Advanced Transition Metal Chemistry – Periodic Table
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Lecture – 6
Introduction to Transition Elements

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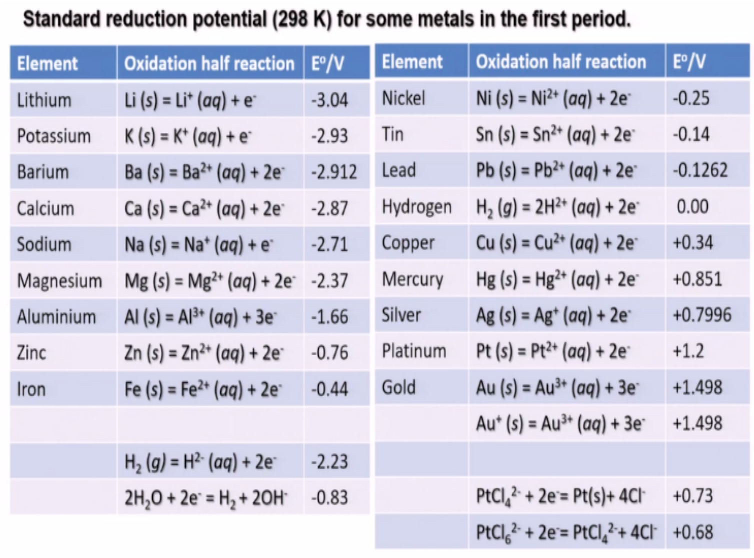

Standard reduction potential (298 K) for some metals in the first period.

Element	Oxidation half reaction	E°/V	Element	Oxidation half reaction	E°/V
Lithium	Li (s) = Li^+ (aq) + e^-	-3.04	Nickel	Ni (s) = Ni^{2+} (aq) + $2e^-$	-0.25
Potassium	K (s) = K^+ (aq) + e^-	-2.93	Tin	Sn (s) = Sn^{2+} (aq) + $2e^-$	-0.14
Barium	Ba (s) = Ba^{2+} (aq) + $2e^-$	-2.912	Lead	Pb (s) = Pb^{2+} (aq) + $2e^-$	-0.1262
Calcium	Ca (s) = Ca^{2+} (aq) + $2e^-$	-2.87	Hydrogen	H_2 (g) = $2H^{2+}$ (aq) + $2e^-$	0.00
Sodium	Na (s) = Na^+ (aq) + e^-	-2.71	Copper	Cu (s) = Cu^{2+} (aq) + $2e^-$	+0.34
Magnesium	Mg (s) = Mg^{2+} (aq) + $2e^-$	-2.37	Mercury	Hg (s) = Hg^{2+} (aq) + $2e^-$	+0.851
Aluminium	Al (s) = Al^{3+} (aq) + $3e^-$	-1.66	Silver	Ag (s) = Ag^+ (aq) + $2e^-$	+0.7996
Zinc	Zn (s) = Zn^{2+} (aq) + $2e^-$	-0.76	Platinum	Pt (s) = Pt^{2+} (aq) + $2e^-$	+1.2
Iron	Fe (s) = Fe^{2+} (aq) + $2e^-$	-0.44	Gold	Au (s) = Au^{3+} (aq) + $3e^-$	+1.498
				Au^+ (s) = Au^{3+} (aq) + $3e^-$	+1.498
	H_2 (g) = H^{2-} (aq) + $2e^-$	-2.23			
	$2H_2O + 2e^- = H_2 + 2OH^-$	-0.83		$PtCl_4^{2-} + 2e^- = Pt(s) + 4Cl^-$	+0.73
				$PtCl_6^{2-} + 2e^- = PtCl_4^{2-} + 4Cl^-$	+0.68

Hello everyone, once again welcome you all to MSB lecture series on advanced transition metal chemistry. In my previous lecture, I was discussing about the redox potential and also activity series. Let me continue from where I had stopped. So, yesterday I showed you this table. I have given redox potential for both the *s*- and *p*-block elements as well as selected *d* block elements.

