Quantitative Methods in Chemistry
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Lecture – 51
Course Revision (Week 08 to 11)

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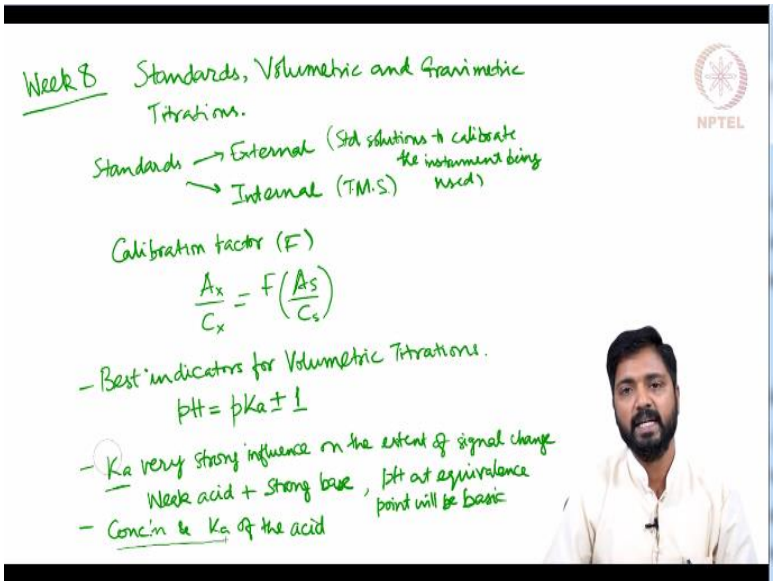

Subsequently we move to Week 8 and week 8 was essentially devoted on the various Standards as well as Volumetric and Gravimetric titrations. So this week had a lot of practical things to be discussed for example while talking about the standards we talked about the external standard as well as the internal standard. For example, we talked about the Tetramethylsilane which is used as a standard in NMR measurements.

And of course external standard refers to the use of standard solutions to calibrate the instrument being used. And we talked of a calibration factor in this case which we called F and we saw that in the case of absorption spectroscopy we had unknown analyte whose absorption and concentration could be estimated if we know either one of these and the calibration factor or the response factor of the instrument which can be estimated by the absorbance of the standard divided by the concentration of the standard.

So in some senses this calibration factor is a proportionality constant between the absorption values and the concentration values of the unknown and the standard. Now when we were talking about the volumetric titrations which actually we undertake quite routinely in our undergraduate classes, we talked about the best indicators for volumetric titrations and here we talked in terms of the pKa value of the indicator.

And we figured out that the indicators who are best in the pH range which is defined by the pKa value of the indicator and a value + - 1 of the pKa value is the regime where our indicator will work the best. And this is also true in terms of the buffers that we use for example when we are using acetic acid and sodium acetate buffer, if we know the pKa range of the acid that we are using we can tell very confidently the pH range at which the buffer would work the best.

In the case of acetic acid for example, the pKa value is about 4.75 so the buffer would work best in 4.75 + - 1 that is 3.75 to 5.75 pH regime. So acetic acid acetate is considered to be an acidic buffer. Similarly, we can think of ammonium salts which can be used as a basic buffer because in those cases the pKa value will be much higher. So while discussing the volumetric titrations we saw that K value of the acid.

So when discussing about the titrations between acids and bases we realized that the K value is having a very strong influence on the extent of the signal change that comes about. And we also saw that when we are titrating weak acid the signal change will be much smaller, and if we are titrating a weak acid with a strong base the pH at equivalence point will be basic. So we can use indicators that undergo color changes under basic regime.

For example, phenolphthalein or even the phenol red can be utilized in such cases, if we are actually using a weak base and a strong acid the vice-versa would be true that means the pH at the equivalence point would be much acetate. So these factors needs to be kept in mind when we are undertaking titrations and we have to choose our indicators that are best suited for the conditions that are being employed for the titration. That means both the concentration and the K value of the acid has to be kept in mind. So these two factors will become very important when we are undertaking titrations.

