Non-ferrous Extractive Metallurgy

Prof. H. S. Ray
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Kharagpur

Lecture No. # 05
General Methods of Metal Extraction

Well friends, I now come to module 3 of this lecture series. In module 2 we ended up by discussing mineral beneficiation techniques, which are use to prepare ore into a product, which will be acceptable to an extraction process industry, I have mentioned that you cannot simply mine an ore and start working on it to extract metals, the ore has to be dressed properly. It has to be sized various minerals will have to be separated, the gang materials have to be rejected and for doing this there are many, many unit operations. Having done that, we now have a dressed ore from which we will have to have a process for extracting metal either as an elemental form or as a compound, may be more than one metal.

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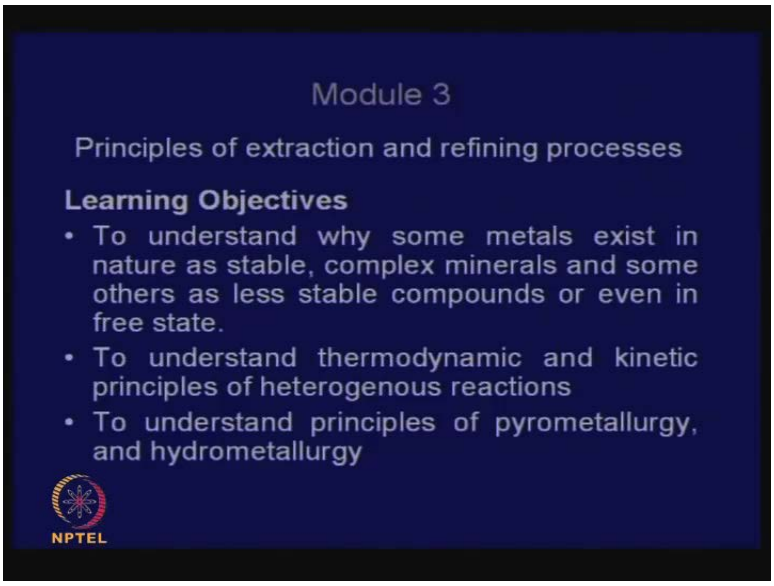

Module 3

Principles of extraction and refining processes

Learning Objectives

- To understand why some metals exist in nature as stable, complex minerals and some others as less stable compounds or even in free state.
- To understand thermodynamic and kinetic principles of heterogenous reactions
- To understand principles of pyrometallurgy, and hydrometallurgy

And in this module, we will discuss the principle of extraction of metals or compounds and the various refining techniques. The learning objectives would be to understand why some metals exist in nature a stable complex minerals and some others has less compound or even in three states, why do I mention this? Because unless we understand the nature of minerals, which depend on the nature of reactivates of elements we really cannot design an extraction process, we would also have to understand some thermodynamic and kinetic principles or heterogeneous reactions, most reactions in extracting metallurgy are heterogeneous means they involve more than one phase, there can be two phases, sometimes there are three phases, solid, liquid, and gas.

And then having done that we will go into the principles of pyrometallurgy and hydrometallurgy, I will discuss electrometallurgy in the next module after several lectures, why I will discuss it later I would explain when I get there.

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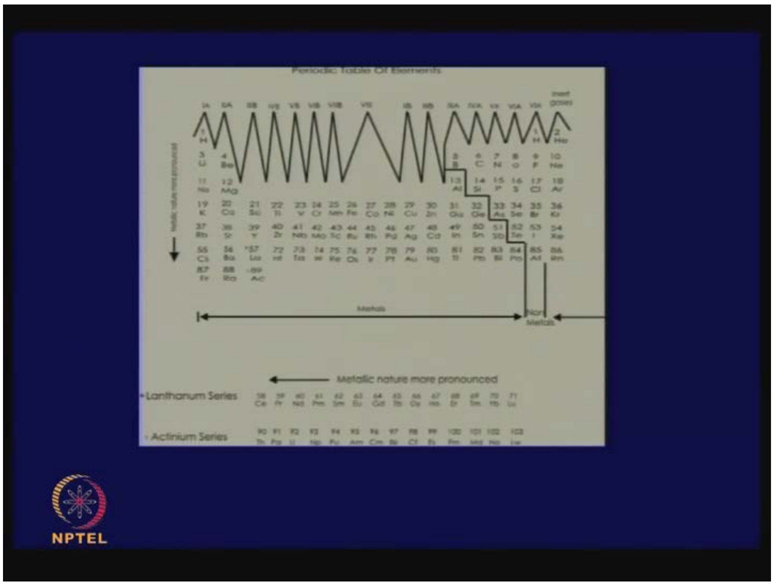

Now before we start we need to know why not all metals are similar in reactivates. Now, first of all you know that we make a distinction between nonmetals and metals, all these are non metals on the right hand side here all non metals, these are all metals almost 55, 56 of them, there are many more because on the lanthanum an actinium series there are many metals, so all these are metals excepting hydrogen which is which have been put there. Now, what is a metal? I have earlier mentioned to you that general we say by the word metal something which has a very typical luster, it has good electronic conductivity as mechanical properties like strength, hardness, and malleability, ductility etcetera, and a metal is a base by the word base I mean a metal reacts with acid, but not all metals, those which are more metallic will react more strongly.

There are some metals which have other properties, but have no reactivity towards us is, so the metallic nature in terms of this properties which are kind of way vary there are also exception, like arsenic and bismuth they are metals, but they are very brutal, so they do not have mechanical strength, on the other hand non metals like iodine and graphite and they have luster, using graphite they shine, and graphite also has a very high conductivity, but none of them is a metal.

And then you know diamond, diamond is a nonmetal but it is a hardest substance now, so the classification between metals and non metals is not so clear cut is been fake, but basically we understand what is a metal what is a nonmetal, but then not all metals are equally metallic, in the periodic table what we see is that the metallic nature increases as we move form right to left, and as we move from top to bottom, the metals in this area are much more metallic then the metals in this area, like they will be much more reactive towards acids than the metals in these areas.