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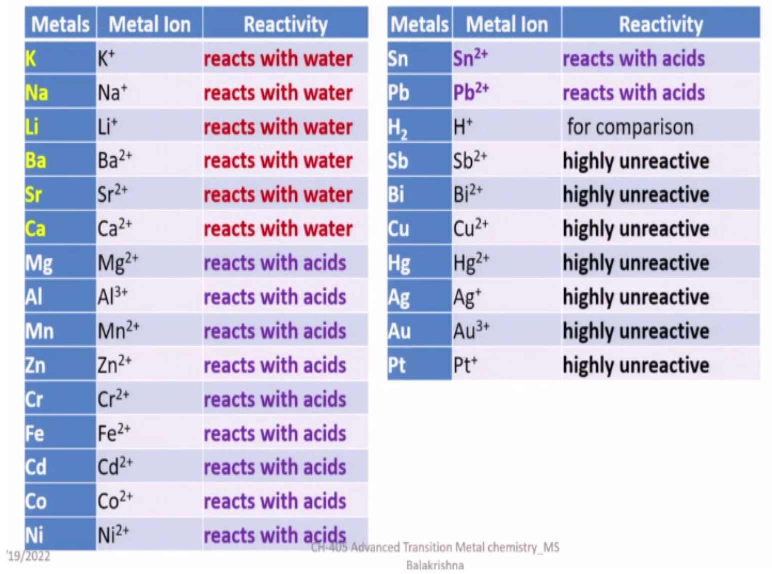

Metals	Metal Ion	Reactivity
K	K^+	reacts with water
Na	Na^+	reacts with water
Li	Li^+	reacts with water
Ba	Ba^{2+}	reacts with water
Sr	Sr^{2+}	reacts with water
Ca	Ca^{2+}	reacts with water
Mg	Mg^{2+}	reacts with acids
Al	Al^{3+}	reacts with acids
Mn	Mn^{2+}	reacts with acids
Zn	Zn^{2+}	reacts with acids
Cr	Cr^{2+}	reacts with acids
Fe	Fe^{2+}	reacts with acids
Cd	Cd^{2+}	reacts with acids
Co	Co^{2+}	reacts with acids
Ni	Ni^{2+}	reacts with acids

Metals	Metal Ion	Reactivity
Sn	Sn^{2+}	reacts with acids
Pb	Pb^{2+}	reacts with acids
H_2	H^+	for comparison
Sb	Sb^{2+}	highly unreactive
Bi	Bi^{2+}	highly unreactive
Cu	Cu^{2+}	highly unreactive
Hg	Hg^{2+}	highly unreactive
Ag	Ag^+	highly unreactive
Au	Au^{3+}	highly unreactive
Pt	Pt^+	highly unreactive

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And here I have given the reactivity series. The reactivity series is a series of metals in order of reactivity from highest to lowest. It is used to determine the products of single displacement reactions. Let us say: a metal A will replace another metal B in a solution if A is higher in that series.

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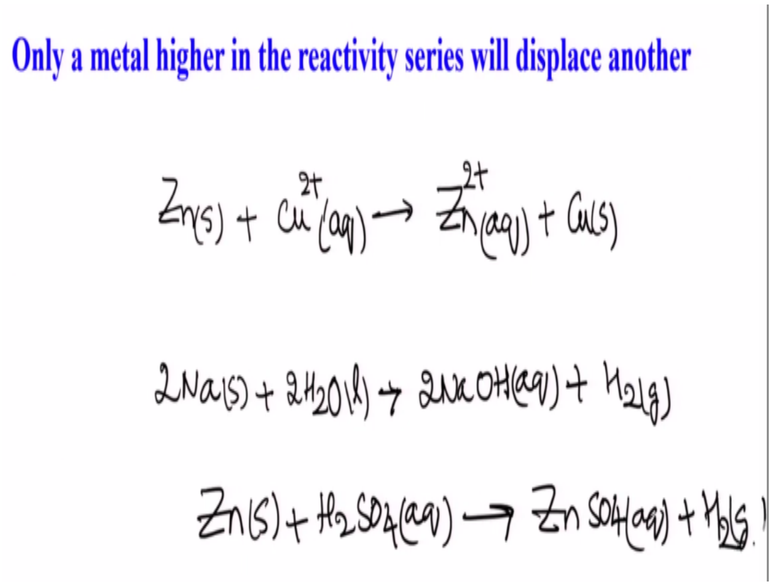

Only a metal higher in the reactivity series will displace another

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$$

$$Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$$

So, only a metal higher in the reactivity series will displace another. A metal can displace metal ions listed below in the series, but not above. For example, zinc is more active than copper and is able to displace copper ions from solution. If you consider this reaction, why this reaction happens can be clearly seen from the redox potential. Here, copper 2+ is reduced to copper, but silver cannot displace copper ion from solution.

So, it is important to distinguish between the displacement of hydrogen from an acid and hydrogen from water. Sodium is highly reactive and is able to displace hydrogen from water. For example, if you take sodium solid and add to water, I am sure you are all familiar with this equation. So, H_2 is liberated here. Sodium is highly active and is able to displace hydrogen from water.

