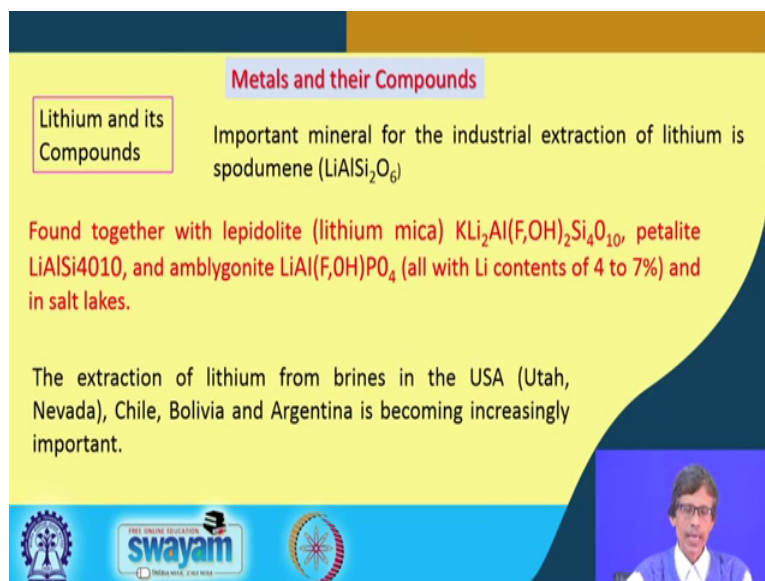


Industrial Inorganic Chemistry
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Lecture – 36
Metals and Their Compounds: Lithium

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Metals and their Compounds


Lithium and its Compounds

Important mineral for the industrial extraction of lithium is spodumene ($\text{LiAlSi}_2\text{O}_6$)

Found together with lepidolite (lithium mica) $\text{KLi}_2\text{Al}(\text{F},\text{OH})_2\text{Si}_4\text{O}_{10}$, petalite $\text{LiAlSi}_4\text{O}_{10}$, and amblygonite $\text{LiAl}(\text{F},\text{OH})\text{PO}_4$ (all with Li contents of 4 to 7%) and in salt lakes.

The extraction of lithium from brines in the USA (Utah, Nevada), Chile, Bolivia and Argentina is becoming increasingly important.

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Welcome back to this class where we are talking about the metals as well as the different compounds of metals. So, now we will be talking about a typical aspects of the Metals and their Compounds and how we get the metals. From a chemists point of view or more specifically from inorganic chemists point of view, because the industrial demand for metals and their processing and making all these things is the typical engineering aspects people can think of, people can talk of which is a typical subject for the people who are dealing with metallurgical engineering, who are dealing with materials engineering.

And this particular class and the following classes what we will see about how we look at the metals and their compounds as an inorganic chemist. Because we will be talking about something, where we think about the basic and the fundamental inorganic chemistry knowledge will be useful. And that basic and fundamental knowledge of inorganic chemistry, how it is useful for selecting the area of introducing that particular industry, where you can get the easy availability of the material for the different types of processing.

So, we will start from the lightest metal iron, after hydrogen say. So, hydrogen helium, and then we have in the periodic table the lithium, because it has a huge demand. So, if you go and ask any particular metallurgical engineer or a metallurgical technologist or a materials engineer that how you get or how you can start a industry for making lithium-ion batteries. So, it is not that you go and start a lithium-ion battery and all these things, you should have a very good level of availability and a cheap source of availability of lithium for that particular purpose.

If work if our country does not have that much amount of supply of lithium, we should not think of establishing a company, which will be dealing with lithium as your lithium-ion batteries. Because, if we think that china has a huge source lithium or any other European country as a huge source of lithium, we cannot compete with them in terms of the price. So, always forget about the fundamental and the economic interest or the economic knowledge, it is the knowledge which will be driven by the market, which will be driven by the economics.