And because they the reactivates differ they form different kinds of compound, the metals in these areas the kind of compound they will form will be different from the metals in this area the compounds that will be found by metals in this area, actually you know that metals like gold they do not form any compounds at all, because they are so stable their reactivates are so small things like lead it is reactivity is small, it does it forms very week compounds.

So, again metallic nature is not the same in all metals, and their reactivates are not the same in all metals, why I am saying it because the fundamental aim of an extraction process is to break a mineral separate the metal form the nonmetal with which it is generally in a command state, and what are the nonmetals it will be mostly oxygen, sulphur or halogen, so most minerals are compounds of metals with oxygen which means there are oxides or with halogen haloids or sulphur.

And of course, there are combinations of oxides so there can be silicates alumino silicates etcetera, so the whole idea would be to break the compound and take the metal out, now there are some compounds which are very week compounds, like cinnabar, mercury sulphide all one has to do is to just heat it and mercury liquid will flow out, because h g will get separated from sulphur, it is very easy it does not need any reduce signature nothing only by heating you can break it, there are some which are very stable component aluminum oxide a l 2 o 3 it is very difficult to break it.

What we have to do is to dissolve it in some solvent and then electrolyze it high temperature, so not only alumina is electrolyzed in a solvent by application of electricity, it also has to be done at a very high temperature, because the solvent in this case would be cryolite which is ah halite, and that would need high temperatures to may it to start.

Something like lead which is which can be very easily converted to oxide, very easily reduced by carbon, because carbon will take out the oxygen and lead will be left behind, so these are the techniques of breaking the compound to liberate the metal, and all extraction processes in a sense are processes of liberating the metal form its state of association with nonmetals like oxygen, sulphur and halogen. Again let me repeat that there are some minerals which are compounds which are very stable, there are some minerals which are very week and very easily decomposed, and that depends on the reactivates of this metals, now how do we define the reactivates, a very common way of defining reactivity of a metal is in terms of electrode potential, which you must have studied in course in thermo dynamics.

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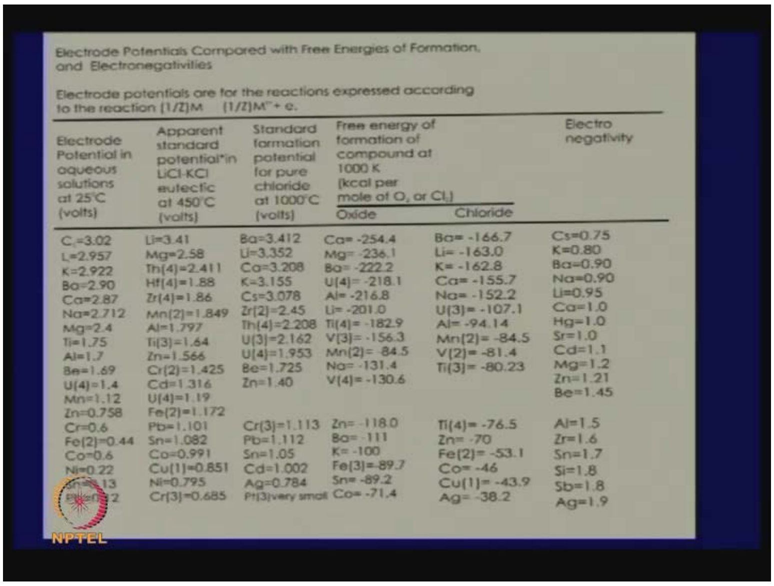

Electrode Potentials Compared with Free Energies of Formation, and Electronegativities

Electrode potentials are for the reactions expressed according to the reaction $(1/Z)M \quad (1/Z)M^{z+} + e$.

Electrode Potential in aqueous solutions at 25°C (volts)	Apparent standard potential* in LiCl-KCl eutectic at 450°C (volts)	Standard formation potential for pure chloride at 1000°C (volts)	Free energy of formation of compound at 1000 K (kcal per mole of O_2 or Cl_2)		Electro negativity
			Oxide	Chloride	
Cs=3.02	Li=3.41	Ba=3.412	Ca= -254.4	Ba= -166.7	Cs=0.75
Li=2.957	Mg=2.58	Li=3.352	Mg= -236.1	Li= -163.0	K=0.80
K=2.922	Th(4)=2.411	Ca=3.208	Ba= -222.2	K= -162.8	Ba=0.90
Ba=2.90	Hf(4)=1.88	K=3.155	U(4)= -218.1	Ca= -155.7	Na=0.90
Ca=2.87	Zr(4)=1.86	Cs=3.078	Al= -216.8	Na= -152.2	Li=0.95
Na=2.712	Mn(2)=1.849	Zr(2)=2.45	Li= -201.0	U(3)= -107.1	Ca=1.0
Mg=2.4	Al=1.797	Th(4)=2.208	Ti(4)= -182.9	Al= -94.14	Hg=1.0
Ti=1.75	Ti(3)=1.64	U(3)=2.162	V(3)= -156.3	Mn(2)= -84.5	Sr=1.0
Al=1.7	Zn=1.566	U(4)=1.953	Mn(2)= -84.5	V(2)= -81.4	Cd=1.1
Be=1.69	Cr(2)=1.425	Be=1.725	Na= -131.4	Ti(3)= -80.23	Mg=1.2
U(4)=1.4	Cd=1.316	Zn=1.40	V(4)= -130.6		Zn=1.21
Mn=1.12	U(4)=1.19				Be=1.45
Zn=0.758	Fe(2)=1.172				
Cr=0.6	Pb=1.101	Cr(3)=1.113	Zn= -118.0	Ti(4)= -76.5	Al=1.5
Fe(2)=0.44	Sn=1.082	Pb=1.112	Ba= -111	Zn= -70	Zr=1.6
Co=0.6	Co=0.991	Sn=1.05	K= -100	Fe(2)= -53.1	Sn=1.7
Ni=0.22	Cu(1)=0.851	Cd=1.002	Fe(3)= -89.7	Co= -46	Si=1.8
Sn=[illegible]13	Ni=0.795	Ag=0.784	Sn= -89.2	Cu(1)= -43.9	Sb=1.8
[illegible]2	Cr(3)=0.685	Pt(3) very small	Co= -71.4	Ag= -38.2	Ag=1.9

Electrode potentials are the potential that is created between metal and metalines in an aqueous media, and it is coated with reference to the electrode potential between hydrogen hydrogen ions.

