

Basics in Inorganic Chemistry
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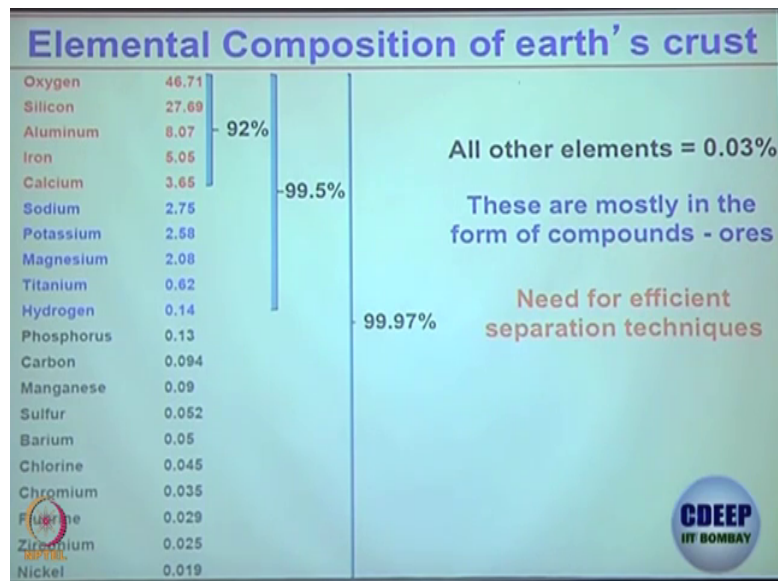
Lecture – 04
Extraction of Metals

The last chapter we have discussed about the periodic table. This is the one where we are trying to see if we can purify the metal from ores. So, usually whatever is available in the form of ore like metal oxide, metal sulphide, metal halides and so on. These are not something we want in our regular life. In daily life we want something in more of a different form more of a pure form.

Let us say we need iron bar, we need pure gold, we need pure nickel, we need pure palladium, we need pure of different metal, but these metals are not given to us by nature by default. So, it is usually existing as in it is oxidized form ok. Invariably all the metal ores we see they are found as metal oxide; that means, metal is in oxidized form right. Metal sulphide again sulphide is you know negatively charged to minus and metal is usually going to be 2 plus or in so on.

So, therefore, what we are really looking for is a method is a technique that can reduce the oxidized form of the metal and give us the pure reduced metal ok. For example, if you have iron oxide iron oxide you from iron oxide we are hoping to get pure iron that is in iron 0 form which is utilized in regular life right. Same is true for almost every metal whatever metal complex or metal form is available with us we are not going to use them we are going to purify them and then only we can use them.

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As we briefly discussed in the last class, fine. So, what we are trying to say we have 105 elements at least more and more every day we are discovering almost not every day regularly I mean let us say in every 10 years we are discovering a new element in the periodic table at least definitely in last few decades if you see we have discovered something or the other ok.



So; that means, that at least those are present in some amount on earth crust or in atmospheres and thereby it allowed to scientists to discover them ok, but invariably what is happened is this is the scenario most often we see that only few elements are present in high quantity. All others are present in very very low quantity.

The challenge is really to get them in pure form even if they are present in very very tiny amount ok. So, this is where I think chemistry becomes very handy. Chemists can help the engineers to isolate the metal in pure form and that is what we are going to discuss today.

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Methods of Separation / Extraction

1. Mechanical separation
2. Magnetic separation
3. Thermal decomposition
4. Displacement of one element by other
5. Electrolytic reduction
6. High temperature chemical reduction
and so on

We are discussing there are different techniques not necessarily each or any technique are going to be only useful it is a combination of things we need to utilize a number of or series of experiments by which from a impure mixture impure metal ores or mixture of ores we will be able to get a pure form of the metal.




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1. Mechanical separation

Based on the density variation
by sieving method

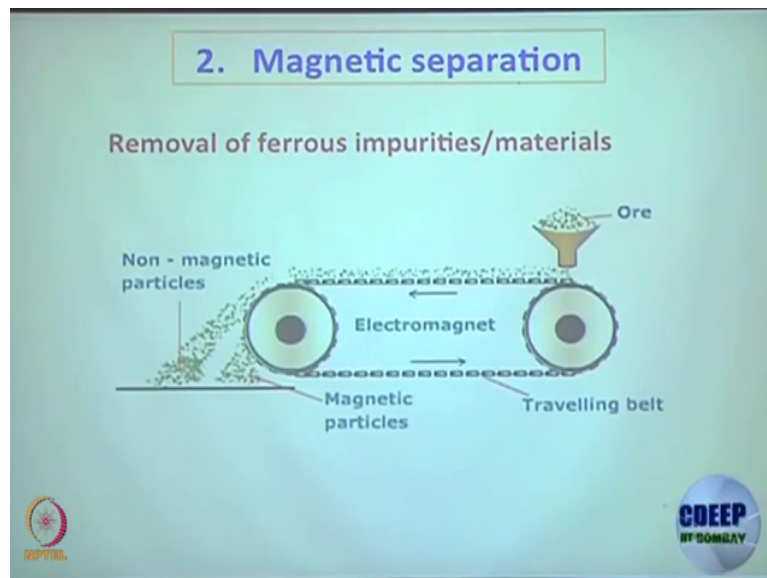
Free elemental form – unreactive elements
Coinage & Pt metals