So, the source of the material as the corresponding source of the ore or the minerals is important. So, we will look at that and what are the feasibility for the typical or the very simple inorganic chemistry, because everywhere we are talking the knowledge level of our inorganic chemistry, how we can apply to get some useful industry, where we can start this for you are making this compound of all these things. So, what are those lithium compounds, we can have? So, lithium sources we should know, how we can process of those for making lithium metal itself first and then the different compound that is why the title of this class is the metals and their compounds.

So, again we should look at the important material that means, where from we get the huge amount of that thing, which is feasible for your industrially possible extraction process is your spodumene s p o d u m e n e is just spodumene, it is a typical name basically I am not asking you that you should remember it nicely, but so long you have the class you if you as appearing for the exam, you just try to remember it. Otherwise, how will you know this particular one.

Once you know that what is your magnetite, what is your ferrite from our school days we know that these are the iron sources or the iron materials, which is available everywhere. Even for our soil sample and everywhere where the soil sample is reddish in colour. So,

we know that there are hematite, there are magnetite and all these things. So, a geologist can go and try to find out the physical characteristics of this particular mineral, they identify it, they take it, they make it grinding and they go for its typical analysis for its lithium component or any other component.

But, this particular oxide mineral is a complex one, if we now look at the corresponding formula of the material, so mineral has a formula of one lithium, one aluminum and two silicon, so is $\text{LiAlSi}_2\text{O}_6$. So, basically is a silicate mineral, so wherever we find is not that you will get as the free lithium as lithium oxide or lithium chloride is not possible like that of your sodium or potassium.

We will come back once again, under the heading of your metals and their compounds, the sodium and potassium, but already we have discussed. A huge amount of that thing that how we get sodium chloride, how you get potassium chloride, in the same fashion you will not get lithium chloride.

So, always remember that the periodic table goes in a particular direction, and always we look at all these things and basically we are looking in different categories and in terms of the periodic table also. So, is basically a silicate mineral, there are large number of silicate minerals we know. And basically, the basic formula of this you can have the bi silicate or di silicate, we call Si_2 , Si_3 , Si_4 , all these more complex materials we have.

Particularly, some useful catalytic material when we recall at the later part of this course, we will find that the zeolites and all these things, which are nothing but silicate as well as aluminum, so we call them as alumina silicate. So, this is nothing but you have double silicate structure that is two silicate ions are there along with one aluminum, this is basically alumina silicate.

And alumina silicate as a particular type of charge, when the whole charge is not being neutralized by aluminum or potassium or sodium, because most of these silicates are sodium salts or the potassium salts like our silicic acid and all. It is naturally available as your lithium salt. So, it is not so easy to get that lithium also, because the during processing your lithium can go out can leach from the medium, so is very difficult to trap that particular lithium and lithium has the different characteristics, different inorganic chemistry and all these things lithium has.

So, it is also found together with some other material. One is your lithium mica. So, mica again has a different structure, but it is again silicate. So, silicate structure of mica, we can have. And in case alumina silicate is there, but there is aluminium are also bound to fluoride as well as hydroxides like your flour apatite or hydroxyapatite molecules, we all know. But, here little bit higher level of lithium, two lithium-ions are there along with one potassium.

So, try to look at the formula of lepidolite, it is lepidolite $\text{Li}_3\text{Al}_2(\text{Si}_4\text{O}_{10})_2(\text{OH})_2\text{F}$. So, lepidolite formula, we will tell you that how nature is giving us, this particular rich material. And the way we are getting people have struggled a lot, basically you have two or three different types of (Refer Time: 08:08) part, because aluminum is within the structure of alumina silicates, but it is not as a pure cationic form. But, you have potassium as the cation, you have lithium as the cation, but that particular salt, this lithium mica we are not getting as the pure K_3 salt or we are not getting it as the pure Li_3 salt.

So, whenever we are getting so nature is also getting this thing, whether it is coming out from the volcanic source or some other sources, initially it can have a molten thing. The molten thing is basically crystallizing out with time and during the crystallization depending upon the availability of your potassium salt nearby or the lithium salt nearby, it is crystallizing as KLi_2 sample.

