go ahead and define a few other parameters that are routinely used in chemistry and also daily life to define concentration of different chemicals. The first one is weight percent. This is more precisely call us mass percent nowadays.

This is defined as the mass of solute in grams divided by the mass of solution in grams multiplied by 100 gives you a percentage along with it. There are also other similar units, I am going to define all of them as we go forward. The other one is volume percent. This is defined as the volume of solute divided by volume of solution. Of course, in the same units if you are using ml it is better to use ml both the numerator and the denominator multiplied by 100 to get percentage.

And the third unit which is also quite common is weight volume percent, which is given by the mass of solute in grams divided by volume of solution in times 100, gives you a percentage. The major differences between all of this is that this is mass by mass and this is volume by volume. On the other weight percent weight by volume percent as mass by volume and similar to molality, one would observe that the mass percent is independent of temperature.

While on the other hand the other 2 percentages are dependent on temperature as the volume of solution could change as a function of temperature. On the other hand volume percent could have volume of solute that also in addition changes in function of temperature. So basically of the 3, only mass percent is independent of temperature. Why do not we take some examples.

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The slide contains handwritten notes with the following content:

- HNO₃ 70% w/w** = 70 g of HNO₃ / 100 g of solution (labeled "biscuit")
- Isopropanol-water 40% v/v** = 40 ml of iPrOH / 100 ml of soln. (labeled "liquid-liquid")
- 9% w/v NaCl chips** = 9 g of NaCl in 100 ml of soln. (labeled "solid-liquid")
- 50% w/w NaOH** calculation:
 - $\rho = 1.53 \text{ g/ml}$
 - $V = \frac{100 \text{ g}}{1.53} = 66 \text{ mL}$
 - 50 g NaOH + 50 g of water
 - 50g / 66 mL
 - $\rho_{\text{NaOH}} \sim 2.3 \text{ ml/g} \sim 30\% \text{ v/v}$
 - $\sim 76\% \text{ w/v}$

So let us start with an example of nitric acid. Nitric acid is generally sold as a 70% weight by weight in the market, this indicates you have 70 grams of nitric acid in 100 grams of solution.

This is a routine concentrated nitric acid we end up using in the laboratories. On the other hand, when you are going for volume, volume, let us take an example. Let us say you have a solution of isopropanol in water 40% volume by volume.

This indicates you have 40 ml of isopropanol in 100 ml of solution and as you are able to realize this is one case where when you are dissolving a liquid in another liquid you are going to be defining it as volume by volume. On the other hand, if you want to take an example of weight by volume 9% solution of weight by volume of NaOH is actually what is used in drips. So this indicates you have 9 grams of sorry NaOH NaCl of NaCl in 100 ml of solution.

So what we are able to see here is that these are very different ways of expressing concentration. And in the last case you are looking at a solid that is dissolved within a liquid and quite commonly are able to understand that weight by weight could be used when you are having 2 solids that mixed with each other. That is one easy way of expressing their concentration. If you take a look at the biscuit packets that you end up eating, at the back of all this you would have the contents that is given in terms of carbohydrates, fats and proteins given per 100 grams.

So basically they would have said carbohydrates are 70 grams that is present within the 100 grams of a given biscuit. This indicates you have a 70% weight by weight of carbohydrate that is present in the biscuit that you are eating okay. Now that we have seen at one has to be very careful when something is defined okay, I am giving you X% of something this makes no sense unless and until you say it is a weight by weight that is a mass percent or volume percent or a weight by volume percent.

Let us take an example here yet again 50% weight by weight, NaOH which has a density of 1.53 units grams per ml. So now let us try to convert this 50% NaOH from weight by weight to weight by volume, so you are able to realize in this case you have 50 grams of NaOH which is a pellet. These are nice, small pellets that you will see + 50 grams of 50 grams of water. In this case, what is going to end up happening is that you have 100 grams of water.

But remember the density is 1.53. So the overall volume is going to be 100 divided by 1.53, which is approximately equal to about 66 ml. So now when you go back and do the calculation of what how does this transpire, how does a 50% weight by weight transfer into weight by volume, you are going to have 50 grams per 66 ml of solution. This roughly translates to something like 76% weight by volume.

So one has to be extremely cautious. Of course, you can do the exercise again, by trying to convert the weight by weight into volume by volume, which we will do in a moment but when one is able to see is that if you have not clearly mentioned whether the 50% is weight by weight, or weight by volume, you are going to have a confusion and how would we determine what is the volume by volume of this entire solution would be that we have calculated the volume of solution here.

