Non-ferrous Extractive Metallurgy

Prof. H. S. Ray

Department of Metallurgical and Materials Engineering

Indian Institute of Technology, Kharagpur

Module No. # 01

Lecture No. # 10

Refining of Metals - Chemical Methods

So far, we have been discussing principles of methods of production of metals using Pyrometallurgy, Hydrometallurgy and Electrometallurgy. We will now discuss some techniques of refining, in other words, we would like to go from impure metal to pure metal.

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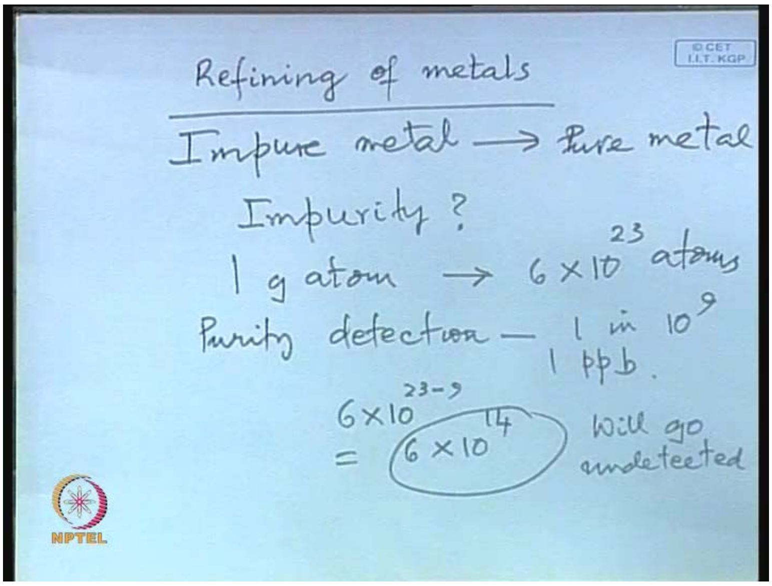

Refining of metals

Impure metal → Pure metal

Impurity ?

1 g atom → 6×10^{23} atoms

Purity detection — 1 in 10^9

1 ppb.

$6 \times 10^{23-9}$

$= 6 \times 10^{14}$ will go undeteeted

Now, I think, we should first be very clear as to what we mean by the word impurity. Theoretically speaking, there is nothing in this world which is totally pure; it is because we have no method of knowing if something is totally pure. You know according to Avogadro's hypothesis, 1 gram atom of anything will have 6 into 10 to the power 23 atoms, but our purity detection level say in the chemical laboratory will at most go to finding 1 in 10 to the power 9 that is 1 parts per billion.

Now, that implies that 6 into 10 to the power 23 minus 9, that is 6 into 10 to the power 14. So many atoms in a gram atom will go undetected, so if there were other atoms and many atoms impurity atoms at this level it it looks very large, but it is below 1 part per million, 1 part per billion, so it cannot detect.

So, if we find something and we find it absolutely pure according to today's analytical techniques, it is going up to 1 parts per billion; we should not think it is totally pure, there are other impurity atoms below that level, which we are not able to detect. Fortunately, with what we can detect, below that perhaps very often impurity levels are not important; as a matter of fact we should say that, an impurity is an impurity when it has an undesirable effect on the intended use. Consider for example copper, now copper is a metal which is used in electrical applications.

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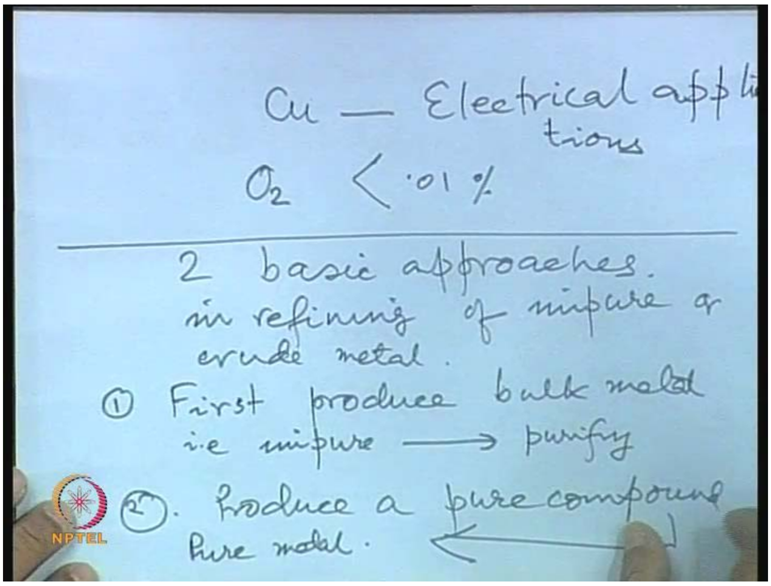

Cu — Electrical appli
tions

$O_2 < \cdot 01\%$

2 basic approaches.
in refining of impure or
crude metal.

① First produce bulk metal
i.e impure ⟶ purify

②. Produce a pure compound
Pure metal. ⟵

See, if a copper for electrical applications, there oxygen is a very serious impurity, it has to be less than 0.01 percent sometimes, why? Because, if you allow oxygen to be there, then the electrical conductivity is very badly affected, some oxides we precipitate at the grain boundaries, so oxygen is a serious impurity, whereas if you have to make a sculpture out of copper alloy or copper or copper in coinage, if there is some oxygen it does not matter because, it does not affect the intended use. So, we always look at purity, from the point of view of the question, whether the impurity is affecting the intended use, if it is not affecting the intended use, we we can ignore that. But then, in many situations we find that, we have impurity elements, which must be removed, otherwise we cannot use the metal for the intended use.

Now, the first thing to know is that, there are two basic approaches in refining 2 basic approaches in refining of impure or sometimes we call it crude metal; approach one is, first produce bulk metal that is impure, then purify. Now the aim is, in the beginning the aim is to produce as large quantity as possible, bulk recovery and after you get the bulk recovery, then you worry about the impurity contents. In the second approach, right from the beginning we try to produce a pure compound and which will automatically give pure metal. So, you see the two basic approaches, they are quite different from each other.

What do we do in iron and steel making, we do not worry about producing pure iron, pure steel or pure anything, we just produce as much of iron as possible as pig iron, it has a whole lot of things: carbon, manganese, silicon, phosphorous, sulphur whatever, we then go for steel making, a purified version of pig iron. So, we are first producing bulk quantities, then you are purifying, whereas you will find there will be examples where we cannot use this approach, right from the beginning, the aim would be not to produce metal in the bulk, but a pure compound and once you have got the pure compound, from there automatically the metal you will get will be pure.