KLi_2 plus, the whole charge is 3 plus with it, so that particular one neither Li_3 nor K_3 is forming, not even K_2Li . So, this is the thing that you try to remember this in this fashion, because you have to take this particular material, where it is economically very feasible, economically it is beneficial for isolation of your lithium metal from this particular material.

Then we have another one is your petalite. Petalite is $\text{LiAlSi}_4\text{O}_{10}$. So, this Si_4O_{10} business is similar to that of your this Si_4O_{10} business of lithium mica, but is of different type, because you do not have potassium. Then amblygonite; amblygonite is again lithium aluminum only no potassium, but again one is to one. And all with these your lithium component is not very less not even very more, it is 4 to 7 percent of lithium, it is pretty good amount of lithium is available. And you not only get as the mineral from the earth crust, but it can also be available from the different salt lakes.

So, the salty water of the lake material lake can give rise to this particular material, how we get that. So, lithium bearing or the lithium containing brine water that means, the salt water which is coming out from the different salt lake. Sometimes, we get those that the crystallized forms also from those salt lakes as the flakes salt flakes are also available.

So, those salt flakes also you can have, and you see that know where the country, which are producing huge amount of this one or the extraction is visible is only US, Chile, Bolivia and Argentina. Not even the entire US, some pockets always be there, it is the state which is your Utah and the Nevada. So, Utah, Nevada is the place, where you can have the corresponding amount of deposition of this particular lithium material, then again other places we can get that.

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Lithium precipitates out as the poorly soluble lithium carbonate.

Metallic Lithium

By melt electrolysis of LiCl/KCl-mixture (ca. 1 : 1) at 400 to 460 °C in steel cells with a graphite anode and a steel cathode. The cell voltage is 6.0 to 6.5 V. The metallic lithium formed collects on the surface of the molten salt electrolyte.

Use

In the manufacture of lithium hydride and lithium amide, and for the synthesis of organo-lithium compounds. Used as catalysts in polymerization reactions.

As a reducing agent in organic chemistry and in the refining of metal melts in metallurgy.

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So, lithium during this particular process, the lithium precipitated out as poorly soluble lithium carbonate. So, if you grind it, if you make it in the solubilized form and if you try to get that lithium-ion, which is a very small ion which in presence of water that means within water, it is always highly solvated, because the solvation power is more in lithium compared to your sodium as well as potassium.

So, highly solvated lithium-ion you have and if you try to supply either in the term terms of alkaline supply of CO₂ or the addition of carbonate any other carbonate salt. So, what you get that that you can have the corresponding precipitate of poorly soluble lithium carbonate.

So, you have highly soluble all these things, highly soluble lithium mica or lithium any other alumina silicate in your hand, so you grind it, you make it powder, you put water, so lithium will be leached out from the material. And that material is very difficult to crystallize, it if you think of that I will crystallize it as lithium chloride or I will crystallize it as lithium nitrate or I will crystallize it as lithium sulphate is not so easy.

So, if you just quickly compare the solubility differences of all these lithium salts nicely, you just select them your natural intense or natural intuition rather. We will tell you that it is the lithium carbonate, which will be very much useful for you to give you the corresponding separation from this material as lithium carbonate. So, we have the lithium carbonate and how you make that particular one. So, from the ore or the mineral, you get the material as lithium carbonate. Now, your condition is that how you get metallic lithium out of it.

So, the best way of getting these like that of your sodium as well as potassium and all other alkali metal ions, we all know you should go for the corresponding electrolytic technique and melt condition not in solution condition. In solution condition otherwise, you will end up with the electrolysis of water only. So, you get the melt and for increasing the conductance you add potassium chloride. So, you have a lithium chloride, potassium chloride mixture and at a higher temperature say is always not very easy to make, easy to do is 400 to 460 degree centigrade in closed chamber in steel cells with a graphite anode and steel cathode.

So, two of the material for anode and cathodes are very much specific, because that particular potential. Only those material can give you the required suspense surface for its removal that means for its oxidation or for its reduction of the particular material, whether you are talking about the corresponding reduction of m plus that means, Li plus or the corresponding oxidation of other part to at the other electrode.

