Quantitative Methods in Chemistry

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Lecture-32

Standards And Volumetric/Gravimetric Titrations Part 04

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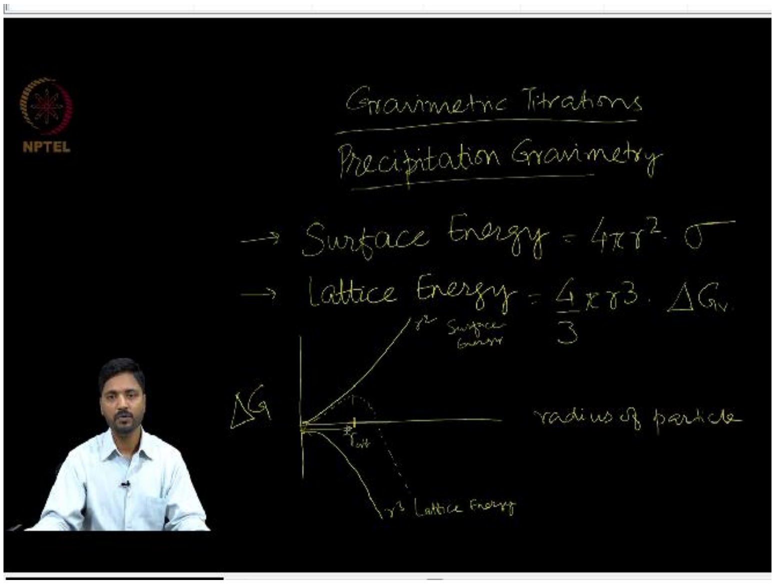

Gravimetric Titrations

Precipitation Gravimetry

→ Surface Energy = $4\pi r^2 \cdot \sigma$

→ Lattice Energy = $\frac{4}{3}\pi r^3 \cdot \Delta G_v$

So, while talking about gravimetric titrations or what is also known as the precipitation gravimetric, what are the points that we need to consider and under what conditions will we be able to generate homogeneous large particles that are easy to separate. So this is more of a practical consideration here, when we are undertaking precipitation gravimetry, because the quality of the precipitate will decide how easy will it purification.

And it is separation from the reaction mixture would be. So, let us look at what are the forces that are in play when a particle is being formed. So, that 2 sort of opposing forces that are to be considered here, one is coming due to the surface energy of the forming particle and the other one is the lattice energy of the particle that is being formed. Now being surface energy, it is mainly dealing with the surface of the particle.

And for a spherical particle this will go as 4 pi r square into what we can call as sigma or the surface tension. Similarly, when we talk in terms of lattice energy, this is more of a volume 3. So, this will be 4 by 3 pi r cube into something like what we call as the delta Gv. So, these 2 forces act simultaneously on the particle and if I plot the free energy of particle formation with the radius of the particle what we see is that the surface energy will scale as an r square value.

And the lattice energy is an exothermic thing and it will scale as the r cube. So, this is what we will call as the interfacial or surface energy and this will be the contribution coming from the lattice energy. So, what we observe here is that some of these 2 energies will be the total energy of the particle that is being formed and this will follow a profile like this. So, up to a certain constant radius of the particle which we denote as the r critical.

The particle formation is not an energetically favorable process, because the surface energy term dominates over the lattice energy term. And as we as the particle becomes bigger and bigger, the lattice energy term starts dominating on the total free energy of the particle and it becomes a spontaneous process for the particle to grow. So, we can also consider that this initial phase till reaching the r critical value is the phase of nuclear where the particle is forming.

And re dissolving into the solution and only a certain fraction of these nuclei that are formed will continue to grow into bigger particles. And once this threshold of r critical is crossed, he will be able to create bigger and bigger particles during the growth phase.

