Shellyza Moledina, February 2004

Introduction to...

Transition Elements:

- **Elements in the central part of the Periodic table**
- **Generally, Strong, lustrous, high mp, high bp, high ΔHvap, malleable, ductile and good conductors.**
- **There are ten of them (in the 4th period), periods 5 and 6 also contain transition series.**
- **The elements in the first transition series – (fourth period) show remarkable similarities in atomic radii, IE, mp, bp, and oxidation states...**

(Answer: From one transition element to the next, the nuclear charge increases by 1 unit, and the number of electrons also increases by 1. Since each additional electron enters the 3d shell, it helps to shield the 4s electrons from the increased nuclear charge, with the effect that the effective nuclear charge remains fairly constant across the series of transition elements. The atomic radii, the first ionization energies are therefore very similar, and the elements have comparable electropositivities.)

So WHY are they so similar?

- So at first, you think you have a pretty good pattern here: I mean, *1s*. Then *2s* and *2p*. Then *3s* and *3p* and.... well it should be *3d*. But it isn't.
- **When we look at the transition metal electron configurations... we state 4s before 3d**
- i.e: Sc: [Ar] $4s_2 3d_1$)
- ***WHY?***
- Answer: When we go down the periodic table, we have more overlap between energy levels. Does this seem kind of vague? Well so did another student, until this professor explained it further...
- (Please don't think I drew the characters . The following 'stuff' is copy-paste material)

Crossover Energy Levels

What's happening here, roughly, is this: you can think of the series of primary levels as being based on the electrons' attraction to the protons; each successive row moves another "step" away from the nucleus. But once you start getting a *lot* of electrons around, they begin repelling one another like crazy and messing up this nice pattern.

That sounds kind of vague to me. How does the repulsion of other electrons mess up the energy levels?

Well...the fundamental difference between the various sublevels is that higher sublevels have more angular momentum. If you don't know what that means, don't worry; all you need to understand is that more angular momentum tends to fling an electron farther out from the nucleus. When there are many other electrons around, a screening effect occurs.

So that's why the different sublevels have different energies.

Yes. Furthermore, when the number of electrons becomes large, this screening effect becomes so strong that it actually begins to overlap the next primary level. An added electron will then prefer to enter that next level rather then go to the orbital where it "should" be.

(if you didn't understand that, read it over again ... or just skip it ☺)

- How to remember that: USE THE PERIODIC TABLE!!!!!!!!!!

THE ELECTRON CONFIGURATION PERIODIC TABLE

$1s^1$																$1s^2$
$2s^1$	$2s^2$											2p	2p	2p	2p	2p	2p
3s	3s											3p	3p	3p	3p	3p	3p
4s	4s	3d	3d	3d	3d	3d	3d	3d	3d	3d	3d	4p	4p	4p	4p	4p	4p
5s	5s	4d	4d	4d	4d	4d	4d	4d	4d	4d	4d	5p	5p	5p	5p	5p	5p
6s	6s	5d	5d	5d	5d	5d	5d	5d	5d	5d	5d	6p	6p	6p	6p	6p	6P
7s	7s																

Go left to right. Always. So the first row you have 1s1 and 1s2. If you continue on to the fourth row, you have 4s and then 3d.

s before d. (that's the clincher)

The Copper/Chromium problem

- We’ve heard in class that Chromium and Copper are some sort of ‘exceptions’ to the rule. How? Why? Well, first lets state the electron configuration for each transition metal (shortcut way of course)

Sc: [Ar] $4s_2 3d_1$
Ti: [Ar] $4s_2 3d_2$
V: [Ar] $4s_2 3d_3$
Cr: [Ar] $4s_1 3d_5$
Mn: [Ar] $4s_2 3d_5$
Fe: [Ar] $4s_2 3d_6$
Co: [Ar] $4s_2 3d_7$
Ni: [Ar] $4s_2 3d_8$
Cu: [Ar] $4s_1 3d_{10}$
Zn: [Ar] $4s_2 3d_{10}$

- Look at Chromium and Copper carefully. They only have one 4s electron, where all the others have two.
- ***WHY?***
- Well, we all know (or should know by now) that:

➔ s has 1 orbital --> 2 electrons.
➔ p has 3 orbitals --> 6 electrons
➔ ***d has 5 orbitals --> 10 electrons.***

The clincher is 10 electrons. Think of d as a very ‘picky’ guy. It always wants to be stable, or in other words, have 10 electrons.