So, less active metals such as iron or zinc cannot displace hydrogen from water but do readily react with acids and liberate hydrogen. For example, if you take zinc and treat with sulfuric acid it, forms zinc sulphate plus H_2 will be deliberated.

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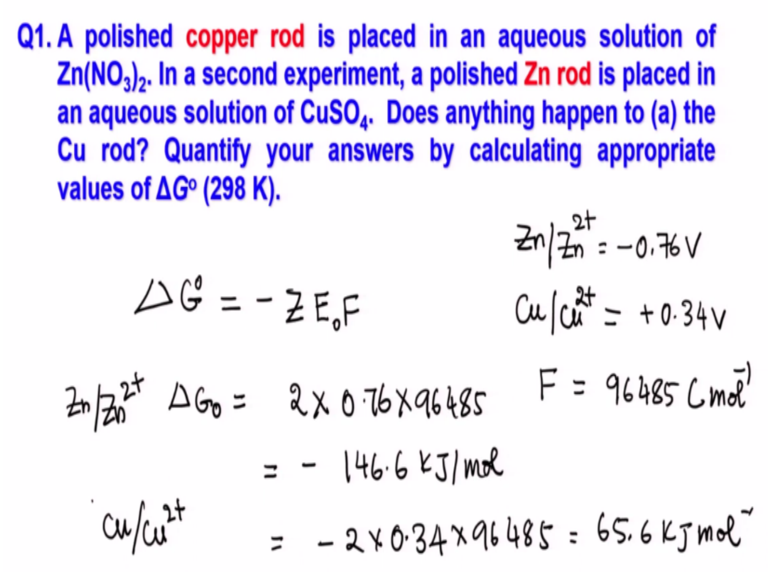

Q1. A polished copper rod is placed in an aqueous solution of $Zn(NO_3)_2$. In a second experiment, a polished Zn rod is placed in an aqueous solution of $CuSO_4$. Does anything happen to (a) the Cu rod? Quantify your answers by calculating appropriate values of ΔG^o (298 K).

$Zn/Zn^{2+} = -0.76 V$

$Cu/Cu^{2+} = +0.34 V$

$$\Delta G^0 = -Z E_0 F$$

$F = 96485 \text{ C mol}^{-1}$

Zn/Zn^{2+} $\Delta G_0 = 2 \times 0.76 \times 96485$

$= -146.6 \text{ kJ/mol}$

Cu/Cu^{2+}

$= -2 \times 0.34 \times 96485 = 65.6 \text{ kJ mol}^{-}$

So, let us look into some problems related to these topics. I have given a question here. A polished copper rod is placed in an aqueous solution of zinc nitrate. So, in a second experiment, a polished zinc rod is placed in an aqueous solution of copper sulphate. Does anything happen to the copper rod? Quantify your answers by calculating appropriate values of ΔG^o at 298 Kelvin.

So, what we have to do is, from redox potential table you can get the information about redox potential for copper and zinc couple. The values are here. Similarly, we have to calculate now ΔG and I am sure you are all familiar with this equation and where F you know Faraday's constant that is equals 96485 coulombs per mole. So, just if you use this one, in both cases, we should be able to determine ΔG in each case.

So, ΔG here if you use in case of zinc it is = 2 x E_o = 0.76 x 96485. So, this gives a value of –146.6 kiloJoules per mole and then if you do the same; this is for zinc couple. If we do the same for copper we can get here too, so what do we get is here 65.6 kiloJoules per mole. So, this is positive and this is negative you know that. Zinc cannot replace copper, whereas copper can readily replace from copper sulphate and it can form Cu.

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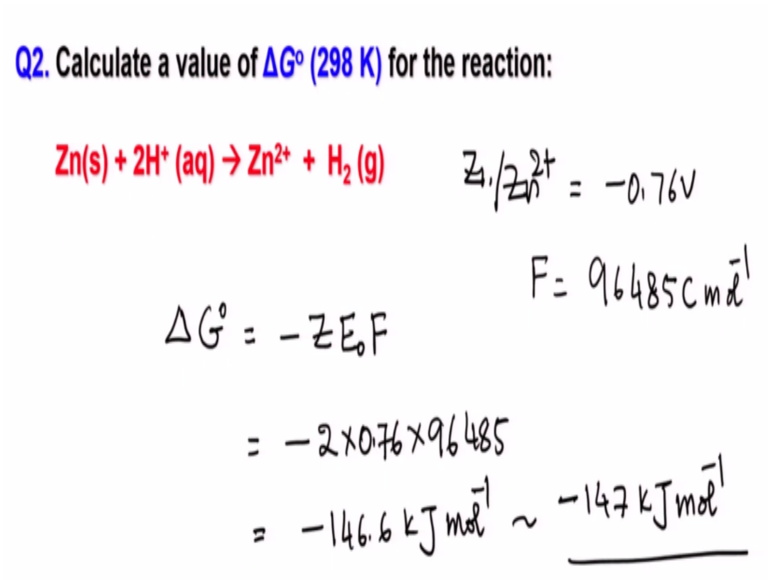