And then all that we need to ask how much volume does 50 grams of NaOH occupy. And for this you need the density of NaOH pellets. And that is about 2.3 units. So what you are able to see here is that the volume is going to be somewhere close to 20 ml. So you have a 20 by 66 ml, so which is going to be approximately one third . So you can imagine something close to 30 to 40% volume by volume.

So one is able to understand if the units are not appropriately provided, you are going to have different numbers that come up for the same amount of chemical that is present in the total volume of solution. So therefore, whenever you mentioned percentage always good the units that you are working with.

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parts per million

$$C_{\text{ppm}} = \frac{\text{mass of solute}}{\text{mass of solvent}} \times 10^6 \text{ ppm}$$

dilute $\sim 1 \text{ g/mL}$

$$C_{\text{ppm}} \sim 6 \text{ ppm} = \frac{\text{mass of solute (mg)}}{\text{mass of solvent (kg)}} \times 10^9 \text{ ppm}$$

$C_{\text{ppm}} \sim 6 \text{ ppm}$ $6 \text{ mg in } 1 \text{ L soln.}$

$C_{\text{ppb}} \sim 4 \text{ ppb}$ $4 \text{ } \mu\text{g in } 1 \text{ L soln.}$

Similar to the mass percent that you have learned there are also units that go as parts per million in concentration is given by the ratio of mass of the solute to that of the mass of the solution times 10 power 6, and you are able to realize the 10 power 6 factor is what makes it parts per million. If you multiply this by 10 power 9, that is going to make it parts per billion and of course 10 power 12 would make it parts per trillion and so on and so forth very dilute solutions.

And the important thing one is able to realize is that going back to parts per million, this can be rearranged in a way where if you are expressing the mass of the solute in milligrams, and then the mass of the solvent in liters, so you are going to end up the definition where mass of the solute in milligrams to that of mass of solvent in kilogram would be the definition of ppm.

And if you are discussing, if you are assuming that the solutions are dilute, then one can imagine that the density will be equal to 1 gram per ml. So therefore, what ends up happening, the denominator, one can understand is to switch mass into volume and the kilogram will get converted to liters. So basically, if somebody says concentration in ppm, let us say 6 ppm of a given ion, this indicates you have 6 milligrams in 1 liter of solution.

So, that is basically the definition of parts per million. And once again as I said this is very similar to the mass percent that you have seen a few moments earlier. And similarly, when someone says the concentration of something in ppb is something like 4 ppb, this indicates you

have 4 micrograms and 1 liter of solution okay. So, now that we have seen these 2 definitions, the next thing that we will be moving towards is the definition of some of the thermodynamic parameters.

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The slide contains the following handwritten equations and notes:

$$aA + bB \rightleftharpoons cC + dD$$

$$\Delta G = \Delta G^\circ + RT \ln Q \rightarrow \text{reaction co-ef.}$$

$$Q = \prod_i a_i^{\nu_i}$$

at equilibrium $\Delta G = 0 \Rightarrow \Delta G^\circ = -RT \ln K_{eq}$ (equilibrium const.)

$$K = \prod_i a_i^{\nu_i}$$

$$K_{eq} = \frac{a_c^c \cdot a_d^d}{a_A^a \cdot a_B^b}$$

$$K_{eq} = \frac{a_c^c \cdot a_d^d}{a_A^a \cdot a_B^b}$$

Before I move ahead, I would like to define what is equilibrium. Let us take a simple example of $aA + bB$, where A and B are reactance and small a and small b are their stoichiometry coefficients. This is in the formation of $cC + dD$, where capital C and capital D are the products and small c and small d are the stoichiometry coefficients, then for such an equilibrium, the delta G is going to be given by $\Delta G = \Delta G^\circ + RT \ln Q$ of the reaction coefficient.

The reaction coefficient is nothing but the product of the activities of all of the engaging chemicals raise to the power of the stoichiometry. When equilibrium is established, delta G goes to 0. This implies $\Delta G = 0 = -RT \ln K_{eq}$ where this K equilibrium is your equilibrium constant. What is the difference between the reaction quotient and the equilibrium constant is that as the reaction has not reached equilibrium, Q is determined by the concentration of the various components in that reaction at that given point of time.