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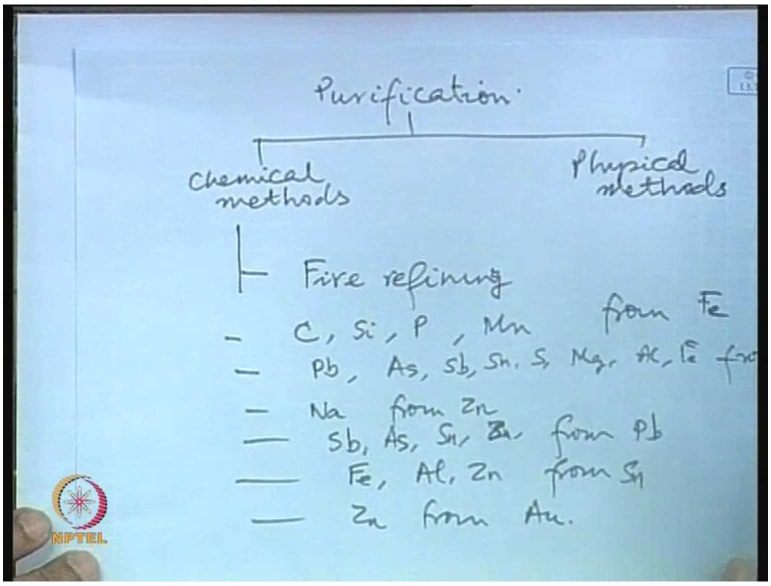

Purification

Chemical methods

Physical methods

Fire refining

- C, Si, P, Mn from Fe
- Pb, As, Sb, Sn, S, Mg, Al, Fe fr
- Na from Zn
- Sb, As, Sn, Zn from Pb
- Fe, Al, Zn from Sn
- Zn from Au.

There are many, many ways of doing it, and we can say that purification can be achieved by chemical methods or by physical methods. I will very quickly indicate some of these methods and what I say, I am going to say is not a total picture, but some of the important ones I would certainly mention.

Under chemical methods, the most important method is fire refining, a method that can be used from time in memorial for thousands of years, fire has been used to eliminate from the crude metal, impurity elements or elements we do not want. Say for example, consider iron and steel, simply by keeping it under fire in the molten state or by injecting oxygen through that, we can remove carbon, silicon, phosphorous, manganese from iron, this is how, pig iron is purifying in iron and steel industry from pig iron to steel; steel is a purified version of pig iron, we eliminate carbon, silicon, phosphorous, manganese as stable oxides by blowing an oxygen or in the open hearth furnace, simply by keeping the metal for long hours under oxidizing conditions.

The idea is to produce oxides of carbon, silicon, phosphorous, manganese, which preferentially form prior to forming of iron oxides. Of course in the process, the pool of metal gets very saturated to dissolve oxygen, which has to be removed later on by a process of deoxidation that is a separate matter.

Now similarly, we can remove a whole lot of metals, lead, arsenic, antimony, tin, sulphur, magnesium, aluminum, iron, etcetera from copper. Copper in molten state we treat them and an oxidizing atmosphere, and the impurity elements will form either volatile oxides or solid oxides, which will separate out as sludge; we can remove sodium from zinc, we can remove antimony, arsenic, tin, zinc from tin, and zinc from lead and there are many others, we can remove iron, aluminum, zinc from tin, and zinc from gold.

Now, in all this cases, the things that are being removed, obviously are forming more stable oxides compared to the to the metal that you want to purify, when we come to discussing production and purification of individual metal, some of these will be repeated.

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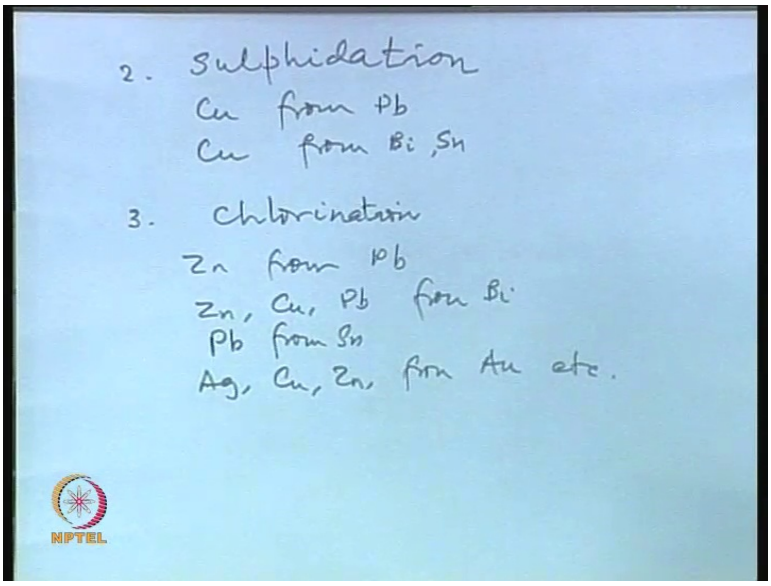

2. Sulphidation
Cu from Pb
Cu from Bi, Sn

3. Chlorination
Zn from Pb
Zn, Cu, Pb from Bi
Pb from Sn
Ag, Cu, Zn, from Au etc.

We can also do sulphidation means, preferentially form sulphides of impurities as compared to the metal being purified, copper can be separated from lead, copper can be separated from bismuth and tin, because this will form stable sulphide as compared to the rest.

A very effective way of removing impurities is through chlorination, we can remove zinc from lead, because if you have lead and zinc in the molten state, if you pass chlorine, zinc chloride will form vapours will come out, lead chloride will will not form when zinc chloride is forming. Zinc, copper, lead can be removed from bismuth, lead from tin and other examples are there like this one, silver, copper, zinc from gold etcetera.

So, the basic principle in this this sort of fire refining is very simple, that we are keeping the crude metal in the molten state under oxidizing conditions, we control the partial of pressure of oxygen various levels, we can remove the impurity elements either as volatile oxides or as solids which would come out as a slag, which should be skimmed of periodically, very standard technique.

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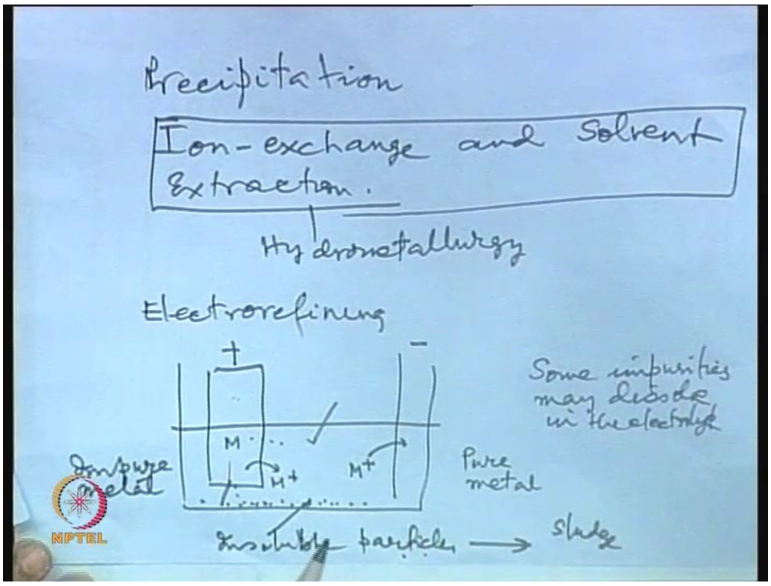

The other methods of that will make use of chemical processing, of course would be in hydrometallurgy precipitation if everything is taken into solution it can precipitate, impurity elements as oxides or carbonates or sulphates or whatever. Then, there are some special processes call ion exchange and solvent extraction, exclusively used in Hydrometallurgy, widely used in Hydrometallurgy, I will discuss that little later.

