

Main Group Chemistry
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Lecture – 55
Chemistry of Group 12 Elements

Welcome to MSP lecture series on main group chemistry. This is fifty fifth lecture in the series, today I would like to drive your attention to the chemistry of group 12 elements. Group 12 elements have intermediate properties between main group elements as well as transition elements of course, we have 3 elements zinc, cadmium and mercury although these 3 elements are faced with d block elements have properties much similar to main group elements rather than transition elements, and all these 3 elements have $d^{10}s^2$ electronic configuration with a group oxidation state of plus 2, due to the laws of the 2 s electrons and of course, Hg₄ was theoretically predicted in 1994.

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The Group 12 elements

Group 12 Elements: Zinc, Cadmium and Mercury

Although placed with d-block elements, have properties close to main group elements rather than transition elements.

All three elements have $d^{10}s^2$ electronic configuration with a group oxidation state of +2 due to the loss of the two s-electrons.

[Hg₄ was theoretically predicted: Inorg. Chem. 1994-33-2122]

	11	12	13
			B
			Al
Cu	Zn		Ga
Ag	Cd		In
Au	Hg		Tl

Element	First	Second
Zn	+913	+1740
Cd	+874	+1638
Hg	+1013	+1816
Be	+906	+1753

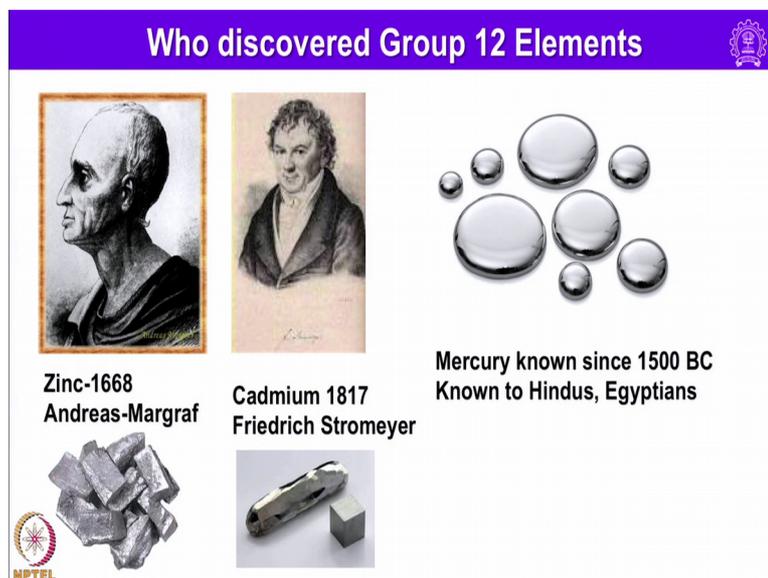


If you just look into the ionization energies for zinc, cadmium, and mercury, we can see here the first ionization energy for zinc, cadmium, mercury are given along with beryllium that is 913, 874, 1013 and 906 kilo joules per mole and similarly second ionization potential is expected to be little higher. In case of zinc it is 1740 kilo joules per mole, where is in case of cadmium mercury and beryllium these values as 1638, 1816 and 1763 kilo joules per mole. From these data it is very clear that these 3 elements

resemble very close to beryllium in terms of their first and second ionization enthalpies. Let me before I proceed further let me give some idea about the people who discovered this 3 elements, zinc was discovered in 1668 by Andreas Margraf we can see here.

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Who discovered Group 12 Elements



Zinc-1668
Andreas-Margraf

Cadmium 1817
Friedrich Stromeyer

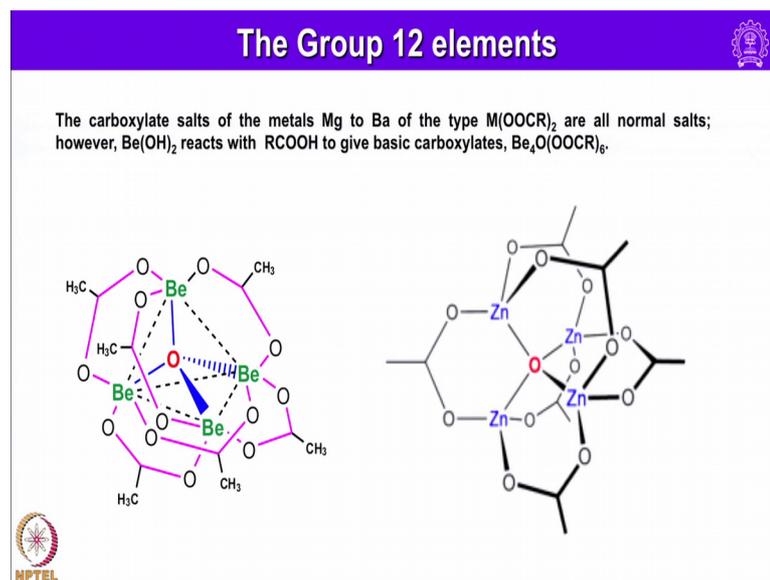
Mercury known since 1500 BC
Known to Hindus, Egyptians

NPTEL

This is how zinc looks like and cadmium was discovered in 1817 by Friedrich Stromeyer and of course, mercury known in ancient days since 1500 BC and of course, it was known to Hindus even much earlier and also Egyptians new how to extract mercury from its ore cinnabar.