But it does get some degree of stability when it’s half full. (5 out of 10 electrons)

Now Chromium SHOULD have had **Cr: [Ar$3d_4$] $4s_2$**.

But the 3d was very ‘picky’ and wanted to have SOME degree of stability. Why not BORROW an electron from the ‘4s’ --> to get 5 out of 10 electrons?

So in the end, Chromium ends up being Cr: [Ar] $3d_5$ $4s_1$.

Copper does the same thing --> except it's not half stability this time, its FULL STABILITY.

Let me explain.
Copper should have had: **Cu: [Ar] $3d_{9}$ $4s_{2}$**.

But the 3d had nine out of ten electrons, and it wanted to be stable (10/10). So it borrowed an electron for the 4s to get

Cu: [Ar] $3d_{10}$ $4s_{1}$.

D- Block: an element which forms some compounds that possesses an incomplete inner shell of d-electrons.

Why Scandium and Zinc are not Typical Transition Metals:

Scandium: Since scandium only has one 'd' electron, we can pretty much assume that it forms $3d_{0}$ in a compound.

Zinc: Zinc compounds have a filled 3d shell --> $3d_{10}$

The typical properties of compounds of transition elements are associated with partly filled d orbitals, i.e. d-block are defined as elements which form some compounds in which there is an incomplete subshell of d-electrons ------- ONLY.

Formation of Ions

(very important – follow steps slowly)

1. When *electrons* are LOST in a neutral atom, there are more protons then electrons.
2. Therefore the atom becomes POSITIVE.
3. Since there is more positive charge in the nucleus, the electrons in the NEARBY shells get pulled closer to the nucleus. Let's say that this includes all the electrons in the first three energy levels: $1s_2$, $2s_2$, $2p_6$, $3s_2$, $3p_6$, and 3d
4. Notice that this includes the 3d but not the 4s . That's important.
5. So 3d gets pulled towards the nucleus, and 4s doesn't.
6. Let's try to lose electrons from a neutral transition metal now. We look at the transition metal's atomic structure, and see that 4s is more far away from the nucleus than 3d is. So we start pulling electrons from the 4s FIRST – and then from the 3d.

For transition elements: both the (n-1)d and the ns electrons are considered valence electrons.

Stability

How many times has a chemistry teacher said this word? Too many to count – but you have to understand, that the word 'stability' can mean many things. If we copy and paste from Mrs. Pall's notes...

Stability can be achieved with the loss of...

1. All 3d and 4s electrons giving a noble gas configuration.
2. The 4s electrons only, leaving the 3d untouched.
3. The 4s and some 3d electrons, leaving the 3d sub-shell half-filled.

That's pretty easy to understand once you think about it. For the first one, if you look at the **electron configuration periodic table on** page 3, you can see that if we take any transition metal, and take all the 3d and 4s electrons away, then we really end up with a noble gas.

The second one is a bit queer. If you take away the 4s electrons only (remember from before – the formation of ions section -- you can take the 4s away first), your remaining 3d has some degree of stability.

The third is something we've already talked about in Chromium, if you take away the 4s first, and then some 3d, leaving a HALF FILLED d (or 5 out of 10 electrons), you get some stability.

Oxidation States

(this is basic stuff, but you have to know it well to understand a major part of this unit)

"Oxidation numbers are denoted in chemical names by bracketed roman numerals placed immediately after the relevant element. For example, an iron ion, with an oxidation state of +3 is expressed as iron (III). Manganese with an oxidation state of +7 present in manganese oxide is given the name manganese (VII) oxide. The motive for placing oxidation numbers in names is only to distinguish between different compounds of the same elements. The actual charge (positive/negative) of the ion is not expressed because it is not necessary for this purpose." (Copied from: Wikepedia)

You know that... obviously – from last year if you were in a good science teacher's class... and from this year if otherwise. ☺

Well, when we look at the varying oxidation states of ionic compounds, its always useful to look at the anion.