Under chemical methods of purification, one should also include electro refining, there the idea is that, in a suitable electrolyte, we will have the impure metal as anode, we will have a sheet of pure metal as cathode and we will do electro refining. When this impure metal M will dissolve as M plus ions or whatever with the balancing, this will go and deposited on the pure cathode, so which time this will begin to become thinner and this will become thicker.

So, from an impure thick anode, we will produce a pure thick cathode. What will happen to the impurities that are there in the impure or crude metal? Two things can happen: from here, some impurities may dissolve in the electrolyte, this is electrolyte, some impurities will dissolve, some will precept, some will not dissolve, but as the metal is taken out of this, they will simply drop as insolvable insolvable particles called sludge. So, two things can happen, we will produce a pure cathodes from the impure anode, impurities will be released some will go into the solution, some will be deposited at the bottom or sludge.

Now, both of them may be very valuable, we can recover by-products from the sludge, we can recover some impurities, if they have their uses from the solution also, so these are some of the chemical methods.

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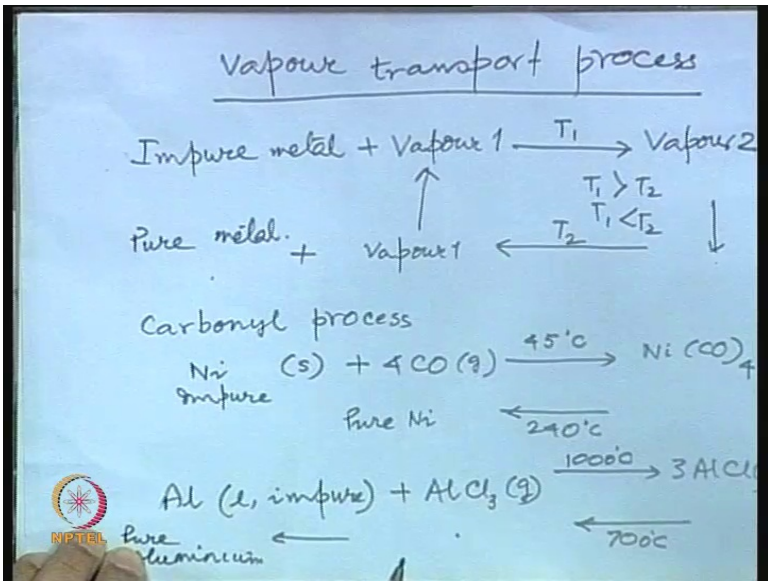

Vapour transport process

Impure metal + Vapour 1 $\xrightarrow{T_1}$ Vapour2

$T_1 > T_2$

$T_1 < T_2$

Pure metal. + Vapour1 $\xleftarrow{T_2}$

Carbonyl process

$Ni(s) + 4CO(g) \xrightarrow{45^\circ C} Ni(CO)_4$

impure

Pure Ni $\xleftarrow[240^\circ C]{}$

$Al(l, impure) + AlCl_3(g) \xrightarrow{1000^\circ C} 3AlCl$

Pure aluminium $\leftarrow$ $\xleftarrow[700^\circ C]{}$

Now, before I go into a solvent extraction and electro refining, let me discuss a very interesting method, which come under the class of vapour transport processes. Vapour transport process, this is not suitable for large scale large scale production, but it is an extremely sophisticated technique for producing pure metals from impure metals and it is applicable for many metals.

But, the reason I am discussing is, it is based on a beautiful thermodynamic concept, see a whole idea here is, that we will take an impure metal, make it react with a vapour or gas, say we call it vapour or gas 1 to produce another vapour 2 means, that vapour which is the the gaseous reactant reacts with the impure metal and takes it into a gas phase, vapour 2 at some temperature T1. This vapour is taken out and at another temperature, T 1 can be greater than T 2 or sometimes T 1 can be less than T 2, this reaction is reversed means, we will produce, we will generate the vapour 1, but now we will have pure metal, I hope you understand this scheme.

We have impure metal and we create an intermediate gas phase vapour 2 using a gaseous reactant vapour 1 and then this intermediate gas phase that we have created is at another temperature, which may be higher or lower decompose to regenerate that vapour and produce pure metal. Obviously, this thing cannot be done in the same chamber, the idea is that, once you have produced the vapour 2, you take it out into another chamber and then you decompose to get the pure metal and this vapour of course will be recirculated.

In the source system, there is no consumption of the reactant which is taking the metal into the gas phase; there is a very interesting example, application of this in the case of purification of nickel. Now, that has a special name called carbonyl process, where nickel, impure solid nickel is made to react carbon monoxide which is gas at about 45 degrees, at such low temperatures it can be converted to nickel carbonyl. This nickel carbonyl at a higher temperatures 200 and 40 degree centigrade decomposes and the reaction goes this way, so you regenerate carbon monoxide and now you have pure nickel; it looks very easy but, such a process is very, very dangerous, carbonyl is is a very poisonous gas everything has to be done in a closed chamber.

Similar reaction is applied in the case of aluminum - liquid, impure one can react with aluminum tetra chloride gas to form at 1000 degrees aluminum mono chloride gas, so using this gaseous species, we are taking aluminum into a gas phase and then this gas decomposes at a lower temperature to regenerate this and of course pure aluminum. So, essentially at one temperature, we produce an intermediate gas by gasifying this metal to a reaction with a gaseous species and then the reaction is reversed at another temperature, which can be at a higher temperature or at a lower temperature.

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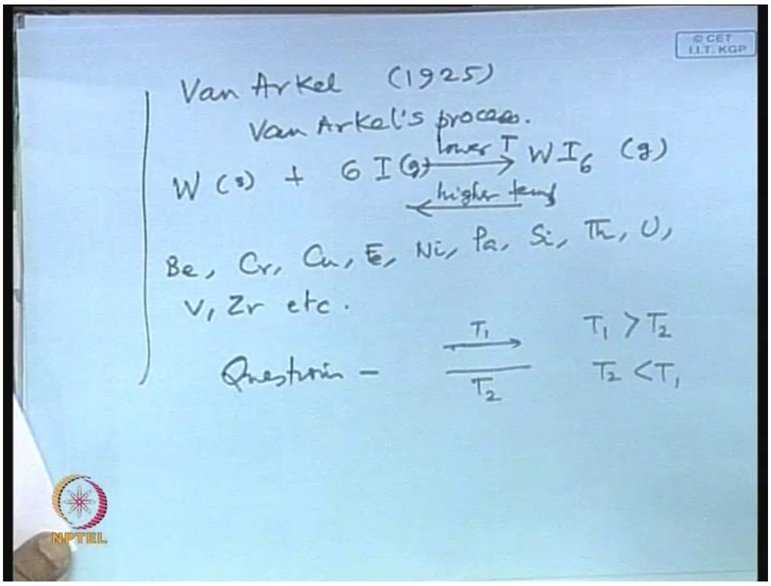

Van Arkel (1925)

Van Arkel's process.

$$W(s) + 6I(g) \underset{\text{higher temp}}{\overset{\text{lower } T}{\rightleftharpoons}} WI_6(g)$$

Be, Cr, Cu, E, Ni, Pa, Si, Th, U, V, Zr etc.

Question – $\underset{T_2}{\overset{T_1}{\rightleftharpoons}}$ $T_1 > T_2$ $T_2 < T_1$

Now a gentlemen called Van Arkel achieved some similar things around 1925 and it is called Van Arkel’s arkel’s process, very famous process, where impure tungsten solid is reacted with iodine gas, I am writing I, because of the temperatures, where this reaction is taking place, iodine is atomic to produce tungsten iodide gas, gas at another temperature it will reversed.