In many aspects as I had already mentioned zinc and cadmium compounds are very similar to the analogous magnesium compounds and have the same structures. Mercury compounds have a greater degree of covalent character often with low coordination numbers, and plus one state is quite well established for mercury, but it is very unstable in the case of zinc and cadmium and zinc has much more similarities to beryllium, both have similar first and second ionization energies and though zinc 2 plus is larger than beryllium with different coordination numbers. Of course, when we look into beryllium it has a maximum coordination number of 4 whereas, zinc can have 4, 5 or 6 coordination. Both metals react with acids and alkali and both form a basic ethanoate are acetate of the type and m 4 o 6 acetates you can see that one in the next slide.

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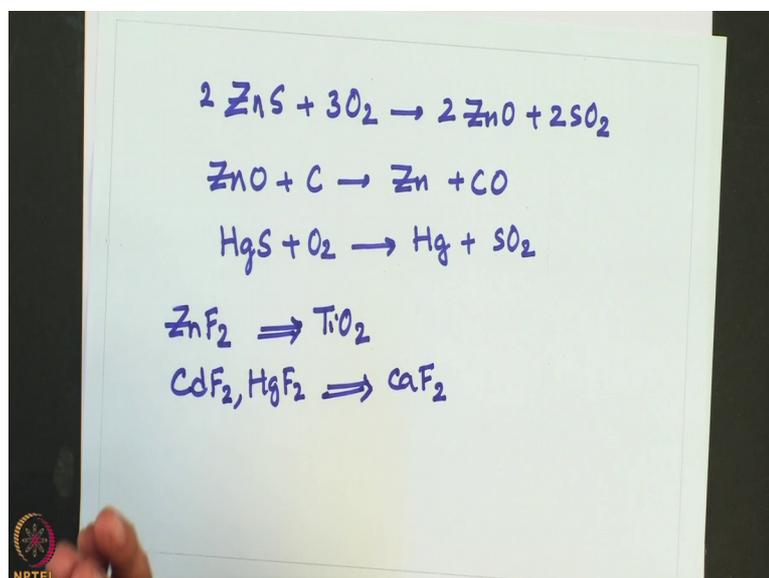


You can see here this is how the zinc acetate looks like of course, the carboxylates salts of the metals magnesium to barium in a have this type of normal salt structure of course, beryllium hydroxide also reacts with carboxylic acid such as acetic acid to give basic carboxylates, that I had discussed while discussing the chemistry of group 2 elements. This one is very similar to this beryllium basic carboxylate yeah. So, we have one tetra bridging oxygen and bridging acetates, because of the youngest electrons in the zinc, cadmium and mercury are tight bound; they are relatively unavailable for metallic bonding and. So, the metals are volatile with low melting and boiling points. In fact, mercury is a unique metal being a liquid at room temperature, and forming a monatomic gas let us look into the occurrence of these 3 elements.

Of course zinc, cadmium and mercury are chalcophilic; that means, they have strong affinity for the chalcogens such as cell for selenium and tellurium, and they occur naturally as sulphide minerals. For examples zinc occurs as a zinc bland also known as paralite, having the composition z and s and also contains trace amount of cadmium, and mercury is obtained from its major ore cinnabar that is HgS and of course, HgS mercury sulphide is unstable above 400 degree centigrade and decomposes to the metal, the zinc oxide and cadmium oxide or reduced to the metals using carbon, and in case of mercuric sulphide one can go for auto reduction in that process what one has to do is mercuric sulphide has to be combined with controlled amount of oxygen to form mercury oxide. So, that carbon can be used for reduction; however, because of low decomposition

temperature of mercuric sulphide before it could convert to mercuric oxide, it decomposes, so that pure metal can be obtained.

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In case of zinc one can do again auto reduction zinc sulphide can be converted into zinc oxide and then on treatment with carbon, it gives zinc plus carbon monoxide.

