LECTURE 1
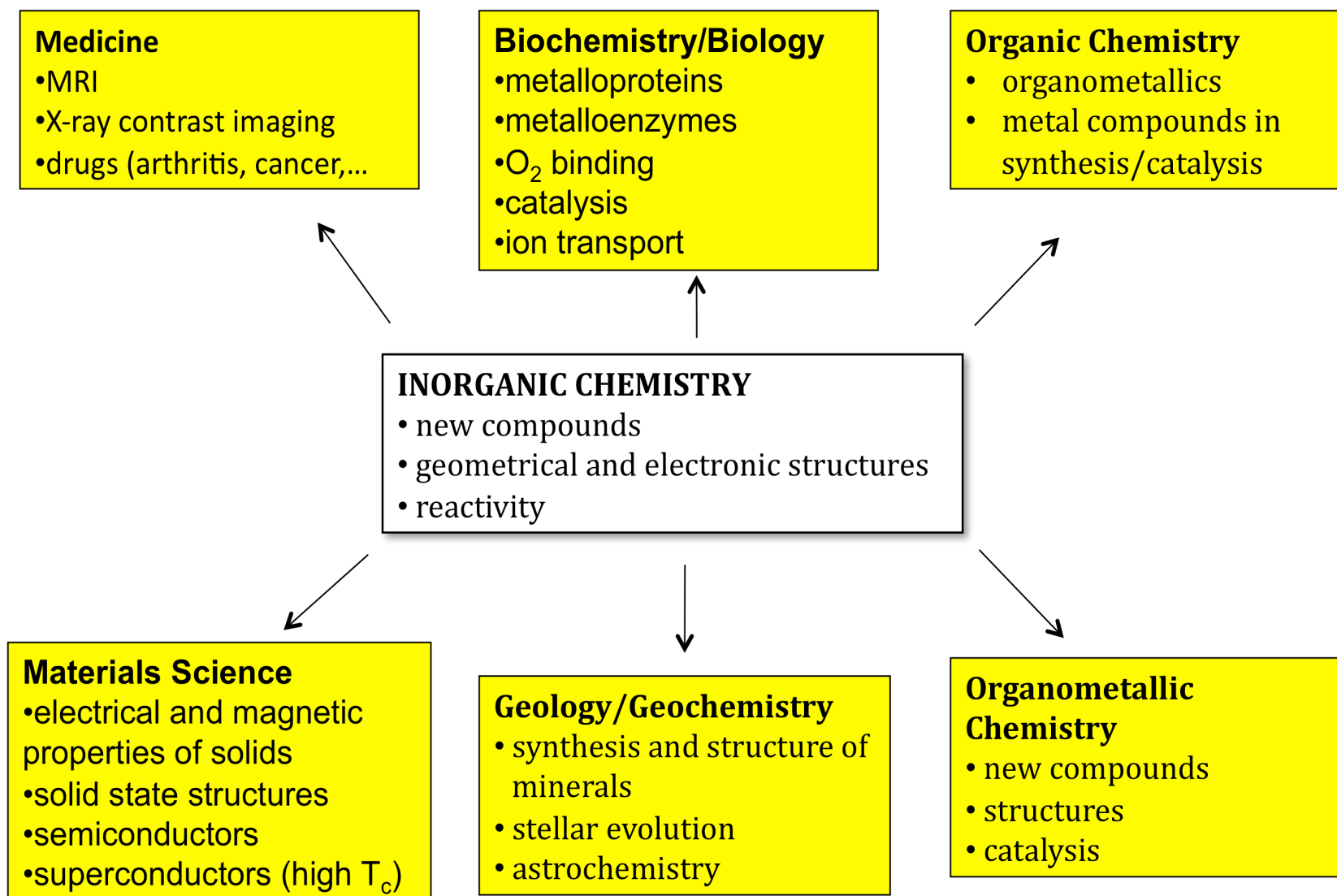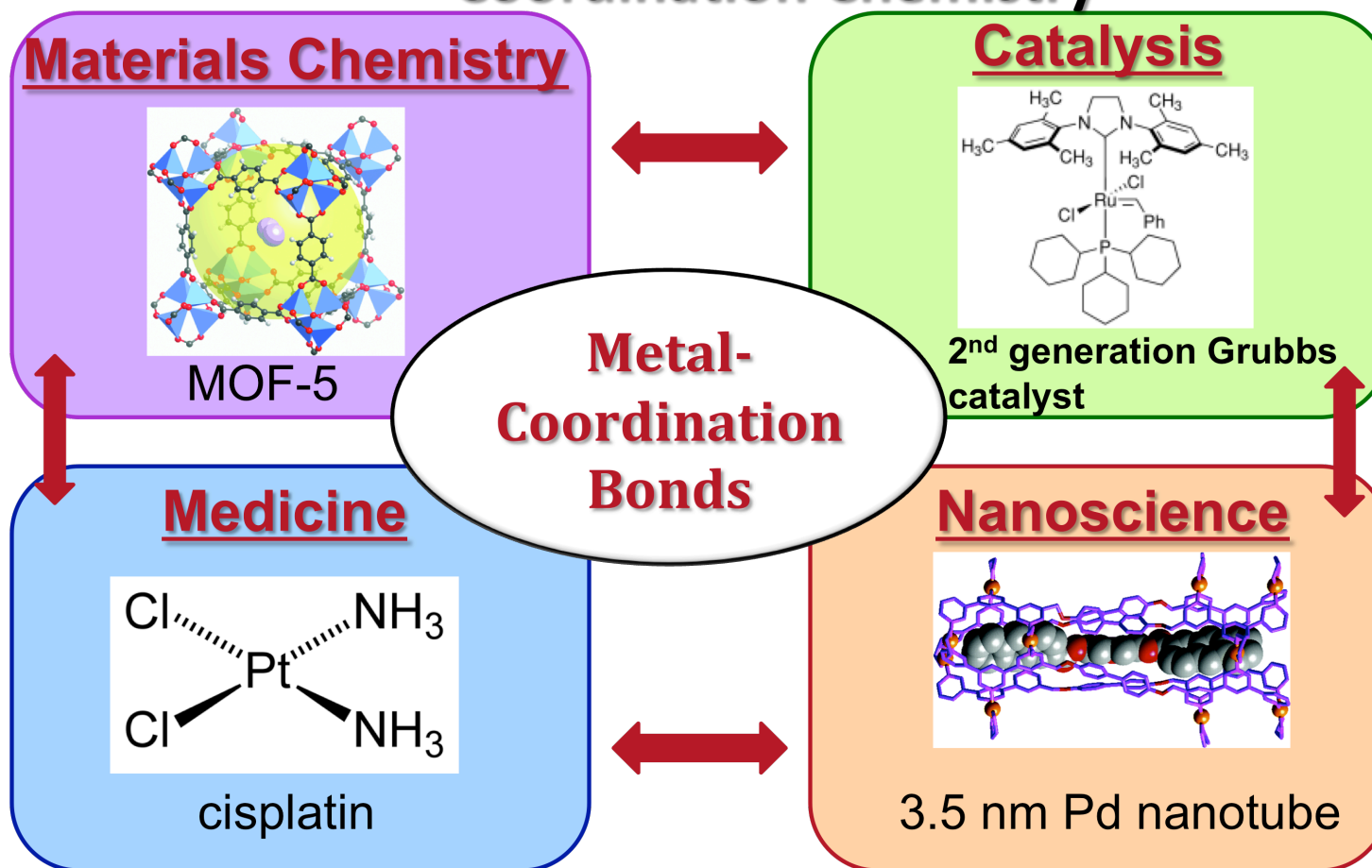# Goals of the Course

1. To be familiar with the periodic table and how it is organized according to the relationships among the elements.

2. To have a firm grasp of fundamental physical principles regarding energy (thermodynamics) and reaction rates (kinetics) such that you can use this knowledge to make predictions.

