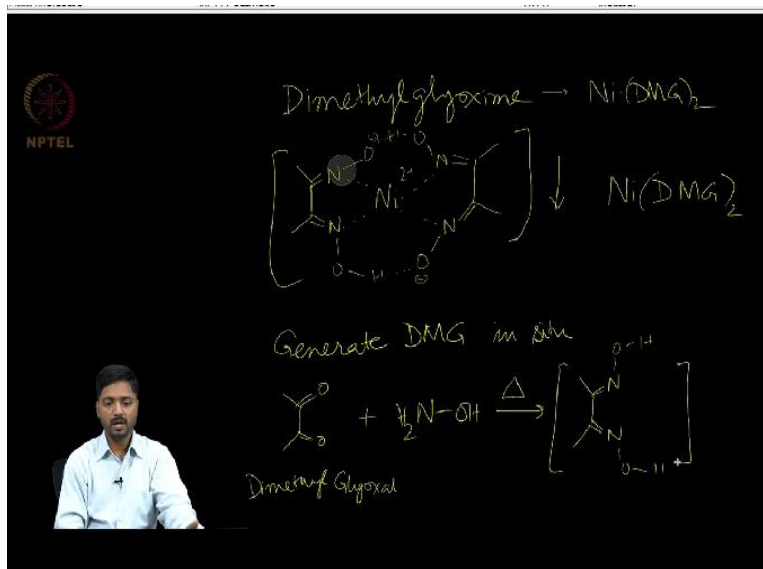


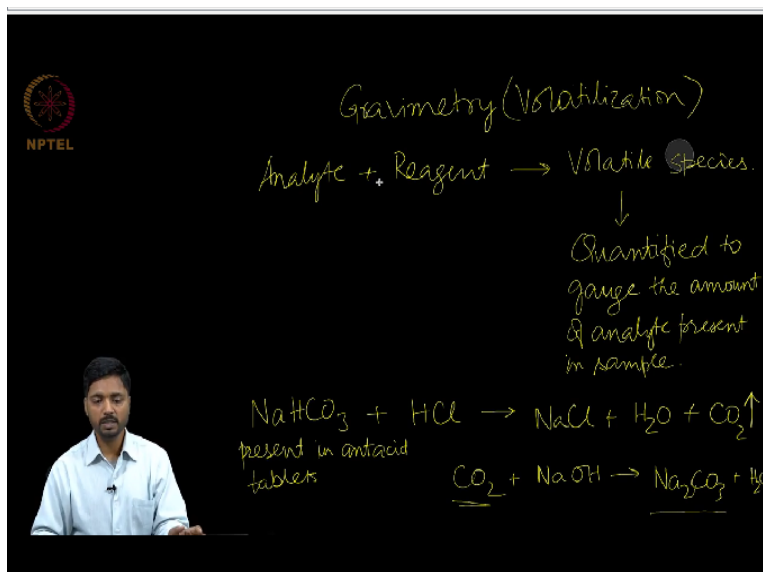
Quantitative Methods in Chemistry
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Lecture-33
Standards And Volumetric/Gravimetric Titrations Part 05

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So, one type of gravimetry which is a little counterintuitive is what is known as volatilization gravimetry. So, far whenever we think of gravimetry we have been thinking of a precipitate

being generated and the precipitate being separated in gravity weighed and then the analyte concentration evaluated using the amount of precipitate that is being generated. In volatilization gravimetric completely inverse protocol is followed that is the reaction between the analyte and the reagent.