In case of mercury same thing when atoms are made to convert mercuric sulphide into mercuric oxide, it decomposes to give mercury plus SO₂, why this sulphide ores had to be converted into oxide is we do not have a suitable reducing agent, that can extract sulphur from these sulphide ores, only option we have is carbon disulphide or carbon monoxide or CS. CS does not have any independent existence and CS₂ is not a suitable reagent for the reduction. So, as a result one has to convert into oxide and then use carbon or carbon monoxide to reduce the corresponding metal. Let us look into the chemistry of grouped all elements, the reactivity decreases down the group similar to other group elements. Although zinc and cadmium have high first and second ionization energies, their redox potentials are quite large and negative going to the high solvation energy that drives the reaction. So, they readily dissolve in non-oxidizing acids.

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The Group 12 elements

Chemistry

The reactivity decreases going down the group.

Although Zn and Cd have high First I Es, their redox potentials are quite large and negative owing to the high solvation energy that drives the reaction, so they readily dissolve in non-oxidizing acids.

$$\text{Zn}_{(s)} + 2\text{H}^+_{(aq)} \rightarrow \text{Zn}^{2+}_{(aq)} + \text{H}_2(g)$$

In contrast, mercury will only dissolve in oxidizing acids, such as nitric acid.

Reaction	E° (V)
$\text{Zn}^{2+} + 2e^- \rightleftharpoons \text{Zn}$	-0.76
$\text{Cd}^{2+} + 2e^- \rightleftharpoons \text{Cd}$	-0.40
$\text{Hg}^{2+} + 2e^- \rightleftharpoons \text{Hg}$	+0.85

So, you can see here. So, it can readily form Zn 2 plus ions and despite having very high ionization energies. In contrast mercury will only dissolve in oxidizing as its such as nitric acid. So, the standard redox potential also I have given here for zinc, cadmium and mercury. Of course, in case of mercury it is positive that is in case of zinc, it is negative minus 0.76 6 whereas, in the case of cadmium it is minus 0.40 volts and of course, in case of mercury it is plus 0.85 volts. So, let us look into the halides of zinc, cadmium and mercury all combinations of halides and metal or known for the group. The fluorides are ionic having very high melting point for example, zinc fluoride crystallizes with rutil structure rutil means TiO 2 structure, while cadmium fluoride and mercuric fluoride resemble that of calcium fluoride ok.

And off course zinc fluoride and cadmium fluoride similar to magnesium fluoride they are poorly soluble in water. Chlorides, bromides and iodides of zinc and cadmium are largely ionic, but covalent character for the combination of cadmium with heavier halides increases. In contrast mercury halides are covalent solids which are only slightly soluble in water and are only dissociated into mercury 2 plus and x minus ions.

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The Group 12 elements

ZnF_2 crystallizes with rutile structure, while CdF_2 and HgF_2 have the fluorite structure (CaF_2).

ZnS crystallize in two forms: the low-temperature **zinc blende** (sphalerite) and the higher-temperature **wurtzite** form.

FCC
Tetrahedral coordination around F^-

Ca^{2+}
 F^-

S^{2-}
 Zn^{2+}

ZnS

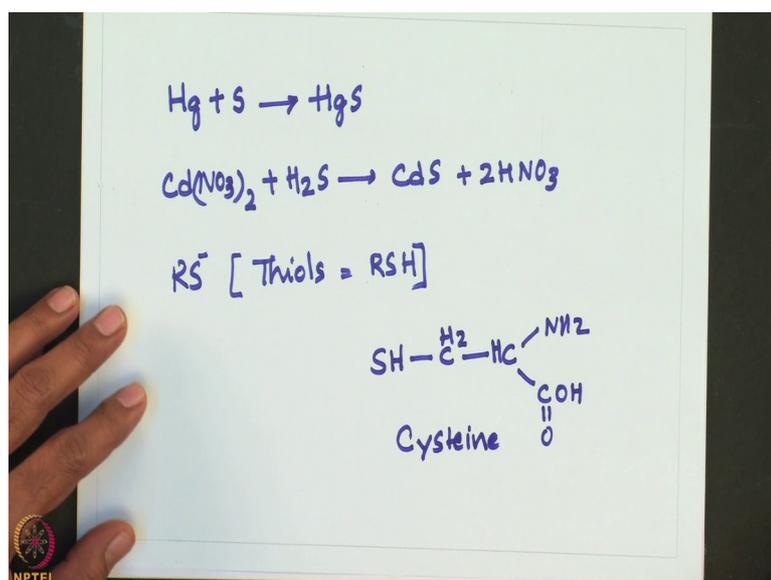
The structure of wurtzite

S
Zn

You can just see the structures of zinc fluoride, as I mentioned it crystallizes with structure of course, one should remember the rutile structure in which titanium is surrounded by 6 oxygen atoms whereas, the oxygen tetrahedral in nature. While cadmium fluoride and mercury chloride have the fluoride structure similar to calcium fluoride structure I have shown, and the zinc sulphide crystallizes in 2 forms, in low temperature zinc blende has sphalerite and the higher temperature wurtzite form, we can see here the wurtzite structure is shown here.