And the cell voltage is also not very much, it is only 6 to 6.5 volt. And it is formed and collects on the surface of the molten salt electrolyte. So, on the molten salt electrodes, if you have molten salt electrolyte, you are electrolyzing that molten salt through the insertion of the electrodes. And whatever lithium is forming that will be floating on the surface of the electrolyte. So, from the surface, you can have some exit. If you know the height of that particular surface above the electrolyte, you can have the regular exit

channel and through that exit channel, you can take out that particular material for its isolation.

Then we think off the typical uses, because you have the ore, you get it as the corresponding electrolytic procedure. And now how you use it particular one, particularly the metallic one the metallic lithium. So, one of the most important material that we know from our school days once again in organic chemistry classes and everywhere, we know that lithium aluminum hydride is a very good reducing agent.

And when we talk in terms of the corresponding material as your some lithium mica, lithium aluminum silicate, but it is not so easy to understand it that there is no procedure available to our still that whether that one containing both lithium as well as aluminium, to convert it directly to lithium aluminum hydride through the supply of hydrogen gas or any other hydride material or any other hydrogen containing agent, it is not so easy, so that way the chemistry process or the process chemistry is completely different.

In the reaction will not go for this particular reaction, but we can think of that your raw material has both lithium and aluminum and your compound which is pretty costly, the market has a huge demand. The bigger chemical companies, they are producing for the laboratory use also lithium aluminum hydride. So, we should go to some other ways that means, you have to convert it to lithium hydride first that means, this lithium whatever available as the metallic form of lithium will be converted to lithium hydride. And luckily, we should have some mechanism; we should have some procedure or the industrial technique, where the lithium metal can be converted to lithium hydride.

Then we can have like potassium amide KNH_2 , we can have $LiNH_2$, these are very useful reagent for organic transformations, pharmaceutical industries, any other industries. And for the synthesis of any other organo-lithium compound, so organo-lithium compounds we all know. These are organometallic compounds and most of the organometallic compounds we all know.

Like your Grignard reagent, which is the organ of magnesium compound. We also study from our school days that organo-magnesium compound, what you can have that particular organo-magnesium compound is useful for some good techniques. Similarly, the corresponding organo-lithium compound; even the methyl-lithium, if we consider that l i m e.

So, methyl-lithium type of thing can be very useful organo-lithium compounds. And sometimes these organo-lithium or some other modified compounds are also useful in as catalysts. Why we are making a very small compound of all these things, if you require a certain amount of bulk, industrial we are producing several tones we are producing.

But, if we require only a small amount of this for the laboratory purpose for your drug making business or the pharmaceutical industry or the perfume industry or the food industry, what you can think of that the consumption for the laboratory use definitely of a high grade analytical reagent or the guaranteed reagent form, your consumption is more, but your value addition is more and more compared to your bulk material of lithium and lithium metal.

But, if you move from that material for day-to-day laboratory use or the industrial laboratory use also, industrial r and d use also, you can go for the making these as that useful catalyst. Because, the catalyst requirement very small amount only some milligrams scale, some time it can go to Nano gram scale also, but it is a catalyst which is not changed after the reaction also, so it is unchanged after the reaction also.

So, in the polymerization reaction, so the whole polymerization industries the polymer industries, basically will be dependent on some of these lithium bearing compounds. Because, if you have very useful organo-lithium compound, can serve as a catalyst, which you cannot get from your corresponding organo-sodium or organo-potassium or organo-transition metal compound.

As I told you that it is a very useful one as lithium aluminum hydride L A H making. So, is the reducing agent in organic chemistry, and also in refining of metal melts in metallurgy. So, when you use is as reducing agents and the refining industry also in the metallurgical industry, already we are talking all the time that how you handle the metal by the metallurgical engineer. So, in metal melts in the metallurgy, we use also the lithium for its regular supply.

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Li/Mg-alloys are used in aerospace applications.

Lithium is very important in nuclear technology e.g., nuclear weapons manufacture.
As anodes for batteries with a high energy density and long term stability.