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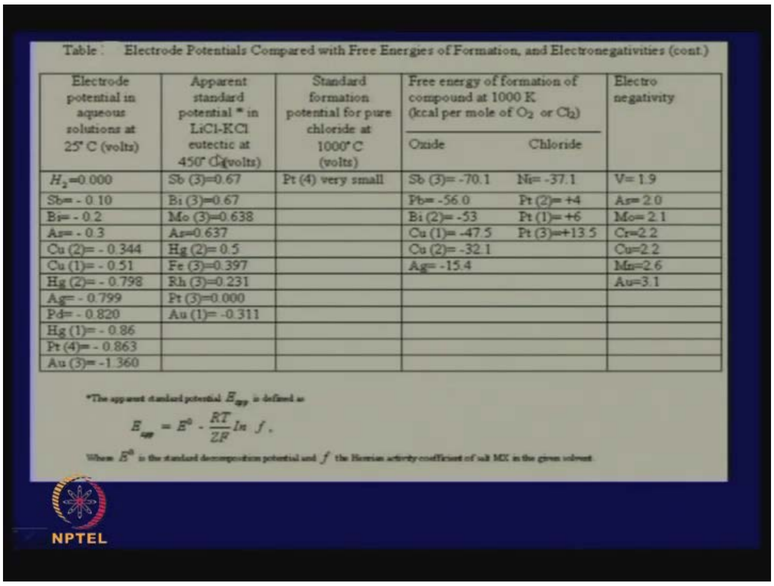

Table : Electrode Potentials Compared with Free Energies of Formation, and Electronegativities (cont.)

Electrode potential in aqueous solutions at 25° C (volts)	Apparent standard potential * in LiCl-KCl eutectic at 450° C (volts)	Standard formation potential for pure chloride at 1000° C (volts)	Free energy of formation of compound at 1000 K (kcal per mole of O_2 or Cl_2)		Electro negativity
			Oxide	Chloride	
H_2=0.000	Sb (3)=0.67	Pt (4) very small	Sb (3)= -70.1	Ni= -37.1	V= 1.9
Sb= - 0.10	Bi (3)=0.67		Pb= -56.0	Pt (2)= +4	As= 2.0
Bi= - 0.2	Mo (3)=0.638		Bi (2)= -53	Pt (1)= +6	Mo= 2.1
As= - 0.3	As=0.637		Cu (1)= -47.5	Pt (3)=+13.5	Cr=2.2
Cu (2)= - 0.344	Hg (2)= 0.5		Cu (2)= -32.1		Cu=2.2
Cu (1)= - 0.51	Fe (3)=0.397		Ag= -15.4		Mn=2.6
Hg (2)= - 0.798	Rh (3)=0.231				Au=3.1
Ag= - 0.799	Pt (3)=0.000				
Pd= - 0.820	Au (1)= -0.311				
Hg (1)= - 0.86					
Pt (4)= - 0.863					
Au (3)= -1.360					

*The apparent standard potential E_{app} is defined as

$$E_{app} = E^0 - \frac{RT}{ZF} ln\ f ,$$

Where E^0 is the standard decomposition potential and f the Henrian activity coefficient of salt MX in the given solvent

Now, the hydrogen electrode potential at 25 degrees is defined as 0, it is at 0, there are metals whose electrode potential is below hydrogen, means this potentials are negative, and there are good number whose electrode potentials are positive and higher than hydrogen. What this means is that these are more active than hydrogen, so if we have hydrogen ions in an acid, its dilute H2SO4, these elements will replace hydrogen liberate hydrogen and dissolve themselves, that is why zinc; if you put zinc in an acid it will dissolve and hydrogen will be liberated, this is a true with all of them, so all these are electropositive in the sense they are positive potential as compare to hydrogen.

Whereas these elements metals which have negative hydrogen potential will not liberate hydrogen form acids, you have heard you have learned this in your thermo dynamics course, so this electrode potential indicates relative reactivates of metals, now I mentioned that an element placed higher compare to hydrogen will liberate hydrogen from an acid, similar principle operate in the case of elements other than hydrogen. Like the metal calcium should be able to liberate the metals placed below form their compounds, and form a more stable compounds and liberate that metal, this will be the basis of metallo thermic reaction to which I will come later on.

So, what I am trying to say is when you have a series like this which indicates relative reactivates, we can say that the metals placed higher above being more reactive will replace those below that form their compound, all or you place hydrogen from aqueous media and these of themselves.

Now, there are other kinds of series I am talking about eco solutions, what about say such a series in haloids, it is possible to have electrode potentials of metal, metalions in molten chlorides, with reference to chlorine chlorine ion electrode potential, and we will have a series, but it is may not be identical to this, the very active reactive metals will still be placed high above in that, but the relative the order may not be the same, the another thing that we criteria that we use to understand reactivates is free energies of formation of oxides chlorides and other compounds.

Metals which are placed high in the electrode potential series which are very reactive they form very stable compounds, and stable compounds will be characterized by more negative values for free energies of formation of their compounds, so you see for calcium oxide it is minus 254 kilo calories per mole unit whereas, for those which are placed below calcium the values are less negative, means compounds of calcium would be more stable, compounds of sodium will be less stable.

Now, again the relative the ordering of metals according to this criterion may not be the same as ordering here, but generally those which are placed higher here will be placed higher here as well, look at for example, the stability of chlorides you find here that this metal is placed higher in the chloride series whereas, calcium is placed higher in the oxide series.

The other criterion is electro negativity, I will not discuss that now because perhaps you study it in your thermo dynamics course, but what you should understand form a series like this is that there is a very clear cut way of understanding which metals are more active as compared to the other metals, in terms of values of electrode potentials in eco solutions as compared to hydrogen electrode, or electrode potentials in haloids melts in terms of the corresponding halogen electrode, and also in terms of the free energies of formation of various compounds mostly we code values of oxide and chloride, there are some other ways of also assigning relative reactivity, but we need not discuss that.