Let us just look into the (Refer Time: 11:13) generates and related compounds of zinc, cadmium and mercury of course, because of chalcophilic nature zinc cadmium and mercury form stable compounds with Sulphur, selenium and tellurium as well ok.

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Similarly, if cadmium nitrate on treatment with hydrogen sulphide gives cadmium sulphide through the formation of HNO_3 , and mercury has a strong affinity for thiolate ligands that is RS^- . So, and of course, if H is there they are called thiols, thiols are essentially RSH , and these kind of compounds RSH are essentially known as mercaptans because of their affinity towards mercury, thiolate complexes of zinc, cadmium, and mercury are very important in biological systems. In enzymes, zinc is often bonded to the S atom of the amino acid that is 16, if you have forgotten this structure of the system here it is ok.

So, this has more affinity, because of the representation of Sulphur towards mercury and to an extent zinc and cadmium as well. So, let us look into the oxygen compounds.

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The Group 12 elements

Oxygen compounds

Zinc has a relatively high affinity for oxygen, whereas mercury does not.

Metals react directly with oxygen on heating, however, above 400 °C, HgO decomposes to the metal and O₂.

ZnO adopts the wurtzite (ZnS) structure which has a tetrahedral coordination of zinc ions, whereas in CdO the larger Cd²⁺ ion is better accommodated by the NaCl structure, which has six-coordinate Cd ions.



Zinc has a relatively high affinity for oxygen whereas, mercury does not. Metal react directly with oxygen on heating. As I said earlier above 400 degree centigrade, mercuric oxide decomposes to the metal and oxygen and zinc oxide adopts wurtzite or zinc sulphate structure which has a tetrahedral coordination of zinc ions, where as in case of cadmium oxide the larger cadmium 2 plus ion is better accommodated by NaCl structure here having 6 coordination surrounding nickel cadmium 2 plus ion.

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The Group 12 elements

ZnO is amphoteric, dissolving in both acids and bases. With excess base, the hydrated zincate anions $[\text{Zn}(\text{OH})_x(\text{H}_2\text{O})_y]^{(x-2)-}$ are formed, and solid salts such as $\text{Na}[\text{Zn}(\text{OH})_3]$ and $\text{Na}_2[\text{Zn}(\text{OH})_4]$ can be crystallized.

CdO is not amphoteric. However, small amount of cadmate anions may be formed, since $\text{Cd}(\text{OH})_2$ dissolves in hot and very concentrated KOH solution.

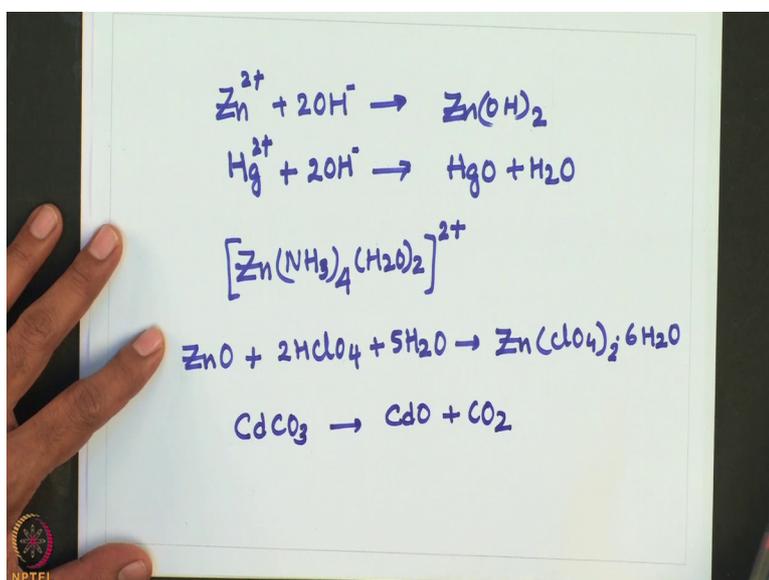
Addition of M²⁺ ions precipitates Zn(OH)₂ and Cd(OH)₂; Hg(OH)₂ does not exist and instead yellow HgO is formed.