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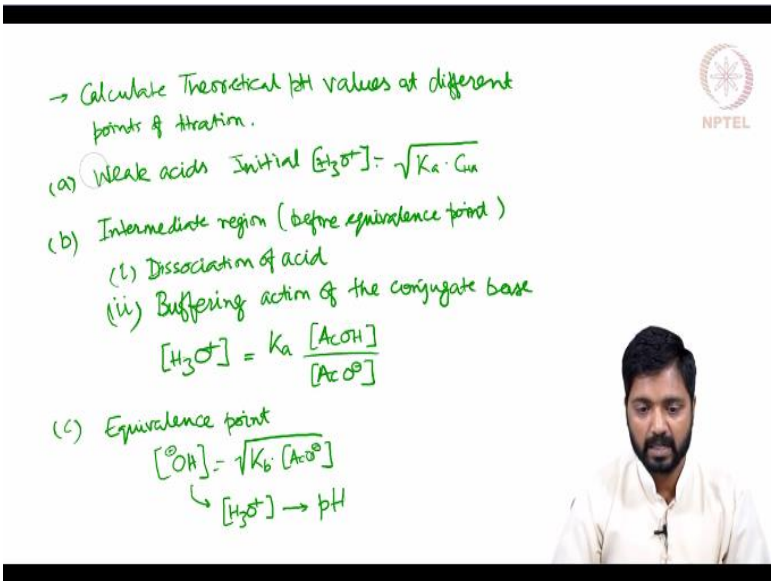

We also discussed that in these cases we could calculate theoretical pH values at different points of titration. For example, when we are dealing with weak acids the initial pH or the initial hydronium ion concentration can be obtained simply by using this equation which takes into consideration the K value and the concentration of the acid and as we keep adding the base into this we reach an intermediate region which is before equivalence point.

And here we have to consider two factors one is the extent of dissociation of the acid and the second thing which becomes very important now is the buffering action of the conjugate base. And we exemplified it by considering the titration between acetic acid and sodium hydroxide and we saw that when sodium hydroxide is added to acetic acid we have the formation of sodium acetate in the mixture and this sodium acetate and acetic acid mixture now starts acting as a buffer and hence the pH needs to be calculated accordingly.

And we figured out that this is; can be estimated in terms of the hydronium ion concentration which is nothing but the K into the concentrations of the acid divided by the concentration of the acetate ions present in the medium. Finally, we reach the equivalence point, and here essentially we estimate the hydronium ion concentration in an indirect manner we estimated first the hydroxide ion concentration which was formed to be square root now Kb into the say the acetate

ion concentration and from here we estimated the H3O+ concentration and from there we can estimate the pH value. So all these things we undertook in our week 8.

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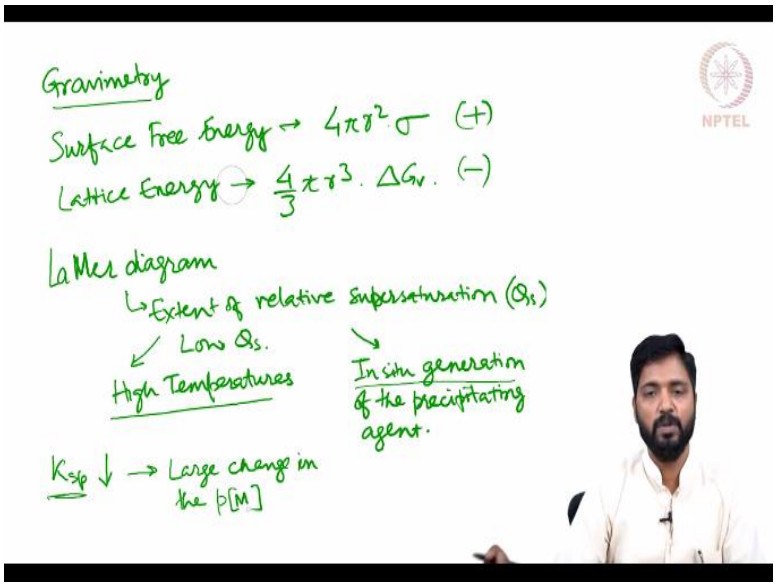

And in addition to that the concepts related to Gravimetry were also discussed. Basically, we talked in terms of the surface free energy of a particle that was being formed and this was given in terms of the surface area of the particle into the surface free energy value. And similarly, we have the lattice energy of the particle which has a volume contribution. So for a spherical particle this would turn out to be something like this.

So we saw that while the surface free energy has a positive value the lattice energy is a stabilizing energy and it has a negative value. Consequently, we pass through a stage where the formation of particle is initially energetically unfavorable up to a certain particle size but as we keep adding more material to the growing particle the formation and growth of the particle becomes energetically favorable beyond a critical radius.

Then we talked in terms of the LaMer diagram to discuss how particles are formed based on the extent of relative supersaturation. And we discussed in this case that we would want to have a low relative supersaturation that means we could use both high temperatures and In-situ generation of the precipitating agent and we discussed in the context of the sulfide ions where the use of hydrogen sulfide would have created excess of the sulfide.