3. To accumulate a database of descriptive chemistry of the inorganic elements (facts are important!)

4. Ultimately, to achieve a basic understanding, through the knowledge of facts, of the periodicity of structure, bonding and reactivity patterns.
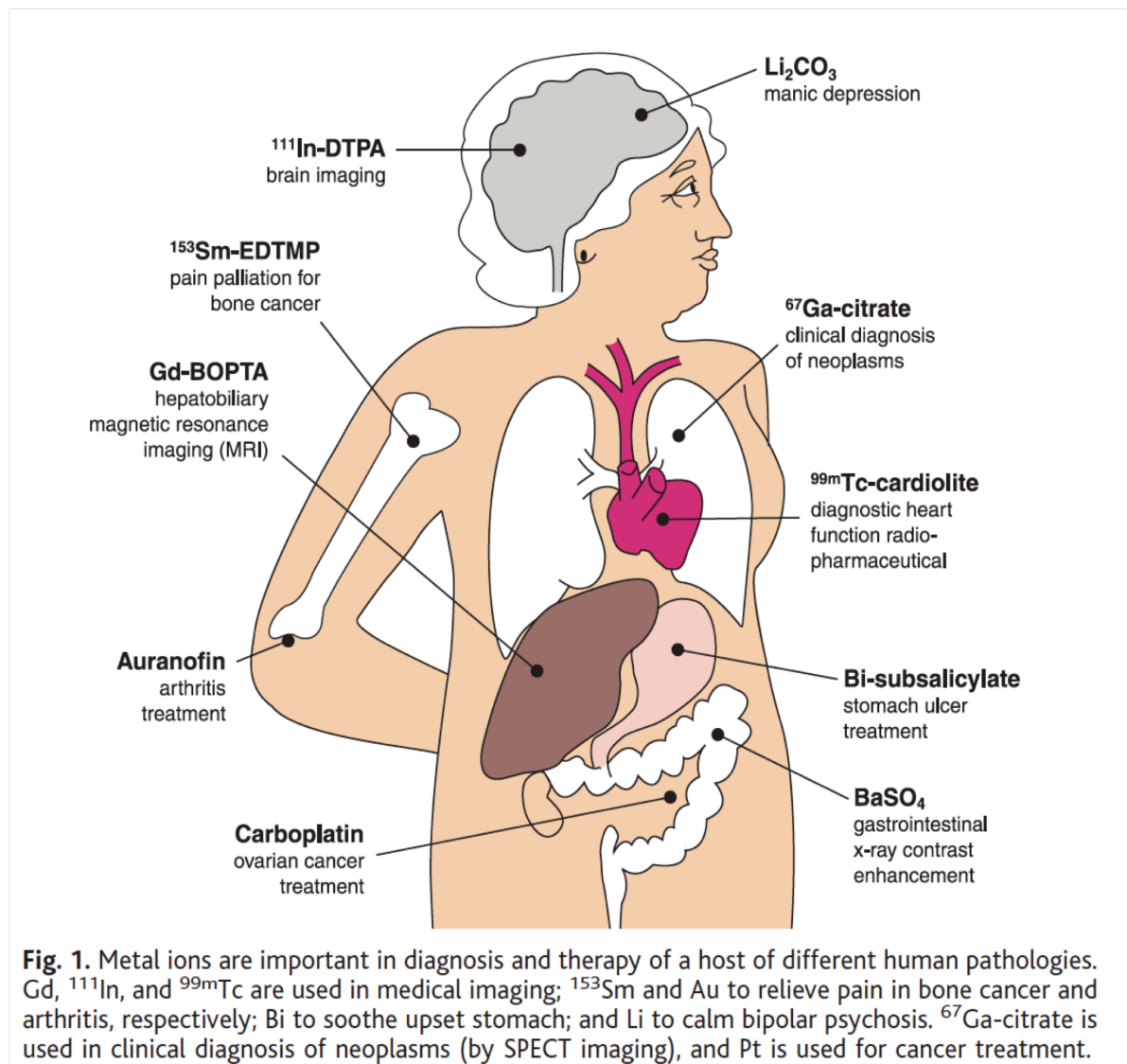
The Scope of Inorganic Chemistry

Medicine
•MRI
•X-ray contrast imaging
•drugs (arthritis, cancer,…

Biochemistry/Biology
•metalloproteins
•metalloenzymes
•O_2 binding
•catalysis
•ion transport

Organic Chemistry
• organometallics
• metal compounds in synthesis/catalysis

INORGANIC CHEMISTRY
• new compounds
• geometrical and electronic structures
• reactivity

Materials Science
•electrical and magnetic properties of solids
•solid state structures
•semiconductors
•superconductors (high T_c)

Geology/Geochemistry
• synthesis and structure of minerals
• stellar evolution
• astrochemistry

Organometallic Chemistry
• new compounds
• structures
• catalysis

Modern Inorganic Chemistry Revolves around Coordination Chemistry

Materials Chemistry

MOF-5

Catalysis

2nd generation Grubbs catalyst

Metal-Coordination Bonds

Medicine

cisplatin

Nanoscience

3.5 nm Pd nanotube

Omar M. Yaghi et al. *Acc. Chem. Res.* **2001,** *34,* 319 . M. Scholl, S. Ding. C. W. Lee, R. H. Grubbs, *Org. Lett.* 1999, **1**, 953.
T. Yamaguchi, S. Tashiro, M. Tominaga, M. Kawano, T. Ozeki, M. Fujita *J. Am. Chem. Soc.*, **2004**, *126,* 10818.

An Excellent Example of the Importance of Inorganic Compounds is Their Use as Drugs

Metals in Medicine

Fig. 1. Metal ions are important in diagnosis and therapy of a host of different human pathologies. Gd, ^{111}In, and ^{99m}Tc are used in medical imaging; ^{153}Sm and Au to relieve pain in bone cancer and arthritis, respectively; Bi to soothe upset stomach; and Li to calm bipolar psychosis. ^{67}Ga-citrate is used in clinical diagnosis of neoplasms (by SPECT imaging), and Pt is used for cancer treatment.

Orvig, Science 300, May 9, 2003

PERIODIC TABLE GROUPED INTO CLASSES
ACCORDING TO ELEMENT VALENCE ORBITALS s, d, p, and f

Group	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period																			
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	*	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