Zinc oxide is amphoteric; that means, it dissolves in both acids and bases with excess base similar to aluminium the hydrated zincate anions, that is I had shown here $Zn(OH)_x$ where x is 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, whole to the power of x minus 2 minus or formed and solid salt such as tri hydroxy zincate and tetrahydroxozincate can also be conveniently crystallized, and in contrast to zinc oxide cadmium oxide is not amphoteric.

However small amounts of cadmate anions may be formed, since cadmium hydroxide dissolves in hot and very concentrated potassium hydroxide solution, and addition of m^{2+} plus ions precipitate zinc hydroxide and cadmium hydroxide, mercuric hydroxide does not exist and instead yellow mercuric oxide is formed.

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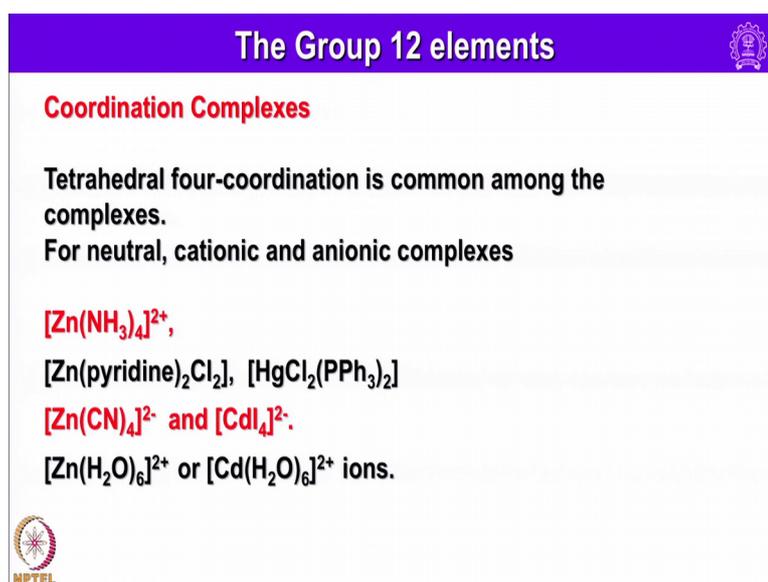


Zn^{2+} plus $2OH^{-}$ gives $Zn(OH)_2$, similar attempts to make mercuric hydroxide leads to the formation of mercuric oxide. Zinc and cadmium hydroxides also dissolve in aqueous ammonia solutions by the formation of ammonia complexes, for example, this type of compounds are known where zinc is hexa coordinated surrounded by 4 ammonia ligands and 2 water ligands ok.

Salts of oxy acids are known for all 3 metals including nitrates, sulfates and chlorides synthesized by reaction of the oxide with acid followed by crystallization. For example, zinc oxide on treatment with perchloric acid in aqueous medium gives zinc perchlorate. Of course, here this is the counter anion and it is surrounded by 6 water molecules. So, having (Refer Time: 17:10) octahedral geometry. Zinc and cadmium carbonates are rather unstable

to heat as a result of the polarizing effect of the small zinc 2 plus and cadmium 2 plus ions, causing the composition to the oxide very similar to alkali and alkaline earth metal carbonates for example, if you take CdCO_3 , it gives cadmium oxide though the liberation of carbon dioxide.

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The Group 12 elements

Coordination Complexes

Tetrahedral four-coordination is common among the complexes.
For neutral, cationic and anionic complexes

$[\text{Zn}(\text{NH}_3)_4]^{2+}$,
 $[\text{Zn}(\text{pyridine})_2\text{Cl}_2]$, $[\text{HgCl}_2(\text{PPh}_3)_2]$

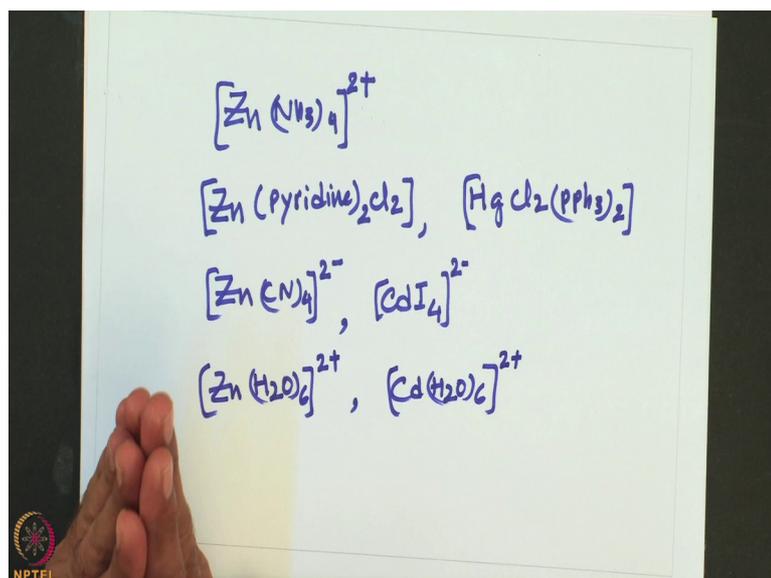
$[\text{Zn}(\text{CN})_4]^{2-}$ and $[\text{CdI}_4]^{2-}$.