Q2. Calculate a value of ΔG^o (298 K) for the reaction:

$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+} + H_2(g)$

$Zn/Zn^{2+} = -0.76 V$

$F = 96485 C mol^{-1}$

$\Delta G^o = -zE_oF$

$= -2 \times 0.76 \times 96485$

$= -146.6 kJ mol^{-1} \sim \underline{-147 kJ mol^{-1}}$

Let us look into one more question here. Calculate a value of ΔG for the reaction. Of course here again, the same answer you can anticipate that I showed you in my previous solution. Here what we have to do is: of course once again, we have the value of 0.76 volts and F is known 96485 coulombs per mole. What we have to do is, we have to calculate ΔG minus, so if you put here values, so this comes around –146.6 kiloJoules per mole. It can be rounded off to –147 kiloJoules per mole This is the ΔG value for this reaction. Similarly, by knowing the redox potential, ΔG for any reaction can be calculated.

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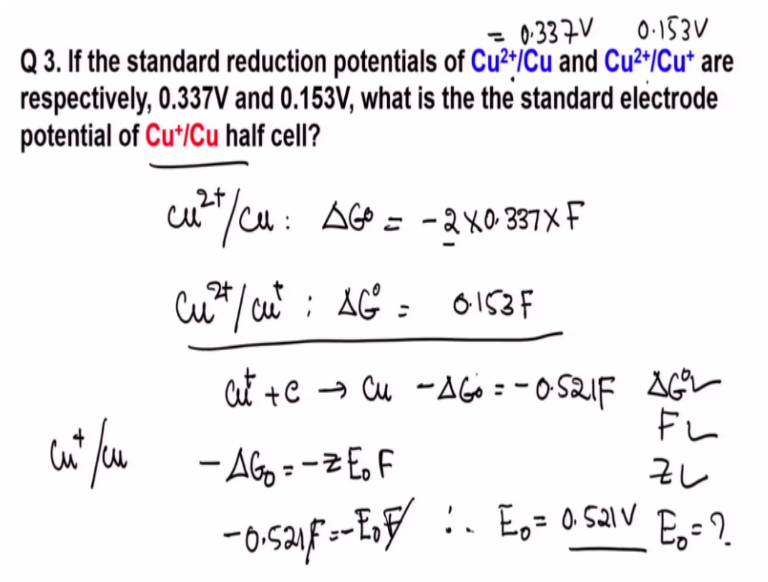

$= 0.337V$ $0.153V$

Q 3. If the standard reduction potentials of Cu^{2+}/Cu and Cu^{2+}/Cu^+ are respectively, 0.337V and 0.153V, what is the the standard electrode potential of Cu^+/Cu half cell?

$Cu^{2+}/Cu : \Delta G^o = -\underline{2} \times 0.337 \times F$

$Cu^{2+}/Cu^+ : \Delta G^o = 0.153F$

$Cu^+ + e \rightarrow Cu \quad -\Delta G_o = -0.521F \quad \Delta G^o ✓$

$F ✓$

$Cu^+/Cu \quad -\Delta G_0 = -zE_0F \quad z ✓$

$-0.521\cancel{F} = -E_0\cancel{F} \quad \therefore E_0 = \underline{0.521V} \quad E_0 = ?$

So, let us look into one more question here. If the standard reduction potential of Cu^{II} to Cu and Cu^{II} to Cu^{I} are given as 0.337 and 0.153 volts, respectively, what is the standard electrical potential of Cu^{I} to Cu half-cell? So, what is given here? The values for this is given here, this is 0.337 and for this one it is 0.153 volts. So, now let us calculate for this one ΔG.

