## Industrial Inorganic Chemistry Prof. Debashis Ray Department of Chemistry Indian Institute of Technology, Kharagpur

## Lecture – 43 Manganese and it is Industrially Important Compounds

Hello, good evening everybody welcome to the class where we are talking about the different chromium salts and there is fullness in industrial production.

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В	asic Chromium(III) Salts	
Obtained as a by-product in the dichromate oxidation of anthracene to anthraquinone		
$Na_2Cr_2O_7 + 3 H_2SO_4 + $ $\longrightarrow$ $H_2O_6 + Na_2SO_4 + 2 Cr(OH)SO_4 + H_2O_6$ Chrome tanning agents: it is the crosslinking of the collagen carboxyl groups		
in animal hides with the help of Cr(III) compounds.		
Metallic Chromium	Utilized in: turbine blade chromium alloys and in co	and the second sec
$\begin{array}{l} \textbf{Preparation} \\ \mathrm{Cr}_2\mathrm{O}_3 + 2 \ \mathrm{Al} \longrightarrow \mathrm{Al}_2\mathrm{O}_3 + 2 \ \mathrm{Cr} \end{array}$	Reduction Cr(III) oxide b	IV AI
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So, we have considered so many like your dichromate your chromate and all these things. So, today we will just finish with the single slide that what is your basic chromium salts and how we can manufacture it industrially and how these are very important. So, this can be obtained as one of the by product also when we are talking in terms of their corresponding dichromate oxidation because we have seen earlier that how we can prepare sodium dichromate, potassium dichromate or ammonium dichromate.

Now, the same dichromate can be used for oxidation of anthracene. So, this will be something very much similar to the production of hydrogen peroxide as we have seen long back, where these anthracene and anthraquinone type of thing or the anthraquinone to hydroquinone type of thing can be utilized those molecules can be utilized as a very useful reducing agent where we can deduce the dioxygen molecule, the O 2 molecule to hydrogen peroxide.

Now, if we go or if we use the same strategy for the corresponding reduction of the dichromate species because whatever we have seen so far is your sodium chromate NaCrO 4 or sodium dichromate or potassium dichromate where the chromium oxidation state was plus 6. It was the highest possible oxidation state of chromium and it is highly oxidizing. Therefore, that is why the chromium compounds including your titrimetric method the redox titration use; that means, the use of potassium dichromate or sodium dichromate. We utilize all these things for the use of chromium in the hexavalent state and during the process because that hexavalent chromium center available from your dichromate or potassium chromate it can be utilized for it is reduction to any other chromium 3 salts.

Now, if the same thing that we know now that the basic chromium salts any chromium salt the chromium chloride is the CrCl 3 is a simple chromium salt of the trivalent chromium, but the basic chromium salt will have one hydroxide group attached to it. So, we will utilize the corresponding oxidation of anthracene, anthracene is your this molecule simple tri cyclic hydrocarbon like benzene we all know that if you have a one cyclic ring of these.

This is your benzene if we put second one this is naphthalene and when the third one is there it is anthracene and it is very much susceptible for it is oxidation to the anthraquinone derivative and that anthraquinone derivative is nothing, but your central part is getting oxidized like your corresponding hydroquinone formation. And that hydroquinone formation we know that earlier we required the quinone to hydroquinone formation, but here we directly provide 2 of the oxygen atoms on these carbon 2 carbon centers.

So, it is basically the oxygen insertion reaction or oxidation reaction of these 2 carbon converting your CH, this was CH, this was CH also, it was not COH, but it was COH so that CH can be converted to C double bond O. And during this particular process we are utilizing sodium dichromate Na 2 Cr 2 O 7 and in presence of sulfuric acid because most of the chromium based compound; that means, your titration or your other salts we use these as your corresponding acids. So, that basically gives us the corresponding chromium salts as the sulfate derivative or the corresponding basic form where one of the hydroxide group is attached to the chromium center.

So, if you see on the right hand side that what we are getting, we are getting nothing, but your corresponding anthraquinone sodium sulfate is for me because this sodium was there and the sulfate is basically coming from your sulfuric acid and 2 of the chromium centers which were present as your Na 2 Cr 2 O 7. These 2 chromium centers were the hexavalent chromium centers and will be reduced to chromium 3.