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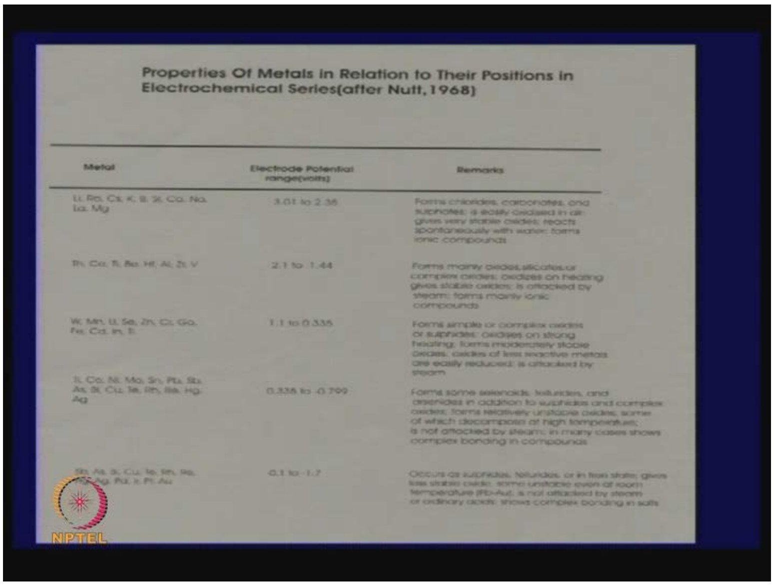

Properties Of Metals in Relation to Their Positions in Electrochemical Series(after Nutt, 1968)

Metal	Electrode Potential range(volts)	Remarks
Li, Rb, Cs, K, Ba, Sr, Ca, Na, La, Mg	3.01 to 2.36	Forms chlorides, carbonates, and sulphates; is easily oxidised in air gives very stable oxides; reacts spontaneously with water; forms ionic compounds
Th, Ce, Ti, Be, Hf, Al, Zr, V	2.1 to 1.44	Forms mainly oxides, silicates or complex oxides; oxidises on heating gives stable oxides; is attacked by steam; forms mainly ionic compounds
W, Mn, U, Se, Zn, Cr, Ga, Fe, Cd, In, Tl	1.1 to 0.335	Forms simple or complex oxides or sulphides; oxidises on strong heating; forms moderately stable oxides; oxides of less reactive metals are easily reduced; is attacked by steam
Tl, Co, Ni, Mo, Sn, Pb, Sb, As, Bi, Cu, Te, Rh, Re, Hg, Ag	0.338 to -0.799	Forms some selenoids, tellurides, and arsenides in addition to sulphides and complex oxides; forms relatively unstable oxides, some of which decompose at high temperatures; is not attacked by steam; in many cases shows complex bonding in compounds
Sb, As, Bi, Cu, Te, Rh, Re, Hg, Ag, Pd, Ir, Pt, Au	0.1 to -1.7	Occurs as sulphides, tellurides, or in free state; gives less stable oxide, some unstable even at room temperature (Pt-Au); is not attacked by steam or ordinary acids; shows complex bonding in salts

Now, if we have understood that not all metals are similar in terms of reactivity, and if they are not similar what will happen they will obviously form different kinds of compounds, I have listed some characteristics here, that we have seen metals with electrode potential values range the more reactive ones in this range one group, then another group, then another group and at the bottom are those where you see you got negative electrode potentials, and there we have some precious metals or absolutely not metals like gold also.

Now, the most reactive metals are characterized by lower values of electro negativity, higher electrode potentials and the free energies formations of their compounds like oxides and haloids are more negative. The order according to these criteria as I have mentioned again are not identical, but their moods of occurrence in nature will depend on their reactivates, we can make some general statements such as the following, highly reactive metals which are characterized by factors such as high electrode potentials and high negative free energies of formation of compounds occur in nature as simple compounds very often.

Thus the alkali or alkaline earth metals are mostly found as chlorides; carbonates or sulphates, simple oxides of these metals are however rare as they will react with other acidic oxide such as silica, so they will end up forming mineral such as alumino silicates and silicates. And then we come to those which occupy intermediate position become lower down, there we find the metals principally founded silicates, some of these which are placed higher up in the intermediate position may form simple oxides as well, those occupying a lower position may be found abundantly also a sulphides, and sulphides become more important from the point of view of winning up for metals placed in the lower of the series, and metals occupy very low position so an increasing tendency to occur either a selenides, tellurides, arsenides or antimonides or they may be available in the native state.

Now, all the metals that appear below lead in the first column in the table I had shown may be found in Free State, and this becomes the most state of common state of occurrence for silver and all metals placed below it. Now, we I have given a table here to indicate this in little more detail, if you look at the first group which is the lithium lead by lithium and electrode potential value is 3.01 to 2.38, these metals forms chlorides, carbonates, sulphides they are easily oxidized in air, they gives very stable oxide reacts spontaneously with water and forms ionic compounds. If you come to the metals below that values of electrode potential 2.1, to 1.44 they form mainly oxides silicates or complex oxides, oxides on heating they will not oxide in left in air, if they are heated they will form oxides and they will give stable oxides they are attacked by steam they will not be attacked by water they will attacked by steam, and they will form mainly ionic compounds again.

Then you come to again another group lower down in electrode potential values, these will form simple or complex oxides or sulphides, they will oxidize on strong heating and forms moderately stable oxides, oxides of list reactive metals are easily reduced and they are attacked by steam. Then we come to this group, which are again less reactive with values of electrode potentials from 335 to minus 0.799 they forms as I mentioned earlier, selenides, stylolites and arsenide in addition to sulphides and complex oxides forms relatively unstable oxides, some of which decompose at high temperature like mercury sulphide, they are attacked by steam in many cases show complex bonding in compounds.