So, for the first one equals –2 x 0.337. Let us keep F as it is okay. Similarly, let us look into this couple here 0.153 because only one electron is involved in this one, here two electrons, so here it is one. So, let me write this way and now Cu^{I} plus one electron, gives Cu. So, minus ΔG = –0.521. You have to sum up, so you get the value. Now, we can use for this reaction. Now, for this reaction we know that ΔG is known and F is known and z is known.

We have to find out E_o, E_o equals what? So, let us put this equation minus ΔG, so this is for Cu, Cu couple = –z E_o F. So, this value is already there, this is the F. So, I shall put –0.521 F equals here z is 1, simply this is E_oF. So, it goes and this is also minus, therefore E_o. So, standard electrode potential of Cu^{I} Cu = equals 0.521 volts. So, this is the answer. So, this is how unknown quantity can be found out.

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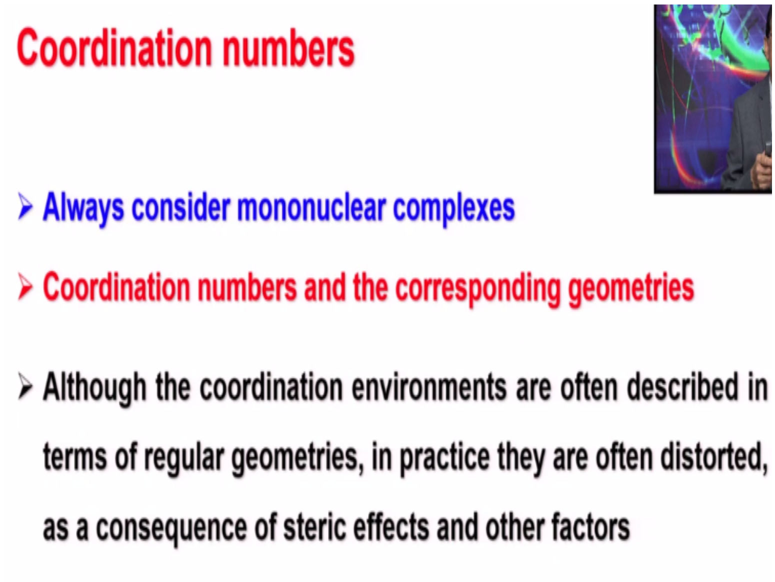

Coordination numbers

- Always consider mononuclear complexes
- Coordination numbers and the corresponding geometries
- Although the coordination environments are often described in terms of regular geometries, in practice they are often distorted, as a consequence of steric effects and other factors

So, let us look into the coordination numbers now. So, always consider mononuclear complexes while deciding the coordination number. And coordination numbers and the corresponding geometries should be looked into it. For example, if you have coordination number 2, it is supposed to have linear geometry. If coordination number 3, it should have trigonal planar geometry.

So, it continues, I shall elaborate more when we go to valence bond theory and bonding concepts. Although the coordination environments are often described in terms of regular geometries, for example when coordination number is 4, the sheer number can only tell you about the geometry, whether tetrahedral geometry or square planar geometry, but it does not tell you information about whether it is irregular geometry or distorted geometry.

So, this information can come from actual bonding and also by looking into the nature of the ligands and all these things are very nicely understood when we go for crystal field theory where we come across spectrochemical series, where we know whether a given ligand is strong ligand or weak ligand. So, that means the consequences of steric effects and other factors can influence the geometry and hence we can see some distortion in them.

So, discussion of a particular geometry usually involves bond parameters such as bond lengths and bond angles that can be determined in the solid state by doing single crystal X-ray diffraction, and of course, here several other factors also influence these parameters including crystal packing forces. And when the energy difference between possible structures is small, for example, when we have coordination number 5 and coordination number 8.

If they possess more than one type of geometry and the energy difference between those two geometries are small, then they can exhibit fluxionality in solution, and sometime that can be monitored at lower temperature, using various spectroscopic methods. The small energy differences may also lead to the observation of different structures in the solid state.

That means, if they have preference for a particular geometry, at a particular temperature, by controlling the temperature, we can crystallize in a particular geometry for a given complex or a compound.