So, 3 plus 3 it is a 6 electron reduction process and by doing so what we get we were able to produce some more amount of this particular anthraquinone derivative and some amount of hydroxide groups. So, during this oxygen insertion reaction in anthracene, we also get some compound where the hydroxide groups is available in large amount and that hydroxide group will be attached to chromium center and chromium is basically giving a very useful salt known as your basic chromium 3 salt, where the trivalent oxidation state of the chromium center will be satisfied by hydroxide ion. That means, HO minus or SO 4 2 plus.

So, 1 plus 2 3 that is you get the corresponding crystallized form from the reaction medium as your basic chromium 3 sulfate. It is very much useful for other industrial sectors like the leather industry where we use it as the chrome tanning agent. Earlier we have seen also that the hexavalent chromium compounds were also useful for giving you the corresponding reagent for your tanning operation; that means, removal of the hairs of the corresponding leather.

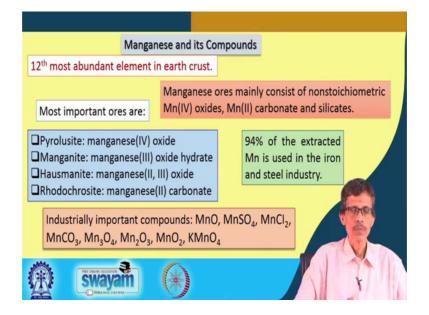
So, in leather industry basically it is used for the cross linking the collagen carboxyl groups in animal hides with the help of chromium 3 compounds. So, the chromium 3 compound still can control this particular process; that means, it is a very useful tanning agent and it is very much used in a your industry. Then metallic chromium we can utilize so if we are able to produce metallic chromium from the different chromium ores, it can be utilized in different turbine blades as we have already seen that the chromium is a useful component for your steel material then some of these chromium can be used in alloys and in cermet.

So, this particular iron free chromium alloy; that means, iron will not be there, but some other metal or the other metallic species will also be there and the chromium is the corresponding alloying compound or the alloying metal, which can improve the corresponding quality or the corresponding use of this particular alloy and this particular one is the cermet, cermet is nothing, but the chromium which is there and utilization of that chromium for the metallurgical industry.

So, this particular one can be very easily prepared by a reaction where the aluminum the metallic aluminium and aluminium powder can be utilized for the reduction of the trivalent compound now it is nothing, but your chromous oxides Cr 2 O 3. And that Cr 2 O 3 can be utilized for reduction to metallic chromium with the help of metallic aluminium. So, aluminium reduction process can go for your corresponding reduction of the chromium from chromium oxide that the chromous oxide not your Cr O 3. That means, the hexavalent chromium, but it is trivalent chromium converting your aluminum powder whatever we use for this particular reduction process is converting that to alumina; that means, Al 2 O 3.

Because the aluminum has higher affinity for your oxygen and that oxygen or the oxide ion O 2 minus it is there and that O 2 minus is basically now attached to aluminum as aluminum 3 plus aluminum centers will be oxidized giving you aluminium 3 plus and the further attachment of your O 2 minus will giving you Al 2 O 3. So, the production of this is from aluminium as alumina and by doing so we basically convert your chromium oxide to the metallic chromium which is very much useful in industry. So, is the process is therefore, the typical reduction of chromium 3 oxide by aluminium.

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So, after chromium if we see another 3 D metallic state or the 3 D metal which will be very much useful for our industrial sector or industrial purpose some of the use where we can go for typically the metallic manganese and it is some useful compounds. So, what are those and how we can utilize those for our isolation and production?

So, the amount what is available on the earth crust is also 12 the numbers. So, it is the twelfth most abundant element in earth crust that we can find and that we can identify and that we can isolate and the different ores basically what is available geologically are consists of non stoichiometric manganese 4 oxides. Manganese 2 carbonate and some of them will be combined to as the corresponding silicates.

So, it is basically like that of the silicon ore we know that the feldspar and other silicates are available, but if it are able to trap manganese as is bivalent manganese compound as manganese carbonate. So, is the complex mixture of your manganese sample and your silicates similarly the manganese 4 oxide we all know that the most common commonly available manganese oxide is your MnO 2 the pyrolusite.