And presence in the precipitating mixture resulting in a high relative supersaturation value which will be detrimental to getting uniform or monodisperse particles particle sizes on the contrary when we use sulfur generating or sulphide generating reagents such as thiourea or thioacetamide. There is a slow and continuous generation of the H2S in the reaction medium by the decomposition of these precipitating agents.

And this results in a more homogeneous particle population in the reaction mixture. So this technique of using both the high temperatures and In-situ generation of the precipitating agent is widely used in the area of creating monodisperse particles whether these are Nanoparticles or Nicroparticles in both the cases we use these ideas or principles. Finally, we talked about the fact that the Ksp value or the solubility product value is also to be considered when we are talking about gravimetry.

And this has a very profound effect on the change in the Pag or Pcd value for example, the concentration of the metal and in the solution will change according to how large or how small the Ksp value is. So if the Ksp value is significantly low we have a very large change in the in the p value of the metal ion being consider.

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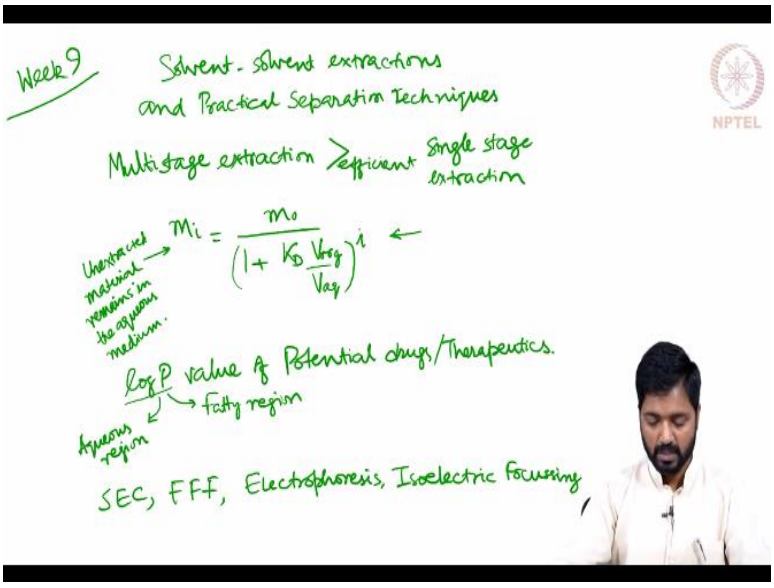

Week 9 of the course as you can recollect was dedicated mainly to Solvent - solvent extractions and also covering various practical separation techniques that are available to us. Now during the Solvent - solvent extractions we realized that a multistage extraction is more efficient than a single stage extraction and we prove this through the use of mathematical equations. We also talked in terms of the unextracted material that remains say in the aqueous medium after i iterations of extractions.

And it depends intricately on the distribution constant of this material or this compound between the organic and the aqueous layer and the volumes of the two employed during the extraction. So if we do i number of extractions multiple times so we have this equation which can explain or which can quantify how much of the unextracted material remains in the aqueous medium. Importantly, we also discussed this point in terms of the log P value of potential drugs or potential therapeutics.

And this log P value could tell us whether the drug will partition into the fatty regions of the body or the aqueous regions of the body and this is an important factor to be considered when undertaking drug design. This was followed by discussing the various separation techniques whether it is the size exclusion chromatography, whether it was the field flow fractionation or when dealing with charged particles whether it was electrophoresis or isoelectric focusing.

So all these aspects are utilized in our day-to-day lives as researchers to purify and separate compounds as well as polymers and proteins for characterization as well as for finding out the structure property relationships.

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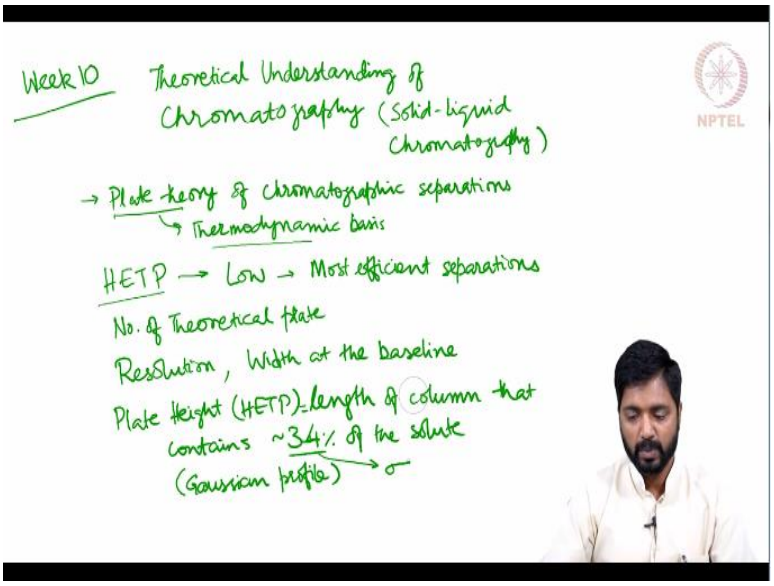

