Basics in Inorganic Chemistry

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Lecture - 06
Thermit Process and Zone Refining

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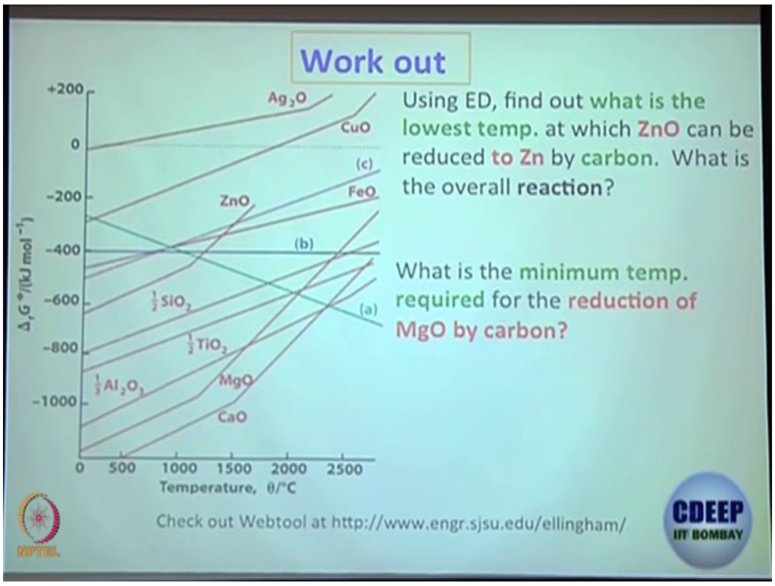

Work out

Using ED, find out what is the lowest temp. at which ZnO can be reduced to Zn by carbon. What is the overall reaction?

What is the minimum temp. required for the reduction of MgO by carbon?

Check out Webtool at http://www.engr.sjsu.edu/ellingham/

Now work out this one, so this is a question using ED means Ellingham Diagram. Find out what is the lowest temperature at which zinc oxide can be reduced to zinc bicarbon. Let us say zinc oxide curve is this one which is the temperature, you are going to use or which is the temperature that is required to convert zinc oxide to zinc by using carbon.

Student: (Refer Time: 00:49).

So, this is the temperature right. So, the carbon monoxide curve is in the green, zinc oxide curve if this is the one, this is the temperature around. Let us say 1250 this point around 1250 you need to convert zinc oxide to zinc by using carbon right. What is the minimum temperature required for the reduction of magnesium oxide by carbon?

Student: (Refer Time: 01:19) more than 2000.

More than 2000 because this is the green curve, this is the magnesium oxide curve and that is the point where you are having that intersection and that is more than 2000 let say 2150 So, at that point at this point carbon going to carbon monoxide formation is thermodynamically more favorable compared to magnesium going to magnesium oxide. So, net reaction will be magnesium oxide reacting with carbon giving you carbon monoxide, that means carbon monoxide formation is favorable magnesium oxide is converted to magnesium ok.

Student: Ok.

So, there are some website is given, you can play with that or you can look at that.

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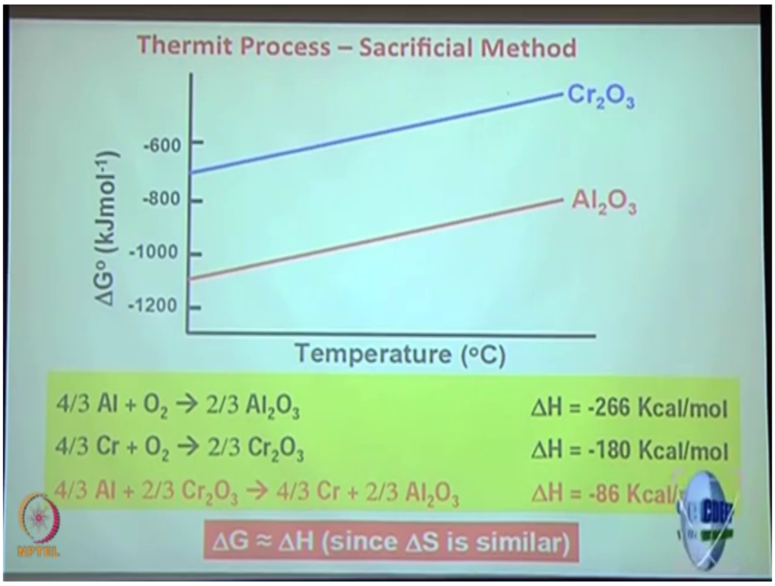