Lastly we have the least reactive group of metals they may occur as sulphides, stylolites or they may occur in free state, they will give very less stable oxides, some unstable even at room temperature such as oxides of lead and gold, they are not attacked by steam or ordinary acids and they show complex warning in source. So, you see the way they exist in nature the kind of compounds they found, the minerals they form they all depend really on their relative reactivates, and we measure reactivates in terms of electrode potentials or free energies of formations of compounds. So, the obviously we need to have different kinds of processes for extraction of metals from different kind of metals, those which are formed very weak compounds there will be very easy to break and their it will be very easy to liberate the metal, or there will be somewhere will have to have very special processes for liberating the material metal, because it is very strongly bound with the nonmetal.

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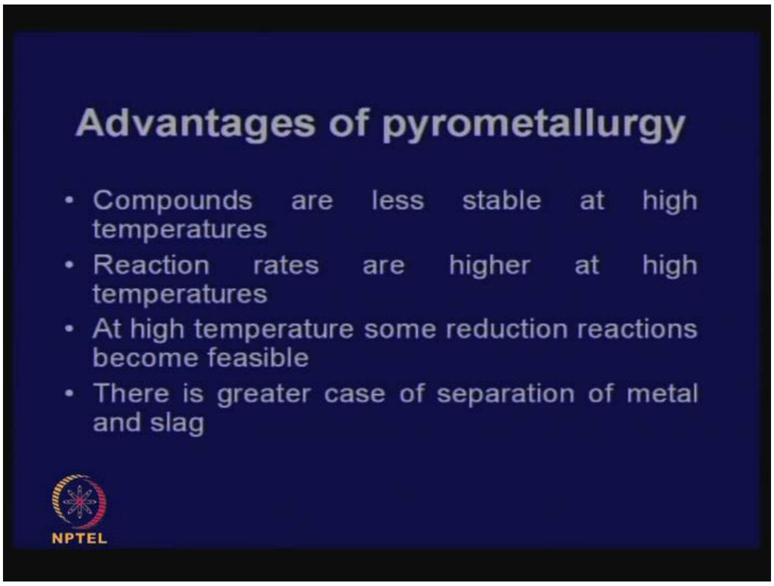

Advantages of pyrometallurgy

- Compounds are less stable at high temperatures
- Reaction rates are higher at high temperatures
- At high temperature some reduction reactions become feasible
- There is greater case of separation of metal and slag

Now, the history of extractive metallurgy actually starts with pyro metallurgy, because you have discussed how the ancients produce metals, it is always with the application of fire, unless we leave aside what they found in the native state, the iron from the poly matroids or gold that was found here and there. But when they started producing copper or bronze or zinc and then iron it always works with application of fire, and many processes were developed by trial and error, and many we understood much later, the science of it we understood much later by analyzing what was being done and why it was being done, but our ancients did not go into science, they found somehow that this is how we should work to produce this metal or that metal.

Now, pyro metallurgy definitely have has some distinct advantages, first of all compounds become less stable at high temperatures, because temperatures create vibrations amongst atoms and molecules, so that is how you make things unstable, and when you have made them unstable you can use various techniques you can apply electrical potential or you can bring in a reducing agent or whatever to take out the metal and separate the rest. There is another advantage of using high temperatures, at high temperatures reaction rate are accelerated, you know many reactions are highly temperature sensitive, give an ordinary example, if sugar is not dissolving in water if you heat the water the dissolution will be speeded up sugar will dissolve much faster, so the process of dissolution of sugar is temperature sensitive, we say such processes as thermally activated processes, and in pyro metallurgy we use heat to accelerate processes by use of high temperatures.

Then there is a third advantage, when you go to high temperatures thermo dynamically many reaction becomes feasible which were not feasible at lower temperatures, means no matter how much you heat you give you may not you cannot do that at lower temperatures. Even mercury sulphide cinnabar h g s which is a very weak compound, which dissociate some heating it needs a minimum temperature, it will not dissociate at a at room temperature, to dissociate when you go to couple of 100 degrees 600, 700 degrees or so I do not know exact figure then only it will decompose, which means decomposition is made possible thermo dynamically only at a particular temperature, take simple example, of say decomposition of calcium carbonate, calcium carbonate on heating decomposes to calcium oxide and CO2.

Now, in theory as you keep increasing the temperature the partial pressure of CO2 increases, so it is not that it suddenly decomposes, like you should know water if you have water at room temperature it has a vapour pressure. But we say boiling of water is 100 degrees when the atmospheric pressure is 1, because at 100 degrees its partial pressure becomes 1 atmosphere similarly, calcium carbonate will have some PCO2 at lower temperatures, but it will really decompose at one atmospheric pressure only when you go to about 910 degrees or so exceed 900 degrees.

So, mercury sulphide at 100, 200 degrees may have a small vapour pressure of mercury, but to really decompose it and get the metal in large quantity they have to go to a certain temperature. Similarly, when we talk about reduction by carbon or reduction or some process, everywhere thermo dynamics dictates the minimum temperature you need, and many reactions become possible only when you when you go to a minimum temperature.

The fourth advantage of pyro metallurgy is that at higher temperatures many phases become molten, metal may will melt then the gang materials which are flux to make what we called slag will melt, so there is a clear separation between metal and slag. Consider for example, steel making in the blast furnace we charge iron ore, we charge coke, we also charge fluxes that is limestone quartz.

So, we form to start with calcium silicate phase many other gang materials go into that, and then you form a phase called slag which dissolves a lot of impurities from iron ore, so that we will finally, get a metal which is relatively pure, and the slag phase takes out the gang materials, so we have a greater ease of separation of metal and slag at high temperature, these are the advantages of pyro metallurgy.