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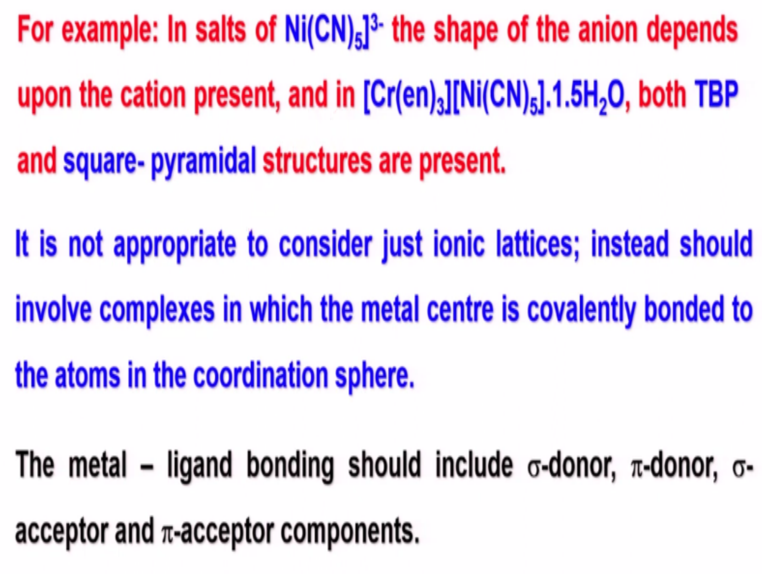

For example: In salts of Ni(CN)$_5$]$^{3-}$ the shape of the anion depends upon the cation present, and in [Cr(en)$_3$][Ni(CN)$_5$].1.5H$_2$O, both TBP and square- pyramidal structures are present.

It is not appropriate to consider just ionic lattices; instead should involve complexes in which the metal centre is covalently bonded to the atoms in the coordination sphere.

The metal – ligand bonding should include σ-donor, π-donor, σ-acceptor and π-acceptor components.

If you consider pentacyanonickelate anion where nickel is in +2 state. The shape of the anion depends upon the cation present. So, that means here when the coordination number is 5 in this case, you can anticipate trigonal bipyramidal geometry or it can also have square pyramidal geometry, however, the geometry adopted by this anion depends on the type of cation we have with this, and similarly in case of trisethylenechromium, (Cr(en)$_3$, is a counter cation here, chromium is in +3 state and in this one nickel is in +2 state, it is a trianion.

So, here this one can exhibit both TBP and square pyramidal geometries. So, this particular combination of cation and anion can exhibit both TBP as well as square pyramidal geometries. That means, it is not appropriate to consider just ionic lattices, instead should involve complexes in which that metal centre is covalently bonded to the atoms in the coordination sphere.

That metal-ligand bonding also should include not just sigma-donor, but also pi-donor and also sigma-acceptor as well as pi-acceptor components. Of course, you can understand these things very clearly when we talk about the classification of ligands. I should tell you again whatever the ligands, we have at our disposal as coordination chemists, can be simply classified into three categories.

One category is pure sigma-donors, the complexes having pure sigma-donors, the examples are: ammonia and water complexes, aqua complexes or primary and secondary aliphatic amine complexes. And the second category belongs to those complexes having ligands which are capable of acting as sigma-donors as well as pi-donors, that means electron rich ligands exhibit this property.

For example, if you consider halides such as fluoride, chloride, bromide and iodide, so they have low energy filled sigma-orbitals and low energy filled pi-orbitals. So, they are called as sigma-donor and pi-donor complexes, and the third one is: carbon monoxide and phosphine and other related compounds, we call them as sigma-donor and pi-acceptor. So, that means all ligands should fall into one of these categories.

We shall look into more and more examples when we go to the bonding concept. That means these ligating properties have significant influence on the geometry adapted by a particular metal complex.

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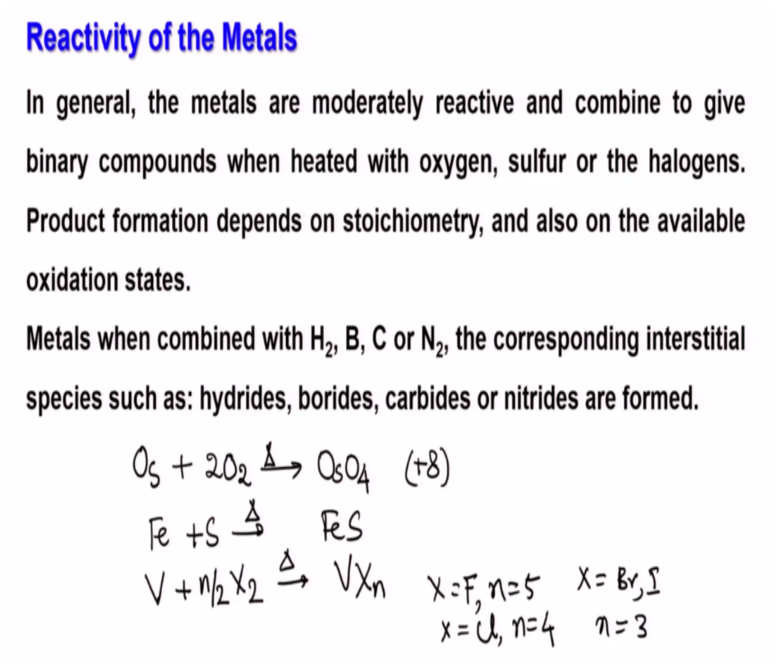

Reactivity of the Metals

In general, the metals are moderately reactive and combine to give binary compounds when heated with oxygen, sulfur or the halogens. Product formation depends on stoichiometry, and also on the available oxidation states.