Thermit Process – Sacrificial Method

$4/3\ Al + O_2 \rightarrow 2/3\ Al_2O_3$ ΔH = -266 Kcal/mol

$4/3\ Cr + O_2 \rightarrow 2/3\ Cr_2O_3$ ΔH = -180 Kcal/mol

$4/3\ Al + 2/3\ Cr_2O_3 \rightarrow 4/3\ Cr + 2/3\ Al_2O_3$ ΔH = -86 Kcal/

ΔG ≈ ΔH (since ΔS is similar)

Now, so this is the reaction which is used in thermit process, all of you are familiar with thermit process, you have heard of ok.

Student: Yes.

So, technically speaking as I was telling you can utilize aluminia, aluminum to react with chromium to get pure chromium, because aluminum this you know diagram from this Ellingham diagram you can see aluminum is having more delta G or more negative delta G compared to chromium. So, chromium oxide can be converted to chromium by using aluminum because, aluminum oxide formation is more favorable than chromium oxide right. This is the standard reaction kind of reaction which you should not forget, what when you are looking for Ellingham diagram you must remember something like these whatever is at the bottom that will be getting oxidized ok.

Not the other way around, this chromium is not going to react with alumina to give you the reverse reaction. So, this is in these case alumina is going to be your sacrificial reagent, it is going to sacrifice itself to give you the pure form of the other one. How is the delta G working out here or more to say since this is almost a two both the reactions are similar, aluminum oxygen stereometric everything is exactly same. Aluminum solid, chromium solid, oxygen gas, oxygen gas and then you are going to get alumina and chromium or chromium oxide right.

So, nothing is changing, since nothing is changing in terms of their state like solid liquid and gas or overall stereometric are all same. If you are taking or thinking about delta delta G or the delta G formation for the whole reaction only thing perhaps you need to worry about the delta H, that is the only difference because delta S is going to be similar or exactly you know comparably you can just cut it out.

So, delta G equals delta H minus T delta S. So, overall delta delta G the difference between the delta G is going to be equivalent to the difference in their delta H ok. So, since delta S is similar T delta S term you can kind of delete it ok. So, over here if delta G for this reaction is minus 266 delta S is minus 180 what overall you are having is for this reaction delta G is going to be minus 86 k cal per mole right.

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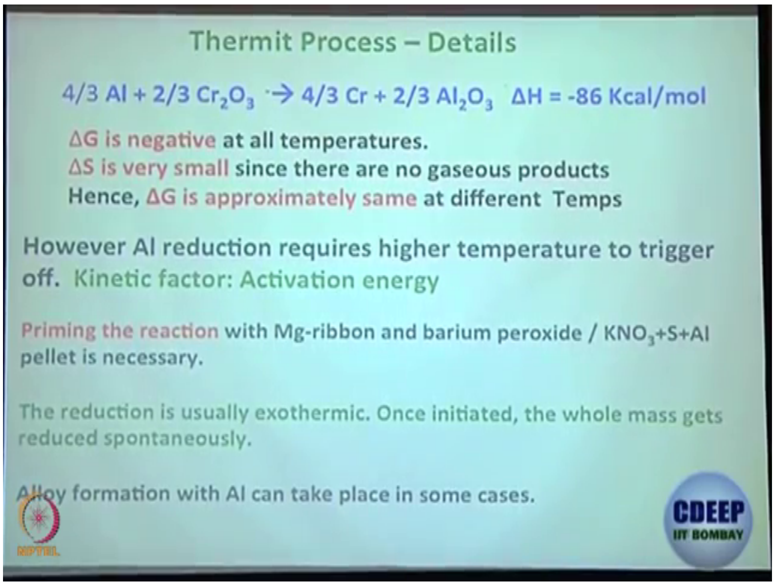