This method can be applied for in a small scale for many metals like, beryllium, chromium, copper, iron, nickel, palladium, silicon, thorium, uranium, vanadium, zirconium, etcetera, this is the reason, why I want to discuss it in a few minute, because it is a it it is a it is in a class of its own. A very interesting process, some call it Van Arkel’s process, we have the other names like carbonyl process for nickel, and in general, they are called vapour transport processes, because we are transporting impure metal through a gas phase to a pure metal form; in this cases, we are taking the crude metal at a lower temperature and we decompose it at a higher temperature.

Questions that come to our mind is, when will the temperature for the forward reaction T 1 and temperature for the T 2, when will T 1 be more than T 2? When will T 2 be less than T 1? When this is achievable and when this is not achievable? What are the thermodynamic conditions for that? I would like to discuss that.

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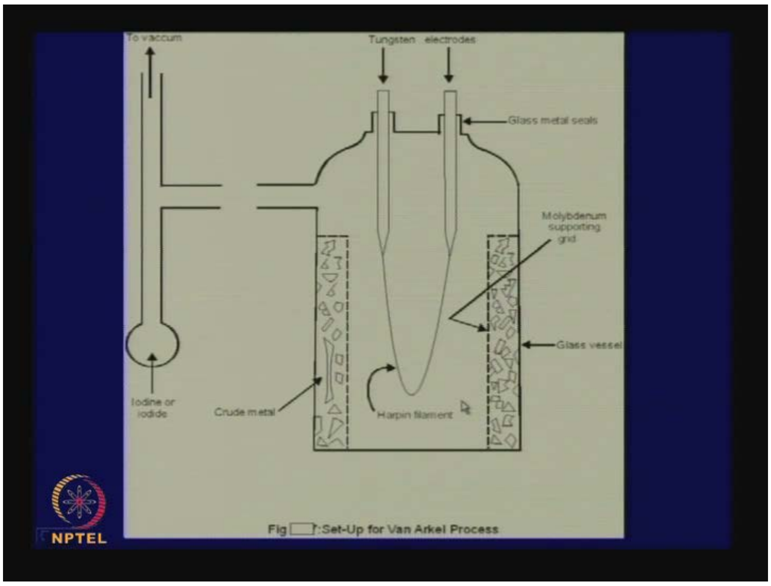

Fig [ ]:Set-Up for Van Arkel Process

But before I proceed, let me give to show you this diagram, this diagram figure shows how purification of tungsten is done by Van Arkel’s process. These are the two tungsten electrodes; this is a tungsten filament and by passing current, this filament is kept at a high temperature. The rest of the chamber is at a lower temperature, but the filament inside is at a higher temperature, because a current is passing through. This heat generated here may heat the chamber, if necessary it can be heated from outside also.

Now, iodine comes to this chamber separately and we have a vacuum arrangement to maintain whatever pressure we want, what happens is that the crude metal is kept along the periphery, in a cage we have molybdenum supporting grid, means there is a cage all around but there are perforations, so the gases can come and go.

Now, in this case, we have seen the temperature required for forming tungsten iodide, I have not given the temperature, but I will give it little later, it it forms at a lower temperature. So, in this chamber tungsten iodide vapour will form and when it goes and hits the filament, if this region it gets heated, so pure tungsten is deposited and then iodine vapour is rejected; so the iodine vapour will keep coming here, react with to form tungsten iodide and move there and it will get decomposed tungsten when deposit.

So, you transport titanium tungsten from this cage to the filament, the filament grows thicker, this filament grows thicker and from here, you lose crude metal gradually, whatever impurities are there in the tungsten will be left behind in this place.

Now, this is one design, essentially we are able to have in the same chamber two temperature zones: one zone is here, another zone is here and the way it is it is done is very convenient that the crude metal stays here and the pure metal goes at another place and iodine is coming here picking up a tungsten from here, going there and getting disassociated the tungsten iodide and it keeps on going on and that material goes, when we have got a very thick filament, we will we will cut it off put another tungsten wire and we will put more tungsten here a crude tungsten and we will do the purification.

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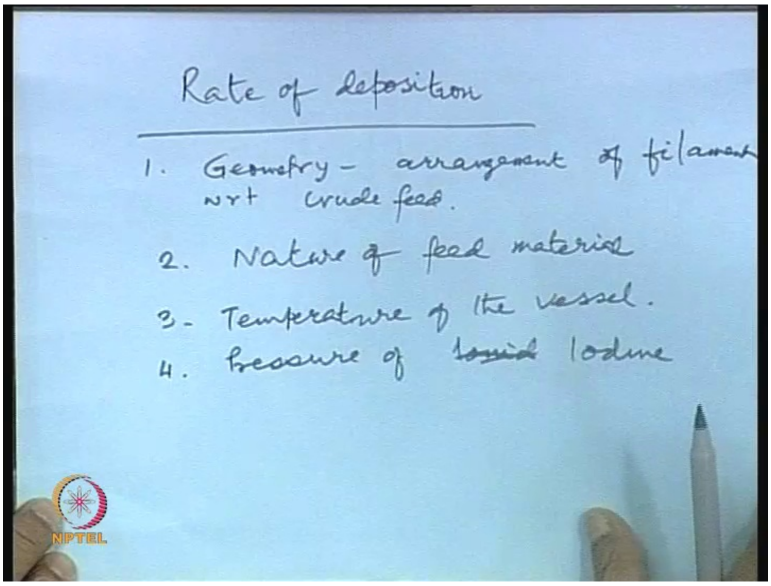

Rate of deposition

1. Geometry – arrangement of filame
   wrt crude feed.
2. Nature of feed material
3. Temperature of the vessel.
4. Pressure of ~~liquid~~ Iodine

Of course, it is a a very schematic diagram, the rate of deposition will depend on many things; rate of deposition, rate of deposition will depend on factors like geometry, arrangement of filament with respect to crude feed. One has to optimize the distance between the filament and the crude feed, the dimensions of the chamber, it would depend on a nature of feed material, it will depend on temperature of the vessel, at what temperature, it will depend on the pressure of iodine gas that is maintained within the chamber etcetera, etcetera, etcetera.