So, the other ores apart from your pyrolusites so when we consider the tetravalent state of manganese which is manganese oxide which is MnO 2 which is pyrolusite, similarly if we go down to manganese 3 oxide hydrate, Mn 2 O 3 which is manganite, then manganese 2 3 oxide; that means, the mix oxide like your iron oxide Fe 2 O 3 we consider as a mixed oxide or Fe 3 O 4 also. So, they are basically mostly the manganese will type of mixed oxide thing and where both the oxidation states can be available of different stoichiometric of manganese 2 plus and manganese 3 plus.

Then rhodochrosite is typically the manganese 2 carbonate so, when we go for oxide you can have the all the possibilities starting from bivalent to tetravalent oxides, but when we are able to isolate it in some other form of the ore where the anionic present is your carbonate anion in that carbonate anion can give you only the manganese 2 carbonate. So, these are our very useful material starting material for isolation of manganese or getting some other useful manganese compounds.

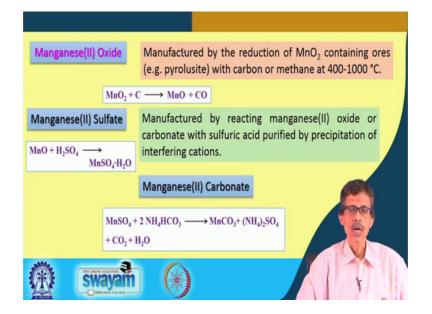
So, for iron and steel industry we require huge amount of manganese and 94 percent of these can be extracted as the manganese and is used in both these 2 industries and like these. So, these are the set of 4 manganese compounds which are important industrially

these are your source material or the starting material for manganese industry or the manganese in industrial chemistry if we talk about.

And if we just simply quickly see that what are those important compound because we are talking in terms of both manganese; that means, what we can get as elemental manganese, manganese in the metallic state or in very high quality manganese in the elemental form and also some very useful compound where you can have MnO; that means, the manganese in bivalent state oxide, manganese sulfate, chloride, carbonate, manganese oxide, again another manganese oxide, pyrolusite and KMnO 4.

So, these MnO 2 though formula wise it is MnO 2 so, if it is a pure compound we consider it will be MnO 2 we will not talk in terms of your pyrolusite, because the pyrolusite is basically a mixture, there are large number of other impurities you can have carbon black also in it, you can have other charcoal derivative, because it is a huge black product so, purity is definitely very less. So, if we can use that particular one for the production of pure quality of manganese dioxide because industrially all these compounds are very useful as we all know that manganese dioxide is very useful while we make the dry cell batteries. So, the use of this manganese dioxide as a phase in dry cell battery can come only if you know the corresponding purity and the quality of the manganese dioxide.

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So, the first thing what we will now see is your manganese 2 oxide; that means, the lowest possible oxidation state what we are talking from 2 to 4 and it is stabilized by your corresponding oxygen as O 2 minus.

So, how we go we typically take pyrolusite and we go for the reduction. So, chemistry wise it is very simple and definitely your corresponding industrial chemistry of manganese is also would be very simple. If we just simply look at the corresponding process what we will be utilizing for the production of your manganese 2 oxide. So, if we take pyrolusite that pyrolusite we know it is a tetravalent manganese and is manganese O 2 which should be reduced basically by any other reducing agent and industrially useful and industrially important and industrially readily available reducing agents are not like that of our laboratory use reduction reactions what we perform by very sophisticated or more precise reducing agent like borohydrate or anything.

So, here if we can use carbon that only charcoal based carbon or the carbon as a coke also and methane CH 4 and a temperature range pretty high 400 to 1000 can be used for the reduction of your manganese from your MnO 2 which is in pyrolusite to MnO only. Not that this particular procedure can give you the formation of elemental manganese; that means, you cannot go up to manganese as manganese elemental form or the manganese metallic state, but we go for these reduction of manganese dioxide with carbon to MnO and CO.