Thermit Process – Details

$4/3\ Al + 2/3\ Cr_2O_3 \rightarrow 4/3\ Cr + 2/3\ Al_2O_3$ $\Delta H = -86$ Kcal/mol

ΔG is negative at all temperatures.
ΔS is very small since there are no gaseous products
Hence, ΔG is approximately same at different Temps

However Al reduction requires higher temperature to trigger off. Kinetic factor: Activation energy

Priming the reaction with Mg-ribbon and barium peroxide / KNO_3+S+Al pellet is necessary.

The reduction is usually exothermic. Once initiated, the whole mass gets reduced spontaneously.

Alloy formation with Al can take place in some cases.

Now, this is what we know as Thermit process. So, delta H is the minus 86 delta G is negative delta S is very small, delta G is approximately same at different temperature. So, with respect to temperature you are not going to see any or much difference with respect to delta G, whatever temperature you do the reaction you are supposed to get this thermit process.

Alumina plus chromium this alumina formation and this chromium oxide you can convert, because it is becoming independent of temperature. But what usually you need to do is you need a kinetic you need to cross a kinetic barrier; you cannot just mix at room temperature alumina and chromium ok. You need to prime the reaction almost like you know igniting your, you know your what your this explosive or any of those and you know what are those.

Student: Fireworks.

Fireworks yes I can see that. Now, this is a kinetic say you need a prime you need something called priming we are done going to be done very soon. So, you need to prime the reaction with magnesium re bond, but once you initiate the reaction it is a auto catalytic process once you initiate one time. If you have let us say whole mass of huge mass of this reaction right after initiation you do not have to worry about it, because the reaction it is elf will take care of the later on ignition period ok. So, it is a very you know auto catalytic type of thing once you catalyze it will be catalyzed forever sorry.

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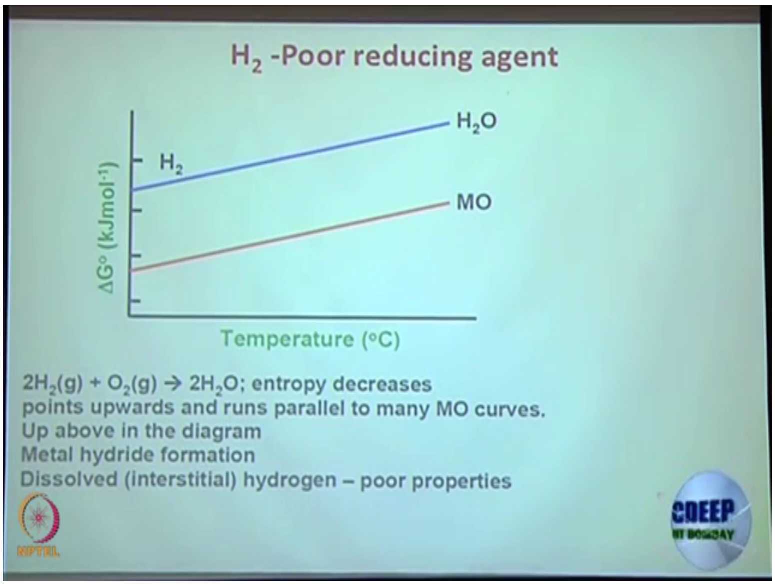
H_2 -Poor reducing agent

$2H_2(g) + O_2(g) \rightarrow 2H_2O$; entropy decreases
points upwards and runs parallel to many MO curves.
Up above in the diagram
Metal hydride formation
Dissolved (interstitial) hydrogen – poor properties

Student: Priming.