So lets look at: Fluorine, Chlorine, Iodine and Bromine in their ionic states. (F^{-1}, Cl^{-1}, I^{-1} and Br^{-1})

Chlorine is easily polarized, so it can form high oxidation states. If you're not sure what that means, look at the quote in italix... it's part of the definition of oxidation states from *Wikepedia.*

Diagram Summary of common oxidation states (THIS IS COPY – PASTE FROM MRS. PALL'S SITE)

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
				7					
			6	6	6				
		5	5	5	5				
	4	4	4	4	4	4	4		
3	3	3	3	3	3	3	3	3	
	2	2	2	2	2	2	2	2	2
	1	1	1	1	1	1	1	1	

For the above table, the following pattern in oxidation states may be summarized

☆ 1) From Sc to Mn, the maximum oxidation state commonly occurs. This involves loss (or partial loss) of all 4s and 3d electrons giving a noble gas structure

☆ 2) From Mn to Zn, an oxidation state involving only the loss of 4s electrons commonly occurs. This suggests that the removal of the paired 3d electrons is less easy.

Note: The maximum oxidation state is two more than the number of unpaired 3d electrons, i.e. the maximum oxidation states only use 4s electrons and unpaired 3d electrons.

MAKE SURE YOU UNDERSTAND THE THINGS MARKED WITH THE **COOL YELLOW STAR.**

And if you don't understand it....

Well from Sc to Mn, the atoms usually get 'stable' by losing all their 4s and 3d electrons. When these atoms (from Sc to Mn) do this, we call it "MAXIMUM OXIDATION STATE"

The remaining transition metals, Mn to Zn, the atoms get 'stable' by LOSING THEIR 4s ONLY! (now you know why the 'stability' lesson was important ☺)

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Coloured Compounds

What's a ligand?

A ligand is any atom or compound is able to act as an electron pair donor, i.e. a Lewis Base.
That seems kinda vague, but we'll use it as our 'working' definition.

So why are elements coloured? Elements are coloured, because they absorb light. The light is then reflected, so a person can see it.

However, there's something WRONG with this explanation. Did you know that a green leaf appears green because it absorbs every single colour of light – *except for green*? And a blue copper sulphate solution appears blue, because it absorbs *red light*.

Each colour of light ***emitted*** coresponds to a certain wavelength. This wavelength, using $c=f\lambda$ and $E=hf$, can correspond to a specific ENERGY

But where is this energy coming from?

Well by now you should know that when electrons in a higher energy level jump to a lower energy level, some energy is released.

This energy, is the one we're talking about, this energy can correspond to a certain *wavelength*, which in turn, corresponds to a color of light *reflected*.

Well, each color of light ***absorbed*** also corresponds to a certain wavelegth. Using this wavelength, we can find the Energy *needed* when an electron goes from a LOWER energy level, to a HIGHER one.

The Crystal Field Theory

So far, we've been saying that in an isolated transition metal atom, the five d-orbitals are degenerate, that is, they are all at the same energy level.

We assume it, when we're looking at this diagram (that was included in our quantum number unit :)

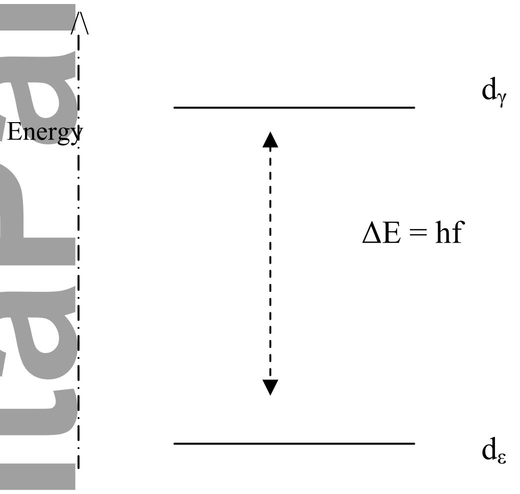
__ __ __ __ __3d ←
__ 4s

__ __ __3p
__ 3s

__ __ __ 2p
__2s

__ 1s

But, in a complex ion, the d-orbitals differ slightly in energy as a result of overlapping differently with the ligands, ligands raise some d-orbitals slightly and lower some d-orbitals slightly: now they are non-degenerate. Let's take her diagram now:



Electrons can jump from one d-orbital to another if they absorb energy.
The energy difference between two 'd' orbitals can be measured by using the formula $\Delta E = hf$, for most transition metal complexes, the frequency of light absorbed in these energy transitions is in the visible region of the spectrum, and thus the ion appears coloured.
If there's a large split between orbitals d_γ and d_ε, then there will be a large **energy difference** between the two d orbitals as well.