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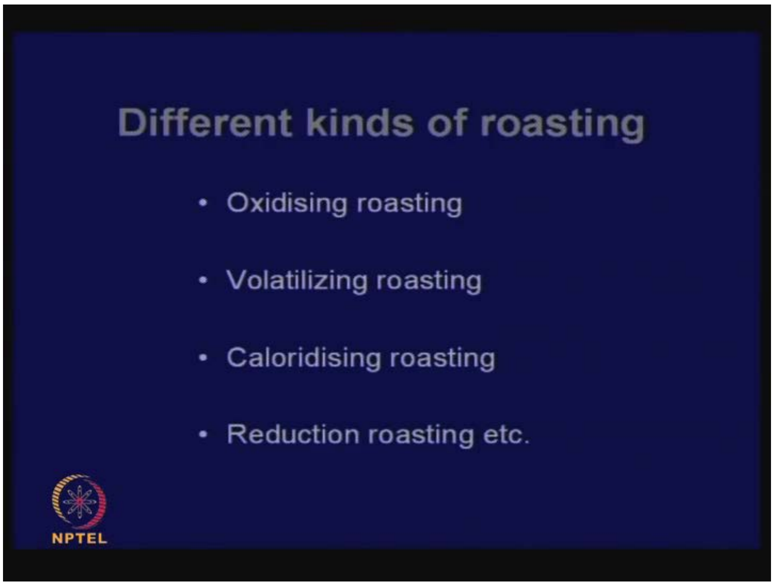

Different kinds of roasting

- Oxidising roasting
- Volatilizing roasting
- Caloridising roasting
- Reduction roasting etc.

Then pyro metallurgy there are three terms which are very used very frequently and you should know what they mean, these are unit processes previously we have talked about unit operations where the nature physical and chemical nature of the mineral is not change, by unit process we mean an operation what we change the physical and chemical nature of the processes for example, by calcinations we mean heating to decompose minerals to eliminate product such as CO2 or even water, so if you have calcium carbonate we heat it to around 900 degrees it decomposes to produce calcium oxide and CO2 goes out.

So, we have produce calcium oxide form calcium carbonate by calcinations, so that is the meaning of the word calcinations, do not think that if we have water molecules associated with a compound a mineral they will all go out at 100 degrees no, there are many minerals which have water molecules in them not all of it will go at 100 degrees, actually some may require several 100 degrees temperature rise to release that water molecule. And that would also be under in a calcination process what you completely cancel to eliminate all water, now the calcination temperature of various carbonates like this, you have magnesium carbonate decomposite at 417, manganese carbonate 377, iron carbonate 400, hydrates like A l 2 o 3 with X H 2 O decompose at lower temperatures less than 700, for and the so they kills up to the operated like that, so this is calcination.

Then there is the word called roasting, the word roasting means heating the ore below its fusion points, you have to you have to very careful not to fuse it, it still solid but you heat it near below the fusion point so as to change its chemical nature, and a very common thing will be to heat the sulphides to convert the sulphide into oxide, lead sulphide roasted to form lead oxide, copper sulphide roasted to form copper sulphide etcetera. There can be other kinds of roasting also and some of the first one I mentioned is oxidizing roasting, where the idea is to produce an oxide, by the word volatilizing roasting I mean that you allow a some part of that mineral to get separated through volatilization, and by caloridising roasting we mean that we heat it below the fusion point using a caloridising agent like hydrochloric acid or chlorine to produce either a liquid chloride or a gaseous chloride will out some element from the aggregate of other elements they will get separated out.

So, suppose you have several metal compounds one is able to be chloridized, one forms chloride easily, so by reacting with the chloridizing agent we can separate it out as a liquid or as a gas, that will be call chloridizing roasting, there can be other kinds of roasting for example, reduction roasting, we may have a an ore which has in it F E 2 O 3 as well as many other oxides, and if we reduce it partially and produce F E 3 O 4 in place of f e 2 O 3, then we would be able to separate it out by magnetic separation, this will be called reduction roasting. We can also reduce something to a lower valance state which will be more amiable to leachy by separation, so reduction roasting is when during heating you are bringing in a reducing atmosphere to go to a lower value state of one particular metal, there are also other kinds of roasting reactions and we need not discuss all that now.

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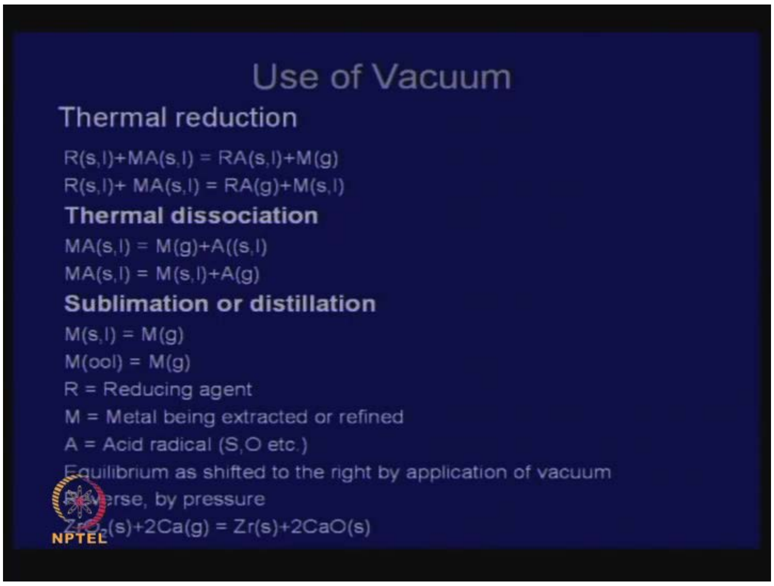

Use of Vacuum

Thermal reduction

$R(s,l)+MA(s,l) = RA(s,l)+M(g)$

$R(s,l)+ MA(s,l) = RA(g)+M(s,l)$

Thermal dissociation

$MA(s,l) = M(g)+A((s,l)$

$MA(s,l) = M(s,l)+A(g)$

Sublimation or distillation

$M(s,l) = M(g)$

$M(ool) = M(g)$

R = Reducing agent

M = Metal being extracted or refined

A = Acid radical (S,O etc.)

Equilibrium as shifted to the right by application of vacuum

Reverse, by pressure

$ZrO_2(s)+2Ca(g) = Zr(s)+2CaO(s)$

There are some very interesting operations in pyro metallurgy, and let me mention some examples, I had mentioned that there are some oxides some compounds which are very weak like here I have mentioned mercury sulphide, I say m a it can be solid or liquid actually a is the nonmetallic part, and simply by heating we can dissociate that, and during dissociation we can may produce metal in the gas phase, or we may produce the metal in the solid or liquid phase. And if in the right hand side if we have something in the gas phase then you know by application of vacuum we should be able to encourage the reaction to go to the right side, now when we talk about reduction processes if we have the metal as a compound solid or liquid, if we have a reducing agent solid or liquid, then we may we can produce the metal either as a gas or solid or liquid, but suppose the other the reducing agent produces a gas then in either case the reaction become sensitive to vacuum, you can apply vacuum and help to go the reaction forward.