Sorry.

Student: What is priming?

Priming is like initiating, initiating the reaction ok. You have to initiate the reaction you have to provide enough activation you need to start. The reaction activation barrier is there for the reaction then activation barrier the moment you cross that activation barrier everything is down in. So, thermodynamically everything is going to work out from there on ok.

Now, of course, life would perhaps the world would have been a very good place or much better place, if we perhaps need not use charcoal. I think one or few of you are having the queries it is going to produce carbon monoxide or carbon dioxide anyway it is a bad thing right. Of course, lot of this greenhouse effect lot of global warming everything is due to let say blame it on Ellingham diagram ok, it is a charcoal you are using right.

Now, the problem is there is no other solution, perhaps the best solution could have been this hydrogen right. If hydrogen plus oxygen going to give you water that water has it been gas ultimately it is liquid right hydrogen plus hydrogen plus oxygen two gas you are consuming and you are forming something water that is liquid.

Has it been something gas ok, more of a water has been you know if it is stable form has been gas, then what would have happened that instead of that carbon Ellingham diagram that carbon going down you perhaps would have seen hydrogen to water formation, hydrogen plus oxygen going to water formation or hydrogen plus metal oxide going to form the water formation that would have been in a negative slope right and water being very friendly you would not have any problem.

Since most of the cases what you see that this hydrogen going to water or hydrogen reacting with metal oxide going to water is running parallel to that of the metal oxide curve. You are not going to use the hydrogen efficiently for conversion of metal oxide to metal and that is unfortunate, I think and most of the problem world's problem would have been really really solved ok.

But that is how it is, but of course, there are some reaction you have to you have to know relatively where hydrogen is with respect to other metal oxide curve in the Ellingham diagram. So, some reaction you can utilize hydrogen for the reduction of corresponding metal oxide to the metal. But it is not a generalized solution the generalized solution is charcoal that is where everywhere you see the charcoal.

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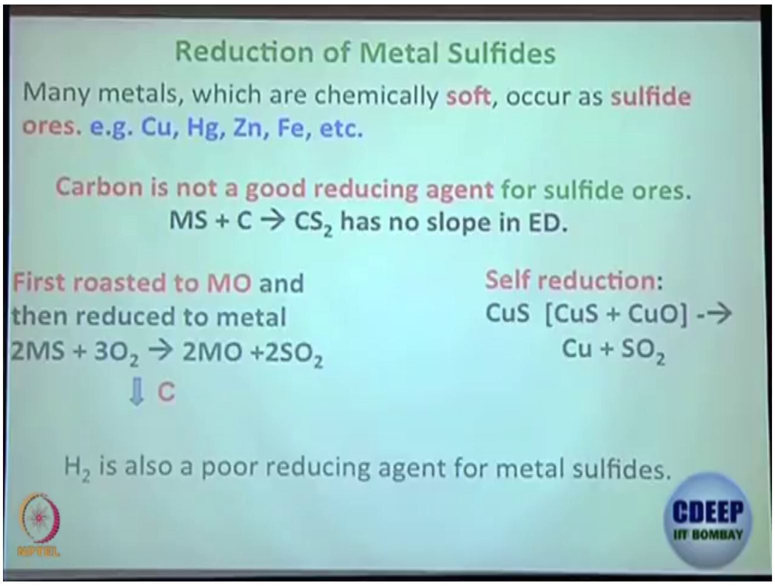

Reduction of Metal Sulfides

Many metals, which are chemically soft, occur as sulfide ores. e.g. Cu, Hg, Zn, Fe, etc.

Carbon is not a good reducing agent for sulfide ores.
$MS + C \rightarrow CS_2$ has no slope in ED.

