

Chem 103 Lecture 10a and 10 b Summer 2009

Admin: reminder Final Exam is Monday 8-1030am

Review Session Wednesday at 10-11am PS 607

Last time:

- 1) rate of nuclear decay (1st order)
- 2) half life calculations
- 3) radioactive dating: ¹⁴C etc.

today:

- 1) origin of elements (21-1)
- 2) transition elements & coordination cmpds (chapt. 22-1, 22-6)
- 3) Crystal field theory (22-7)

Important

(0) Know (i.e. read up on):

nuclear radiation
effects and units:

units of absorption dose:

gray (Gy) = si unit for 1 J/kg

rad = radiation absorbed dose = .01 Gy

Roentgen = 93.3×10^{-7} J/g tissue

REM = roentgen equivalent mammal

Bkground radiation: average = 360 mrem /yr

(1) Origin of elements: where did the elements come from?

Cosmologists who study of the universe postulate the Big Bang 15 billion years ago.

Extremely high temperatures

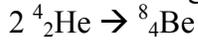
-cooled down to allow H and He to form
Massive nebula (cloud) form rich in H and He
These condense due to its own gravity
They form many protostars (heating up as they
for coalesce). At 15 million°C, fusion starts
and these protostars become stars

glowing and releasing energy by fusion:
Note that fusion releases heat (as long as element
is less massive than Fe

hydrogen burning:



helium burning:



Etc...

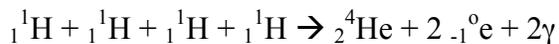
Until it reaches Fe, star starts to cool down
If it is a supergiant, it will start to collapse very
quickly (1 minute), supernova

s(slow) process can form heavier elements by slow
capture of n.

r(rapid) capture of n.

After Fe, fusion

1) H to Fe: hydrogen burning:



after billions of years:

Helium burning:



then ${}^8_8\text{O}$ then ${}^{10}_{10}\text{Ne}$ then ${}^{12}_{12}\text{Mg}$

C and O burning gives Si

Elements up to Fe-56 (and Ni-58) form by fusion.

Higher elements form during supernova:

By 2 process:

S process "slow" bombardment by n

n capture places element above belt of stability: leads to beta emission, increase in atomic #

very rapid process "r" process leads to radioactive elements: in a matter of seconds during a supernova: nucleus may capture many neutrons and become very heavy elements...high z due to series of beta decays

Transition elements

d-block elements contain d-orbitals partially or just fully filled.

When they ionize, ns electrons lost before (n-1)d electrons

Naming complex ions

Ligands

(2) Transition elements

d-block elements contain d-orbitals partially or just fully filled.

When they ionize, ns electrons lost before (n-1)d electrons

(1a) Coordination bonding

What is coordination covalent bond?

A covalent bond whose pair of electrons is donated by only one atom.

2 theories used to explain coordination complexes

a) **crystal field theory** can best explain:

magnetic properties (spin)

stability of coordination compds

b) **valence bond theory**

insight on geometry

Write down the e config of transition elements:

say: 30Zn :

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} \dots = 30$

(Zn a 2B element = has properties similar to 2A like Mg which has $3s^2$)

Elements between: 21-29 are first row transition elements (they are in 4th row of periodic table. We'll limit ourselves to this first row transition elements.)

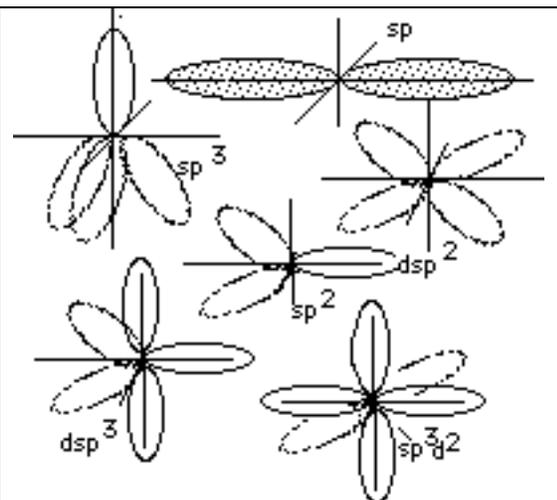
Say 29Cu: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$
(note that $3d^{10}$ is filled first before $4s^1$)