But what determines how much distance there are between d orbitals?

Or, you could say, what determines the energy difference between d orbitals?

It all depends on the 'ligand' that is interfering with it.

We said before, that a ligand is a compound or atom that 'interferes' with our transition metals.

So basically we have these weird compounds somehow making our transition metal's d-orbitals more or less further apart from each other.

Lets look at some examples of ligands:

(Copy-paste from Mrs Pall's website)

$\mathbf{CN^{-1} > NO_2{}^{-1} > NH_3 > H_2O > F^{-1} > OH^{-1} > Br^{-1}}$

Large orbital splitting	Small orbital splitting
Large ΔE	Small ΔE
Strong field ligands	Weak field ligands

Ligands such as Cyanide and Nitrate cause large d-orbital splitting in a transition metal.

Ligands such as Hydroxide and Bromide cause small d-orbital splitting in a transition metal

EXAMPLE THAT YOU SHOULD UNDERSTAND BY NOW

In the solid $CuSO_4$, the Copper ion is surrounded by $SO_4{}^{2-}$ ions. The d-orbital splitting is such that the absorption of light by the Cu2+ cation is not in the visible spectrum, and therefore the substance appears white.

However, in aqueous solutions, the Cu^{2+} ion is surrounded by the H_2O ligands --> $Cu(H2O)_6{}^{+2}$. These complex ions absorb light in the visible region and appear blue.

WHY DO THEY DIFFER?
In the first case, SO_4 acted like a strong ligand. It made Cu have a large d-orbital splitting, and therefore have a large energy difference. This large energy, corresponded to a large wavelength – that was not included in the electromagnetic spectrum.

In the second case, H2O acted like a weaker ligand. It made Cu have a small d-orbital splitting, and therefore a small energy difference. This small energy difference corresponded to a smaller wavelength than before. This wavelength was included in the electromagnetic spectrum.

The colour of the ion is complementary to the colours absorbed.

NOTE: COLOURLESS COMPOUNDS

Sc $^{+3}$ has no electrons in the 3d or 4s orbitals. It resembles a noble gas. So we obviously can't do any electron transitions within the 3d orbitals, and no energy is released. So the Sc $^{3+}$ ion is colourless.

Zn $^{+2}$ and Cu^{+1} have complete 3d subshells, with a d^{10} configuration, no d – d transition is possible since the 3d subshell is full, and these ions are thus colourless.

Complex Ions

Just when you thought you could forget about Lewis acids and bases....
Well we have to bring it up again

- All Ligands are Lewis BASES, electron pair DONORS
- All Transition Metals are Lewis ACIDS, electron pair acceptors

Let's take one of Mrs. Pall's examples. It's quite simple.

$$M^{+n} \quad + \quad :NH_3 \longrightarrow [M \leftarrow NH_3]^{+n}$$

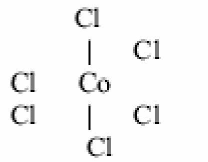
Lewis acid + Lewis Base Lewis acid- base complex formed by a co-ordinate covalent bond.

She's saying that a transition metal, bonds with a ligand (:NH3)

The ligand donates its electron pairs to the transition metal, (the acceptor which has empty orbitals to accommodate them) – forming a CO-ORDINATE COVALENT BOND BETWEEN THE TWO.

~*~*~*~*~*~*~*~*~*~*~*~*~*~*~*~

An example of a transition metal/ligand compound is CoCl6. Chlorine is the identified ligand, (the Lewis base), in this case.