First roasted to MO and then reduced to metal
$2MS + 3O_2 \rightarrow 2MO + 2SO_2$
$\Downarrow$ C

Self reduction:
CuS [$CuS + CuO$] $\rightarrow$ $Cu + SO_2$

H_2 is also a poor reducing agent for metal sulfides.

Now, the point of this reduction of metal sulfides; so of course, as you mentioned many metals which are chemically soft you know it is again that hard soft acid base principle. Oxide is hard so metals which are in harder form or hard cation metal oxide will be formed and those are the metal oxide we see in the ore let say calcium oxide calcium 2 plus is oxide 2 2 minus is hard calcium oxide is going to be favorable form.

Calcium sulfide may not be that favorable that much favorable, but because calcium two plus is hard sulfide is softer relatively softer. So, calcium sulfide or let say magnesium sulfide formation or whatever titanium sulfide if you form, these are not going to work out these are not going to be a stable conformation.

So, similarly when you have metal which is not hard, but more of a soft on a softer side, then metal oxide formation will not be preferable. You would get metal sulfide in the ore you will get metal sulfide. Now, these are the for example, these are the cases copper marker zinc iron these are the cases of course iron can be iron oxide as well. But, still it can give you the sulfide form. Now, the reason why we cannot utilize this reaction is very simple.

The metal sulfide plus carbon this carbon dioxide carbon di sulfide formation has more slope almost it is a constant slope in Ellingham diagram carbon going to carbon monoxide you have seen it is going down running down. But, carbon reacting with metal sulfide it is a generalized form we have given metal sulfide is not just like metal and sulfide. It is of course, sometime it is as you have seen Fe2 O3 it is a simplified form we have given metal sulfide ok, metal oxide mo it is not necessarily mo it can be m 2 o 3, similarly metal sulfide can be of different form anyway.

This is the problem why we cannot utilize the charcoal for carbon di sulfide formation. It is therefore, easier or it is advisable I think you have almost no choice, but to convert metal sulfide to metal oxide one step and then utilize charcoal to reduce those metal oxide to the corresponding metal right. So, first metal oxide is roasted or metal sulfide is roasted to metal oxide and then reduced to metal.

So, metal sulfide plus oxygen going to metal oxide plus sulfur dioxide plus charcoal giving you the metal and corresponding; of course, another possibilities are there, where yourself reduction is a viable technique. What is self reduction you take copper sulfide you try to do this reaction copper sulfide plus oxygen you try to get copper oxide, the moment copper oxide is formed copper sulfide and copper oxide together can give you copper and sulfur dioxide under that high temperature condition right.

So, this is like a self sorting self reduction, of course hydrogen is also a poor reducing agent for metal sulfide. So, you have to see the relative curve if there you know hydrogen going to water is delta G for that reaction is it less or more negative compared to the metal going to metal sulfide that is all you need to care. So, this the Ellingham diagram for metal sulfide as you can see these are you know in the metal oxide curve we were seeing minus 2000 3000 and so on.

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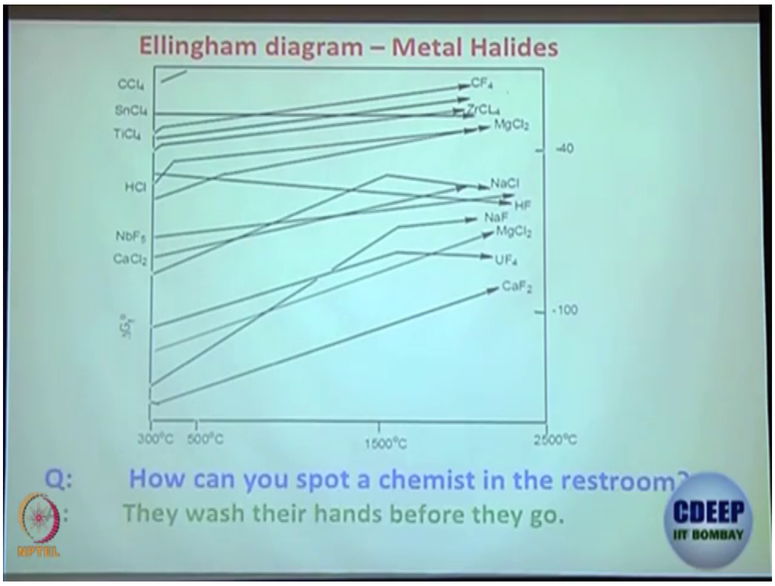

Ellingham diagram – Metal Halides

Q: How can you spot a chemist in the restroom?