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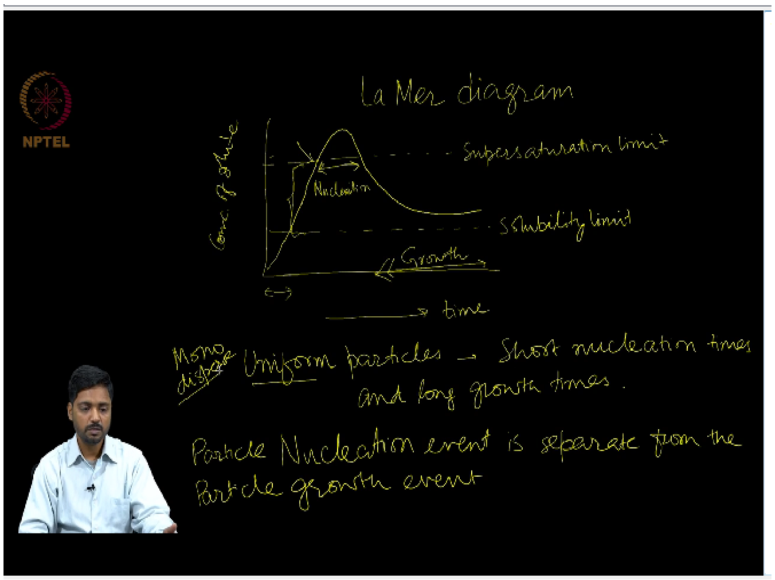

La Mer diagram

Mono disperse Uniform particles → Short nucleation times and long growth times.

Particle Nucleation event is separate from the Particle growth event

So, this concept is also very nicely explained by the lamer diagram, which essentially plots the change in this concentration of solute verses time and so, this is the change in the solute which is undergoing precipitation. So, initially the solute concentration will keep increasing, it will hit a point where we can no longer keep adding more and more solute into the medium and the solute starts precipitating and after a while we reach equilibrium condition.

So, this point is known as the solubility limit and a point somewhere here is known as the super saturation limit. So, as we see that initially we have in this time regime, we have the concentration of the solute being lower than the solubility limit. So, it would be nicely soluble in the medium in which the particle is being formed. As we cross the solubility limit, the particle does not immediately start forming.

However, we reach a regime which is known as a super saturation regime, which we can consider as this regime. So, this regime is what we will call as the super saturation regime, where the concentration of the solute will be somewhat higher than the solubility limit and it keeps crossing the super saturation limit which is indicated here. And as it does that, in this regime the nucleation process will start happening.

And as nucleation keeps happening, the concentration of the solute in the medium will start decreasing and ultimately the nucleation will give way to the growth of the particle. So, in this regime, we observe the growth of the particle. So, this concept is utilized quite extensively, both in say nanotechnology as well as in gravimetry where we want to create uniform particles and for that to create uniform particles we need short nucleation times and long growth types.

So, we will consider how this is to be achieved and what we also need for achieving mono dispersed particles is that the nucleation event is separate from that growth event. So, we can also rewrite is as the particle depletion event is separate from the particle growth event. So, these 2 needs to be separate for achieving uniform or mono dispersed particles. So, how do we practically achieve this is what we will see in the rest of this class.

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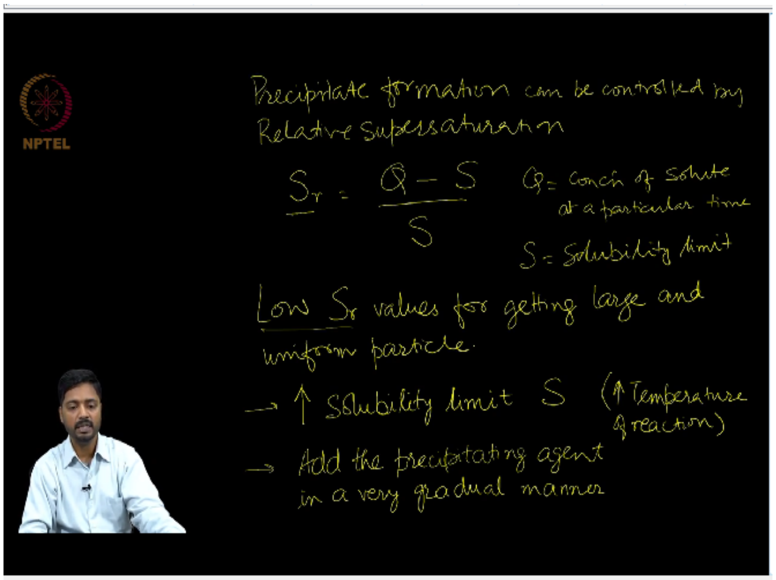

Precipitate formation can be controlled by Relative supersaturation

$$\underline{S_r} = \frac{Q - S}{S}$$

Q = Concn of solute at a particular time

S = Solubility limit

Low S_r values for getting large and uniform particle.