While after having reached equilibrium, the net concentrations of neither the reactants or the products are going to change. So, the equilibrium constant is determined by taking such a ratio. So, once again K has a similar definition of $\prod_i a_i^{\nu_i}$ to the μ_i , where the reaction has reached

equilibrium in this case, and the important thing one has to understand, in the reaction given about the K equilibrium will be given by activity of c to the power C times activity of D the power d times activity of a power - a, an activity of B to - b.

So basically, that is what we are trying to say, μ_i is determined whether you are going to be in the reactants or the products, the products being the positive reactions are multiplied by - 1. So, therefore, you get $\sum \nu_i \mu_i$. Of course, in standard textbooks, you are going to see this as something like this. So, this is nothing but the equilibrium constant which is expressed in terms of activity.

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The image shows handwritten notes on a slide. At the top left is the NPTEL logo. At the top right is the logo of the Indian Institute of Technology Bombay. The main text is written in blue and red ink. It starts with the word 'Activity' underlined. Below it, 'SOLVENT' is circled in red, followed by 'Raoult's Law'. To the right, the equation $K = \prod_i a_i^{\nu_i}$ is written. Below that, $a \propto X_{\text{solvent}}$ is written, followed by $a \rightarrow X$ and $X \rightarrow 1 \Rightarrow a = \gamma X$. A red arrow points from $a = \gamma X$ to $a = X$. Below this, $\gamma \rightarrow 1$ is written. To the right, $a = X$ is written in red. Below this, 'SOLUTE' is circled in red, followed by 'Henry's Law'. To the right, $a \propto X_{\text{solute}}$ is written, followed by $a = \gamma X_{\text{solute}}$. A red circle is drawn around $X \rightarrow 0$, with a red arrow pointing to it from the word 'low' written in red. Below this, $\gamma \rightarrow 1$ and $a \rightarrow X$ are written.

Getting to the discussion of activity we are trying to understand activity because we are expressing the equilibrium constant in terms of the products of activities of the involved species. So now let us try to define activity for a solvent and this comes back from a Raoult's law where when 2 solutions are added we tried to determine the partial vapor pressure that they exert . And therefore we try to determine what is the actual vapor pressure versus the determined vapor pressure to understand any deviations between the interaction that would end up coming between the 2 entities that you are interacting.

And in this definition, the activity would go proportional the mole fraction and as we all know, that the Raoult's law will be behaved when this solvent is more pure to itself. So meaning that

activity will tend to the mole fraction, when mole fraction tends to 1, this indicates a small fraction tends to 1 the activity coefficient gamma also tends to 1, that is for a pure solvent, the activity coefficient is imagined or is assumed to be 1.

On the other hand for solutes this is determined from the Henry's law. The Henry's law helps you understand how much amount of solute gets dissolved in a solvent. And we know that Henry's law obeyed when the concentration of solute is low. So, going back to the definition of activity once which is once again proportional to the mole fraction. So, let me define this as solvent and in this case a small fraction of solute.

Here activity will be equal or close to the constant the mole fraction of solute with gamma absolute when chi tends to 0, so in this condition gamma tends to 1 and activity tends to chi okay. So, what we are able to understand here is how was activity approximated to the concentration in terms of mole fraction for solute versus a solvent, that we iterate that for a solvent, when the solvent is pure, you tend to associate activity to its small fraction.

On the other hand in terms of a solute, when the solute is present at very low concentrations, you tend to approximate activity to its mole fraction.

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NPTEL

write - $K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \gamma \rightarrow 1.$

$aA + bB \rightleftharpoons cC + dD$

p-value
p-function

$pH = -\log [H_3O^+]$ ←
 $pX = -\log [X]$ → Molarity.

$2 H_2O \rightleftharpoons H_3O^+ + OH^- \quad a_{pure} = 1$

$K_w = \frac{[H_3O^+][OH^-]}{[H_2O]^2} = [H_3O^+][OH^-]$

$25^\circ C \quad K_w = 10^{-14} \Rightarrow [H_3O^+] = 10^{-7} = [OH^-].$

$pH @ 25^\circ C = -\log [10^{-7}] = 7$

14

Traditionally in chemistry is that the K equilibrium will be given by the concentrations of the reactants and the products directly. Of course, here we are assuming the fact that the activity coefficient tends to 1. So this is a major assumption that we end up doing. And remember, whenever we say concentrations, it does not mean that concentration is given molarity it is actually referenced with a unit concentration that ends up coming up in these cases.

So that is in each of this case, the given concentration is a reference to 1 molar are 1 molar. So this will ensure that the concentration of the units of equilibrium remain unit less okay, now that we have understood this, let us quickly go ahead and understand what is that we are trying to here, we have defined for equilibrium reaction $aA + bB \rightleftharpoons cC + dD$. How is the equilibrium constant define.