: They wash their hands before they go.

But you see this metal sulfide these curve are not that much thermodynamically favorable ok. That is a good thing because and then you can convert that into the metal oxide and so on ok.

There are also Ellingham diagram possible for metal halides, there is no way you need to remember these things most often I think few things you should remember.

But most often you will be provided with the Ellingham diagram ok. But, you know of course which is most electro positive metal and there by what should be the curve for it these are few things you should know. But these are metal halide these are metal halide this is metal halide Ellingham diagram. Of course, so we have seen oxide Ellingham diagram sulfide Ellingham diagram and metal halide Ellingham diagram ok.

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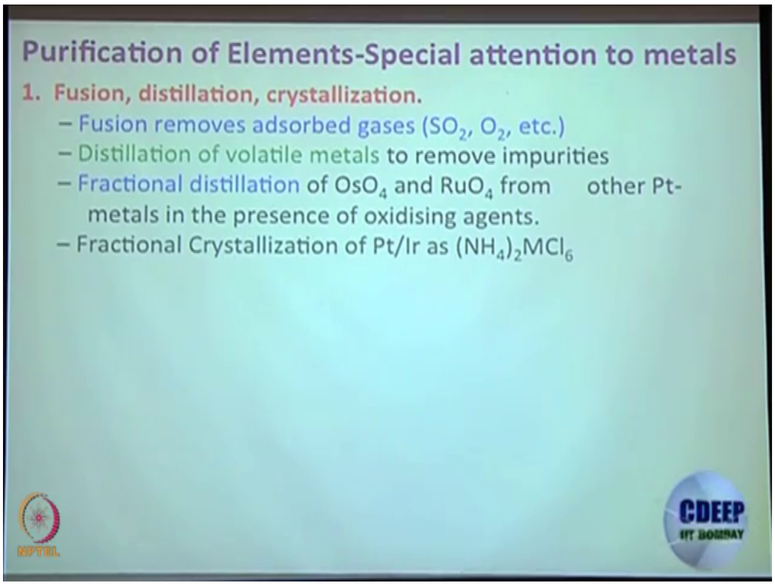

Purification of Elements-Special attention to metals

1. Fusion, distillation, crystallization.
   - Fusion removes adsorbed gases (SO_2, O_2, etc.)
   - Distillation of volatile metals to remove impurities
   - Fractional distillation of OsO_4 and RuO_4 from other Pt-metals in the presence of oxidising agents.
   - Fractional Crystallization of Pt/Ir as $(NH_4)_2MCl_6$

Now so let me summarize by telling you this part, we have seen different techniques as simple as mechanical separation electromagnetic separation and thermal decomposition you can heat it and decompose it, these three things are very easy to understand. Of course almost everything is easy to understand, but these are none of these are kind of you know self contained method you cannot just use one method to purify your ores and get the metal in pure form.

Often you have to use the combination of method. Of course, you can use one metal to reduce another metal oxide right, also you can use the electro catalytic reduction where cathode and anode you can have right. The one which is perhaps most important for us is the Ellingham diagram, where we take a metal oxide use charcoal reduce the metal oxide to corresponding metal and then we form carbon in oxidized form carbon monoxide or carbon dioxide right.