$[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ or $[\text{Cd}(\text{H}_2\text{O})_6]^{2+}$ ions.



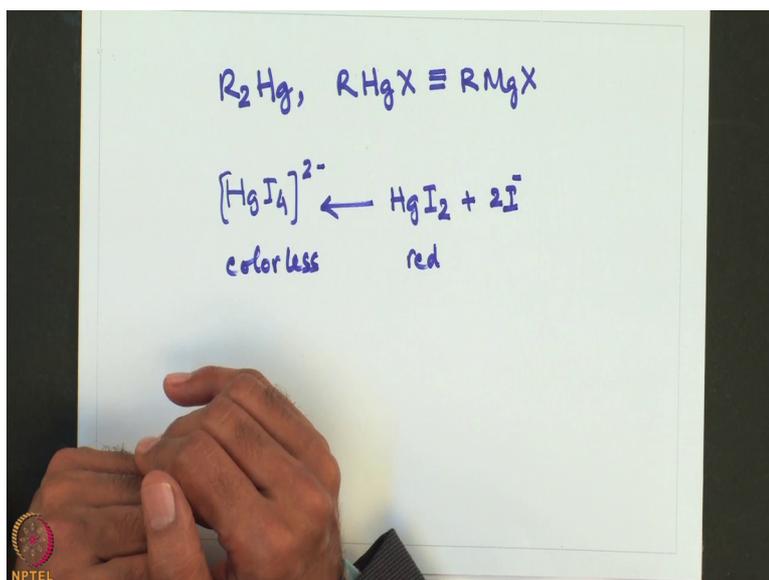
Several coordination coordination complexes of zinc cadmium and mercury are known; and tetrahedral 4 coordination is the most common for group 12 elements, and also whether they exist a neutral cationic or anionic form, coordination number 4 is the most stable one.

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Let me write few examples here for example, tetra amine zinc is known it is cationic. Neutral compounds also known for example, zinc chloride and treatment with 2 equivalence of pyridine will form this type of compound, similarly mercuric chloride on treatment with 2 equivalence of triphenyl phosphine forms neutral compound of this type. Similarly anionic compounds are also known for example, tetrasynozincate and tetraiodocadmet are known. Of course, they form neutral compounds and cationic compounds with water as a ligand as well having coordination number 6. So, these are few examples of coordination compounds of zinc, cadmium and mercury. Mercury has a strong tendency to adopt lower coordination numbers then cadmium and zinc, it often displays linear 2 coordination in compound such as di alkyl mercury and also compound having a composition or Hg_x resembling I did not reagent two coordination with compounds of this type or quite known.

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Now. So, in this case also it is 2 coordinated and this is very similar to $RMgX$. So, otherwise 4 coordination is quite common for mercuric compounds as well. So, colorless HgI_4^{2-} can be formed starting from mercuric iodide for example, if it is taken this is red ink color, and it is treated with 2 equivalents of iodide it forms this one this is colorless and; that means, treatment of this one with potassium iodide solution gives this tetraiodomercurate to minus ion.

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The Group 12 elements

Low-valent compounds

Cd_2^{2+} and Zn_2^{2+} species are known but are unstable; they are formed only in anhydrous conditions and readily disproportionate in water to give the metal and M^{2+} .

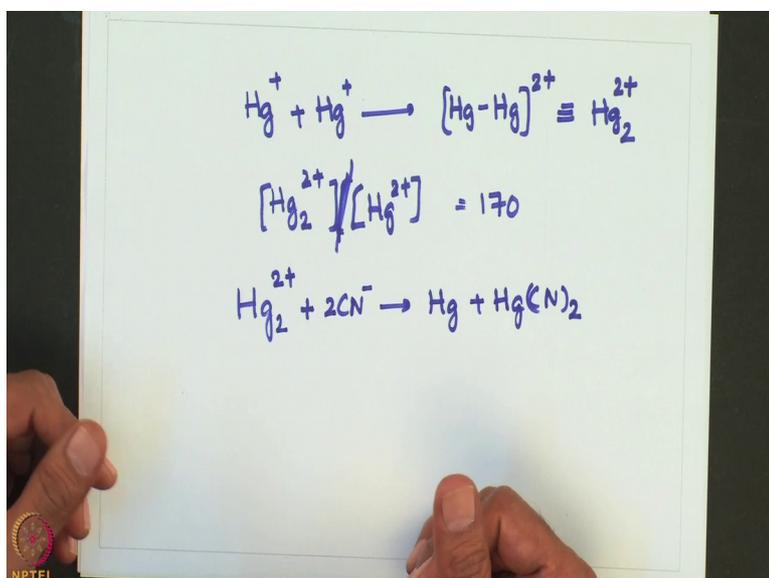
In contrast, Hg_2^{2+} ion is the most stable, and the best known example of a monovalent species formed by the group.