Lithium Compounds

Most important: Li_2CO_3 , LiOH , LiH , LiCl

Lithium carbonate: Enriched and calcined spodumene is digested e.g. with concentrated sulfuric acid at $> 250\text{ }^\circ\text{C}$, leached with water and finally reacted with sodium carbonate.

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Then another useful important in application is making of lithium, as I told you that organo-lithium compound, but it can be incorporated in alloy making also, because these are very useful compounds. The way we say that when we talk in terms of when we will be talking, in terms of your transition metal ion say palladium and platinum.

When we are talking about the corresponding diesel exhaust, the NOX removal, we have seen that also we can have the catalytic converter. And those catalytic converters are only on very precious metals like palladium, like platinum, like iridium, like rhodium, but lithium is not so costly, because we are using we have started using, we are still using the lithium-ion batteries.

And if you have the magnesium, so the lithium-magnesium alloys, magnesium is a very lighter element, lithium is also very lighter one, but individually their characters are different. But, when you go for making this corresponding alloy of lithium magnesium, you get a new product or new alloy material, which can find a very useful application in aerospace industry, because is very lighter one.

So, for making aircraft, aircraft components and other thing such that in a lighter way that means, your things should not be heavy. Even if you make a motor, even if you make a window, even if you make a some structure, you can use this, because the lighter one. So, aerospace industry is very much dependent on this sort of alloy and people are also working on it.

How we can improve the corresponding allowing nature by using some other third metal ion or metal center for allowing process or improving the corresponding composition or the process, it is also very much useful or very much applicable for nuclear application also. While we make nuclear weapons manufacturing, because if it is not very much destructive one. And if it is highly resistant for all the different types of nuclear reactions that means, neutron bombardment, gamma bombardment, alpha particle bombardments, so if it is at the typical resistance, we can use it in nuclear technology.

And the thing what we are talking in terms of its making the lithium batteries, it is functioning as an anode. So, making these batteries as the anode material with a high energy density, because these are the typical characteristics. When people are working on the electrical engineers are working, then others the energy engineering is another branch of engineering, because we are having shortage of the fossil fuels that means, the coal is limited, the oil is limited, many other thing the solar cell also does not have that much applicability.

So, we can go for all these things that means, the lithium-ion bearing batteries and high energy density and long term stability, it is stable because you can use it for several years that is also very important. So, these two component high energy density and long term stability of the lithium metal. Makes this very useful material for giving you the lithium-ion based batteries, so that is again a huge area. If you are interested, you can read it, you can also learn it that how only that one particular metal ion, which we know that how we can get it starting from your ore material, starting from your minerals, starting from your lithium metal to get that particular lithium-ion batteries.

Now, we like that of your lithium-aluminum hydride, what other lithium compounds we can have but most importantly those are lithium carbonate, lithium hydroxide. Already I told you how you get the lithium hydride and lithium chloride the chloride salts always very much useful.

The first one how we make it, and how we get it, we should start from spodumene again. So, the calcined spodumene that means is the heated and you have the corresponding breaking and making the powder of this thing. So, enriched material or enriched mineral, what we call it as the enrichment in terms of the corresponding lithium percentage.

Then is digested with concentrated sulphuric acid, so sulphuric acid is needed. So, concentrated high sulphuric acid, which is highly corrosive one. So, we will basically break the corresponding microstructure or corresponding alumina silicate structure in the spodumene, whatever inert material as its an ionic part was there are only idea is that.

In acidic medium, we should take out that particular lithium from there as the corresponding lithium-ion. So, a high temperature is also applied. So, as the high temperature reaction, so it is basically leached with water and finally reacted with sodium carbonate. So, lithium is taken away through this particular procedure. And taking of that particular lithium from that material is next is used for its reaction with sodium carbonate, because the sodium carbonate reaction will give you directly the your lithium carbonate formation.

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Li_2CO_3 applications: aluminum manufacture, glass, enamel and ceramic industries medicine.

Lithium hydroxide

$$\text{Li}_2\text{CO}_3 + \text{Ca}(\text{OH})_2 \longrightarrow \text{CaCO}_3 + 2 \text{LiOH}$$

Industrially important in the manufacture of greases e.g. on the basis of lithium stearate.