What we try to also say that similar things are possible for sulfides and halides metal sulfides and metal halides. But those are not of really that great importance compared to oxide, metal sulfide almost invariably is converted to metal oxides first and then that is converted to the corresponding metal. Why metal sulfides are converted? Because, the carbon di sulfide curve is not having a negative slope as we are seen carbon monoxide case ok; that is all now there are other techniques.

Lot of other techniques which are utilized quite routinely these are fusion distillation crystallization ok. Fusion is something let us say you have a rock; you have a rock, now if you fuse that rock what will be happening inside that rock some dissolved or some amount of gas will be there. So, if you melt it those gas will be evaporated right, so the trapped gases will be evaporated. Of course, that is a purification technique you can distil you can distil means.

Let us say you would start with a liquid you heat it at a particular temperature let us say 200 degree centigrade. So, those which are having boiling point suitable less than 200 degree C, selectively sum up those or all of those which are having boiling point less than 200 degree C that will be selectively coming out rest of the material will be in the container where you started with.

So, you can both collect the material that is left of and material that is going to get boiled and you collect it you can collect it in fraction wise, one fraction two fraction and you can increase or decrease the temperature adjust the temperature slowly you can increase the temperature. So, that one by one compound can come out, let us say you heat it at 1000 degree c one metal oxide comes out ok. You heat it further 1500 degree c another metal comes out.

So, by heating at 1000 degree C you get that in pure form one ore in pure form by heating just let us say 1500 or 1400 you get another one, so this is another technique. So, what essentially this extraction technique tells you, it is a combination of things you need to have knowledge both of course, engineering knowledge when you are going to do it practically engineering knowledge is essential.

Because you cannot just heat without knowing what is going to happen ok, you have to have those knowledge in addition. Of course, you can have let us say crystallization technique you have let us say you have a five things, five solid material combined, you try to add some solvent, solvent let us say could be water solvent could be something else and selectively one of those material get dissolved in that solvent right. So, you take it out you try to grow crystal or you know that is what is in pure form.

So, solubility can be utilized either to grow the crystal or to wash it off or take it off take of particularly one of the metal or metal oxide. So, there are there are other lot of other techniques it is not necessarily you have to read in detail. But it is important that you do understand that those things exists.

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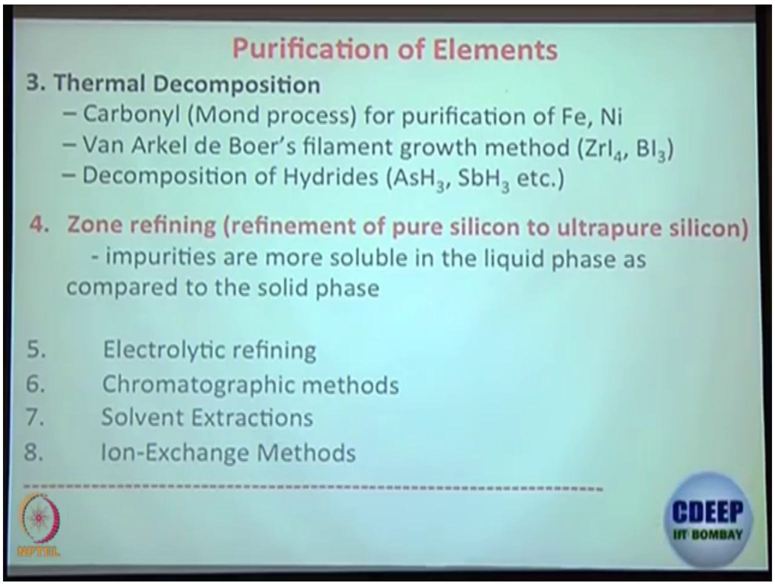

Purification of Elements

3. Thermal Decomposition

- Carbonyl (Mond process) for purification of Fe, Ni
- Van Arkel de Boer's filament growth method (ZrI_4, BI_3)
- Decomposition of Hydrides (AsH_3, SbH_3 etc.)