→ ↑ Solubility limit S (↑ Temperature of reaction)

→ Add the precipitating agent in a very gradual manner

So, one way through which the precipitate formation can be controlled is by controlling what is known as the relative super saturation, how do we define relative super saturation, the defined relative super saturation is S r being Q - S by S. Here, Q is the concentration of solute at a particular time during our reaction or titration or making of the particle and S is the super saturation limit or the solubility limit.

And in nutshell, we need low S r values for getting large and uniform particles. So, what can we do to achieve uniform particles in a practical manner is we can increase the solubility limit S and the simplest way to increase the solubility limit is by increasing the temperature of the reaction.

That is why if you see literature, scientific literature, you will find that many of the very uniform particle synthesis is undertaken at very high temperatures of about 300 to 350 degrees Celsius.

Similarly, what we can also do here is to add the precipitating agent in a very gradual manner. So, we need to do a slow addition of the precipitating agent, so that the relative super saturation value remains low and that will help us to get uniform and mono disperse particles. Now, one way through which researchers have found it to do this practically is by precipitating from uniform solutions.

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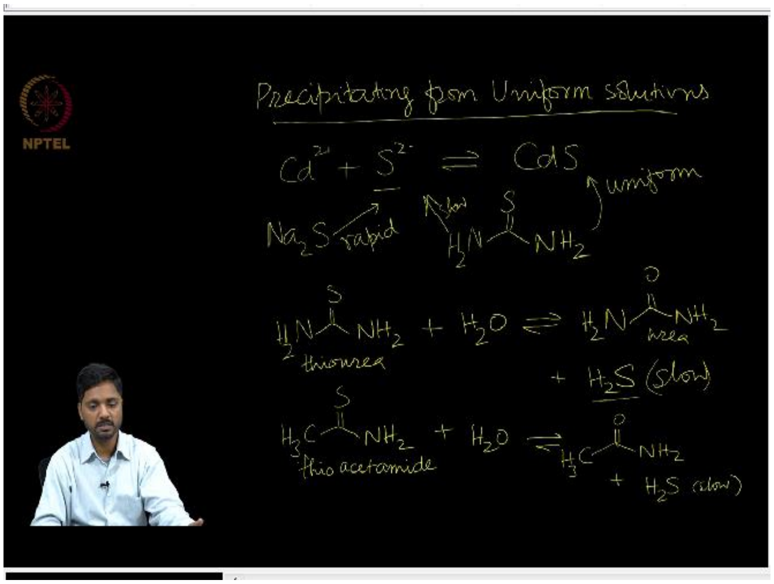

So, again the concept here is same that we need to keep the relative super saturation values low and we will generate the precipitating agent either in situ or in a slow manner. So, a very simple example is when we are making particles like reaction of cadmium with sulfide giving rise to cadmium sulfide nanoparticles are particles, we generate the sulfide reagent in the reaction medium in a very slow manner by using a precursor to the sulfide.

So, we can either use sodium sulphide, which will give very rapid. However, what researchers found out is that using organic sulfur precursors such as thiourea will help us generate the sulfide ions in a slow manner and will hence give us unique access to uniform cadmium sulfide or metal sulphide nanoparticles. So, what reaction happens here is that you take thiourea, you react it with water at high temperatures and you generate urea from this reaction and hydrogen sulfide.

Now, one reason why the carbon sulfur bond breaks and the carbon oxygen bond forms is because carbon sulfur bond is weaker and that is being replaced by the thermodynamically more stable carbon oxygen bonds. But this process happens more gradually and results in slower generation of the hydrogen sulfide gas in the reaction medium. Another such precursor would be the thioacetamide that are made which on reaction again with water at high temperatures will give rise to acetamide and H 2 S in a slow and steady fashion.

So, this is a very commonly employed technique in preparing uniform and mono disperse metal sulphide particles. Another example is when we need to increase the pH gradually.