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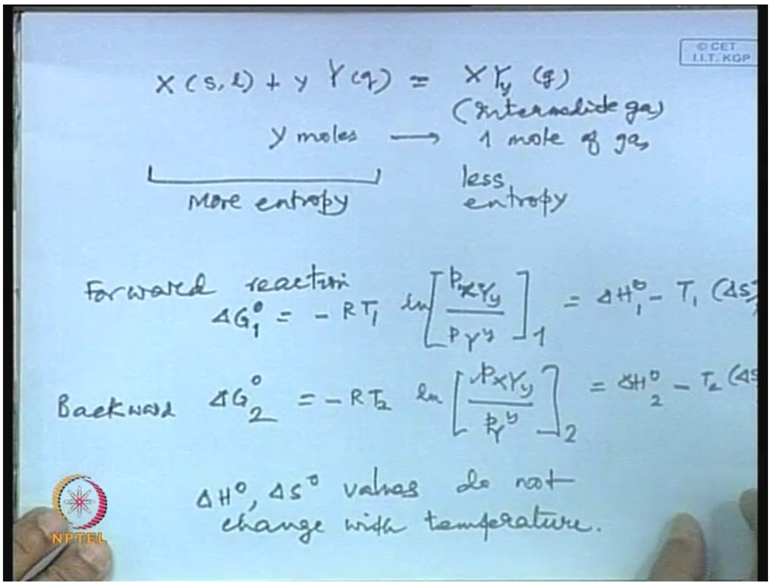

$X(s,l) + y\,Y(g) = XY_y\,(g)$

(intermediate gas)

y moles ⟶ 1 mole of gas

More entropy

less entropy

Forward reaction

$\Delta G_1^0 = -RT_1 \ln\left[\frac{p_{XY_y}}{p_Y{}^y}\right]_1 = \Delta H_1^0 - T_1\,(\Delta S$

Backward $\Delta G_2^0 = -RT_2 \ln\left[\frac{p_{XY_y}}{p_Y{}^y}\right]_2 = \Delta H_2^0 - T_2\,(\Delta S$

ΔH^0, ΔS^0 values do not change with temperature.

Let us look at this reaction in little more detail. Essentially the reaction is that, a metal X solid or liquid is reacting with a gas Y to generate an intermediate gas, this is the intermediate gas. Now, there are y moles of gas giving only one mole of gas, in this side we have more entropy, because the gas is disappearing in the reaction, creating less gas we have less entropy, so we have an entropy change in this which is negative.

Now, we can write for the forward reaction, delta g naught 1, minus r t ln p x Y y we are dealing with two gaseous species y y, it is happening at temperature T 1 delta H naught 1 minus T 1 delta s naught 1. And for the backward reaction, we can similarly write ln p x Y y p Y y. Now, I have mentioned before that normally delta h naught, delta s naught values do not change with temperature, so we can actually get rid of the the notations of 1, 2, etcetera with delta h naught minus T 1 delta s naught, delta h naught minus t delta s naught.

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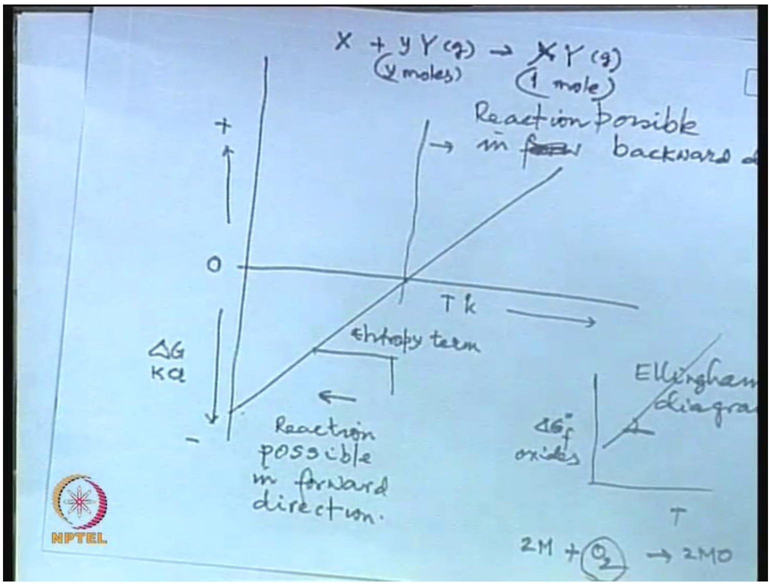

Now see, kind of things we can derive from the simple looking at the simple thing, what we really want is that, a situation like this, we need to ensure that the free energy change in the reaction or free energy change formation of the intermediate will go from negative to positive side, so for the forward reactions, it should be below 0 in this direction, below this temperature, beyond this temperature, this line must cross the 0, so that the reverse reaction becomes possible.

You will recall that, in the case of Ellingham diagrams, where free energies of formations of oxides plotted against temperature, basically it was metal always in terms of 1 or 2 and we are writing 2 M O, the picture is somewhat similar. In this also entropy is reduced, because a gas phase on the left hand side disappears, so there is an entropy change and that is why all the lines move upwards and I had always mentioned that, this is the entropy term, same thing here the slope here will depend on the entropy term.

So, basically, you go back to the previous picture, the reversal of the reaction whether we can go from in the forward direction and then at another temperature, come to the left hand side, it will depend on several factors. First of all, suppose there was no heat of reaction, if delta h naught was 0 then T 1, T 2, T 2 T 2 cancel out, which means, the reaction becomes insensitive to temperature changes.

If there was no entropy change, then it would not be possible to reverse the reaction at all because, delta G naught does will not depend on delta on temperature anymore, temperature would get cancelled out; on the other hand, if the delta h naught term was very large, then also will be a problem, because delta h naught actually is the intercept also in Ellingham diagrams you had seen.

It means, if the line was something like this, the temperature was so high, that it was inconceivable that will go to such a high temperature for decomposition, so there is a restriction here, should not be 0, should not be too high; interestingly this is a critical term because larger the slope of this line, the faster will be able to reverse that, but if it is very shallow, then something we have might have to go to very high temperature reverse. But, if it is strip then, we should quickly be able to ensure reversal and that will depend on the entropy change, which will depend on what kind of intermediate gaseous gaseous species you are making, you are able to generate.

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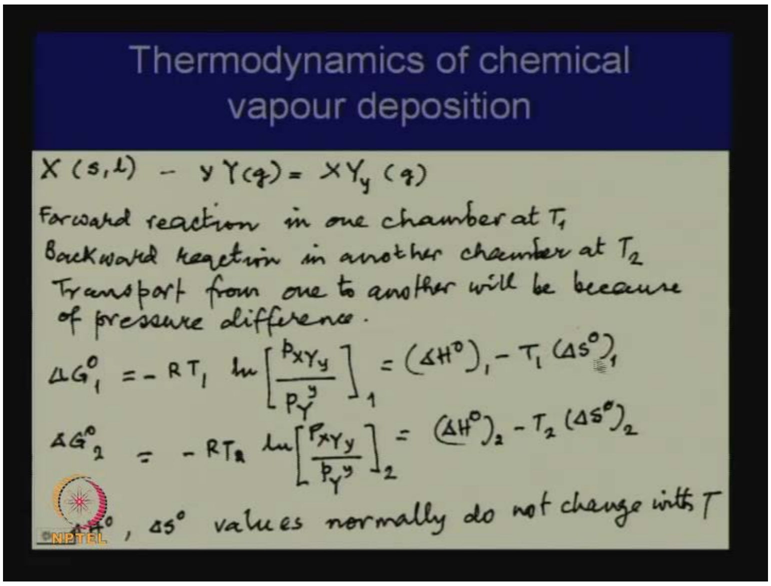

Thermodynamics of chemical vapour deposition

$X(s,l) - yY(g) = XY_y(g)$

Forward reaction in one chamber at T_1

Backward reaction in another chamber at T_2

Transport from one to another will be because of pressure difference.

$$\Delta G^0_1 = -RT_1 \ln\left[\frac{p_{XY_y}}{p_Y^y}\right]_1 = (\Delta H^0)_1 - T_1(\Delta S^0)_1$$

$$\Delta G^0_2 = -RT_2 \ln\left[\frac{p_{XY_y}}{p_Y^y}\right]_2 = (\Delta H^0)_2 - T_2(\Delta S^0)_2$$

ΔH^0, ΔS^0 values normally do not change with T

So, this is the equation and as I have mentioned, if there is no delta H naught in the reaction, then T 1 would get cancelled out and therefore, this term will not depend on delta on temperature anymore, reaction becomes insensitive. This is critical, this will tell us how fast or how slow the things can happen (Refer Slide Time: 38:14).