Lithium hydride

$$2 \text{Li} + \text{H}_2 \xrightarrow{700^\circ\text{C}} 2 \text{LiH}$$

Important as a source of hydrogen and as a reducing agent in organic synthesis.

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So, this particular lithium carbonate if you make that lithium carbonate has huge application in different areas is for aluminium manufacture, so manufacturing of aluminium is also dependent. Because sometimes it is the ingredient for aluminium production from bauxite, then glass making, then enamel, ceramic industries and the medicine also, because, small amount of lithium can help as a medicine also.

Because, the neurodegenerative problem or the bipolar problem people have started using this one, but we should not forget something that historically this particular material the lithium carbonate is functioning as the medicine and we are using say 100

years back or 75 years back, now it has been discontinued. Because, we find that it has can have certain disadvantages, certain side reactions and it is may be harmful for some other organs of our life.

But, you should know historically that how these molecule that means, the small lithium center, the lithium-ion is useful, when we know that we have in our body the corresponding channels of sodium as well as potassium, whether that is hampering that or the signals the neuro signals in our brain is governed by corresponding and potential of that different gradient of sodium and potassium, whether those are affected by lithium.

So, the traditional knowledge is useful, you may not apply it for industrial production of lithium, but future application and all these things are required. So, your knowledge bits should be very high is not that the material what is you what is needed to know is for huge production, and which has a huge demand in the market. You may not know that the basic or the academic interest of all these things can have some future application.

So, like that of your lithium, which was present in your lithium mica or lithium aluminum silicate that also tells you that nature is accumulating that particular mica or the material with a lithium as its component. So, why not synthetically, when we make or when we produce glass, when you make enamel and when you make ceramic, why you should not incorporate lithium that means, lithium has some role definitely to play to improve the corresponding properties of this thing.

Similarly, lithium hydroxide from carbonate, directly we know the inorganic chemical reaction. So, inorganic chemical reaction will tell you how quickly, you can make lithium hydroxide. So, again from your knowledge sake, from your query sake, from your question sake, what you should know that what are the materials? If I ask you how lithium hydroxide can be prepared from a useful material or useful lithium compound, and your choices are given. So, the right compound for this reaction is your lithium carbonate.

And why you use calcium hydroxide, you why you are not using other hydroxides also that you should ask yourself. So, you have a very standardized reaction, which is known for the 100 or 200 years. And how you can lead that particular reaction for industrial production such that always you think of whenever you write a and b for a particular

type of reaction, why we are not thinking the other hydroxides, why you are not thinking about the other carbonate materials or other lithium material for its production.

So, industrially this particular one is important in the manufacture of greases, well based thing which is nothing but your lithium stearate is the long organic molecule we all know, so that organic molecule, when gives you the corresponding lithium salt not the sodium salt, because the sodium permitted, sodium stearate we know the common household soap.

When it is lithium, it is the thick one and it is the greasy material which is industrially very important. Then lithium hydride from the direct reaction of your lithium and hydrogen can be obtained, at a very high temperature say 700 degree centigrade. You have a direct reaction of lithium with hydrogen giving you lithium hydride, which will be utilized for making your lithium aluminum hydride as well. So, getting this lithium hydride is very important, and that lithium hydride for the production of lithium hydride is also very important. So, it is a important source of hydrogen as a reducing agent in organic synthesis.

So, directly either lithium hydride you use or you convert it to lithium aluminum hydride, because it is very easy to use is a very user friendly also. Because, lithium hydride storing up the material in the laboratory, storing of the laboratory in the material in the industrial sector is also very difficult.

So, it shelf life we call, how long you can keep in the laboratory shelf, how can you can keep in the laboratory cupboard? So that is also very important. Because, the day you purchase within the next 7 days, you are not consuming the whole material that is why, it gives stability compared to your lithium hydride, to make or convert it to lithium aluminum hydride. So, we will continue our in our next class that how we can finish this lithium and any other useful metal centers or the metal ions and their useful compounds.

Thank you very much.