*Lanthanoids	*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
**Actinoids	*	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No
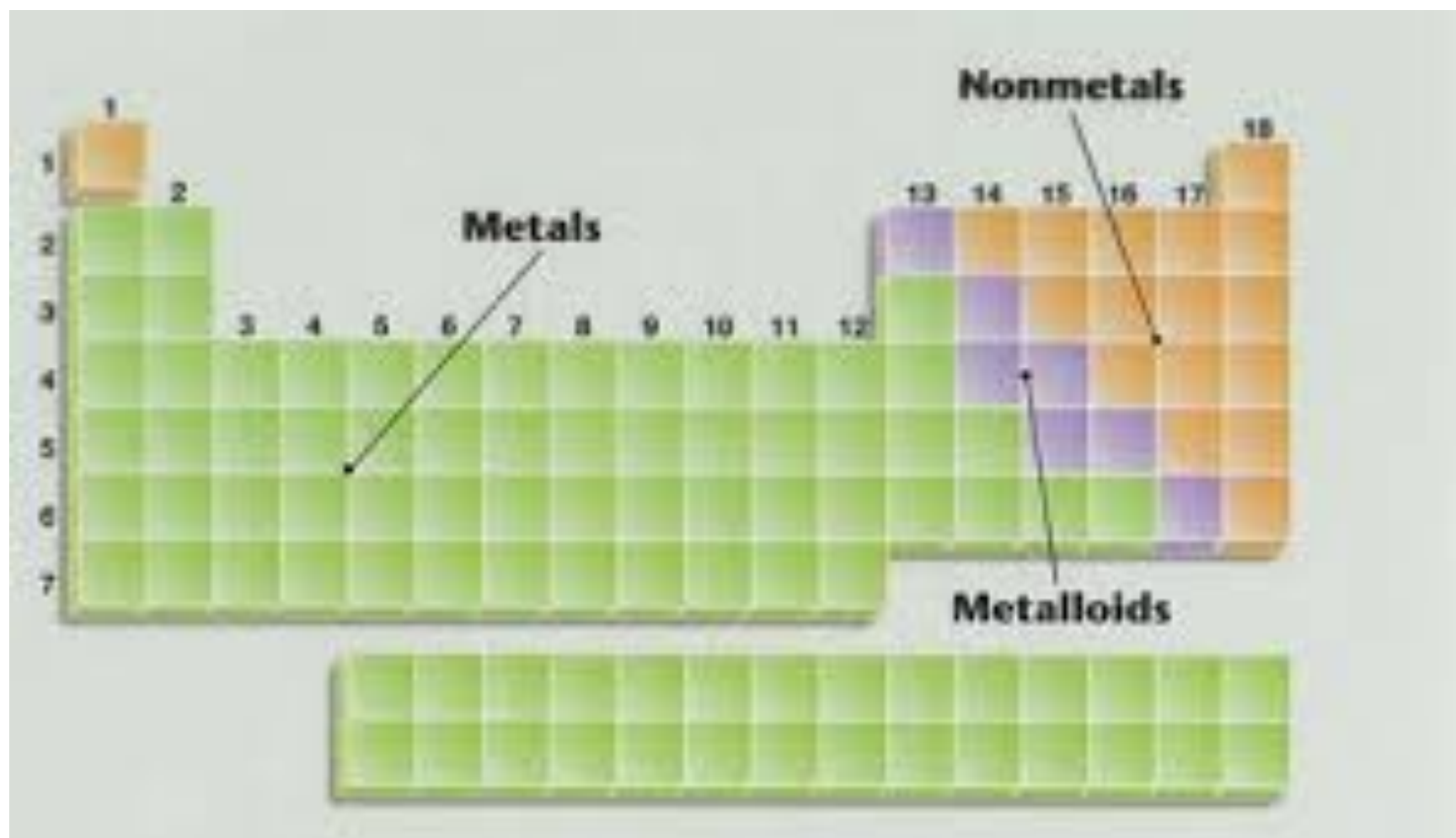
BASIS FOR COMPARISON	METALS	NON-METALS	METALLOIDS
Meaning	The metals which exhibit the highest degree of metallic behaviour is known as metals.	Non-metals are such elements which do not possess any metallic behaviour.	Metalloids are such elements, which possess some of the properties like metal, while some like non-metal.
Place in the periodic table	Metals are placed on the left side of the periodic table.	Non-metals are placed on the right side of the periodic table.	Metalloids are placed in the middle of the periodic table.
Location in blocks	Located in s, p, d, and f blocks.	Non-metals is located in s and p blocks.	Metalloids are located in p block.
Appearance	Metals have a shiny appearance.	Non-metals have a dull appearance.	Metalloids have a shiny and dull appearance.
Conductivity	Thermal and electrical conductivity is high in metals.	It is very low in non-metals.	Thermal and electrical conductivity is good though it is less than metals.
Electronegativity	Metals have low electronegativity.	Non-Metals have high electronegativity.	Metalloids neither possess a too high or too low value of electronegativity.
Ductility and malleability	Metals show ductility and malleability.	Non-metals do not show ductility and malleability.	Metalloids also do not show this property.

The Elements According to Relative Abundance

A Periodic Chart by Prof. Wm. F. Sheehan, University of Santa Clara, CA 95053

Ref. Chemistry, Vol. 49, No. 3, p 17–18, 1976

Colors suggest relative electro-negativity
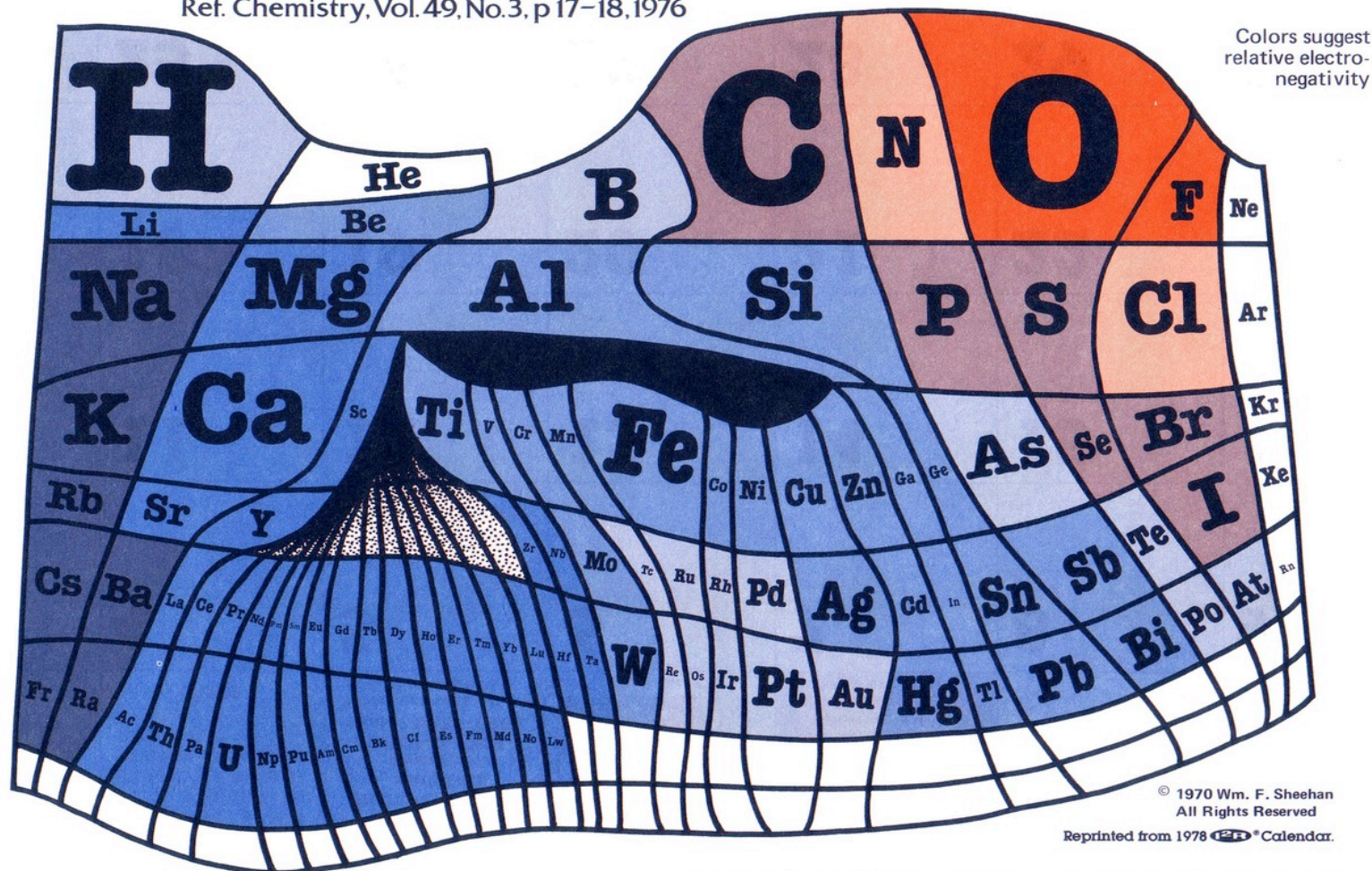
Roughly, the size of an element's own niche ("I almost wrote square") is proportioned to its abundance on Earth's surface, and in addition, certain chemical similarities (e.g., Be and Al, or B and Si) are suggested by the positioning of neighbors. The chart emphasizes that in real life a chemist will probably meet O, Si, Al, . . . and that he better do something about it. Periodic tables based upon elemental abundance would, of course, vary from planet to planet. . . **W.F.S.**