So, many pyro metallurgy operations make use of vacuum of course, it will be true form sublimation or distillation also, like if you have a metal we want to purify it and if you heat it if forms a gas, this is now 0 0 l it should be metal in solution, all this cases vacuum will help. Now, in these things r is a reducing agent, m is a metal being extracted or refine, a is the acid radical which could be sulphur oxygen etcetera. And in all cases equilibrium is shifted to the right by application of vacuum, there can be a reverse thing also, like consider reduction of zirconium dioxide by calcium, this is can be achieved by gases calcium reducing solid zirconium to produce zirconium solid and 2 calcium oxide solid.

In this case it is pressure which is going to drive this reaction to the right, because you have a gas phase on the left hand side, so there will be examples like this in pyro metallurgy, where we will see that we can use vacuum of pressure to make things happen at appropriate temperatures.

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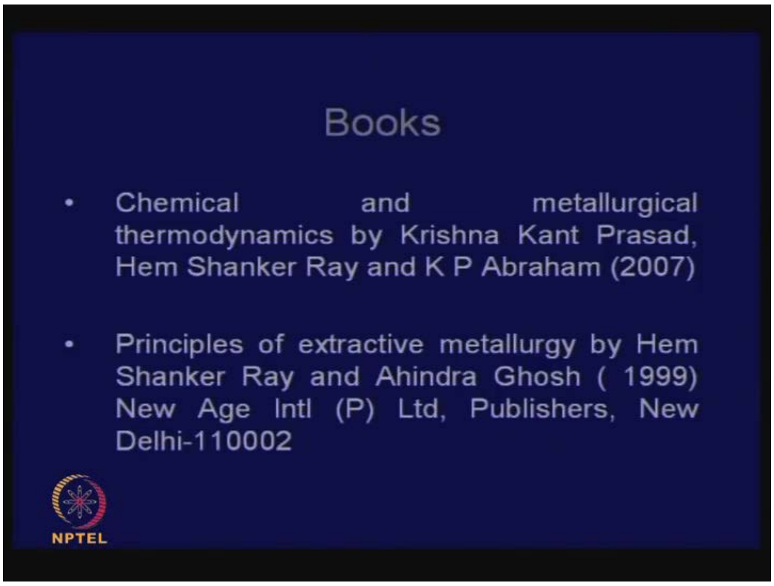

Books

- Chemical and metallurgical thermodynamics by Krishna Kant Prasad, Hem Shanker Ray and K P Abraham (2007)
- Principles of extractive metallurgy by Hem Shanker Ray and Ahindra Ghosh (1999) New Age Intl (P) Ltd, Publishers, New Delhi-110002

Now, in pyro metallurgy there is extensive application of thermo dynamics and kinetics, and there are many books which discuss these, I can suggest the 2 books where I am a co-author they are very simple books, one is called chemical and metallurgical thermodynamics by K K Prasad and myself and also K P Abraham. And another which is which is quite older actually principles of extractive metallurgy by A Ghosh and myself, that was published many years ago 1999, but it still very useful, you will have to read these things.

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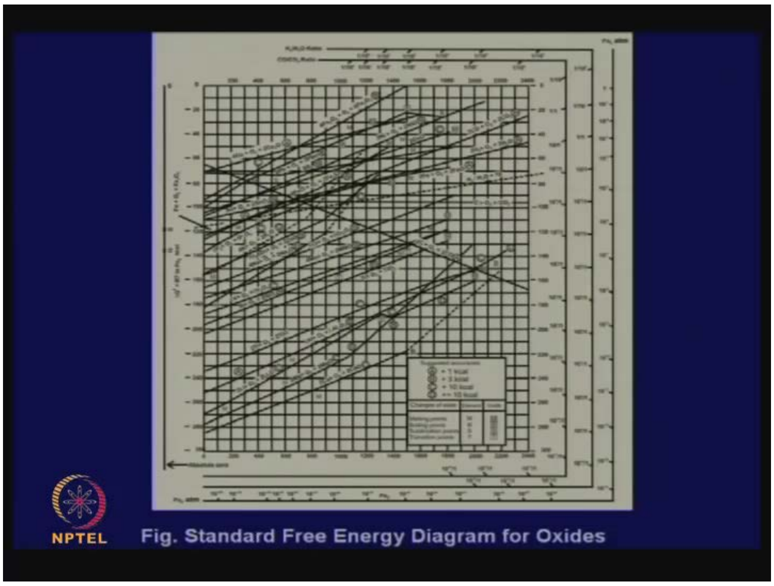

Fig. Standard Free Energy Diagram for Oxides

Now, one of the most fundamental concepts thermodynamic concepts that finds extensive application in understanding metallurgical reduction processes is what we call Ellingham diagrams, this will be discussed extensively in your thermo dynamics course. And I kind of assume you have studied it already, I will very briefly say what it what does the diagram shows and what we learn from the diagram, Ellingham diagrams actually plot free energies of formation of oxides as against temperature, free energies of formation of oxides versus temperature. Now, they are plotted always by writing the reaction with one oxygen molecule, like we write 2 t I plus o 2 is equal to 2 t I o 2, so it is giving free energies of formations of 2 t I o 2, not 1 t I o 2, it will take it vanadium it plots free energies of formation when the reaction is this it is not 1 lead to 5.

The idea is if we write always a reaction in terms of 1 o 2, then we can add these figures to find what will happen when a more reactive metal replaces another the more reactive replaces a less reactive metal forms oxide, all you have to do is to subtract 1 value of free energy formation form the other, I would explain that later on. But please take note of this, that all these lines represent values of free energies of formation of the compound, when the reaction is written in terms of 1 o 2, so reaction is t I plus o 2 t I o 2, here it will be 4 k no sorry four no no where do I go lithium t I o 2, s I plus o 2 s I o 2, 4 c u plus o 2 2 c u 2 o, so all these oxides are represented their free energies of formation are represented by these lines.