This is going to be crucial because we are going to be defining a p value of concentration. Let us start with the easiest p value one can understand that is the pH , pH is defined as $-\log$ of H^+ of hydronium ion concentration in solution. So, basically what we are trying to say for any parameter or any chemical x , the pX value the p value of the p function is defined as $-\log$ of concentration of X in molarity.

And this comes from the fact that okay pH definition is defined this way. Now therefore, let us ask for water. What is the value of pH . I am pretty sure all of you are going to write me answer, the pH value for water is 7, but let us take a look at how does that come up. So, 2 molecules of water is going to end up breaking into hydronium ion and the hydroxide ion. So, for such a process, K_w is going to be given by $H_3O^+ + OH^-$.

The product of concentrations of the hydronium ion and the hydroxide ion divided by the concentration of water square, because the coefficient for water here is 2. But remember activity of a pure solvent is set to 1, so therefore, the denominator goes to 1. It is a general consumption among students that we tend to put water as 1 just because it is a next that is not correct, we put the activity of anything that is pure to 1.

So, therefore, the denominator goes to 1. Thus K_w gets reduced to the product of concentrations of hydronium ion to that of the hydroxyl ion. So, now when you have something like this, one is able to understand why only when the hydronium ion is found via the hydroxyl ion. So the concentrations of hydronium ion and the hydroxyl ion are going to be same. So this can be reduced to the concentration of hydrogen ions square.

When these experiments are done to understand what is the K_w of water, let us say at 25 degrees Celsius, it was determined that K_w is 10^{-14} . So immediately, you are able to understand the concentration of H_3O^+ is 10^{-7} which is also the same concentration as the hydroxide ion. So what ends up happening pH at 25 degrees of pure water, and the $-\log$ of 10^{-7} , that will become 7.

So this is how you actually see the concentration of water under neutral conditions. Let us take a quick look how does pH change with temperature, I was very careful in trying to tell you the pH of water at 25 degrees is 7. Now let us take a look at what happens if the temperature changes.

(Refer Slide Time: 22:32)

NPTEL Van't Hoff eq.

$$\ln\left(\frac{K_1}{K_2}\right) = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

eq. const. enthalpy change Temp. 1 atm

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

"dissociates" "supply energy" $\Delta H^\circ = +ve$ $R = 8.314 \text{ J/Kmol}$ $T = \text{Kelvin}$

$$\ln\left(\frac{K_1}{K_2}\right) = -\frac{\Delta H^\circ}{R} \left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$T_2 > T_1 \rightarrow +$

$K_1 < K_2$
$T_1 \quad T_2$
25°C 50°C
$K_w = 10^{-14} \quad 10^{-13}$

$K_w(T_2) 10^{-13} \Rightarrow pH = 6.5!$

$\ln\left(\frac{K_1}{K_2}\right) = -ve$

This takes us to the Van't Hoff equation which relates equilibrium constant capital K to that of the enthalpy of reaction and temperature in this fashion. So when you have this equation, of course, this is under the equilibrium conditions, one is able to understand you relate equilibrium

constant to that of temperature assuming entropy change is a constant as a function of temperature. This is assumption in which this has been derived.

And the 0 here indicates is done under 1 atmosphere pressure, this does not indicate temperatures are constant because you are indeed varying the temperature. So, now, when you have an equation like this one has to understand what will be the enthalpy change when water dissociates to form hydronium ion and hydroxide ion. As I just mentioned the word dissociates we are able to imagine that okay you got to supply energy.

Generally breakage is associated by supplying of energy bond formation ends up releasing energy. So when you mean you are going to supply energy, this indicates that the enthalpy change for such a process, it is an endothermic process because you are going to supply energy meaning that energy is taken from this surroundings. Therefore, you are going to have ΔH , which is going to be positive for such a process.

So, what ends up happening your lawn of K_1 or K_2 is going to have a number R is the universal gas constant, which is also positive. And when you do a quick arithmetic here, what is going to end up happening is $T_2 - T_1$ by $T_1 T_2$ where T is an absolute and Kelvin scale, absolute temperature in Kelvin scale. So, if for a case that T_2 is greater than T_1 , what is going to end up happening. This entire thing will be a positive term.