The Hg_2^{2+} ion is diamagnetic and M^+ ion would be paramagnetic with one unpaired electron, so dimerization occurs through Hg-Hg bond formation, giving Hg_2^{2+} ion.

Let us look into low valent compounds of cadmium and zinc, you can see here Cd 2 2 plus and zinc 2 plus species are known, but are relatively unstable compared to analogous mercuric compound. They are formed only in anhydrous conditions and readily disproportionate in water to give the metal and die cationic corresponding metals.

In contrast mercury Hg 2 2 plus ion is the most stable, and the best known example of a monovalent species formed by this group. Hg 2 plus ion is diamagnetic and m plus ion would be paramagnetic, with one unpaired electrons. So, dimerization occurs through Hg Hg bond formation giving Hg 2 plus ion.

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Hg plus plus Hg plus gives 2 plus this also can be written as Hg 2 2 plus. So, here there is an equilibrium between Hg 2 plus and Hg 2 plus ion, which has an equilibrium constant of about 170 so; that means, Hg 2 2 plus and Hg 2 plus is about 170. So that means, in an aqua solution of mercuric 2 salts there will be less than 0.5 percentage of Hg 2 plus presenting solution, if a Hg 2 plus ions are removed by complexation with ligands which form stable complexes are insoluble compounds with say cyanide then the dis proportionation goes to completion.

So; that means, Hg 2 2 plus on addition of cyanide ligands gives mercury plus mercuric cyanide. So, this is called disproportionate reaction plus one is giving 0 and 2 plus species, and opposite reaction is also called comproportionation reaction. So, now, let us look.

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Ask a Question

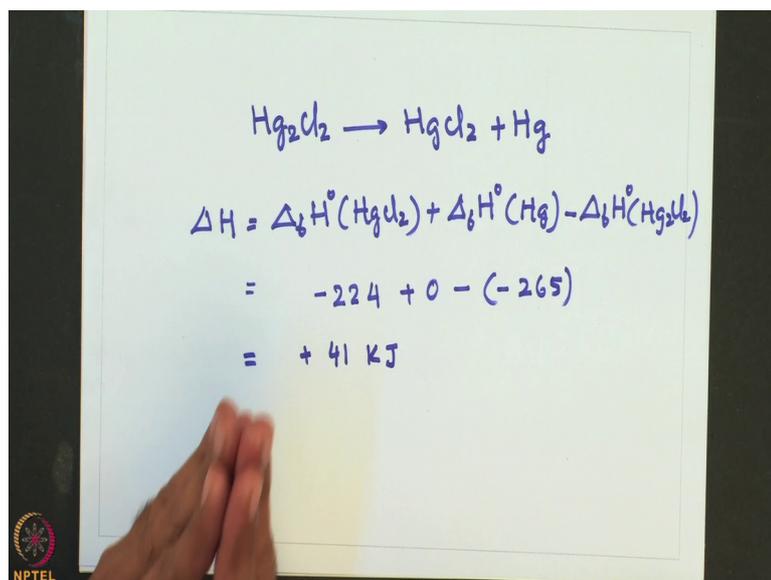
Using the following thermodynamic data, show that Hg_2Cl_2 is unstable with respect to HgCl_2 and Hg :
 $\Delta_f H^\circ(\text{Hg}_2\text{Cl}_2) = -265 \text{ kJ mol}^{-1}$; $\Delta_f H^\circ(\text{HgCl}_2) = -224 \text{ kJ mol}^{-1}$;
and show with an appropriate balanced chemical equation the outcome.



Into now example here one question, using the following thermodynamic data that I have given here, show that mercury is chloride is unstable with respect to mercuric chloride and mercury; that means, its unstable with respect to the disproportionation reaction and here this thermodynamic data are given $\Delta_f H$ of mercurous chloride is minus 265 kilo joules per mole and $\Delta_f H$ for mercuric chloride is minus 224 kilo joules per mole.

Now, with this show with an appropriate balanced chemical equation, the outcome of course, balanced chemical equation one can write easily.