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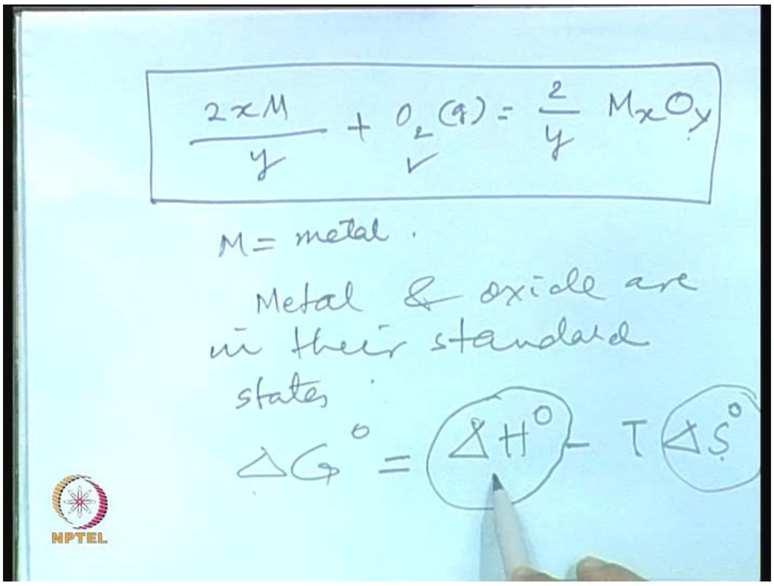

$$\boxed{\frac{2xM}{y} + O_2(g) = \frac{2}{y} M_xO_y}$$

M = metal.

Metal & oxide are in their standard states.

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

So, reaction in general for these lines can be written as 2 x M by y plus O 2 g equal to 2 by y M x O y, all these lines are written in terms of 1 oxygen molecule, here of course, M is metal, and these lines also represent that metal and oxide are in their standard states in their pure states. An oxygen will react with metal in the standard state to produce the oxide in the standard state, and the equations for these lines obviously would be delta g naught t delta H naught minus t delta s naught. Now, I am not writing delta g naught t, because after all or t here because delta g naught values and g s naught H naught values generally do not change with temperature, I would not explain why they do not change with temperature, they more or less remain independent of temperature, this is the equation of every line, so we have delta g naught delta h naught is the intercept delta s naught is the slope, this explains why the lines are more or less parallel.

Because every reaction is so written that you see there is entropy and the left hand side in the gas phase which is disappearing as the oxide is forming, entropy changes positive and they all of them are positive lines, delta s naught is always positive and with higher and higher temperature this term becomes more positive, so delta g naught becomes less and less negative, that is how we get all these parallel lines, I hope you understand that why these lines are sloping upwards, and why most of them are nearly parallel, the slope of each line is referring to the entropy change for disappearance of the oxygen.

Now, look at this line here this equation is for c plus o 2 plus c o 2 in this reaction there is no entropy change, because you have a gas phase on the left hand side, the same amount of gas on the right hand side, the gram moles same volumes and therefore, since same number of gram moles on the left hand side, same number of gram moles on right hand side there is no entropy change therefore, delta s naught is 0 and therefore, this line is horizontal, this there is no entropy change in this. Now, all these lines are parallel because you have written them in terms of only o 2, and that is why if we did not write it in terms of o 2 if we represented this lines writing in terms of one molecule of the oxide then things will get complicated, so you have understood that these lines represent variation of free energies of formation with variation in temperature, the slope giving the positive slope is because of delta s naught, which is because of disappearance of oxygen the entropy represent the oxygen in the left hand side.

There is one very interesting line which goes downwards, and this reaction that is 2 c plus o 2 giving you 2 c o, this is the only one line here which is sloping downwards, why it is sloping downwards? Because you have one molecule of gas on the left hand side o 2, we have 2 molecules of gas on the right hand side, so you are creating lot more gas out of this reaction, so the entropy here is increasing on the right hand side. So, now this give you a negative slope, that is why when the these lines have a positive slop this has a negative slope, now this of course, is a very important observation, and absolutely the most important thing in process metallurgy, and I will come to that in a minute.

You will find there are some lines will suddenly go up we change their slope, come here then change their slope, this is explained by a heat of melting of the metal or the oxide, because if there is a melting of the metal or melting of the oxide that is being formed then the slope will change, because this value will change the intersect value will change. So, you must understand in some cases it should go up, and in some case it should go down, if the oxide was to melt the slope will go this way, so now we have understood the Ellingham diagrams. The importance of this line we must understand now, this line shows that as the temperature increases carbon monoxide becomes increasingly stable, because free energies of formation of carbon monoxide becomes less more and more negative.

So, if we reduce an oxide by carbon monoxide then chances are that somewhere or other it will get reduced, and where it will get reduced we find from the intersection, consider this reaction a particular which is very clear, it is a 2 2 t I o 2 t I plus o 2 plus 2 2 t I o, the free energies of formations intersect here, which means beyond this temperature c o becomes relatively more stable as compared to t I o 2 and therefore, t I o 2 get reduced by carbon to form c o. So, as this line which is carbon forming carbon monoxide moves downwards intersects all of them, so in theory we can reduce any oxide by carbon to from carbon monoxide, and carbon can take out that oxygen from that oxide, I will continue with this in my next lecture because this is the heart of reduction by carbon and this we have to understand very thoroughly.

So, in this lecture we have just started with the relative reactivates of metals, and try to understand why not all metals form same kind of compounds of free energies of formation, or in terms of electrode potentials, and depending on their relative order in that series they form different kinds of compounds, some more stable some less stable. And then you have started with principles of pyro metallurgy saying what are the advantages of pyro metallurgy, at high temperature some reaction becomes feasible or reactions are accelerated, phases are become molten so that there is a separation very easily etcetera, and then I have come to reduction by carbon which has been the back bone of extractive metallurgy. I would continue with this in the next lecture. Thank you