And we just knew or we just summarized that the enthalpy change for dissociation of water is endothermic. So that is going to be R is positive. So this will result in the fact that lawn K_1 over K_2 is going to be negative. This just indicates the fact that K_1 is smaller than K_2 . And I just mentioned, let us say K_1 is a temperature T_1 and K_2 is a temperature T_2 . And let us say you are a 25 degrees Celsius to start with, and you increase the temperature to 15 degrees, what is going to end up happening is that the K_2 is going to be smaller.

Let us just assume some numbers. These are not exact numbers, just giving a feeling it is K_w is 10^{-14} at 24 degrees and the number has to go higher. That means that we can imagine something like 10^{-13} . So what ends up happening, K_w at T_2 would be let us say it is 10^{-13} .

power - 13. This would result in pH of water at neutral conditions to be 6.5. So this indicates that the neutral pH reference as a function of temperature changes.

Basically the amount of hydronium ions and hydroxide ions, as you change temperature also changes. So that is the important lesson that you end up learning out of this exercise. But I hope I have made you understand what is the pH scale.

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The slide shows a whiteboard with the following content:

- Top Left:** NPTEL logo.
- Top Right:** IIT Bombay logo.
- Center:**

$$pH = -\log [H_3O^+]$$

neutral 7 @ 25°C

pH < 7 acidic
pH > 7 basic

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$K_A = \frac{[H_3O^+][A^-]}{[HA][H_2O]} \rightarrow 1$$

$$-\log K_A = -\log [H_3O^+] - \log \left(\frac{[A^-]}{[HA]} \right)$$

$\underbrace{-\log K_A}_{pK_a}$ $\underbrace{-\log [H_3O^+]}_{pH}$ $\underbrace{-\log \left(\frac{[A^-]}{[HA]} \right)}_{\text{Henderson Hasselbalch equation}}$

$$pH = pK_a + \log \left(\frac{[A^-]}{[HA]} \right)$$

$\log(10) \rightarrow 10^x$
- Left Side:**

Hcl

Acetic acid

CH_3CO_2H

$H_2PO_4^-$
- Bottom Left:** A person in a blue shirt is visible, looking at the whiteboard.

Basically, it is going to be $-\log$ of H_3O^+ , we tend to say the pH of neutral water is 7 at 25 degrees Celsius. And what is going to end up happening if you have a pH less than 7, you call it acidic. And pH greater than 7 you call it basic. So similar would be the definition of pX, where X is any solute that you would like to quantify. Let us continue definitely these thermodynamic parameters for also other type of chemicals.

It is not just for water, we would like to define it. Let us try to define it for a weak acid something like HA. What do I mean by a weak acid, let us take for an example acidic acid. What do you mean by a weak acid. Let us first define a strong acid, so that our life is easy. Something like Hcl is a strong acid, because all the ions are diluted enough concentrations is going to dissociate completely to H^+ and Cl^- ions. On the other hand, when you have acidic acid, this will not undergo complete dissociation to H^+ ions and the acetate anion, largely because this is not an ionic compound.

These are actually covalent bonds that are formed between the oxygen and hydrogen. So what ends up happening is that you are still going to form the hydronium ion and the conjugate base of the weak acid. But what is going to end up happening this is going to be an equilibrium, which does not completely go to completion, meaning that unlike HCl, which totally dissociates to H^+ and Cl^- - here that does not happen.

So why do not we write the equilibrium constant, assuming low concentrations of the weak acid. So what is going to end up happening, you want to express it in terms of concentrations of the hydronium ion, the product of the conjugate base A^- divided by HA times H_2O , as we just mentioned, H_2O is in its pure state, so we will approximate to 1. So then what ends up happening is that we can take a quick logarithm on both the sides - $\log K_A$ is going to be - \log of H_3O^+ + - \log of A^- concentration of A^- divided by HA .

Now what ends up happening will be the definitely of pK_a is very similar to the pH this is nothing but - \log of K_a . And this we have already defined this is going to be pH . So, a quick rearrangement is going to help you understand pH will be given by $pK_a + \log$ of concentration of A^- divided by HA . This is a very important equation called the Henderson Hasselbalch, what this Henderson Hasselbalch equation helps us understand is that when you have a solution whose pH is very close to the pK_a of the weak acid, any small addition of base or acid does not change the pH too much.

So what do I mean by this. Let us take for an example phosphoric acid, phosphoric acid has 3 different pK_a s, one of the basic condition close to 12. Another close to neutral conditions 7.1 and another that is close to 2 which is acidic. So when you have such a situation and let say you want to prepare a buffer at pH 7, what you would end up doing is to have the diprotonated salt of the phosphoric acid and its conjugate base which will be HPO_4^{2-} - that you will combine in specific ratio to get the pH of the solution close to 7.