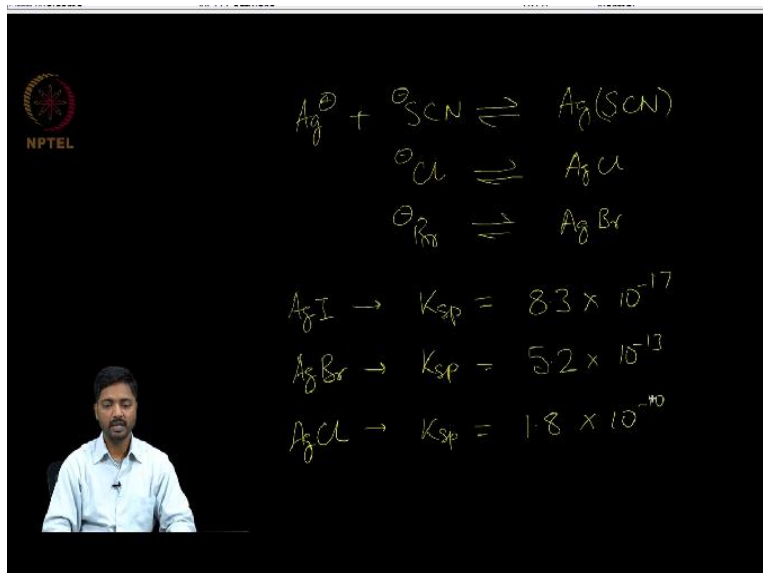
So, analyte plus reagent generates a volatile species and this volatile species is then quantified to gauge or to measure the amount of analyte that is present in our sample. Let us take a very quick example of such a volatilization gravimetry. This can be used very well in quantifying the amount of say sodium bicarbonate or baking soda in antacid tablets. So, what we do is, we take the antacid tablet containing the sodium bicarbonate and reacted with an acid say hydrogen chloride or hydrochloric acid and this generates carbon dioxide.

Now, this carbon dioxide is the volatile product of this gravimetry, which can be quantified and quantification of the carbon dioxide that is being generated in this reaction mixture will lead us to the amount of sodium bicarbonate present in the antacid tablets. So, how do we achieve this, we pass this carbon dioxide into a sodium hydroxide solution which is pre-weighed. And this generates sodium carbonate and water.

This sodium carbonate can be analyzed by various analytical techniques to quantify the amount of carbon dioxide that is being generated. So, it is also very important to note here that this absorption of carbon dioxide by sodium hydroxide is also happening naturally when we keep sodium hydroxide beads or sodium hydroxide solutions exposed to atmospheric air. So, the sodium hydroxide solution or the beads will absorb atmospheric carbon dioxide and give rise to the formation of sodium carbonate.

So, that is also one reason why sodium hydroxide is not considered a primary standard, because it is stoichiometry or its composition undergoes change on exposure to the atmosphere, either in terms of absorbing moisture or in terms of undergoing a chemical reaction with the atmospheric carbon dioxide to generate sodium carbonate. So, in the last part of this class, we will be considering how precipitation gravimetry is undertaken for quantifying various analytes such as silver ions present in our solution.

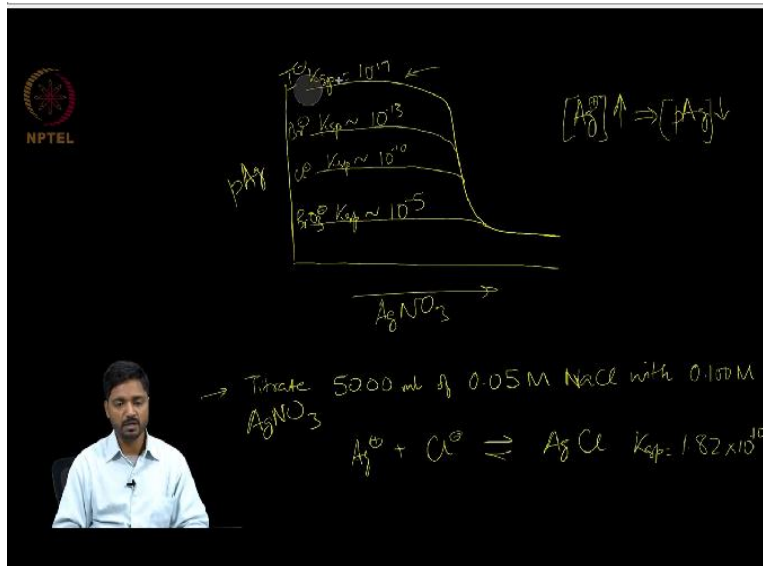
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So this nitration is also very similar to the acid base titration in that we have the silver ions undergoing reaction with either the thiocyanate or the chloride ions or the bromide and ions and this is an equilibrium reaction there we have the formation of either silver thiocyanate, silver chloride or silver bromide. Now, since it is an equilibrium reaction, all of these reactions are having an equilibrium constant for each of these.