The **Co-ordination Number** is the number of atoms forming coordinate bonds with the central atom or ion, i.e. it is the amount of ligands surrounding one central transition metal atom: 2, 4, and 6 are common. In this case, the number is 6. The coordination number of a metal ion in a particular complex depends on the metal ion's size, charge and electron configuration, and on the size and shape of the ligands. The shape of a metal complex depends on the metal ion's coordination number: 2 = linear, 4 = either tetrahedral or square planar, and 6 = octahedral.

Since all LIGANDS are LEWIS BASES

-- Ligands have to have at least *one lone pair* of electrons that can be used to form a *co-ordinate covalent bond to the metal ion.*

The number of co-ordinate covalent bonds formed with the central cation may be classified as:

# of co-ordinate covalent bonds	Type of Ligand	Example Ligand
1	Monodenate	H_2O, $:NH_3$, NO_2^{-1}, OH^{-1}
2	Bidentrate	$C_2O_4^{-2}$
3	Tridentate	(not given)
4	Polydentate	EDTA (ethylene-diamene-tetra-acetate: hexadentate)

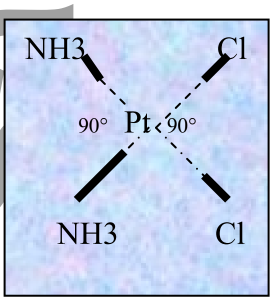
Ligands that can bond through electron pairs on more than one donor atom, are termed polydentate ligands.

In other words ...
Polydentate ligands are known as CHELEATING AGENTS. These are ligands that can form more than one bond to a metal ion.

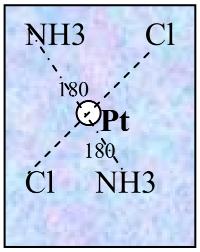
A polydentate ligand generally gives a more stable complex ion than a monodenate ligand, because the greater the number of bonds, the more difficult it will be to remove the ligand, and therefore, the more stable the complex ion.

Geometrical Isomerism

This results when the atoms bonded directly to the metal are sequenced in a different order.
i.e:



Used to treat brain tumors
"Cis"



Physiologically inactive
"Trans"

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Rules for Naming Co-ordination Complexes

1. As with any ionic compound, the cation is named before the anion

   i.e.: K3[Fe(CN)6] is potassium hexacyanoferrate (III)

2. In Complex Ions, the Ligands are named BEFORE THE CENTRAL METAL ATOM/ION

   i.e.: [Cu(H2O)6]+2 is hexaaquacopper (II) ion

3. For MIXED ligands, place the name of the ligand in alphabetical order; ignore the prefixes, di, tri…

   i.e: [Cr(H2O)4Cl2]Cl is tetraaquadichlorochromium (III) chloride

4. For the same KIND of ligands, use the prefix: di- (sometimes bi is used), tri-, tetra-. Etc.

   i.e: [CoCCL2(NH3)4]+1 is tetraamminedichlorocobalt(III) ion

5. When the central atom/ion is positive or neutral, then the name remains unaltered followed by a Roman numeral for the oxidation number.

   i.e: [Ag(NH3)2]+ is diamminesilver (I) ion,
   Pt(NH3)2Cl2 is diamminedichloroplatinum(II)

6. However, if the complex is an anion, the suffix "—ate" is added to the name of the central atom followed by Roman numeral for the oxidation state.

   i.e: zincate and chromate, e.g. [Fe(C2O4)3]-3 is trioxalatoferrate(III)ion

If the metal has a Latin name, then in the complex anion the Latin name of the metal is used, followed by the suffix –ate.

i.e: $[Fe(CN)_6]^{-4}$ is hexacyanoferrate(II)

Note that the metal is not separated from the ligand names by a space (the name of a complex ion is **one word**, with no space between the various ligand names and no space between the names of the last ligand and the metal.)

Square brackets are usually used between the formula of a complex ion and its charge.

Some names that you should remember:

Fe: iron : ferrate.	*Cu: copper: cuprate.*	*Sn: tin: stannate.*
Ag: silver: argentate	*Pb: Lead: plumbate*	*Au: Gold: aurate.*
Al : aluminate	*Cr: chromate*	*Pt: platinate*

7.