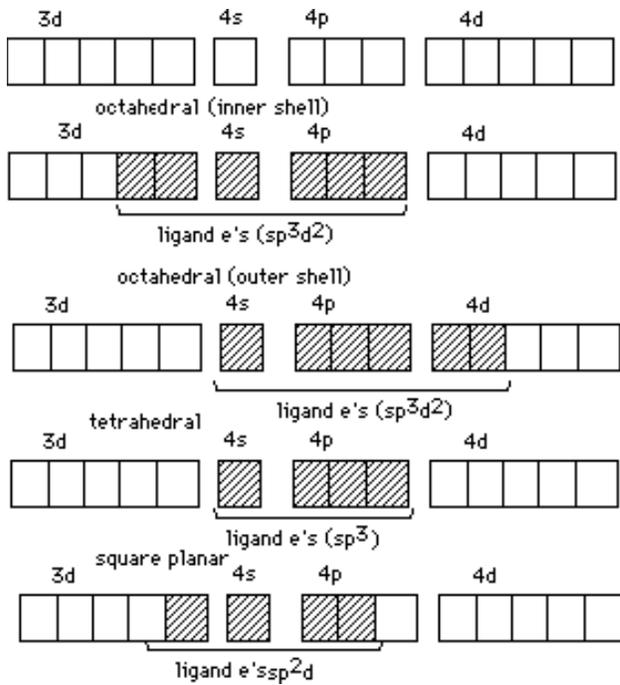
Cu is group 1B

21Sc: [Ar] $4s^2 3d^1$ 22Ti: [Ar] $4s^2 3d^2$
 23V: [Ar] $4s^2 3d^3$ 24Cr: [Ar] $4s^1 3d^5$
 25Mn: [Ar] $4s^2 3d^5$ 26Fe: [Ar] $4s^2 3d^6$
 27Co: [Ar] $4s^2 3d^7$ 28Ni: [Ar] $4s^2 3d^8$
 29Cu: [Ar] $4s^1 3d^{10}$

(2) Valence Bond Theory (VBT) and Crystal(Ligand) Field Theory (CFT) as applied to the octahedral complex. Let us summarize these two theories:

VBT: Involves hybrid orbitals: Review hybrid orbitals(Chapt 9 (p316) if you are not comfortable with these hybridzn orbitals.



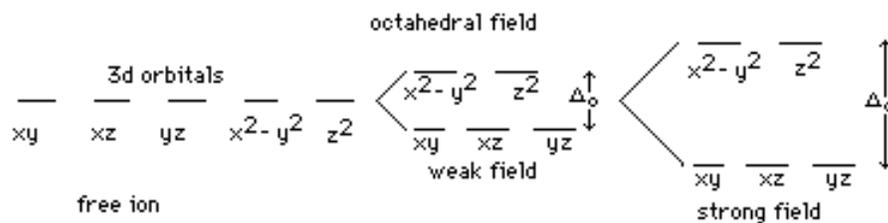


2) Crystal field theory

Crystal field theory treats ligands' interaction as primarily electrostatic in nature. Ligand's electrons exert an electric field (*crystal field*) that affects energy levels of d-orbitals differently.

In crystal field theory, focus is on the **energy levels**:

Again: the energy separations, Δ_o , is affected by crystal's electric field. $\Delta =$ **crystal field splitting energy**



and, tetrah are weak field while sq plan are strong field (none otherwise known contradictory to this generalization).

Transition metals tend to have close-packed structs, with coord # = 12 (recall hcp crystals)

Result: these are very dense; have strong metallic bonds, high melting pts & boiling p, & relatively higher heats of fusion and vaporizn than those of groups 1A & 2A (as well as 2B).

Typical oxidation numbers are:

Sc +3, Ti +4, V+5, Cr+3,+6,

Mn 2+,4+,5+, Fe 2+,3+,

Co 2+,3+, Ni 2+, Cu +1,+2

Read up on properties of the above transition metals: - its ores, its unique props, its usefulness (for your own enrichment)

spectrochemical series: lists weak vs strong field ligands:

halides (F⁻, Cl⁻), C₂O₄²⁻ < H₂O < NH₃ = en < phen < CN

Color depends on perception of complementary color:

400 violet, 500 blue, 550 green, 600 yellow, 700 red.

Recall the color wheel.