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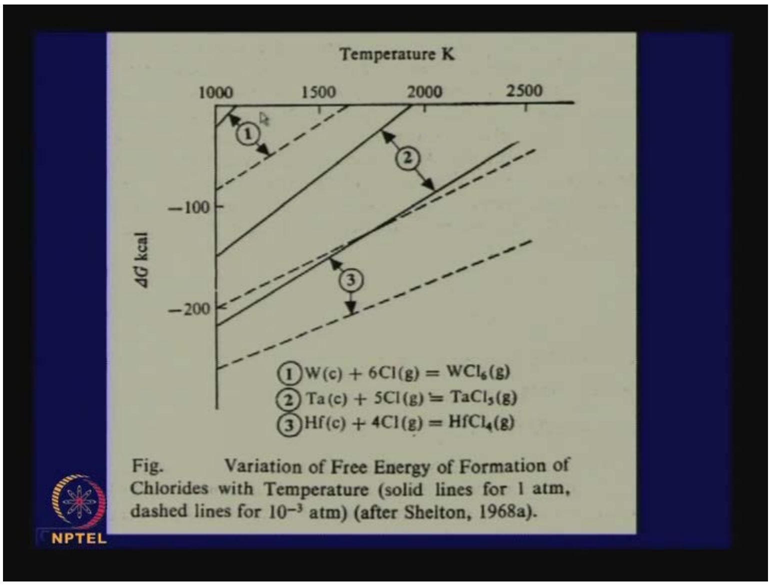

① $W(c) + 6Cl(g) = WCl_6(g)$

② $Ta(c) + 5Cl(g) \leftrightharpoons TaCl_5(g)$

③ $Hf(c) + 4Cl(g) = HfCl_4(g)$

Fig. Variation of Free Energy of Formation of Chlorides with Temperature (solid lines for 1 atm, dashed lines for 10^{-3} atm) (after Shelton, 1968a).

Now look at the actual data, for reactions of tungsten chloride to form w C l 6, this is for tantalum to put T a C l 5, this is hafnium to form hafnium tetra chloride. Now all these seeds can be, impure metals can be purified by this method, form an intermediate gas then, disassociate it with a higher temperature to get pure metal and regenerate the highlight. I am giving you data for chlorine and this data are given for different pressures in the chamber for one atmosphere lines 10 to the power minus 3 atmosphere lines.

Let us ignore that, let us look at the solid lines only, you will find the slope is more, slope of the line is more for tungsten, because here 6 moles of gas are consumed to make one mole of gas, this lot more entropy change, delta s naught is larger; in this case, 5 moles react with the solid to produce one mole of gas, in this case, 4 moles make 1 mole of gas. So, you see the changes in slope of these lines accordingly, it is highest here, it is intermediate here, and it is it has the least slope here, so we will try to ensure that, we form intermediate gas that gives us maximum change of entropy.

Now in this case, because tungsten has a higher valency, if the process becomes very effective for tungsten, because in temperatures below 1000 degrees, we can produce this gas just we go beyond 1000 degrees and the reaction is reversed, I hope you have understood the basic principle.

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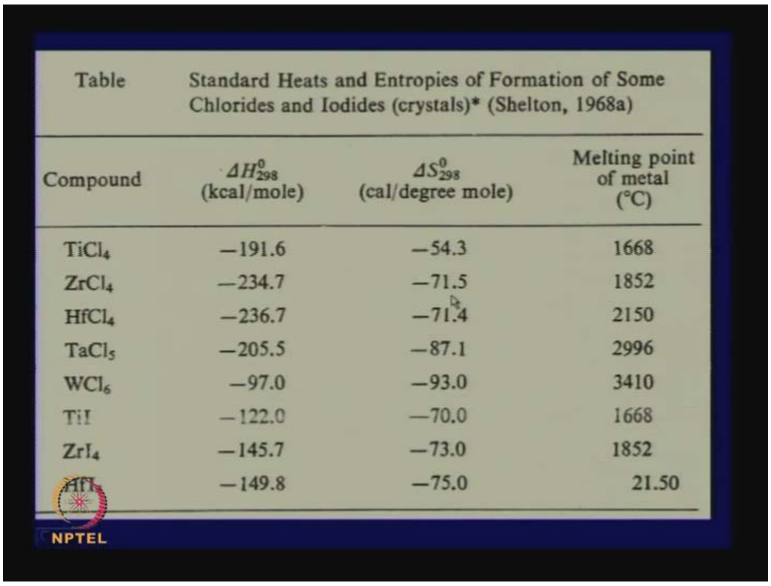

Table Standard Heats and Entropies of Formation of Some Chlorides and Iodides (crystals)* (Shelton, 1968a)

Compound	ΔH^0_{298} (kcal/mole)	ΔS^0_{298} (cal/degree mole)	Melting point of metal (°C)
$TiCl_4$	−191.6	−54.3	1668
$ZrCl_4$	−234.7	−71.5	1852
$HfCl_4$	−236.7	−71.4	2150
$TaCl_5$	−205.5	−87.1	2996
WCl_6	−97.0	−93.0	3410
TiI	−122.0	−70.0	1668
ZrI_4	−145.7	−73.0	1852
HfI	−149.8	−75.0	21.50

I have given some data and you will find that same thing here, that the delta H naught value for tungsten 2 W 6 is higher than that for tantalum pentachloride, which is large and that for hafnium. So, the delta is not the critical parameter this also high is important, because when this is small like in the case of tungsten hexachloride the intercept is small, means here very quickly going to you can quickly cross the 0 point in delta g naught scale.

The larger it is the further away from that line that you have to cross and of course, the these are also important, the melting point parameters, because if tungsten for example, had the melting point been low then what would happen, that in the filament you will not have the solid depositing, you might get a liquid and the liquid will drop off and you would not get a solid filament you will have all kinds of problems; the fact is that, it has a high melting point, it definitely helps and the in the in the kind of apparatus we have. So, there are all this parameters are important in order to show that the most important thing is the entropy parameter.