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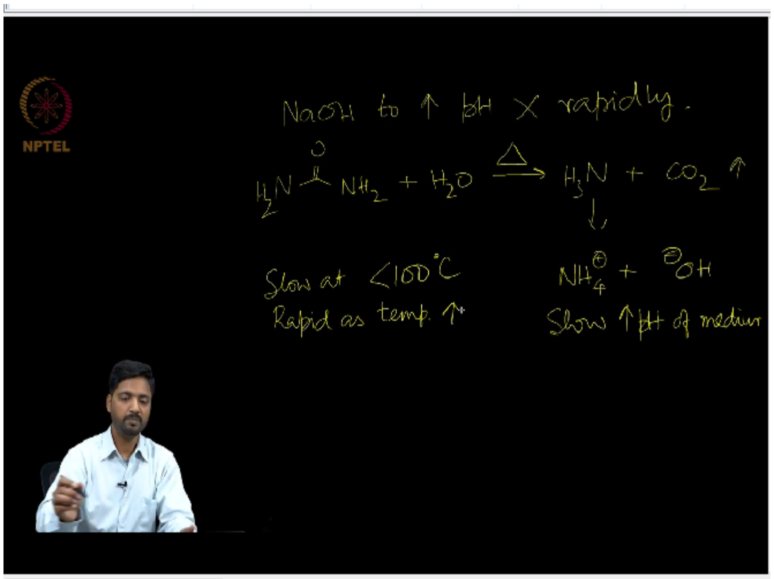

NaOH to ↑ pH × rapidly.

$$H_2N-\overset{O}{\overset{\|}{C}}-NH_2 + H_2O \xrightarrow{\Delta} H_3N + CO_2\uparrow$$

$$H_3N \downarrow NH_4^{\oplus} + {}^{\ominus}OH$$

Slow at < 100 °C

Rapid as temp. ↑

Slow ↑ pH of medium

So, commonly people would use sodium hydroxide to increase pH, but that happens very rapidly which is not what we want. So, a more straightforward solution to this is to use something like urea which upon heating in water will generate ammonia and carbon dioxide. The carbon dioxide will be evaporated and the ammonia in water will give rise to ammonium ions and hydroxide ions. This will result in a slow increase in the pH of the medium.

And this can be utilized to achieve gradual presentation of the material at high pH. So this reaction occurs quite sluggishly at temperatures less than 100 degrees Celsius, but becomes rapid as temperature increases. So, we can use temperature as our convenient tool to control the rate at which the hydroxide ions are being generated in the medium.

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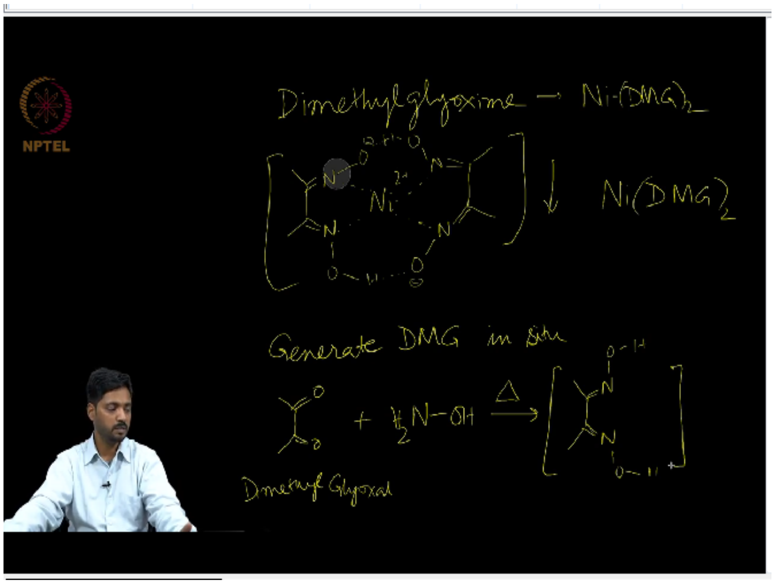

Now, you might have also encountered in your titrations the use of dimethylglyoxime which is used often to form a beautiful pink red complex with nickel ions in the form of nickel DMG twice. So, the structure of dimethylglyoxime nickel complex is something like this, you have and a similar structure is present here. But now with the OH hydrogen bonding with the O – bond present here.

And this 4 nitrogens are the ones which complex with the nickel ions to generate a charge neutral complex which precipitates from the reaction mixture as the nickel DMG twice complex. Now a one straightforward way to generate dimethylglyoxime in C 2 for again a more mono disperse and easily separable precipitate of nickel DMG is to generate DMG in situ. In situ is nothing but in the reaction mixture.

So, for that what is done we take the dimethylglyoxime and react it with hydroxyl amine in the reaction mixture itself and under the right conditions of high temperature you will generate the corresponding dimethylglyoxime which will undergo complexation with the nickel ions present in medium.