So you are able to understand if you have the equal concentration of the diprotic and uniprotic what is going to happen is that \log of 1 is going to be 0, you can set the pH very almost equal to

the pKa of phosphoric acid. Now, let us say even for large additions, let us say you want to add 10 X 10 times more concentration of the base, you are only going to have log of 10, which is going to change the pH of the maximum by 1.

So basically, this is the buffering limit. You can add small amounts of acid or base to the solution to an extent where the pH does not change, while the buffer is buffered close to the pKa of the weak acid. So this is basically the idea where you can exploit the Henderson Hasselbalch equation to prepare solutions that would have constant pH. For instance if you take water by itself although its pH of 7 small additions of strong acid or strong base would end up changing the pH of such a solution.

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The image shows handwritten notes on a whiteboard. At the top left is the NPTEL logo. At the top right is the logo of the Indian Institute of Technology Bombay. The text 'Mole - fractions' is underlined in blue. Below it, 'A and B.' is written. The mole fraction of A is given as $X_A = \frac{n_A}{n_A + n_B}$ and the mole fraction of B is $X_B = \frac{n_B}{n_A + n_B}$. A box contains the equation $X_A + X_B = 1$. Below these, the general formula for mole fraction is $X_i = \frac{n_i \text{ mol}}{\sum_{i=1}^n n_i \text{ mol}}$. To the right of this formula, it is noted that mole fractions are '(unitless)' and 'Temp. Independent'.

Another way of defining concentrations is by mole fractions. Let us assume that you have 2 solutes A and B to start with, and then let us say you have n A amount of chemical A, and n B moles of chemical B, then the mole fraction chi A will be defined as the ratio of the number of moles of A to the total number of moles of A and B. Of course you are able to understand B is going to be defined the same way.

And it makes immediate sense to say okay the sum of fractions should be equal to 1, when you add up all the fractions that go together. So, basically the definition of mole fraction chi i is going to be given by n i divided by sum over n i, where i goes from 1 to n okay. So, this is one

place where we are able to realize you are not worrying about the volume of solution that goes into it, we are not talking about the weight, but you are talking about the number of moles.

And remember the number of moles takes into factor that the ratio between the weight to that of the molecular weight which gives you the number of moles, immediately are able to realize, since this is this has a unit of moles and this is also going to have a unit of moles. The mole fraction is a unit less number. And also the other thing that one has to remember assuming that as a function of temperature the mass does not change.

Then mole fraction is also a temperature independent parameter that one can use for measuring. And this is one parameter that people end up using quite commonly when they are doing phase diagram types, analytical experiments okay. Now let us take a quick review on what all different concentration units that we have been exposed to.

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The slide contains the following handwritten text and diagrams:

- Top left: $M, m, N, \%, ppm, pX$
- Top right: pH, pKa with an arrow pointing to a flask labeled "50 mL of H_2O " and "dilution".
- Center: "50 mL soln. 100 mM NaCl" with a plus sign and "50 mL" below it.
- Left side: "[NaCl] = ?" and "50 mL 100 mM" with an arrow pointing down to "10 mM" and "+450 mL" next to it.
- Below left: $C = \frac{n}{V} \times M$ with arrows pointing to "2" and "1/2".
- Center: $M = \frac{n}{V}$ with "wt" above the "n" and a circled "M" to the right.
- Right side: $C_{initial} = C_{final}$ and $V_i \times M_i = V_f \times M_f$.
- Below right: $50 \times 100 = 100 \times M_f$ with "mL" and "mM" under the numbers.
- Bottom right: $M_f = 50 mM$.

Molarity, which goes as the number of moles per liter of solution in liters, your molality which is the number of moles that is present in 1 kg of solvent. Then we have normality, which goes as the number of moles that is present in 1 liter of solution, times the number of equivalents for that given chemical under the reaction that you are going to end up using. Then we just spoke about in percentages, which is weight by weight, volume by volume and weight by volume.

We also spoke about parts per million, billion, trillion and so on and so forth. Then we also discuss the pX scale where we exemplified it with an example of pH and also pKa. So, at this stage, what we are able to do successfully is that when you are having a solution under equilibrium, you are able to define the concentration of any given chemical in these many different units.