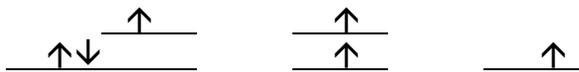
Absorption depends on d to d transitions which depends on splitting energy, Δ

Consider octahedral complexes:

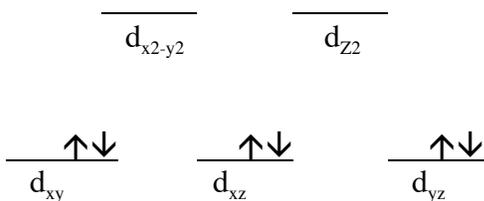
Consider ${}_{26}\text{Fe}^{2+}$ in weak field and strong field:

(Another: ${}_{27}\text{Co}^{3+}$) [Ar]3d⁶:4s²

so if weak: spin=4 (*high spin*)



and if strong: spin=0 (*low spin*)

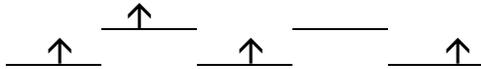
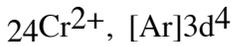


So weak field gives higher spin and so on.

Another example: potassium hexachlorochromate(II):

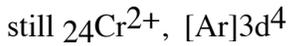
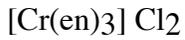


Remember halides => weak ligand; weak field,

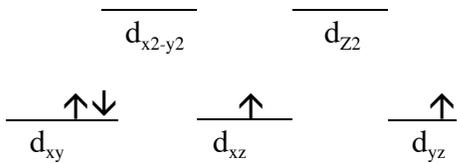


and spin=4.

compare with potassium tris(ethylenediammine)chromate(II):



Remember en => strong ligand; strong field,

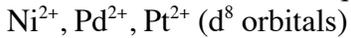


spin=2. (less spin than weak field)

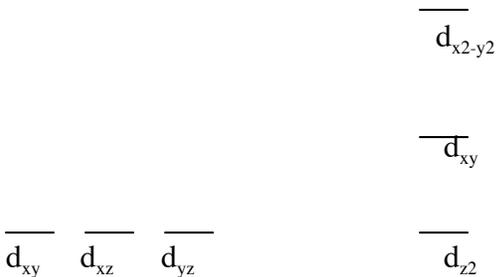
color is different.

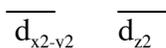
Now, consider square planar complexes:

Metals that tend to have square planar:

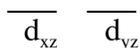


But Ni can have both sq pl & tetrah(F-)





Tetrahedral



Square Planar

This is optional

Hardness or softness of a Lewis acid or base:

Phenomenon is that specific metals tend to form salts with specific anions:

metal

Ca, Mg

Cu, Pb, Hg

Na, K

Al, Ti and Fe

anion

carbonate

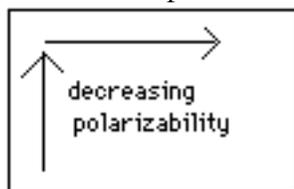
sulfide

Chloride

Oxide

Underlying principle: how tightly bound the metal electrons are:

tightly bound = low polarizability



As effective z increases, the lower the polarizability.

Hard = low polarizability; Soft = high polarizability

Hard acid: acceptor of e^- pair is of low polarizability. eg. most metal ions and atoms. (the smaller the ionic radius and the higher the oxidation state, the harder the Lewis acid).

Hard base: e^- pairs are of low polarizability ; due to high electronegativity of the atom to which the lone pair is assigned.

Soft base: opposite of above. Say the e^- pair is far from the nucleus: eg iodide., then it is polarizable and hence soft. (eg

Soft acids: like Au and Pt. Not affected by oxygen.

HSAB principle

HSAB stands for 'hard and soft acids and bases. HSAB is widely used for explaining stability of compounds and reaction mechanisms and pathways. The theory is used in contexts where a qualitative, rather than quantitative

description would help in understanding the predominant factors which drive chemical properties and reactions. This is especially so in transition metal chemistry where numerous experiments have been done to determine the relative ordering of ligands and transition metal ions in terms of their hardness and softness.

Remember: Hard Lewis acids tend to combine with hard Lewis bases & Soft Lewis acids tend to combine with soft Lewis bases. e.g. (e.g. hard acids = lithophiles : combine with oxides;or halides,carbonates)
soft acids = siderophiles
chalcophiles = found in nature as sulfides