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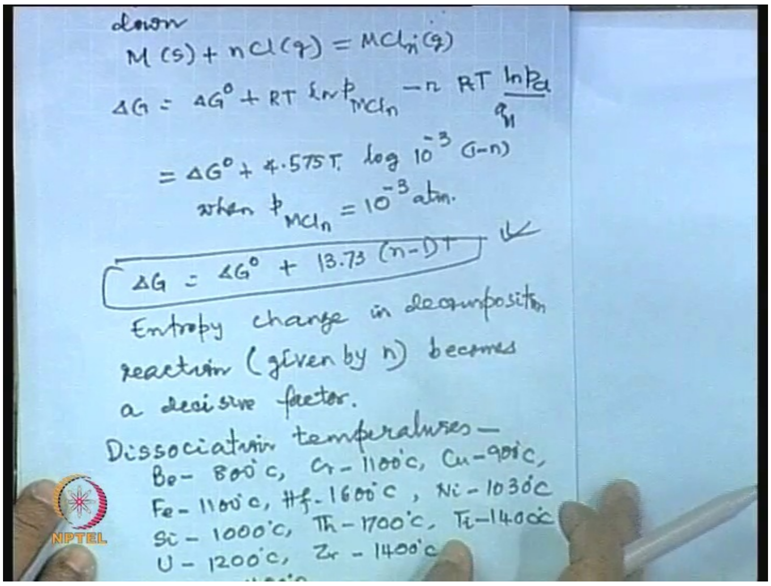

down

$M(s) + nCl(g) = MCl_n(g)$

$\Delta G = \Delta G^0 + RT \ln p_{MCl_n} - nRT \ln \frac{p_{Cl}}{a_M}$

$= \Delta G^0 + 4.575T \log 10^{-3} (1-n)$

when $p_{MCl_n} = 10^{-3}$ atm.

$\boxed{\Delta G = \Delta G^0 + 13.73 (n-1)T}$

Entropy change in decomposition reaction (given by n) becomes a decisive factor.

Dissociation temperatures –

Be – 800°C, Cr – 1100°C, Cu – 901°C,

Fe – 1100°C, Hf – 1600°C, Ni – 1030°C

Si – 1000°C, Th – 1700°C, Ti – 1400°C

U – 1200°C, Zr – 1400°C

Let me just show you another slide here, as I said we are bringing in iodine or chlorine gas, but we are writing in terms of C l because, the temperatures where we are forming the intermediate gas and the C l 2 dissociates, so we can write the reaction as M c l giving you the intermediate gas where n, n can have different values for different metals. For this we have an expression like that, that delta g naught plus R T l n k and that R T l n k will have 3 terms: one pressure of this intermediate gas, ln p this divided by p c l and of course the activity of m which is one, we do not we we can forget about that.

If the pressure in the chamber is 10 to the power minus 3, we finally get an expression like this and when M p m c l n intermediate gas is also in the chamber 10 to the power minus 3, this will be the final expression. So, this gives us the slope and entropy change in decomposition reaction given by n becomes decisive factor as you can see will given by this reaction.

Now the dissociation temperatures for various metals are like this, for beryllium 800 degrees, chromium, copper 900, iron you can see, nickel, silicon, thorium, titanium, uranium, zirconium, tungsten will decompose tungsten chloride 6 only at 1100 degrees, this is all for 10 to the power minus 3 atmosphere equation.

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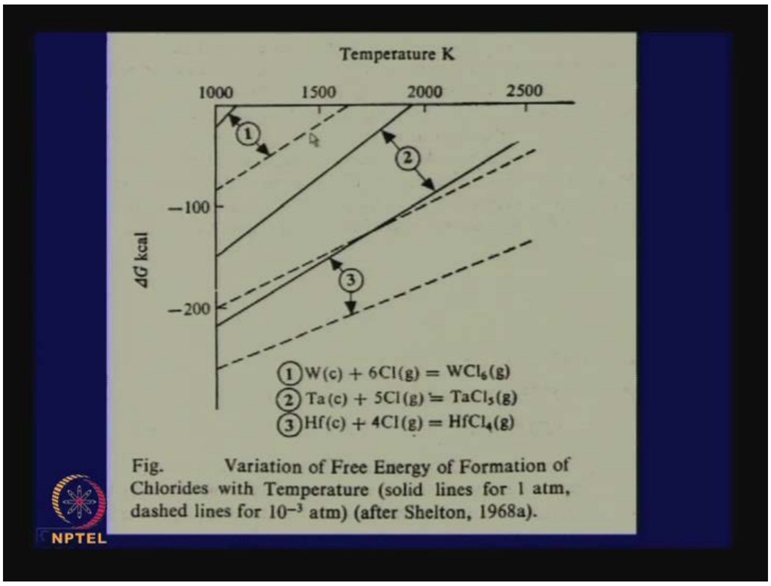

① $W(c) + 6Cl(g) = WCl_6(g)$
② $Ta(c) + 5Cl(g) = TaCl_5(g)$
③ $Hf(c) + 4Cl(g) = HfCl_4(g)$

Fig. Variation of Free Energy of Formation of Chlorides with Temperature (solid lines for 1 atm, dashed lines for 10^{-3} atm) (after Shelton, 1968a).

Because, if we change the pressure from this to that, then actually we are creating a, for us if if we look at the solid line this is for 10 to the power minus 3 no this sorry, this is the solid lines are for one atmosphere and dashed lines are 10 to the power minus 3. For solid line, this is if we have greater pressures, then we have a solid line and if we have a reduced pressure we have the dashed line. Now, if you operate at a very low pressure, you see, you might have to go to very high temperatures for for decomposition, whereas we will be able to do that at a lower temperature if you had higher pressures.

But there are many, many factors to be taken into account as to whether you should operate with high pressures or or low pressures, may be we we need not discuss it now. But, the this gives you the idea that you can do do the reversal reactions over a wide range of temperature. One has to take into account kinetics of that process also with what will be better at high pressures, what will be better to low pressures.

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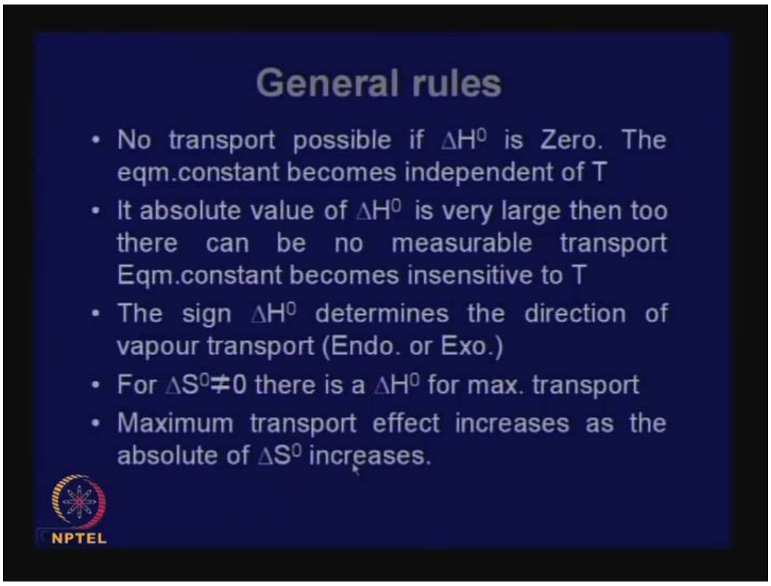

General rules

- No transport possible if ΔH^0 is Zero. The eqm.constant becomes independent of T
- It absolute value of ΔH^0 is very large then too there can be no measurable transport Eqm.constant becomes insensitive to T
- The sign ΔH^0 determines the direction of vapour transport (Endo. or Exo.)
- For $\Delta S^0 \neq 0$ there is a ΔH^0 for max. transport
- Maximum transport effect increases as the absolute of ΔS^0 increases.

Now, there are some general rules for such transport processes and I have mentioned some of them; first is that, no transport is possible if delta g naught value is 0 or very small. If the enthalpy change for that reaction of formation of the intermediate gas phase is a very small, then the process become insensitive. You cannot gasify the crude metal at at one temperature and decompose it another, because equilibrium constant becomes independent of T, again if they absolute if they absolute value of delta g naught are very large, then there can be no measurable transport, equilibrium constant becomes insensitive to temperature.