So, use of carbon basically use of carbon basically converting your manganese dioxide to manganese oxide and by that time while we do so some amount of carbon monoxide will be produced by the end product for your manganese based compound is manganese plus 2 oxide. Then if we have manganese plus 2 oxide or MnO 2 in your hand whether it will be possible for you to convert that manganese directly to manganese sulfate or we take that particular manganese in solution as Mn 2 plus because the challenge is the corresponding difficulty what we can face industrially as that whether the MnO form for your pyrolusite because the pyrolusite is also insoluble in water.

If your MnO form from that is also insoluble in water it is very difficult to take that manganese in solution and convert that manganese to Mn 2 plus. Such that we can add some sulfate salt sodium sulfate or even sulfuric acid to convert that manganese from Mn

2 plus to your manganese sulfate. So, always you should think about their solubility stability and all these thing so, directly if we are able to use it from MnO.

So, MnO plus sulfuric acid; that means, you get something as the typical conversion like that of your Mn 2 plus is there in the solution and addition of sulfate and iron converting the entire amount of Mn present as Mn 2 plus to Mn SO 4 and also that oxygen what was available on manganese oxide will be taken up by the protons available from your sulfuric acid to convert water molecule and that water molecule is getting co crystallize or forming water of crystallization or the within the crystal lattice of manganese sulfate, it is trapped.

So, it is basically reacting reaction of manganese 2 oxide or carbonate because the carbonate can also in a similar fashion can give rise to the reaction of any other salt not that only sulfuric acid, but you can use nitric acid you can use sulfuric acid for that particular conversion. So, getting the corresponding anionic salts of any inorganic acid like chloride, like sulfate, like nitrate, it is always easy to use the correspondings manganese salt or any other metal ion salt as oxide or hydroxide or carbonate.

But if we are lucky enough some time if can we can dissolve the corresponding oxide like that of your this manganese oxide we go the same product very easily. So, we get that everything is in solution and we get the precipitation from the saturated solution and by doing so if we are able to selectively crystallize this mangansulfate monohydrate we will able to remove the all other interfering cations.

Then from this particular process; that means, whether your manganese 2 oxide or manganese 2 sulfate will be useful if we want to make some amount of manganese carbonate, otherwise this manganese carbonate or manganese bivalent carbonate is readily available from the ores. So, starting from manganese sulfate basically, because these all these inter conversions are very useful because some of them can be useful industrially some are not and if we find that makings the corresponding manganese sulfate from there we convert that manganese sulfate to manganese carbonate.

So, simply by addition of ammonium bicarbonate not ammonium carbonate or any other carbonic carbonate source we simply use they are very simple and the cheapest one also the ammonium bicarbonate. An addition of that bicarbonate will give rise to manganese carbonate, ammonium sulfate, carbon dioxide and water. So, this simple and straight cut inorganic reaction can be utilized for the production of manganese 2 carbonate industrially.

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Manganese(IV) Oxide
$\beta\text{-MnO}_2$ is least reactive and amorphous $\gamma\text{-MnO}_2$ is partially active
Activation of Manganese(IV) Oxide
Minerals are decomposed to manganese(III) oxides which reacted with hot conc. $\rm H_2SO_4$
$Mn_2O_3 + H_2SO_4 \longrightarrow \gamma - MnO_2 + MnSO_4 + H_2O \qquad \gamma - MnO_2 \text{ is used in dry batteries}$
Manganese(IV) oxide minerals react with nitrous gases to produce $Mn(NO_3)_2$ and then it decomposed to pure $\beta$ -MnO <sub>2</sub>
$MnO_2 + N_2O_4 \longrightarrow Mn(NO_3)_2;  Mn(NO_3)_2 \longrightarrow \beta \cdot MnO_2 + N_2O_4$

Then manganese 4 oxide why we are coming back again and again to that of the same compound where we considered that manganese 4 oxide is the same thing which we consider as the pyrolusite, but the entire pyrolusite ore is not your manganese 4 oxide. It is not so pure it is a very crude thing and you can have certain percentage of manganese dioxide in it, but the main source of it is your manganese dioxide.