As we go forward, what we are going to end up understanding is how to interconvert these units across each other. So, those are the examples that we are going to end up seeing. Then let us say we are going to dilute solutions, how does the dilution work. So, these are the next parts of the lecture as we go forward okay. So, let us start taking some examples. Let us start with the easy molarity problem.

Let us say that you have 50 ml solution containing 10 or 100 millimolar of NaCl okay. Let us start to have some doodles out here, let us say your conical flask and you have 50 ml of solution that consists of 100 millimolar of NaCl. Let us say to this solution, I add another 50 ml of water. So basically what am I trying to do to already to this existing solution I am adding 50 ml of water.

The question now is what is the concentration of NaCl after this 50 ml has been added. This process I am sure all of us know is called diluted, basically have a slightly more concentrated solution and you want to dilute it and therefore you are adding more of the solvent making up the volume to the extent to which you want the final concentration at the desired level. So when you have something like this, what you are able to understand the amount of NaCl that remains within the conical is not changing.

So, what we are able to understand see *initio* which is the total amount of NaCl that you had initially is going to be equal to c_{final} , meaning that you are not adding any more NaCl into this, let us see we can say is the total amount of weight that you added. So, one is able to imagine that when you are having a molarity definition, you are going something like the number of moles divided by the volume of solution in liters.

As you are able to realize the molecular weight of NaCl is not going to change upon additional water, you are able to realize that this has the weight component in it, which is the concentration that we are trying to talk about. So, what we are able to see here the concentration will be given by the product of the volume times similarity. So, what we end up doing in such a case is that we try to say V_{initial} that is the volume initial times molarity initial will be equal to V_{final} times the final molarity.

So what is the initial volume that you had you had an initial volume of 50 ml. And then what is the initial molarity you had, you had 100 millimolar. And then the final volume after the addition of 50 ml is going to be 100 ml. So, you are asking the question, what is the final concentration of sodium fluoride, of course, very with simple arithmetic, you are able to realize you are going to end up with 50 millimolar.

So, you started with 100 millimolar and you are ending up with 50 millimolar. This is not surprising, because you are doubling the volume. When you double the volume to keep the same concentration, the molarity has to go half. So basically this is dilution. For instance, let us say that you want to go one 10th the initial concentration meaning that from 10 millimolar sorry, from 100 millimolar you want to go to 10 millimolar.

What you will end up doing is the initial solution which is 50 ml, you will end up adding 450 ml of water. So this will reduce the overall concentration of sodium chloride by 10 times. So this is one easy process. Let us take more such examples to understand how concentrations vary when you add different things.

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$50\text{ mL of } 100\text{ mM NaCl} + 50\text{ mL of } 50\text{ mM NaCl}$
 $V_1 \quad M_1 \quad \quad \quad V_2 \quad M_2$
 $V_1 * M_1 + V_2 * M_2 = V_3 * M_3 \quad \quad \quad V_1 + V_2 = V_3$
 $(50 \times 100) + (50 \times 50) = 100 \times M \quad \quad \quad M_3 = ?$
 $M = \frac{5000 + 2500}{100} = \frac{7500}{100} = 75\text{ mM}$
 $50\text{ mL } 100\text{ mM} \quad \quad \quad 100\text{ mL } 50\text{ mM}$
 $50 * 100 + 100 * 50 = 150 * M_3$
 $M_3 = \frac{10000}{150} = \frac{200}{3} = 66.67\text{ mM}$

Unlike the previous example, now let us say you have 50 ml of 100 millimolar sodium chloride, and to this you are adding 50 ml or 50 millimolar sodium chloride. So what will happen in this case, you are able to understand, the amount of sodium chloride is indeed increasing. But what we can try to do let us say this is $V_1 M_1$ and this is volume 2 molarity 2 you are actually adding volume 1 and volume 2 to get volume 3.

We are of course assuming that the volume does not change in such a process. Basically, we are adding V_1 to V_2 to get a V_3 . And you are asking what is the molarity of the final solution. So basically, in this equation, if you once again relate the concentrations before and after the process, what you are going to end up doing is that you are going to have V_1 times $M_1 + V_2$ times M_2 will be equal to V_3 times M_3 .

And let us quickly do this 50 times 100. It is always a good idea to write units, so that you are following which units you are ending up using 50 ml times 50 millimolar will be equal to what is the total volume of solution 50 + 50 that will be 100 ml times molarity, which will be in millimolar. So quick maths will be 5000 + 2500, the whole divided by 100 is going to be molarity in millimolar of NaCl.