For example, for silver iodide formation, the solubility product is what we will use here is quite low as 10 power of - 17. Similarly, for silver bromide, the solubility product is a little higher at 10 power of - 13. For silver chloride, which is what we usually use when we are testing the purity of our distilled water, we see the solubility product as 1.8 into 10 power of - 10.

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So, as we do in titration what we can do here is, we can plot the P function here. In this case it would be the P value of the Ag ions with the amount of silver nitrate that is being added to the solution containing the respective anion. And since it is a P Ag value, the value will decrease as the silver concentration increases. So, this has to be written carefully as the silver ion concentrations increase in the medium the P Ag value decreases.

So, what we observed quite analogous to the acidity constant of the acids is that the P Ag value undergoes the most prominent change when we are talking a K Sp value of 10 power of - 17 which is for the iodide anions when the anion is changed to bromide, the profile becomes less sharp because bromide has a K Sp value of the order of 10 power of - 13. And as the K Sp value decreases further for chloride adds this becomes even less sharp.

And here the case K Sp value was of the order of 10 power of - 10. For something like bromate anions, this difference is so negligible that we will see very significant titration errors if we want to titrate, the bromate anions because the K Sp value here is of the order of 10 power of - 5. So, what we observe here is that the K Sp is in this case analogous to the K a value in the case of acids and we require the lower the K Sp value, the sharper will be the transition between the titration.

So, let us quickly take an example where we titrate 50 ml of 0.05 molar sodium chloride with 0.1 molar silver nitrate solution. So, we will be adding silver nitrate to the sodium chloride solution and seeing the formation of silver chloride and any residual silver ions concentration will be plotted henceforth, and just to remind this as a K_{sp} value of 1.82×10^{-10} .

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(ii) Added 10.00 mL of AgNO_3

$$C_{\text{NaCl}} = \frac{50.00 \times 0.05 - 10.00 \times 0.100}{50.00 + 10.00}$$

$$C_{\text{NaCl}} = 0.025 \text{ M}$$

$$[\text{Ag}^{\oplus}] [\text{Cl}^{\ominus}] = K_{sp}$$

$$[\text{Ag}^{\oplus}] = \frac{K_{sp}}{[\text{Cl}^{\ominus}]} = \frac{1.82 \times 10^{-10}}{0.025}$$

$$= 7.28 \times 10^{-9} \text{ M}$$

$$p[\text{Ag}^{\oplus}] = -\log(7.28 \times 10^{-9}) = 8.14$$

So, let us take an example, where add the pre-equilibrium condition or pre equivalence condition, we have added 10.00 ml of silver nitrate to the sodium chloride solution. Now, our concentration of sodium chloride will does become the original concentration minus the amount of silver nitrate that has been added here divided by the total volume of the medium and now which is 50 ml original plus 10 ml added silver nitrate.

And this will bring the sodium chloride concentration as 0.25 molar. And from here we should be able to calculate the silver ion concentration in the medium by plugging in this value in the solubility product equation and we get the silver ion concentration as K_{sp} divided by the chloride ion concentration, the K_{sp} value is 1.82×10^{-10} . The chloride concentration from the NaCl that is remaining is 0.025.

And this solves out to be 7.28×10^{-9} molar. Now, this can be represented in terms of the $p[\text{Ag}^{\oplus}]$ value and which is nothing but the negative log of 7.28×10^{-9}

solving to 8.14. So, initially, when we have added 10 ml of silver nitrate we have a P Ag value of 8.14.

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(i) At equivalence point (25.00 ml of AgNO_3)
 $[\text{Ag}^+] = [\text{Cl}^-]$
 $K_{sp} = [\text{Ag}^+][\text{Cl}^-]$
 $K_{sp} = [\text{Ag}^+]^2$
 $\therefore [\text{Ag}^+] = \sqrt{K_{sp}}$
 $= \sqrt{1.82 \times 10^{-10}}$
 $= 1.35 \times 10^{-5} \text{ M}$
 $p[\text{Ag}^+] = 4.87$

Now, at equivalence point we will have the total amount of silver ions that have been added as equal to the total amount of the chloride ion present in the medium and we know that the K_{sp} is nothing but Ag^+ ion concentration into chloride ion concentration which solves out to be. So, the Ag^+ concentration at equivalence point is nothing but the square root of the K_{sp} product and that is nothing but square root of 1.82×10^{-10} or 1.35×10^{-5} molar.