The FORMULA of the Ligand.	Root word (we say this when we're **not** addressing the compound as a ligand)	When we address the compound as a ligand, we add an 'o' to the end.
OH^{-1}	Hydroxide	Hydroxo
F^{-1}	Fluoride	Fluoro
CN^{-1}	Cyanide	Cyano
CO_3^{-2}	Carbonate	Carbonato
$C_2O_4^{-2}$	Oxalate	Oxalato
SO_4^{-2}	Sulphate	Sulphato
NO_2^{-1}	Nitrite	Nitro
NO_3^{-1}	Nitrate	Nitroato
SCN^{-1}	Thiocyanate	Thiocyanato
$S_2O_3^{-2}$	Thiosulphate	Thiosulphato

NOW SEE IF YOU CAN USE THESE RULES TO DO HER QUESTIONS ON PAGE 7 OF THE NOTES.

COMPETITION OF LIGANDS

Some ligands form stronger bonds than other ligands with a metal ion, in such a case, the better ligand will displace the poorer one, example:
Let's take a reaction that can go back and forth (is reversible)

$$[Cu(H_2O)_4]^{+2}_{(aq)} + 4Cl^{-1}_{(aq)} \rightleftharpoons [CuCl_4]^{-2}_{(aq)} + 4H_2O_{(l)} \quad K_c = 3.9 \times 10^5\ dm^{12}\ mol^{-4}$$

The equilibrium constant, Kc, also known as the "stability constant" determines if the left or the right side of the equation is most likely to occur. In this case, Kc demonstrates that the equilibrium is 'product dominated' – or in other words:
The Cl-1 molecule is a much better ligand than the H2O molecule.
(If the numerical value of the stability constant, Kc, is large, then the forward reaction is favoured, i.e the reaction is product favoured.)

……………………….

Another example?

$$[Cu(H_2O)_4]^{+2}_{(aq)} + 4NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4]^{+2}_{(aq)} + 4H_2O_{(l)} \quad K_c = 1.5 \times 10^{13}\ dm^{12}\ mol^{-4}$$

Again, Kc demonstrates that the equilibrium is 'product dominated'; the NH3 is a much better ligand than the H2O.

Catalyis involving Transition Elements.

- A catalyst speeds up a chemical reaction by providing an alternative route with lower activation energy.
- NOTE: A CATALYST TAKES PART IN THE SEQUENCE OF REACTIONS, HOWEVER IT IS NOT A ‘REACTANT’ OR ‘PRODUCT’
- Transition metals have high catalytic activity --> how and why?
  - In homogenous ionic solution, there is a variety of oxidation states for each element, therefore a transition metal can take part in a sequence and emerge unchanged in the end.
  - In heterogeneous state: 3d electrons enable transition metal catalyst to form temporary bonds with reactant molecules.

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Haber Process: Manufacture of Ammonia.
REACTANTS: N_2, $3H_2$
PRODUCT: $2NH_3$
CATALYST: Fe, or Fe_2O_3

Contact Process: Manufacture of Sulfuric Acid
REACTANTS: SO_2, O_2
PRODUCT: $2SO_3$
CATALYST: V_2O_5

Manufacture of Anti-freeze
REACTANTS: $2C_2H_4$, O_2
PRODUCT: $2C_2H_4O_2$
CATALYST: Ag
(for more examples, refer to Mrs. Pall’s notes)

Paramagnetism

Paramagnetism

PARAMAGNETIC: A substance which is weakly attracted by a magnetic field.
DIAMAGNETIC: A substance which is weakly repelled by a magnetic field.

Transition elements and their ions are generally paramagnetic – because of the unpaired electrons found in their partially filled d-orbitals; because there is a magnetic moment associated with the spinning electron. The greater the number of unpaired electrons, the more paramagnetic is the ion.
(A substance in which all the electrons are paired is diamagnetic).

FERROMAGNETIC: iron, cobalt, nickel, they are strongly attracted to a magnetic field.)

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Similar Physical & Chemical Properties

There are similar physical and chemical properties between transition metals.

THE GENERAL TRENDS

(a): There is a general decrease in metallic and ionic radii from Ti to Cu.

(b) There is a general, though irregular, increase in first ionization energy from Ti to Cu.

(c) There is a general small increase in electronegativity from Ti to Cu.

Make sure you study all chemical and physical properties provided in Notes, this is just a short summary of them.