So this is 7500. So what you are able to realize here is that when you take equal volumes of one less concentrated solution, when you mix them together, when you take equal volumes of those,

you are going to average 50 and 100 to get 75. Of course, this is only under the assumption that the $V_1 = V_2$. Let us quickly do also another example when V_1 is not equal to V_2 .

So let us assume to the initial solution of 50 ml 100 millimolar. You are adding 100 ml 50 millimolar, the concentration of sodium ions is relatable in these two, so what is going to end up happening 50 times 100 + 100 times 50 which of both are equal to 5000 will be equal 150 times M 3. So in this case, what is going to end up happening M 3 is going to be equal to 10,000 divided by 150.

What you are able to see here is that when you added 100 millimolar and 50 millimolar, but you added more of the 50 millimolar, the concentration tends to get very close to the one that you are adding a lot. So basically, this should give you an idea of framework that when you are adding different solutions, and if you are adding more of one versus less of the other, where do you expect the concentration to be okay.

So as you have seen in this 3 different examples, where you have a dilution versus adding different volumes with different concentrations, you should be able to determine what is the final concentration that comes up. Let us finish off with one simple and last question.

(Refer Slide Time: 42:10)

The slide shows a chemistry problem involving the mixing of two solutions. The initial solutions are 50 ml of 50 mM NaCl and 100 ml of 25 mM KCl. The final volume is 150 ml. The final concentration of NaCl is calculated as $\frac{50 \times 50}{150} = 16.67$ mM. The final concentration of KCl is calculated as $\frac{100 \times 25}{150} = 6.67$ mM. The analytical breakdown shows the dissociation of MgCl₂ into Mg²⁺ and 2Cl⁻, and the resulting concentrations: [Na⁺] = 16.67 mM, [K⁺] = 6.67 mM, and [Cl⁻] = 23.34 mM.

Initial Solutions:

- 50 mM NaCl (50 ml)
- 25 mM KCl (100 ml)

Final Volume: 150 ml

Final Concentrations:

- NaCl: $\frac{50 \times 50}{150} = 16.67$ mM
- KCl: $\frac{100 \times 25}{150} = 6.67$ mM

Analytical:

$MgCl_2 \rightleftharpoons Mg^{2+} + 2Cl^-$

1M 2M

[Na⁺] = 16.67 mM
 [K⁺] = 6.67 mM
 [Cl⁻] = 23.34 mM

16.67
 6.67

 23.34

Let us say you have a 50 millimolar solution of NaCl, let us say 50 ml of it. And you have another solution that is 25 millimolar of let us say KCl that is 100 ml. Let us say you combine both of this together, what will be the final concentration, what you are able to realize here is that you are having different salts that go in together. So in this case, you are having NaCl and KCl. And what you are able to realize is that NaCl you are diluting it to one third.

So you do not have to do any of the math. So you are going to have 50 divided by 3, which is approximately equal to 16.67 millimolar after diluted. On the other hand, you are going 2 thirds to the initial concentration. So you are going to have 25 multiplied by 2 by 3, which is approximately equal to 8.3 times as a 16.6 millimolar is quite interesting both come up to be similar, because I chose numbers in such a fashion.

So let us say if you had about 10 millimolar here, what is going to end up happening over to have 10 times 2 by 3 is going to be 6.6 millimolar. So but I hope you are able to understand the fact that you are diluting things in a way where the final concentration ends up coming since these 2 are not interacting. It is going to be this way. But remember one thing I smartly chose things in a way where you have a common anions.

So now let us quickly take a look at what is the analytical concentration that we are dealing with here. In this case, what is going to end up happening after this dilution you are going to have Na⁺ to the concentration of 16.67 millimolar k⁺ to the concentration let us say you started 10 millimolar, you are going to end up at 6.67 millimolar. On the other hand chloride ion, which comes from both of this is going to be a sum of 16.67 and 6.67.

That is going to end up to be something like 23.34 millimolar. So what you are able to realize is that you have a common anion of course, the concentration of that is going to be more. And a similar example could also be thought about where you have MgCl₂, which dissociates to form mg²⁺ and 2 cl⁻. And let us say you had 1 molar of MgCl₂ you are going to have 1 molar mg²⁺ + 2, but you are going to have 2 molar solution of cl⁻.

So basically what ends up happening here is that you are trying to understand what is the molarity that you started with after you do a certain set of processes, where do you end up and if you add same thing or different things and different concentrations, different volumes, what do you finally end up having.