Now, this can be represented in terms of the P Ag value of 4.87. So, as we see that at equivalence point, which comes at 25.00 ml of silver nitrate addition, the P Ag value is 4.87. However, till 10 ml of silver nitrate addition in the previous case the P Ag value was 8.14. So, we will see that as we keep adding more and more silver nitrate, the P Ag value will undergo significant reduction.

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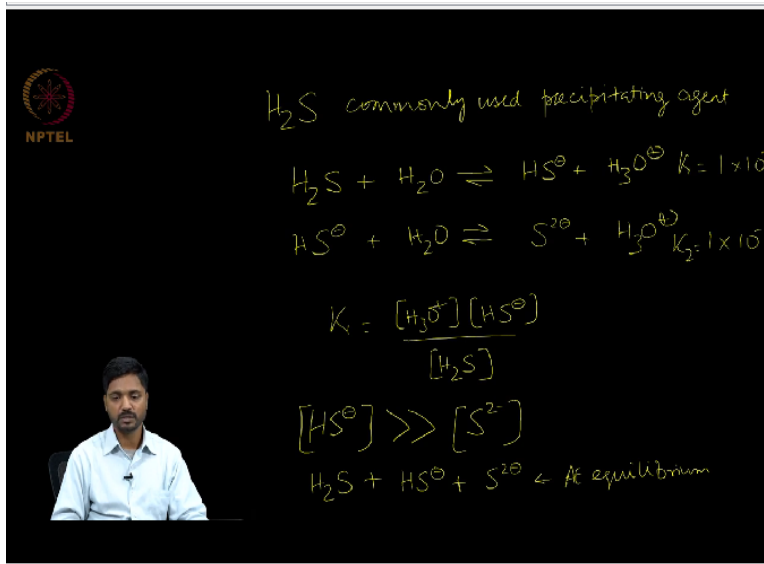
(ii) Beyond equivalence point:
26.00 ml of AgNO_3
$$C_{\text{AgNO}_3} = \frac{26.00 \times 0.100 - 50.00 \times 0.05}{26.00 + 50.00}$$

$$p\text{Ag} = 2.88$$

Let us see what is the P Ag value beyond equivalence point, what we observe is suppose we add 26.00 ml of silver nitrate, in that case we have a little excess of silver nitrate. So, that excess of silver nitrate can be calculated by the total silver nitrate present in the medium minus the initial chloride ions present in the medium divided by the total volume of the medium now, and this solves out to a P Ag value of 2.88.

So, what we see is that from the initial phase, where our P Ag value was 8.14 at equivalence point, this reduced to 4.87. And just after the equivalence point, it reduced even further to 2.88. So, this can again be plotted into a titration curve a theoretical titration curve can be generated from such calculation.

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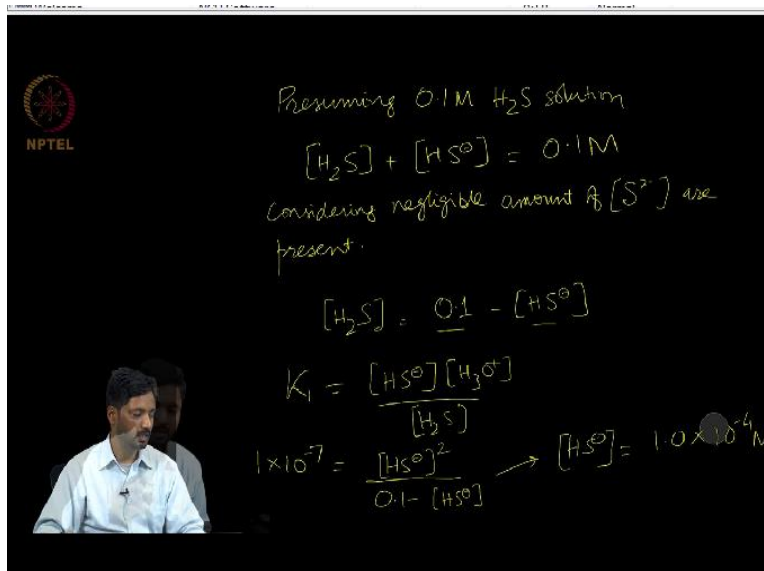
Now you would have also encountered that hydrogen sulfide is a commonly used precipitating agent especially when we are trying to do our chemical analysis. And we will understand today why hydrogen sulfide is used commonly as a precipitating agent. And the answer to this lies in the 2 equilibria that exist here. So hydrogen sulfide being weak as it will donate its proton to water as the first equilibrium.