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So, let me do it for you Hg_2Cl_2 giving HgCl_2 plus Hg . So, this is the balanced chemical equation showing disproportionation of mercurous chloride to mercuric chloride plus mercury and these values are given. So, basically ΔH equals $\Delta_f H^\circ$ of HgCl_2 plus $\Delta_f H^\circ$ of Hg minus $\Delta_f H^\circ$ of mercurous chloride. So, these values are already given if you put these values here minus 224 is given for mercuric chloride and of course, for this is 0 minus into minus 265. So, this will give you a net plus 41 kilojoules. So, that indicates this reaction this proportionate is favored. You know simple summation will show you that this mercurous chloride is unstable with respect to the disproportionation reaction.

So, let us look into the uses and toxic effects of zinc cadmium and mercury.

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Uses and toxic effects of Zn, Cd and Hg

Carbonic Anhydrase
Removes CO₂ from blood and pH of the blood is maintained.
 $H_2O + CO_2 \rightarrow \{H^+ + HCO_3^-\} H_2CO_3$

His(N)
His (N)
His(N)
Zn—OH₂

Of course zinc is very very important in biological system, it acts as a carbonic anhydrase; that means, it removes c o 2 from blood and ph of the blood is maintained you know that h 2 o plus co 2 gives H plus plus HCO 3 minus and this compound is responsible and here (Refer Time: 26:28) nitrogen of histidine is binding here with coordination number of 4, where one of the coordinate site is occupied by OH 2 this is carbonic anhydrase.

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Uses and toxic effects of Zn, Cd and Hg

Liver Alcohol Dehydrogenase
This converts the alcohol present in the liver.

Somebody who is not having this enzyme should not consume alcohol.

Cys(S)
Cys(S)
His(N)
Zn—OH₂

$CH_3CH_2OH \xrightarrow{NAD^+ \rightarrow NADH} CH_3CHO$

Liver Alcohol dehydrogenase

So, another one is liver alcohol dehydrogenase, this complex having 2 systems, and one histidine bond zinc have a one water molecule converts the alcohol present in the liver, one should remember someone who is not having this enzyme should never ever consume alcohol, and you can see here alcohol is essentially normal is ethanol CH_3CHOH and here with this compound basically what happens it is converted into aldehyde now.

So that means, essentially the metabolism of alcohol takes place using this zinc compound is called liver alcohol dehydrogenase.

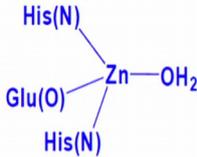
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Uses and toxic effects of Zn, Cd and Hg

Carboxy Peptidase

Peptide bonds of the proteins you consume are hydrolyzed, is known as peptide hydrolysis.

This enzyme hydrolyzes the bonds from the terminal of the protein.



Carboxy peptidase

NPTEL

There is one more called carboxy peptidase, peptide bonds of the proteins we consume or hydrolyzed is known as peptide hydrolysis, this sends them hydrolyzes the bonds from the terminals of the protein this 3 ligands here and then it has one water molecule, this is called carboxy peptidase in all these 3 compounds zinc is the metal ion.

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Uses and toxic effects of Zn, Cd and Hg

The low melting point (234 K) of Hg results in its being a unique metal. Its high thermal expansion coefficient makes it a suitable liquid for use in thermometers, and it has widespread application in barometers, diffusion pumps and in Hg switches in electrical apparatus.

An older use was in mirrors. Some other metals dissolve in mercury to give amalgams; their uses are varied, for example:



So, the low melting point of mercury results in its being a unique metal it is high, thermal expansion coefficient makes it a suitable liquid for use in thermometers and it has widespread application in barometer diffusion pumps and in mercury switches, in electrical operators and older use was in mirrors, some of the metals dissolve in mercury to give amalgam their uses are varied example cadmium, mercury amalgam is a component in the western cell, sodium amalgam is a convenient source of sodium as a reducing agent silver amalgam is used for silver filling in dentistry nowadays it is discouraged because of that toxic effects and volatility of mercury after entering the body as mercury vapor, the metal accumulates in the kidneys brains and testicles it is converted into mercury 2 plus and is readily coordinated by the ion, donors present in the proteins the end result of mercury poisoning is severe damage to the central nervous system.

One of the reasons why the toxicity of mercury so high is that its retention time in body tissue is especially very long; that means, it can stay as many as 65 days in the kidneys. So, after entering the body as mercury vapor, the metal accumulates in the kidneys brain and testicles it is converted into mercury 2 plus and is readily coordinated by thiol, RSH donors present in proteins the end result of mercury poisoning is very severe. I conclude the chemistry of group 12 elements in my next lecture I will be discussing the organometallic chemistry of main group elements, until then have a pleasant reading of main group chemistry.

Thank you very much.