Like, if this is a very large large value then, this term t 1delta naught term becomes to to small compared to this and we we we will not be able to have the reversal. The sign of delta h naught determines the direction of vapour transport, whether it is endothermic, whether it is exothermic will determine, whether you will form the vapour at a lower temperature and decomposition a higher temperature or we will form it at a higher temperature and decomposite at a lower temperature.

Like in the case of nickel, we form the intermediate gas carbonyl at a lower temperature around 40 decompose it at 2 to 40, but in the case of aluminum, we go through a reverse thing aluminum trichloride reacts with crude aluminum to produce aluminum mono chloride at a higher temperature and it decomposes at a lower temperature to regenerate aluminum and trichloride and a pure aluminum.

So you can see for yourself, how it is and by if you look at that equation, the sign will determine the what will happen of course, for delta naught is equal not equal to 0, there is a delta h naught for maximum transport. There has to be a balance between the values of delta s naught, which is critically needed otherwise, we would not be able to have the reversal. There is a value of delta h naught for maximum transport to take place and maximum transport effect increases as the absolute value of delta s naught increases.

So, this is a brief discussion of the vapour transport processes, I discuss it in little more detail, because thermodynamic principles are very interesting and this process makes use of this thermodynamic principles, but it is not for a large scale purification of metals. Let me come to two techniques called ion exchange and solvent extraction, who are extensively employed in hydrometallurgy for purification of leach liquor.

In that case, we are not dealing with a solid impure metal and purifying it, the idea is to have the metallic values in a solution along with a lot of impurity metals assigns. We would like to selectively take out the metallic irons to produce a pure compound, from which we will produce pure metal; we are coming to the second approach in purification.

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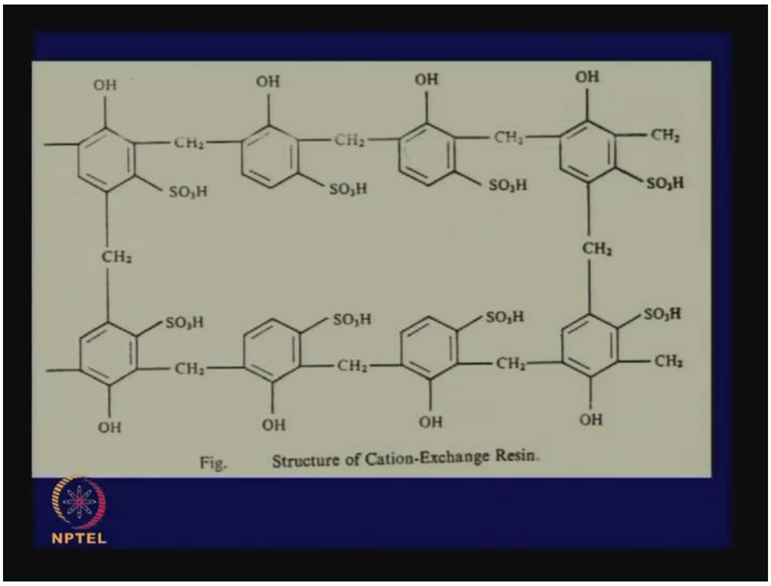

Fig. Structure of Cation-Exchange Resin.

Now, the ion exchange techniques makes use of some complex organic acids or bases, which are insoluble in water the salts that are formed between, because of reaction of this resin and a leach liquor, they are also insolvable in water.

So, basically I am showing you one particular cation exchange resin here, there are many many reason resins, these are all solid organic compounds and the structure has basic or acidic groups, which are capable of ionization and exchange reactions; basically what you see here is a large molecule that comprise of interconnected and cross length chains is a large molecule, there is cross linking also and there is interlinking like this.

In this particular resin, this is the place where an exchange reaction will take place, this mean hydrogen will be knocked off in that place a metal cation will be absorbed, so when you have in the liquid many many metals one or two particular metal, cation would be replaced by this, hydrogen will be replaced by that and then, the metallic value that you are aiming at will be observed by this resin. Now, here what we are showing is a cation exchange resin, because this is where a cationic exchange will take place, we sometimes write is simply as r x means resin matrix and x is the where the exchange will take place, r is the polymer backbone and x is the ion exchange site.

Here the iron exchange site is S O 3 H, where the hydrogen will be replaced by the metal cation by some reaction such as this, say copper sulphate solution is there, it comes in contact with this resin, we are simply writing as R S O 3 8, because S O 3 this is the part where the exchange reaction will take place.

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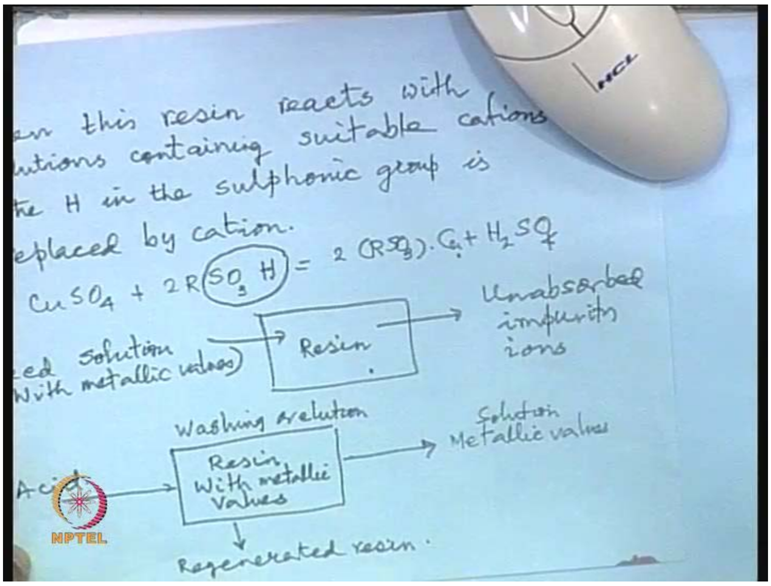

en this resin reacts with
utions containing suitable cations
he H in the sulphonic group is
eplaced by cation.

$$CuSO_4 + 2R(SO_3H) = 2(RSO_3).Cu + H_2SO_4$$

So, in the place of h copper will go H 2 S O 4 will be created, so there are two step process, the feed solution with metallic values will pass through this solid resin, unabsorbed impurity ions will pass off unabsorbed, but the metallic value will be absorbed in the resin and then, that can be washed or eluted through a process of washing or illusion by fresh water, fresh acid, the resin will be regenerated and the solution will take out metallic values.

Now, this is the very simple explanation that basically what all we do, I will I will may be I will I will come to that, when I continue with the lecture, let me now conclude this lecture. We started by discussing purification techniques for metals, we said first of all, define what do you mean by purity, unless the presence of an impurity is affecting the intended use, its not impurity and then, there are different ways we can take out the impurity from a metal; one approach is produced the metal in the bulk and then purify take out the impurity elements.

The other is do not follow that approach, to start with produce a pure compound and then from that you get the metallurgy, there are whole lot of chemical methods. I have discussed fire refining, sulphidation, chlorination, we have talked about intermediate vapour transport process, then I have just started discussing iron exchange, which I will continue in the next lecture, thank you very much.