Example:
Gold; 19.3 g/cm^3 ,
separated by *panning*



The easiest one is the mechanical separation as we were discussing in the last class you just (Refer time: 03:56) off you just wash it off right. So, for example, over here as it shown you just wash off with some solvent let us say water is a usually what it did something if which is usually used you just wash it off. So, unwanted material maybe going off or the you know important materials may be coming out whatever it is you will be able to wash off some of the material that you do not want.

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Next another technique you can use most often you need to use is that is you pass the ore through the through these electromagnetic separation ok. Depending on the nature of the materials you have some of those materials will be isolated completely when you are passing through the electromagnet both magnetic material which are having some attraction for the magnet will be isolated or separated out in a separate place compared to the non magnetic material. These are very easy technique and easy to understand.



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3. Thermal decomposition

Unstable compounds $\xrightarrow{\Delta}$ Constituent elements

- $\text{Ag}_2\text{O} \rightarrow 2\text{Ag} + \frac{1}{2}\text{O}_2$
- Marsh test: As, Sb salt + Zn/H₂SO₄ →
As/SbH₃ → Silver mirror of the metal
- Decomposition of NaN₃ to Na and N₂
Note: Azides are explosives !
- Mond process; production of nickel

van Arkel process Zr or B forms ZrI₄ or BI₃

Of course it is not going to be always that easy. Some more techniques are there such as heating just you take the ore you heat it. What will happen is some of the metal oxide metal sulphide which are not stable you can just heat it and decompose it to corresponding metal. So, that is I guess the easiest, but then there also could be problem. Even if you are able to heat it and break the metal oxide still if the metal is found to be solid usually it is those solid will be really mixed with other metal oxide or metal sulphide.

Still your job may not be full done, but you know sometime this is still can be a good approach. For example, silver oxide not every metal oxide you can heat it at a very low temperature or you know 50 to a 100 degrees you cannot break it. For that I will come to that lingam diagram where you can heat the metal and thereby you can get it, but usually some

something like silver oxide you can heat it and get it also sodium azide from there you can get sodium in pure form.

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Thermal decomposition

Mond's Process: (Reduction followed by thermal)

$$\text{NiO (s)} + \text{H}_2 \text{ (g)} \rightarrow \text{Ni (s)} + \text{H}_2\text{O (g)} \quad 200^\circ\text{C}$$

impure Ni, mixed with iron



$$\text{Ni (s)} + 4 \text{CO (g)} \rightarrow \text{Ni(CO)}_4 \text{ (g)} \quad 50^\circ\text{C}$$
$$\text{Ni(CO)}_4 \text{ (g)} \rightarrow \text{Ni (s)} + 4 \text{CO (g)} \quad 230^\circ\text{C}$$

Kroll Process: (Reductive separation)

Kroll produced Ti by reducing TiCl_4 with Ca/Mg ($950\text{-}1150^\circ\text{C}$)

Van Arkel-deBoer process:

$$\text{Crude zirconium (Zr)} + \text{Iodine} \rightarrow \text{ZrI}_4 \quad 200^\circ\text{C}$$
$$\text{ZrI}_4 \rightarrow \text{Zr (s)} + \text{Iodine} \quad 1300^\circ\text{C}$$

Other processes are there such as Mond's process and (Refer time: 06:10) process which is also mainly dependent on thermal decomposition, but here you have to take care of the chemistry as well. What we are talking about is there is a mixture of at least 3-4 compounds or 10 compounds. From there if you react those mixture of compounds with something like hydrogen not every metal will be converted to corresponding metal oxide will be correspond converted to corresponding metal and water, but only few of them will be converted to metal and correspond you know water right.

So, for a mixture of a lot of compounds you will be able to reduce some of the metal oxide with hydrogen at a given temperature and thereby you will have a mixture of reduced metal

few of the reduced metal and few of the metal oxide which is demand unreactive under that condition.