4. Zone refining (refinement of pure silicon to ultrapure silicon)
- impurities are more soluble in the liquid phase as compared to the solid phase

5. Electrolytic refining
6. Chromatographic methods
7. Solvent Extractions
8. Ion-Exchange Methods

So thermal decomposition of course thermal decomposition, we have seen zone refining this is the last topic two minutes I will take what is zone refining well zone refining is very simply.

Student: (Refer Time: 20:02).

It is a purification done so that you get a high level of material. Let us say you have 99 percent of titanium you want to make it 99.99 percent titanium. How do you do it? Because that is going to be you know in your lot of these metal, all the electronic devices you use it require that your metal be pure in that form, without that impurity you can cost you bounding right. So, you need to really purify the material ok. So, this is what is zone refining one of the technique what you have.

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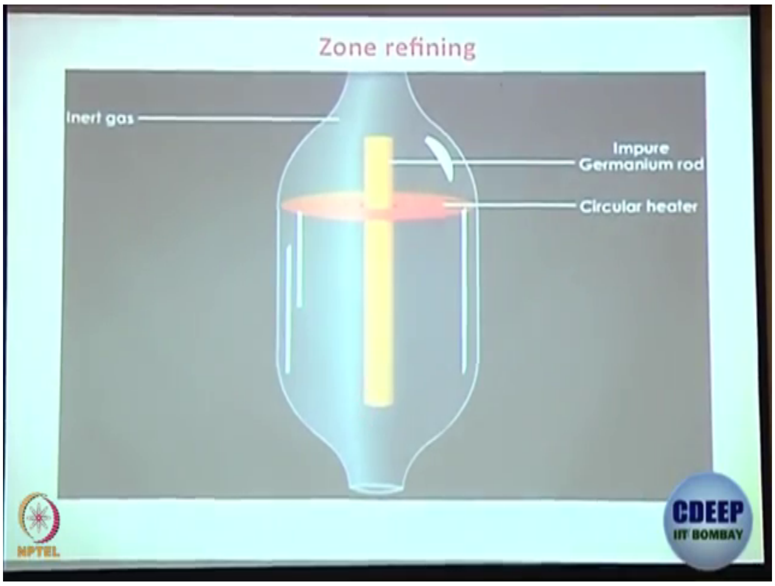
Zone refining

Let say this is your 99 percent or 90 percent pure rod of metal, let us say iron bar or titanium bar or whatever metallic you have. Now, this is a circular heater now circular heater if you have. So, this is our let us say we are having a impure germanium rod let us say this is 90 percent impure germanium rod ok.

Now, it is a circular heater it melts selectively at one position at this position, wherever it is heating it is melting temporarily let us say it is heating here momentarily it heats over there and it melts only that region. It does not melt this region on the top or on the bottom it is a very powerful heater ok, it melts only a selective zone and from top to bottom this circular heater your kind of rotating and bringing it down again putting it back bringing it down.

So, by doing that what is happening is you are melting it and then cooling it, cooling means the moment the circular heater is going out of that zone it is going to cool down. So, impurities when it is going to get solidify impurities will be coming to a particular. So, let us say it is a small zone the top material in that small zone the top region will be pure metal and the impurity will cool down and come at the bottom; that way if because the cooling profile is going to be different for pure metal and impure material whatever is there.

So, that way impurities are going to be on one of them either is it is on the top or on the bottom does not matter. If you keep on doing this you know circular if you keep on heating it, what is happening is one end of this metallic bar one end of it is going to have the impurity concentrated and thereby you can just cut it off you can cut it off that impure part and get almost let say 99.99 percent pure metal you keep on doing.

Let us say if first time is not giving you very high purity, you can keep on heat keep on doing this process after 45 times from 90 percent material pure material you will get let say something like 99.99 percent pure material. So, it is a zone refining you just zone wise very selective area wise you keep on doing this process alright. So, that is how impurities gets collected I think I am done.

Thank you, for your hospitality.