Metals when combined with H_2, B, C or N_2, the corresponding interstitial species such as: hydrides, borides, carbides or nitrides are formed.

$Os + 2O_2 \xrightarrow{\Delta} OsO_4$ (+8)

$Fe + S \xrightarrow{\Delta} FeS$

$V + n/2\, X_2 \xrightarrow{\Delta} VX_n$ X = F, n = 5 X = Br, I

X = Cl, n = 4 n = 3

Let us look into the reactivity of metals. In general, the metals are moderately reactive and combined to give binary compounds when heated with oxygen, sulfur or halogens and product formation depends on stoichiometry and also the oxidation state of the metal we are considering. For example, when you treat metals such as transition metals with hydrogen, boron, carbon or nitrogen, the corresponding interstitial species such as hydrides, borides, carbides or nitrides are formed.

For example, we take osmium here and treat with two molecules of oxygen at high temperature, then it can form osmium tetroxide, and of course here osmium oxidation state is +8. And then if we take iron and heat with sulfur, it can form FeS, and if you take vanadium and treat with halides it can form VX_n. So here it depends on the stoichiometry and also the reaction conditions.

All these things are on heating happens; high temperature reactions, where X can be F, n = 5 and when X = Cl, n = 4 and when X = bromide or iodide, n = 3. So, depending upon the type of halides we are using and the stoichiometry and reaction condition, we can get the corresponding homoleptic oxides, sulphides or halides. So, many *d*-block metals should on thermodynamic grounds liberate H_2 from acid but in practice many does not liberate.

The reason is: they are passivated by a thin surface coating of oxide or by having a high dihydrogen over potential or both. For example, if you consider silver, gold and mercury, they are least reactive elements. Gold is not oxidized by atmospheric oxygen or even by acids except *aqua regia*, that is three to one mixture of hydrochloric acid and nitric acid.

And then when we talk about colour of metal complexes, of course electronic spectroscopy comes very handy in explaining and that we can understand better when you go to crystal field theory. And of course, valence bond theory can also tell you about magnetic properties, but not in detail, especially the temperature dependence of magnetism and all those things can be understood through crystal field theory.

And of course, complex formation and why a complex is more stable and why a particular complex adopts a particular geometry, despite other options are there. So, all these things we should discuss once after completing coordination theory as proposed by Warner and then by understanding crystal field theory and molecular orbital theory. As I mentioned about interstitial hydrates; interstitial hydrates most commonly exist within metals or alloys and their bonding is generally metallic.

So, transition metals form interstitial binary hydrates when exposed to hydrogen. These systems are usually nonstoichiometric with variable amounts of hydrogen atoms in the lattice. In material engineering, one should be extremely careful about interstitial hydrogen present in the lattice, especially when we are using such material for construction. Here if interstitial hydrogen is present in construction material, so the phenomena of hydrogen embrittlement results.

And then what happens, the structure can be weak, that is a reason usually in material engineering, they will ensure that, okay, metal do not contain any interstitial lattice. In case if they are found, it has interstitial lattice some gases, one has to heat it to very high temperature under vacuum and get rid of all the gases, so that this hydrogen embrittlement does not damage the structure.