Subsequently, in the week 10, our focus was exclusively on obtaining theoretical understanding of Chromatography and mainly what we known as the Solid-liquid Chromatography. So here we got introduced to the plate theory of chromatographic separations and we saw that this plate theory has a thermodynamic basis wherein it is presumed that the analyte or the solute equilibrates between the different theoretical plates which are present within a chromatography column.

So we emphasized and I would like to emphasize again that the concept of theoretical plates is actually a conceptual idea to explain that purification of the solute through a chromatographic column and has no real physical basis but it gives us an idea of how good the separations would be what is known as the Height Equivalent of the Theoretical Plate and we wanted this number to be as low as possible to achieve the most efficient separations.

And when we talk about most efficient separations we are implying; achieving very sharp chromatographic profiles and using the lowest illusion times. So both these factors become practically important when we are separating a complex mixture of materials and indeed the extent of chromatographic separations is often shown by taking a real complex mixture of materials or molecules and showing their individual separation through a short chromatographic column.

So by understanding the height equivalent of the theoretical plates as well as the number of theoretical plates present in the column we get an idea of the chromatographic resolutions that possible through the chromatographic separation that is being undertaken. Now here the concept of resolution and the width at the baseline all became important and were discussed during the lecture.

We also realized that the plate height which we also abbreviate as HETP is essentially the length of the column that contains around 34% of the solute. Now this came about because during the chromatographic separations the solute profile or the chromatographic profile adopts; Gaussian profile is seen when the solute eludes through a chromatographic column and we can apply all the concepts that we learnt in the earlier classes of this course to the chromatographic peak that is eluting out of the column. So this was nothing but the sigma value for the chromatographic peak which is coming out and based on that we can estimate how effective is our chromatographic separation.

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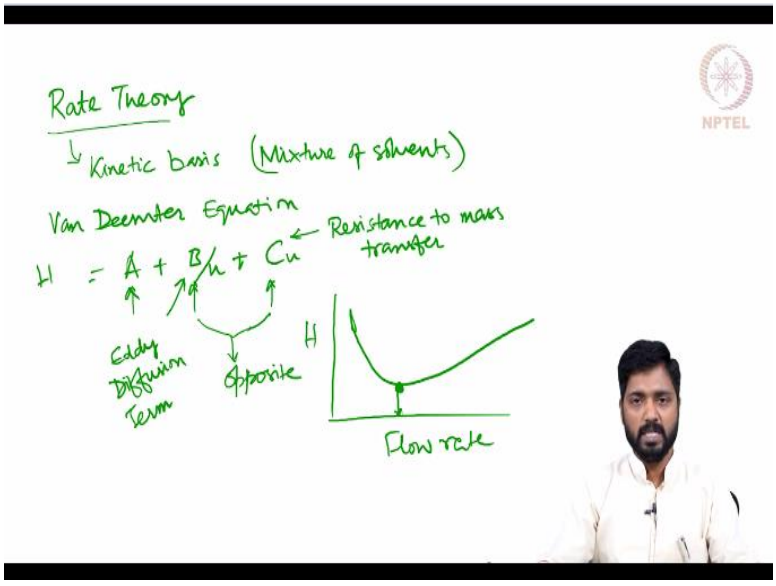

Now in addition to that we talked about the refined theory of chromatographic separation which is known as the rate theory which contrastingly had kinetic bases and could handle mixture of solvents which was not possible for the plate theory because in plate theory only isocratic solution could be considered. Now in the rate theory we got introduced to the Van Deemter

equation where there were 3 terms, the A term, the B/u term and the Cu term that were contributing to the plate height value.

And we also discussed what factors influence all these 3 parameters A, B, C. And we essentially saw that the B and the C terms are sort of opposite to each other so the factors that stabilize or that reduce the B term tend to enhance the C term and vice-versa. Consequently, we observe that a plot of H versus flow rate would ultimately follow a profile like this where at this point we have the lowest or the smallest plate height value or in other words the most efficient separation.

So finally, in the Week 11, we have discussed the various detectors and the various aspects related to practical separations to sort of complete the discussion on chromatographic separations while emphasizing on the quantitative aspects of separations and purifications.