NOTE: TO ACCOMMODATE ALL ELEMENTS SOME DISTORTIONS WERE NECESSARY, FOR EXAMPLE SOME ELEMENTS DO NOT OCCUR NATURALLY.

RELATIVE ELECTRONEGATIVITIES

electronegativity: the power of an atom when in a molecule to attract electrons to itself. Elect
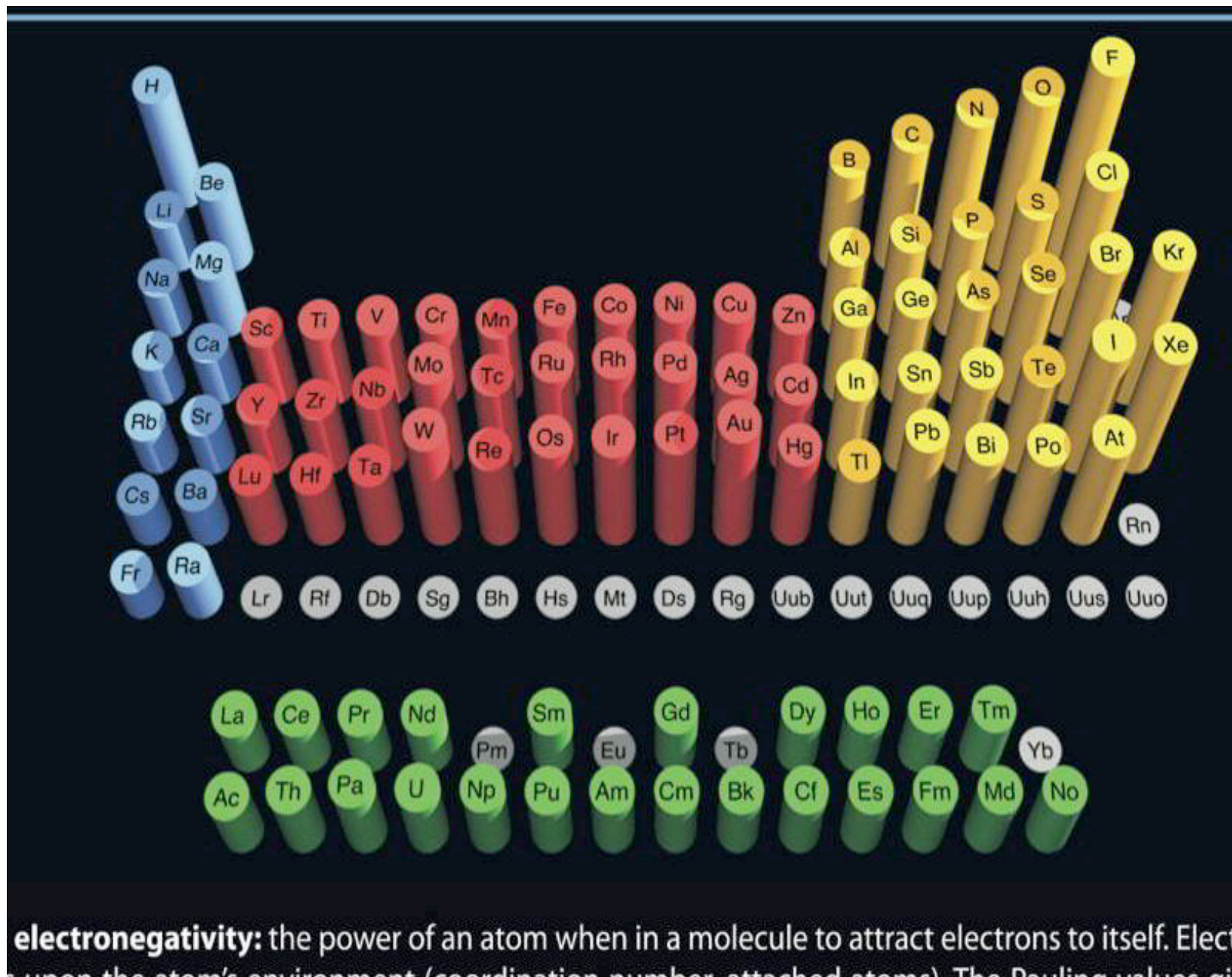
Another interesting way to look at the organization of the Periodic Table
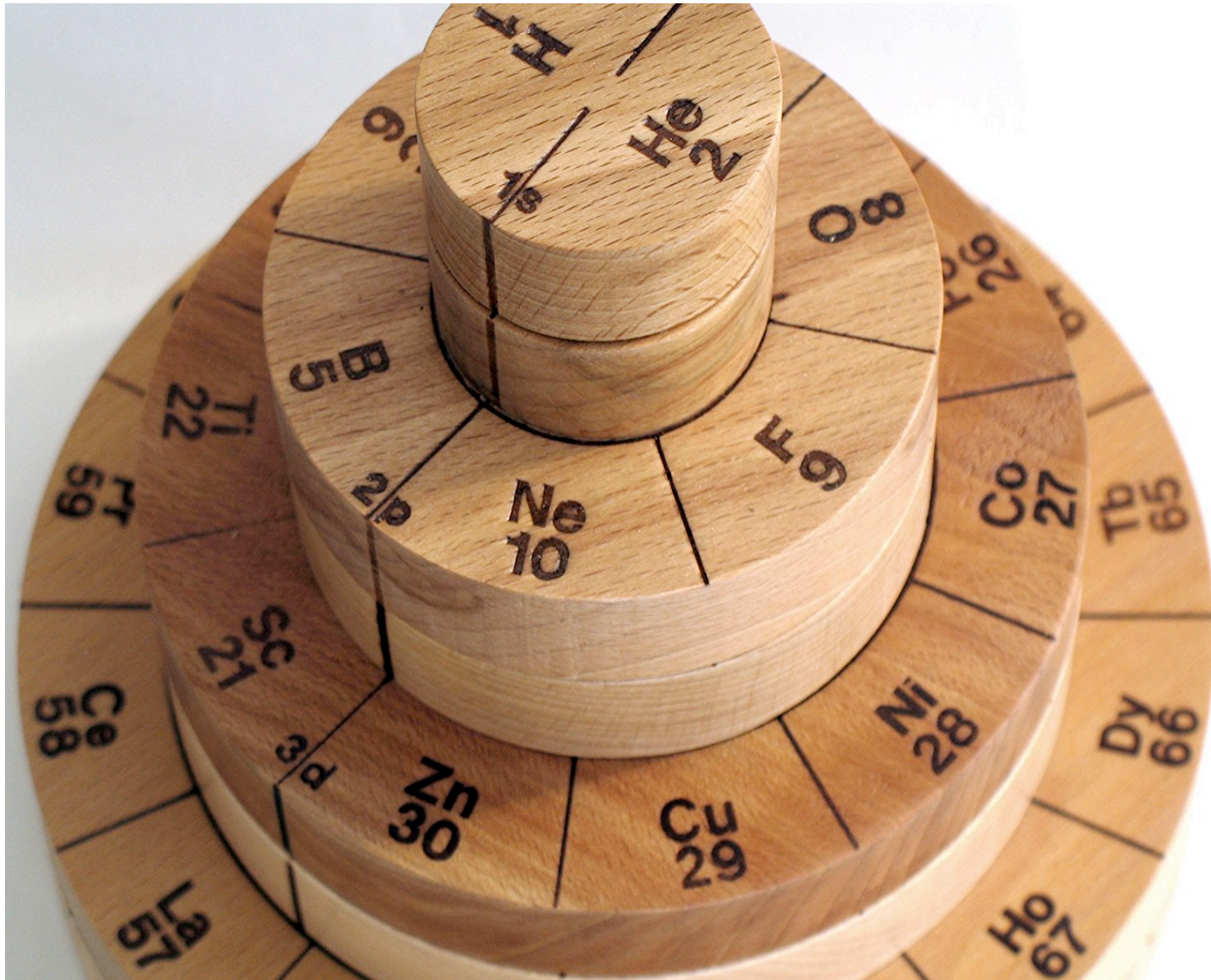
Week 1