So, how we get the pure quality of manganese 4 oxide and that manganese 4 oxide we sometime it is leveled with some other very useful leveling that is the beta form, alpha form, gamma form or epsilon form. So, beta Mn 2 and one we consider as the gamma Mn 2 so is basically the solid state structures are different. The solid state morphology the connectivities are different and the lattice structure is also different, that is why one is leveled as beta and another is leveled as gamma and the reactivity wise and their application solid state applications even are completely different.

And also if we consider after words we will consider that if we consider that these 2 can function as your catalyst. So, heterogeneous catalysis, that these materials are not going into the solution to remaining some other solid state form, but it can so some catalytic activity. So, the solid state catalytic behavior of these will be different if we just simply see that we are able to make beta MnO 2 or gamma MnO 2 which can have the different reactivity because the beta form is this less least reactive and the amorphous gamma form is partially active.

How we go for this activation; that means, activation of manganese 4 oxide. So, minerals are decomposed fast to manganese 3 oxides which is then reacted with hot concentrated sulfuric acid. So, either it is going to the trivalent oxide; that means, trivalent oxide is not that (Refer Time: 21:29) MnO which we have seen just now, but it is MnO 3 like your Fe 2 O 3. So, now, this Mn 2 O 3 will be reacted with sulfuric acid and this process basically giving you one particular form quite easily is the gamma form not the beta form, not the any other form. That means, you should be very well know that 50 percent of that manganese what is coming out from Mn 2 O 3 is being converted to it is gamma form and another 50 percent is going for your manganese sulfate preparation. What we have seen earlier for your MnO, utilization of MnO the manganese oxide MnO for the production of manganese sulfate MnSO 4.

So, this particular reactivity of the solid manganese oxide as Mn 2 O 3 is always very much useful and now this gamma form basically the gamma MnO 2 is used in making dry batteries. So, still we are using huge amount of the dry battery the dry cell batteries for our purposes for our use. So, large amount of this gamma MnO 2 which we can produce through this particular methodology or this particular process we can consume; that means, the battery companies are very much interested to get this MnO 2 by doing this particular reaction for it is production.

Then the 4 oxide; that means, 4 oxide can be prepared nicely for this improvement for your corresponding composition or the improvement of the quantity of manganese dioxide which can react with the nitrous gases; that means, nitric oxide or nitrogen dioxide to produce manganese nitrate. So, direct reaction of the mineral with gas the gaseous region we get the corresponding manganese at this corresponding salt the nitrate salt.

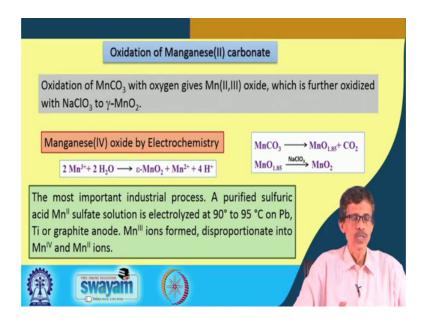
And if we now the decompose that particular nitrate salt will getting the other variety; that means, the beta form. So, making of this beta form will be now useful; that means your nitrogen dioxide is utilized which is basically a dimeric compound, the dimeric form of nitrogen dioxide is a single electron paramagnetic molecule and O 2 is; that

means nitrogen dioxide. So, it immediately dimerizes color is also changing when it is dimerizes.

So, reaction of this and is also very easy to react it basically because handling N 2 O 4 is very easy compared to your only NO 2; that means, nitrogen dioxide. So, direct use of these only produce your manganese nitrate no other side products, no other compound is forming from that particular reaction and that manganese nitrate is now heated for it is decomposition producing beta form of it; that means, beta MnO 2 and N 2 O 4 back.

So, you see if we are very much careful enough in trapping the liberated N 2 O 4 from the reaction medium what we are getting, we are getting basically nothing, but the impure form the most crude form of MnO 2 it can be your pyrolusite also and that crude form of MnO 2 as pyrolusite and some improvement in the purity basically from that pyrolusite and we were able to convert it to the beta form which can be utilized from some industrially important purposes by that process we will also producing back the starting material; that means, your N 2 O 4.