You take that mixture react with carbon monoxide for example, in this process Mond's process selectively only few metal will react with carbon monoxide and thereby for example, this nickel will be reacting to give nickel tetracarbonyl this nickel tetracarbonyl being gas you will be able to collect it in a different container and then you heat it at 230 degree selectively you can get nickel in pure form. So, what we have learned just that it is a generalized approach it is not just a Mond's process. What we are trying to see is we will select a reaction.

That reaction will be somewhat selective for 1 2 or 3 metals. It will not going to be useful at least under this reaction condition let us say 200 degree C. Not every metal oxide will react with hydrogen. Therefore, only out of let us say 10 metal oxide phrase and only 1 or 2 metal oxide will be converted to their corresponding metallic form.

Now still you are left with a mixture of metals what do you do with it you then try to do yet another selective reaction such as you react it with carbonyl. You do that reaction or carbon monoxide you do that reaction at the temperature for example, only one of the metal will react with that carbonyl or carbon monoxide only one metal will react under this condition thereby only selectively from a mixture of lot of solid you selectively get let us say in this case nickel carbonyl which is gas.

Not every metal carbonyls are coming out ok. Selectively only one metal carbonyl is compound is coming out its gas you collect it and then you heat it at 230 degree C. So, basically what telling you is you need to know the chemistry. If you want to apply your knowledge chemistry knowledge then the things are going to be much more simpler.

It is not complex anymore. Just one technique may not be good enough you have to use a series of techniques, but slowly what will happen is let us say you are having only 1 percent of nickel, if you keep on doing this thing like mechanical separation electromagnetic

separation and then thermal process slowly if that 1 percent material will be accumulated and overall from let us say 1 kg of ore you can get 1 gram of pure nickel which is a lot for you.

I mean the it is going to be a lots. Imagine instead of one gram of nickel 1 gram of gold. Now it is making sense more sense. Instead of 1 kg of ore you have 100 kg of ore you get 1 kg of gold that is going to be much more you know attractive method. So, this is a generalized approach right.

Same approach is you know applicable for Kroll's process where we see that titanium oxide is converted selectively to titanium chloride by reacting with charcoal and chlorine gas and this titanium tetrachloride again has to react with calcium or magnesium mixture to get back to that titanium. It is not like we are directly going to the reduced form of the metal from the oxidize we can go up to reduced form of the metal oxidize it back and then reduce it again or read go to the deduct reduced form do some other reaction and then somehow figure out a technique to selectively identify or isolate that compound and then do the thermal decomposition or some other technique.

So, it is going to be always going to be a mixture of approaches. You have to have different approach. You cannot have a generalized approach. As you can see let us say in ore available in Mumbai will I mean you know certain mixture from for nickel separation let us say will be different that is available in let us say Rajasthan it is going to be different right. So, you have to know what are the elements present in your ore and thereby you have to choose what are the techniques you are going to use anyway.

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4. Displacement of one element by other

Metal with lower electrode potential
Greater ability for acting as reducing agent
Can displace other metal of higher electrode potential from ore

$\text{Cu} + 2\text{AgNO}_3 \rightarrow 2\text{Ag} + \text{Cu}(\text{NO}_3)_2$
 $\text{Fe} + \text{Cu}(\text{NO}_3)_2 \rightarrow \text{Fe}(\text{NO}_3)_2 + \text{Cu}$

In principle, any element may be displaced by another element which has more negative E_0 in electrochemical series.

$\text{Cu}^{2+} + \text{Fe} \rightarrow \text{Fe}^{2+} + \text{Cu}$
 $\text{Cd}^{2+} + \text{Zn} \rightarrow \text{Cd} + \text{Zn}^{2+}$
 $\text{Cl}_2 + 2\text{Br}^- \rightarrow 2\text{Cl}^- + \text{Br}_2$

Table 6.10 Standard electrode potentials (volts at 25 °C)

Li^+	Li	-3.05
K^+	K	-2.93
Ca^{2+}	Ca	-2.84
Al^{3+}	Al	-1.66
Mn^{2+}	Mn	-1.08
Zn^{2+}	Zn	-0.76
Fe^{2+}	Fe	-0.44
Cd^{2+}	Cd	-0.40
Co^{2+}	Co	-0.27
Ni^{2+}	Ni	-0.23
Sn^{2+}	Sn	-0.14
Pb^{2+}	Pb	-0.13
H^+	H_2	0.00
Cu^{2+}	Cu	+0.35
Ag^+	Ag	+0.80
Au^{3+}	Au	+1.38

COST and SAFETY !!!! JD Lee Page 18

Let us go on. Another approach which is stands very attractive is that of a you know use of one metal to get another metal. It is a sacrificial method. You sacrifice one metal to get another metal of course, your that another metal has to be very very important or you know precious. You cannot sacrifice goal to get 1 gram of iron right.