Review of Basic Concepts

- **Periodic Table**

- **Thermodynamics & Kinetics**

- **Electronic Structure**

WHAT IS INORGANIC CHEMISTRY?

Inorganic Chemistry is the chemistry of the elements other than that of C combined with H, O, N, S, halogens, and the physical properties that these elements and their compounds exhibit.

Inorganic Chemistry covers a vast area of aqueous as well as non-aqueous chemistry. Types of inorganic compounds range from ionic solids to gases and molecular compounds.

Inorganic Chemistry is the chemistry of life as much as it is the chemistry of metallurgy.

To Name but a few Important Applications:

Main group elements (s, p block) are important in semiconductor technology (*e.g.*, Ga, As).

Transition elements (d block) are found in trace quantities as the active center of enzymes that catalyze all the reactions in our body, and, indeed, are the catalysts that allow us to produce vast quantities of fine chemicals and polymers from petroleum (Rh is one of the most common and is in our catalytic converters in our exhaust systems in our cars).

Rare earth elements (f block – lanthanides and actinides), many of which are radioactive, are important in magnetic materials.

Classes of Inorganic Substances

In the broadest sense, the materials that we shall discuss can be grouped into four classifications: elements, ionic compounds, molecular compounds, and polymers or network solids. The following brief list is presented to show the complicated variety of substances that are encountered in a discussion of inorganic chemistry. Greater detail is presented in the appropriate chapters to follow.

1. **The elements.** The elements have an impressive variety of structures and properties. Thus they can be

   (a) Either atomic (Ar, Kr) or molecular (H_2, O_2) gases.

   (b) Molecular solids (P_4, S_8, C_{60}).

   (c) Extended molecules or network solids (diamond, graphite).

   (d) Solid (W, Co) or liquid (Hg, Ga) metals.

2. **Ionic Compounds.** These compounds are always solids at the standard temperature and pressure. They include
(a) Simple ionic compounds, such as NaCl, which are soluble in water or other polar solvents.

(b) Ionic oxides that are insoluble in water (e.g., ZrO_2) and mixed oxides such as spinet ($MgAl_2O_4$), the various silicates [e.g., $CaMg(Sio_3)_2$], etc.,

(c) Other binary halides, carbides, sulfides, and similar materials. A few examples are AgCl, SiC, GaAs, and BN, some of which should be better considered to be network solids.

(d) Compounds containing polyatomic (so-called complex) ions, such as $[SiF_6]^{2-}$, $[Co(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{4-}$, and $[Ni(H_2O)_6]^{2+}$.

3. **Molecular compounds**. These compounds may be solids, liquids, or gases, and include for example:

(a) Simple, binary compounds, such as PF_3, SO_2, OsO_4, and UF_6.

(b) Complex metal-containing compounds, such as $PtCl_2(PMe_3)_2$ and $RuH(CO_2Me)(PPh_3)_3$.

(c) Organometallic compounds that characteristically have metal-to-carbon bonds. Some examples are $Ni(CO)_4$, $Zr(CH_2C_6H_5)_4$, and $U(C_8H_8)_2$.

4. **Network solids or polymers**. Examples of these substances (discussed in Chapter 32), include the numerous and varied inorganic polymers and superconductors. One example of the latter has the formula $YBa_2Cu_3O_7$.

Classes of Inorganic Structures

Organic compounds are mostly of tetrahedral geometry.
Why?

Carbon requires 4 electrons to complete its valence and a
tetrahedron is the best way to arrange four groups around a
central atom (w/o lone pairs) with s and p orbitals.

Inorganic chemistry is much more complicated.

tetrahedron
cube
octahedron
dodecahedron
Icosahedron

} **These form the basis for
many inorganic
structures**

There are five Platonic solids:
- The tetrahedron, with 4 triangular faces:
- The cube, with 6 square faces:
- The octahedron, with 8 triangular faces:
- The dodecahedron, with 12 pentagonal faces.]
- The icosahedron, with 20 triangular faces:

Less Regular Polyhedra:

Trigonal bipyramid   Trigonal Prism

Phosphorus Pentachloride

Trigonal
Bipyramid

Molecular Geometry
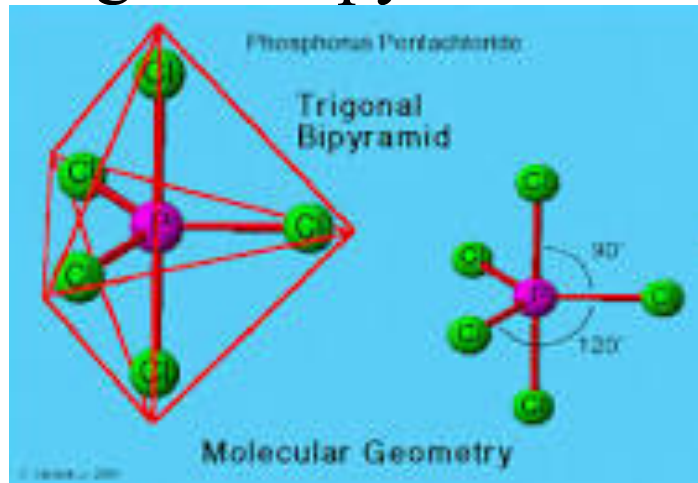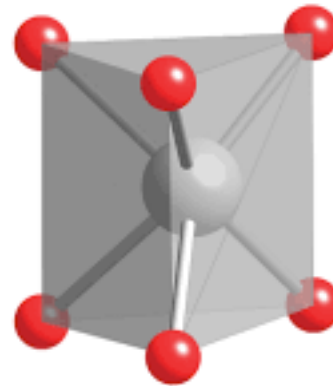
Square prism a **square prism** is a three-dimensional shape with two **square** bases and flat sides. Therefore, all **square** prisms consist of at least two squares, even if not all the sides are squares, as long as the bases are **square**, there is a **square prism**
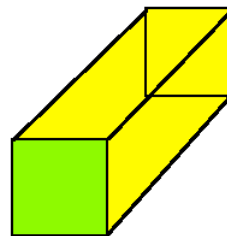
Planar Structures:

Chains

Square planes

Triangles

Are also known for inorganic molecules and materials.
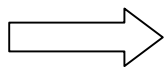
$\Longrightarrow$ **Quite diverse!**

Classes of Inorganic Reactions
## Cotton book cites 12 different ones:

1. **Acid – Base.** According to the definition of Bronsted-Lowry, the neutralization of a proton donor by a proton acceptor. According to the definition of Lewis, the formation of an adduct between an electron-pair donor and an electron-pair acceptor. A lesser known definition is that of Lux-Flood, namely the reaction of an oxide ion acceptor with an oxide.