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Then the manganese 2 carbonate if we use and through oxidation what we will be using or we will be getting. So, another process is basically for your oxidation and that oxidation of MnCO 3 with oxygen basically gives you that M 2 O 3. So, Mn 2 O 3; that means, the corresponding mixed manganese oxide, if we get from carbonate and that mixed oxide that is we are not getting from the decomposition of MnCO 3.

So, at this point you take some time and understand that when we go for the corresponding reaction; that means, the oxidation of manganese CO 3; that means, we are trying to oxidize it is a bivalent compound and we get and we will end up with some mixed oxide, do not worry about the corresponding oxidizing reagent. That means, we can go for your simple oxidation with the air oxygen or oxygen from some cylinder or some higher concentration of oxygen.

So, when it is utilizing for further oxidation by sodium chloride NaClO 3 is a typical reagent for that particular oxidation process and that oxidation process will give you another pathway for making gamma variety of your MnO 2. So, you have MnCO 3 and MnCO 3 we will get giving you the corresponding manganese oxide and that manganese oxide what is form it can be a mixed with some trivalent form.

So, if you have if you write the bivalent form MnO 2, O which we are writing as 1.84 shows the non stoichiometry compound that some of them some of the amount will be your the corresponding trivalent form; that means, the higher amount of oxygen will definitely is not 1. If it is 1 it is MnO, if it is higher than that you can have the corresponding ratio of manganese and oxygen is higher. That means, your oxidation state of manganese is higher and you get that compound and at the particular stoichiometry of 1.85 can very readily react with your sodium chlorate giving you manganese dioxide in gamma form.

And manganese 4 oxide can also be utilized for it is preparation through electrochemistry which is the form which we can make as your epsilon variety is another variety of manganese dioxide starting from trivalent manganese in solution. So, Mn 3 plus in solution in presence of water if we are able to electrolyze it some amount; that means, the 50 percent of it again forming your MnO 2 epsilon variety and another 50 percent is going at manganese in the bivalent state.

So, it is the most important industrial process because whenever we use some industrial process based on electrolysis your purity is comparatively very high and the purified sulfuric acid manganese sulfate solution. So, you take not that you have only water, but it is acidified with sulfuric acid. So, manganese sulfate sulfuric acid mixture is basically electrolyzed at 90 to 95 degree centigrade.

So, it is basically a high temperature electrolysis reaction on either led titanium or graphite anode and manganese 3 ions formed disproportionate into manganese 4 and manganese 2 ions. So, in this particular process basically we get the disproportionation. So, manganese 3 basically we all know that the manganese 3 is very much susceptible for disproportionation reaction and that disproportionation reaction can give rise to a mixture or 1 is to 1 ratio of mixture or manganese 2 plus.

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Then as we can see quickly we will see that how we can use for your ore for preparation of very useful manganese compound which we use in our laboratory also your potassium permanganate. So, it is basically a 2 step process and that 2 step process is you have the melting and then a single step liquid phase process. So, if you have a first step is the 2 step melting; that means, the corresponding fusion reaction that the thermal fusion reaction sometime we call that pyrolusite is taken with KOH and with sufficient amount of oxygen which can be supplied from solid sodium carbonate and that giving you the corresponding K 3 MnO 4.

So, it is basically a manganate form and manganese is present in the pentavalent state and that pentavalent state of manganese can further be oxidized to the hexavalent state that is we also still call is that the manganates. So, manganate plus 5 manganate plus 6 and then finally, that manganate is basically converting to a form where you go for the electrolytic (Refer Time: 30:22) it is a single step liquid phase process is the second phase where you get; that means, the corresponding oxidation one electron loss.

So, oxidation of the manganese hexavalent state to the manganese heptavalent state which we all know is nothing, but your KMnO 4 is your potassium permanganate, by doing so your medium will be alkaline in nature and some amount. That means, 0.5 of your H 2 is forming; that means, the hydrogen production is also taking place over there during the production of these things.

So, this is the production of permanganate and in your next part of our this class is we will talk about the applications of the different manganese compounds we have seen quickly some of these manganese compounds, applications are always useful otherwise we cannot go for it is production because if you have a market demand and that market demand will guide you that which particular manganese compound will be useful for industrial production ok.

Thank you very much.