So, it is other way around if it is true then of course, you are going to use it. So, what determines which metal you are going to sacrifice and this is what is all about these are electro chemical series. What it tells you the one which is at the bottom let us say gold, silver, copper these are going to get reduced very easily. So, you take a oxidized form up those metal that is going to get reduced very easily.

Let us say if you have the metal oxide or sulphide of this element you will be able to reduce those element pretty easily. Their reduction potential is very high. Reduction potential high

means they will be going to the reduced form that is what exactly you are looking for. You want to have the reduced form of these precious metals right. So, what do you do. In order to do that you take let us say anything from top of this series and use those of the reduced form of these metal and oxidized form of the metal at the lower part and you just do a oxidation reduction chemistry.

For example let us say you take a let us say iron just iron with let us say silver. So, iron will be oxidized to iron $+2$ and silver $+1$ will get reduced to silver that is all you are going to do right. For example, over here you take copper; copper is above silver copper is just above silver. So, you take copper. Copper is in metal form metallic copper.

So, copper to copper oxidation is more favourable what is more favourable in this case it is silver $+1$ silver reduction because reduction potential is very high for silver compared to copper. Now, so silver $+1$ will get reduced to silver 0 and copper which is in reduced form will get oxidized to copper $+2$. So, this gives you the basis what you are going to choose or which metal you are going to choose.

So anything that is below or that is existing at the lower part of this electro chemical series that is what you will use in it is oxidized form ok. To get the corresponding metal in pure form or in reduced form the one which is going to be sacrificed is the one on the top clear. Anything with almost any metal combination you can take let us say for example, with gold and lithium you can take right, technically anything that is above anything that is below you can take any combination of these things and in principle you should have an opportunity to do that.

But of course, you have to think about cost and safety which one you are going to choose of course, you have to choose judiciously which is available in large quantity not that very expensive you are going to choose for such reduction.

So, electro chemical series gives you an idea what reaction is favourable what is not. Sometimes that is what I was trying to tell you in the last class. So, it seems like this to this

does not go, but this to this go all right that is basically because you have to look at the potential right.

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5. Electrolytic reduction

1. **Electron** – Strongest known reducing agent
2. Highly electropositive metals, e.g. **alkaline earth metals** are produced this way (Electrolytic reduction of their fused halides)
3. Less electropositive elements, viz., **Cr, Cu & Zn** can be made by electrolysis even from aqueous solution
4. **Ionic materials (salts) are electrolyzed – reduction at cathode**
5. **Excellent method, gives pure metal, but very expensive**

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Anyway another technique which is very effective is that electrolytic reduction. What is that. It is nothing. You just take electro chemical cell where you have a cathode and anode ok. In this case you are not using a sacrificial reducing agent, the reducing agent is your electron.

So, you take let us say gold solution gold you know whatever gold let us say gold chloride Au^{3+} . Now that gold you want to get that gold in cathode because gold is cationic form is in cationic form that is going to be at cathode and going to get reduced from gold $3+$ to gold or silver $+$ to silver or lithium $+$ to lithium right.

So, those reducing agents are provided or reducing equivalents are provided by electron of course, it is not that very you know popular method not everything you are going to get in this way. When you have no option when you have no option left then you are going to turn to this electro catalytic reduction. For example, you want to simplify lithium alright lithium plus 2 lithium as you have seen in the previous one. This this is a electropositive metal. It is tried to stay in plus form electropositive.

It does not want to get reduced right. So, you need some very strong reducing agent. The strongest possible reducing agent perhaps could be this electron. There is almost no sacrificial reagent available chemical available that can chemically reduced lithium plus to lithium. So, this is when you need to use electrolytic reduction ok. So, of course, it is a very good method it is applicable all across the board any metal in plus form in oxidized form you can reduce, but it is very very expensive.

It is a excellent method it gives you pure metal that is for sure, but it is going to be very very expensive. So, you need to use it only at a advance stage when you have the 1 or 2 metal possible you know not lot of mixture of things are possible because mixture of things going to complicate your life. It is an expensive process.

Even want to use a mixture of I mean just you do not want to take ore and want to apply cathode and I mean electrochemical reduction you are not going to do that electrolytic reduction. When things are in very fewer form then only you are thinking to do it or when you do not have any other option to do it.

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Methods of Separation / Extraction

1. Mechanical separation
2. Magnetic separation
3. Thermal decomposition
4. Displacement of one element by other
5. Electrolytic reduction
6. High temperature chemical reduction

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Then you are going to do it ok. So, I think I have covered so far or we have covered so far mechanical separation, magnetic separation, thermal decomposition. These are very kind of easy and then displacement of one element by other and also electrolytic reduction right.