   The general formula for acid–base reactions according to the **Brønsted–Lowry** definition is:
   $$HA + B \rightarrow BH^+ + A^-$$
   where HA represents the acid, B represents the base, BH^+ represents the conjugate acid of B, and A^- represents the conjugate base of HA.
   For example, a Brønsted-Lowry model for the dissociation of hydrochloric acid (HCl) in aqueous solution would be
 $$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$
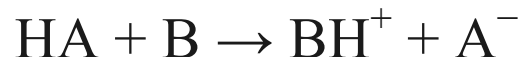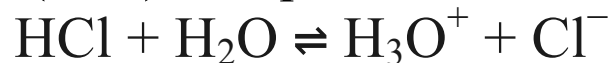
For the **Lewis** definition, a *Lewis base* that can donate an *electron pair* reacts with a *Lewis acid* that can accept this electron pair.

Boron trifluoride, BF_3 is a typical Lewis acid.

$$BF_3 + F^- \rightarrow BF_4^- \text{ is a typical Lewis acid - base reaction}$$

2. **Addition.** A reaction in which a group, molecule, or ion combines with another. Common examples are additions across a multiple bond and addition to an atom that is able to undergo coordination sphere expansion (an increase in occupancy). This reaction is the converse of elimination.

An example of an oxidative addition reaction is the oxidation of Pt(II) with chlorine:

$$[Pt^{II}Cl_4]^{2-} + Cl_2 \rightarrow [Pt^{IV}Cl_6]^{2-}$$
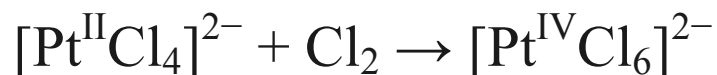
3. **Elimination.** A reaction in which a group, molecule, or ion is separated from another. Examples are dehydrohalogenations, and eliminations from metal centers that are able to undergo coordination number reduction (a decrease in occupancy). This is the reverse of an addition reaction. $[PtCl_6]^{2-} \rightarrow [PtCl_4]^{2-} + Cl_2$

4. **Redox** (a reaction in which an atom, ion or molecule gains (reduction) or loses (oxidation) an electron or electrons. A good example is the reaction between hydrogen and fluorine in which hydrogen is being oxidized and fluorine is being reduced:

$$H_2 + F_2 \rightarrow 2\ HF$$
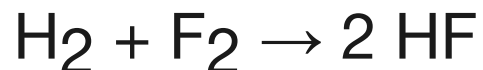
5. **Insertion**. The interposition of a new molecule, group, or ion between atoms in a structure such that the added molecule, group, or ion separates the two parts of the structure that were formerly bound together.
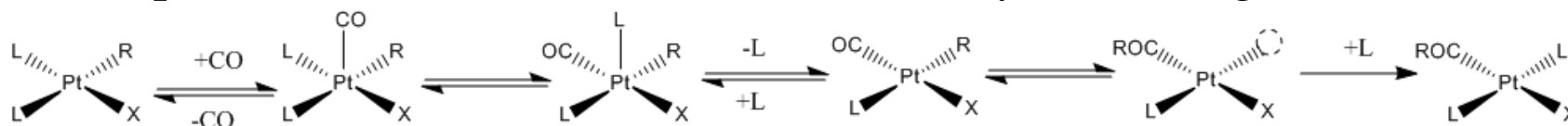
6. **Substitution (Displacement).** The exchange of one atom, molecule or ion for another in a compound.

$$[Pt^{II}Cl_4]^{2-} + 2NH_3 \rightarrow Pt^{II}Cl_2(NH_3)_2 + 2\ Cl^-$$
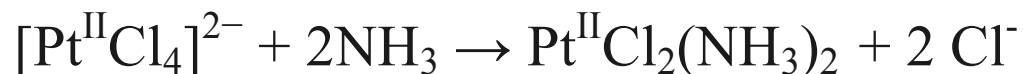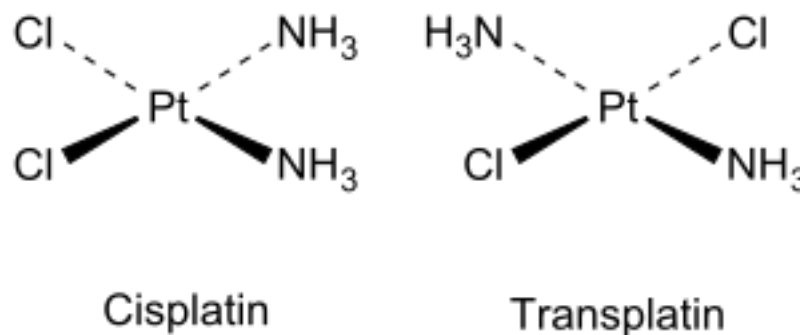
Ligand Substitution Reactions at Inorganic Centers[†]

David T. Richens*

School of Chemistry, University of St. Andrews, North Haugh, St. Andrews, Scotland, KY16 9ST United Kingdom

THIS IS AN EXCELLENT REVIEW ARTICLE

7. **Rearrangement (Isomerization).** A conversion of one isomer into another (cis-trans for example).


Cisplatin   Transplatin

8. **Metathesis (Exchange).** An exchange of comparable groups, such that two compounds form two new ones:

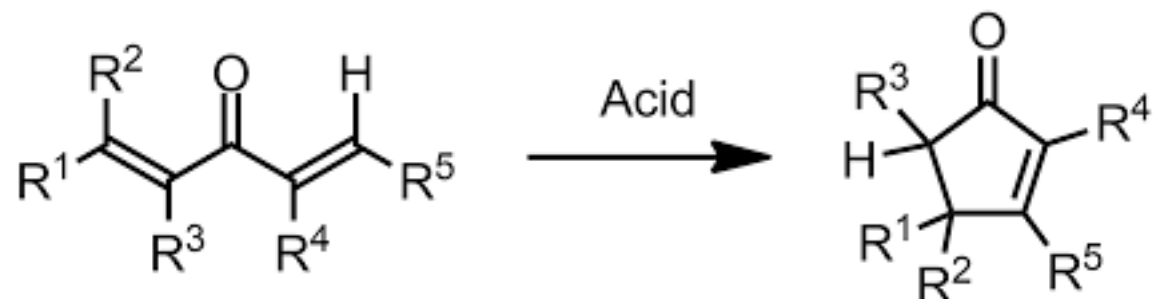$$AX + BY \rightarrow AY + BX$$

9. **Solvolysis.** A reaction with solvent; when the solvent is water it is called hydrolysis.