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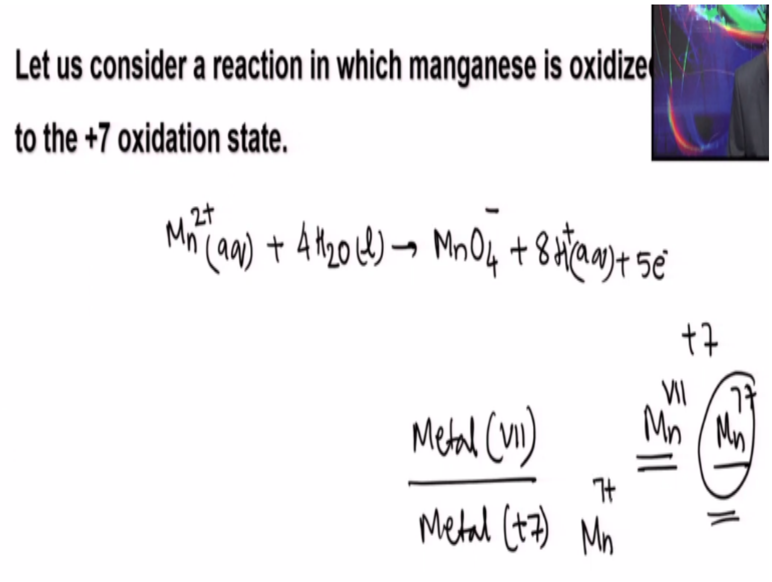

Let us consider a reaction in which manganese is oxidize

to the +7 oxidation state.

$Mn^{2+}(aq) + 4H_2O(l) \rightarrow MnO_4^- + 8H^+(aq) + 5e^-$

Let us consider a reaction in which manganese is oxidized from the +2 state to +7 state. So, when the manganese atom is oxidized, it becomes more electronegative. In the +7 state, this atom is electronegative enough to react with water to form a covalent oxide MnO_4^-. So, it is useful to have a way of distinguishing between the charge on a transition metal ion and oxidation state of the transition metal.

By convention symbols such as Mn 2+ refer to ions that carry +2 charge. Of course, you are familiar with this kind of notation. And one can also use for +7 oxidation state, one can also write something like this Mn^{VII} or someone can also write like this. But, this is more appropriate to write like this rather than writing like this. So, when we completely expand then the metal, so for example when we expand, something like this, metal, then one should write in Roman italic like this.

It is not really appropriate to write like this. So, when we have to use this Arabic numeral, it is better to use symbol and write 7+.

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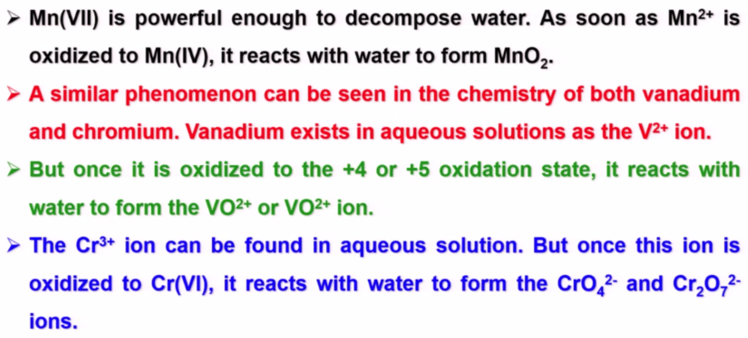

- Mn(VII) is powerful enough to decompose water. As soon as Mn^{2+} is oxidized to Mn(IV), it reacts with water to form MnO_2.
- A similar phenomenon can be seen in the chemistry of both vanadium and chromium. Vanadium exists in aqueous solutions as the V^{2+} ion.
- But once it is oxidized to the +4 or +5 oxidation state, it reacts with water to form the VO^{2+} or VO^{2+} ion.
- The Cr^{3+} ion can be found in aqueous solution. But once this ion is oxidized to Cr(VI), it reacts with water to form the CrO_4^{2-} and $Cr_2O_7^{2-}$ ions.

So, manganese +7 is powerful enough to decompose water. So that means if someone is looking for renewable energy and also to liberate hydrogen through oxidation of water, one should know what kind of metal complex one should use. Usually, they should use early transition metals in their highest possible oxidation state.

And as you can see clearly when the metal is oxidized to highest possible oxidation state, they become very strongly oxidizing in nature because of the increase in electronegativity. So, now in case of manganese(+7) (Mn^{VII}), the electronegativity can be compared to that of fluorine and hence you can see how effective it is in oxidizing most of the substances. A similar phenomenon can be seen in the chemistry of both vanadium and chromium.

Vanadium exists in aqueous solution as V^{II} ion, but once it is oxidized to +4 of +5 oxidation state, it reacts with water to form VO 2+ or VO 2+ ion. Similarly, chromium +3 ion can be found in aqueous solution, but once this ion is oxidized to chromium +6 as in case of potassium dichromate, it reacts with water to form $[CrO_4]^{2-}$ and $[Cr_2O_7]^{2-}$ ions. Let me stop here and continue discussing about reactivity of metal complexes in my next lecture. Until then have an excellent time learning chemistry.