And in the second equilibrium, we can also expect that the hydrogen sulfide will convert into, we can expect that the mono sulfide anion will convert into sulfide anion. And since these are equilibria they can be explained in terms of equilibrium constants. So, let us call this as K_1 and this is of the order of 10^{-7} , the second dissociation becomes much more difficult and this value is almost 10^{-14} .

So, what we see here is that, K_1 can be defined as the H_3O^+ concentration into HS^- concentration divided by the H_2S concentration and typically based on like the equilibria that we just mentioned is that the HS^- - the mono anion concentration is significantly greater than the dianion concentration. And what we can write is that at equilibrium we will have the H_2S present the HS^- present.

And the sulfide ion is in a very small amount presented at equilibrium. Now, presume that we are dealing with a 0.1 molar H_2S solution.

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NPTEL

Presuming 0.1M H_2S solution

$$[\text{H}_2\text{S}] + [\text{HS}^-] = 0.1\text{M}$$

Considering negligible amount of $[\text{S}^{2-}]$ are present.

$$[\text{H}_2\text{S}] = 0.1 - [\text{HS}^-]$$
$$K_1 = \frac{[\text{HS}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{S}]}$$
$$1 \times 10^{-7} = \frac{[\text{HS}^-]^2}{0.1 - [\text{HS}^-]} \rightarrow [\text{HS}^-] = 1.0 \times 10^{-4}\text{M}$$

What we observe is that the equilibrium concentration of H_2S and HS^- is now equal to 0.1 molar considering negligible amount of sulfide ions are present okay. Now, what we can observe here is that the H_2S concentration at equilibrium will be the original concentration of H_2S which was 0.1 molar minus the HS^- concentration. And if we plug it in our K_1 equation what we observe is K_1 is equal to HS^- into H_3O^+ divided by H_2S .

And this solves to the K_1 value being known, the HS^- concentration needs to be calculated. And we will also presume that the equilibrium is the only source for the H_3O^+ ions. Now, when we solve this we get the HS^- ion concentration under these conditions as 1.0.

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NPTEL

HS^- & S^{2-} concentrations are highly pH dependent

$$\text{FeS} + 2\text{HCl} \rightarrow \text{FeCl}_2 + \text{H}_2\text{S}$$

But what is more relevant for our discussion is that the HS^- and H_2S concentrations are highly pH dependent. So based on the pH of the medium the concentration of these 2 can be precisely controlled and this is actually what is being exploited when we are undertaking precipitation of metal ions using H_2S gas as a precipitating agent. So, you can keep this in mind when you are undertaking your chemical analysis using H_2S gas.

And how is H_2S gas generated you must be aware that you have a Fe S separators where iron sulfide is reacted with hydrogen chloride to generate H_2S gas and this can be controlled based on the addition of HCl into the Fe S is controlled based on how much H_2S is being released in that it separators. So, this brings us to the end of this week's lecture, where we have seen how calculations can be undertaken, when titration actions are being performed to calculate the theoretical values of the pH that can be expected in the medium.

We also saw how indicators are to be employed in the choice of indicator will depend upon what is the pH value at the equivalence point. We also understood that the pH at equivalence point is 7.00 only when we are dealing with strong acid and the strong base. If the base is strong and the acid is weak, the pH at equivalence point will be greater than 7. If the acid is strong and the base is weak, the acid will dominate and the pH where the equivalence point will be less than 7.

And then we delved upon how we utilize precipitation gravimetry and what are the principles involved when particles are forming in precipitation gravimetry. Finally, we did a quick calculation of the silver ion concentrations when sodium chloride was being titrated with the silver nitrate, we figured out that the solubility product is in some senses analogous to the dissociation constant in acid based iterations.

And then we saw ultimately that hydrogen sulfide is a very versatile reagent for precipitation because we can generate it at 2 different rates by utilizing either thiourea or thioacetamide and we can also control the dissociation very carefully by control of the pH of the medium. So this brings us to the end of this week's lectures. I will see you next week.