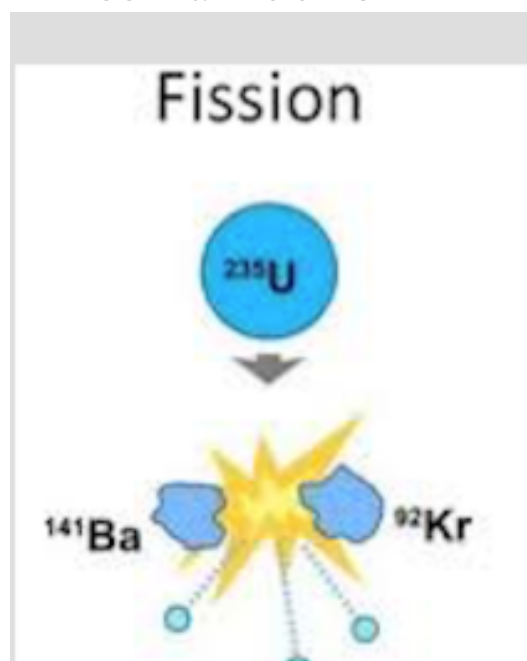$$[Co(NH_3)_5Cl]^{2+} + H_2O \longrightarrow [Co(NH_3)_5H_2O]^{3+} + Cl^-$$
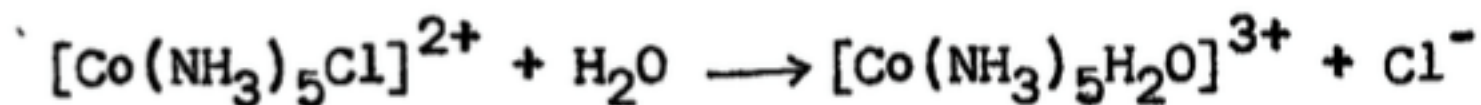
10. **Chelation.** A reaction in which a group (typically called a ligand) is able to bond to a central metal ion simultaneously through more than one donor atom.
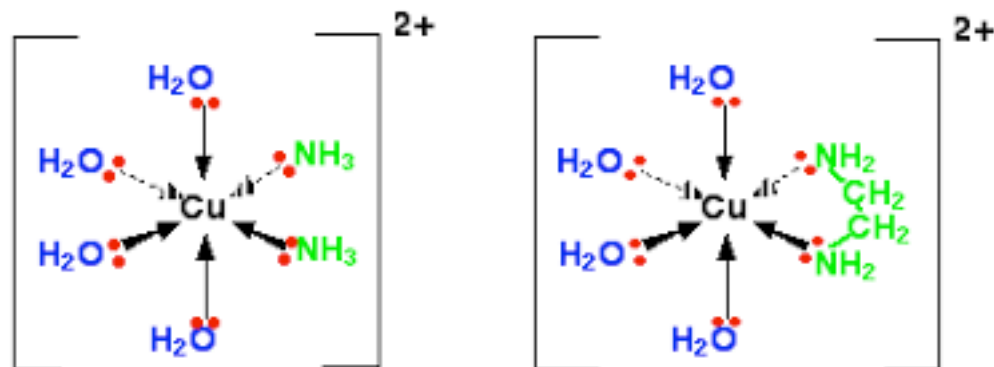
11. **Cyclization.** A reaction that leads to the formation of a ring.

12. **Nuclear reaction**. A reaction that changes the atomic number or mass number of an atom.

Lecture 2

Review of Basic Concepts

Thermochemistry

Enthalpy – H   heat content

 H Changes with all physical and chemical changes

$\Delta H°$ Standard enthalpy (25°C, 1 atm)

(H=O for all elements in their standard forms – by definition)

Exothermic   vs   Endothermic
$\Delta H < O$ $\Delta H > O$
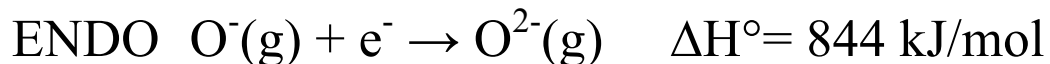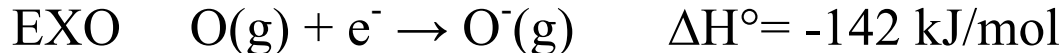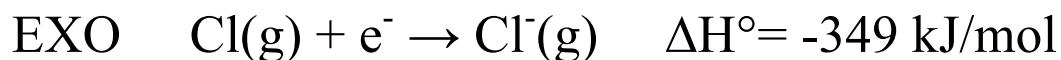Heat is released   Heat is absorbed

Because ΔH = (H products – H reactants)

Many special Enthalpy changes:

- fusion (melting) (s → l)
- vaporization (l → g)
- sublimation (s → g)
- ionization (loss of an e⁻ or electrons)
- electron affinities (capture of an e⁻ or electrons)

ΔH: look at signs and rationalize

e.g.,

EXO $Cl(g) + e^- \rightarrow Cl^-(g)$ $\Delta H° = -349$ kJ/mol

EXO $O(g) + e^- \rightarrow O^-(g)$ $\Delta H° = -142$ kJ/mol

ENDO $O^-(g) + e^- \rightarrow O^{2-}(g)$ $\Delta H° = 844$ kJ/mol

Bond Energies:

Simple case

$$HF(g) \rightleftharpoons H(g) + F(g)$$

$\Delta H = 566$ kJ/mol   ENDOTHERMIC

_____

The enthalpy of this process is the "H-F" Bond energy – the energy released when the H-F bond is formed.

Not so simple case…

$$H_2\text{-}N\text{-}N\text{-}H_2 \rightleftharpoons 2N(g) + 4H(g)$$

$\Delta H = 1724$ kJ/mol
         ↑
NOTE: This is not the bond energy for any of the bonds – It is a total enthalpy change.

Need to <u>Estimate</u>

If we know that:

$$NH_3(g) \rightleftharpoons N(g) + 3H(g)$$

$$\Delta H = 1172 \text{ kJ/mol}$$

Then $E_{N-H} = \dfrac{1172}{3} = 391 \text{ kJ/mol}$

<u>If</u> we assume this number is valid to use for Hydrazine, the formula of which is H_2NNH_2 or N_2H_4

<u>Then</u>

$$E_{N-N} + 4E_{N-H} = 1724 \text{ kJ/mol}$$
$$E_{N-N} = 1724 - 4(391)$$
$$= 160 \text{ kJ/mol}$$

… we have to live with these estimates

Thermochemical data can be tabulated by this method:

Table 1-1 Some Average Thermochemical Bond Energies at 25 °C (in kJ mol⁻¹)

A. Single bond energies

	H	C	Si	Ge	N	P	As	O	S	Se	F	Cl	Br	I
H	436	416	323	289	391	322	247	467	347	276	566	431	366	299
C		356	301	255	285	264	201	336	272	243	485	327	285	213
Si			226	—	335	—	—	368	226	—	582	391	310	234
Ge				188	256	—	—	—	—	—	—	342	276	213
N					160	−200	—	201	—	—	272	193	—	—
P						209	—	~340	—	—	490	319	264	184
As							180	331	—	—	464	317	243	180
O								146	—	—	190	205	—	201
S									226	—	326	255	213	—
Se										172	285	243	—	—
F											158	255	238	—
Cl												242	217	209
Br													193	180
I														151

B. Multiple bond energies

C=C 598	C=N 616	C=O 695	N=N 418
C≡C 813	C≡N 866	C≡O 1073	N≡N 946

Use these values to calculate the energy
that it would take to form a molecule.

Entropy and Free Energy

Two factors in chemical reactions:

1. Enthalpy, H, (kJ/mol)
   Energy (heat) dissipated

2. Entropy, S, ($kJ/Tmol$)
   State of organization
   "order versus disorder"
   which is a statistical probability

   When ΔH is more negative (exothermic)
   and ΔS is more positive (more disordered)
   a reaction is more favored.

   ΔG Free energy which is in kJ/mol
   Involves the relationship between ΔH, ΔS
   $\Delta G = \Delta H - T\Delta S$ (T in degrees K)

<u>Example:</u>

CH_2Cl_2 <u>Heat of formation of Dicholoromethane</u>

    C-H   H= 416 kJ/mol

    C-Cl   H= 327 kJ/mol

$$2 \times 416 + 2 \times 327 = H_{formation} (CH_2Cl_2)$$
$$= 1308 \text{ kJ/mol}$$

<u>Using ΔG° as a Predictive Tool</u>

$$\Delta G° = \sum \Delta G_f° \text{ (products)} \quad - \quad \Delta G_f° \text{ (reactants)}$$

Of course

$$\Delta G° = \Delta H° - (298.15) \Delta S°$$
$$\uparrow$$

(standard temperature)   T= 25°C or 298.15 K

The entropy change for a reaction is the difference between the absolute entropies of reactants and products.

$$\Delta S° = \sum S° \text{ (products)} - S° \text{ (reactants)}$$

Q When is S = 0?

A At absolute zero for a perfectly crystalline solid

Now, what is the relationship between ΔG and the Equilibrium Constant K?

…recall $K = \dfrac{[C]^c [D]^d}{[A]^a [B]^b}$ $aA + bB \rightleftharpoons cC + dD$

$\Delta G = -RT \ln Keq$

at 25°C (298.15 K) we have standard conditions: $\Delta G° = -RT \ln Keq$

rearrange:
$$\ln Keq = - \Delta G°/RT$$
convert
$$Keq = e(-\Delta G°/RT)$$
Gas Constant $R = 8.314$ J/K•mol
Temperature $T = 298.15$ K)

<u>Question</u> for $\Delta G° = 0$ what is K?
<u>Answer</u> 1 because e^0 is 1

Note: The more negative $\Delta G°$ is, the more the reaction proceeds as written *i.e.* K is large.   Conversely, the more positive $\Delta G°$ is, the more the reaction will tend to the **left** ← rather then to the **right**→ as written.

Question How does a reaction become overall thermodynamically favored?

Answer 3 Ways.

First consider $\Delta G° = \Delta H° - T\Delta S°$

1. When $\Delta H°$ and $\Delta S°$ both favor the reaction that is, $\Delta H°< O, \Delta S°>O$

2. When $\Delta H°$ favors the reaction, but $\Delta S°$ does not
   that is, $\Delta H°<O, \Delta S°<O$
   but $\Delta H°$ is still more negative than $T\Delta S°$ is positive

3. When $\Delta H°$ disfavors the reaction, but $\Delta S°$ favors it $\Delta H°>O, \Delta S°>O$ but $T\Delta S°$ is larger

Examples of all three types of situations:

1.formation of CO; SO_2 common case
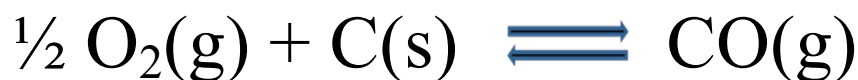
$\frac{1}{2} O_2(g) + C(s) \rightleftharpoons CO(g)$
$\Delta G° = -137.2$ kJ/mol
$\Delta H° = -110.5$ kJ/mol
$T\Delta S° = 26.7$ kJ/mol   In both cases:

Enthalpy favors rxn

$S(s) + O_2(g) \rightleftharpoons SO_2(g)$ *Entropy favors rxn*
$\Delta G° = -300.4$ kJ/mol
$\Delta H° = -292.9$ kJ/mol
$T\Delta S° = 7.5$ kJ/mol

2.synthesis of ammonia (NH_3) common case
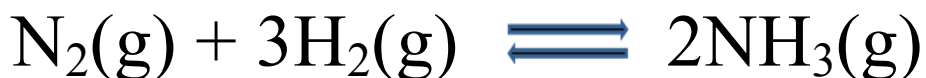
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
$\Delta G° = -16.7$ kJ/mol
$\Delta H° = -46.2$ kJ/mol   *Enthalpy favors rxn*
$T\Delta S° = - 29.5$ kJ/mol   *Entropy disfavors rxn*

3. rare type

$$NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq)$$

$\Delta G° = -2.7$

$\Delta H° = +1.9$ (endothermic) *Enthalpy disfavors rxn*

$T\Delta S° = +4.6$ *Entropy favors rxn*

(less ordered in the dissolved form)

Q Does $\Delta G°$ value (sign) tell you whether a reaction will occur or not?

A NO. It tells you what is thermodynamically possible to attain at 25°C but does not tell you whether it will happen to an appreciable extent at 25°C simply upon mixing reactants.

Q What else needs to be considered?

A Kinetics or the rate of the reaction.

Activation energies for reactants to go to products can be very high, and the reaction will require a catalyst to occur.   e.g. $NH_3(g)$ synthesis
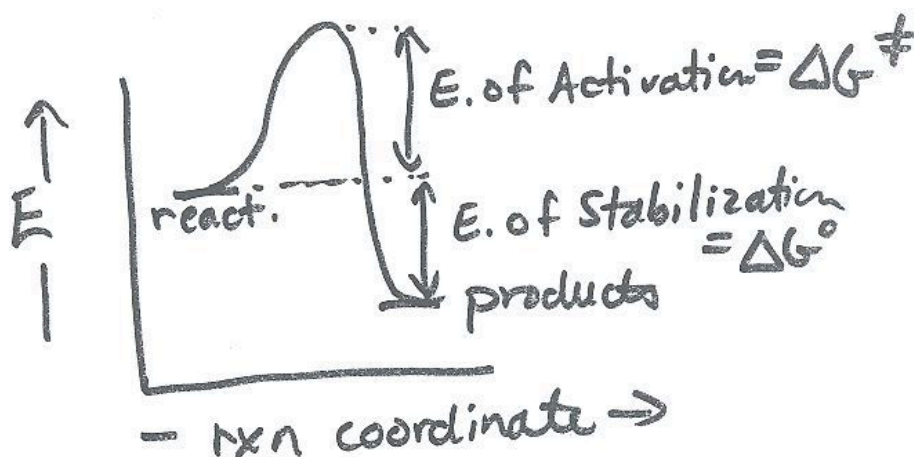
To occur, a reaction needs a negative $\Delta G°$ **and** for the rate to be appreciable.

The study of **Kinetics** is the way we know the mechanism of a reaction → how it occurs.

Reaction conditions affect rate
  • Temperature, concentration, solvent, pressure, presence of a catalyst

One can write a rate law for any reaction

$$4HBr(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Br_2(g)$$

rate constant, k
↓

$$\frac{d[O_2]}{dt} = -k\,[HBr]\,[O_2]$$

rate of disappearance of O_2 is related to the product of the concentration of the two reactants.

Q Did I make a mistake here?

Why isn't the [HBr] concentration reflecting the molar ratio of the reaction?

$$4\ HBr(g) + 1\ O_2(g)\ ?$$
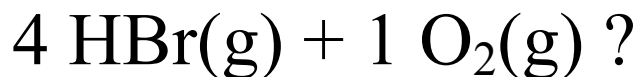
A No mistake. The rate law that best describes the speed of the reaction is the one based on a rate-limiting step. Obviously, in this reaction the rate limiting step is the reaction of one mole of O_2 with one mole of HBr.

$1 + 1 = 2$

2nd order reaction (sum of exponents on conc.)

Q What is a first order reaction?

A One in which the rate law depends on the concentration of only one reactant.
(easy to envision in decomposition reactions)

$2N_2O_5(g) \rightleftharpoons 4\ NO_2(g) + O_2\ (g)$

$$\frac{d[N_2O_5]}{dt} = -k[N_2O_5]$$

Effect of temperature on Rates
Dependence of the rate constant, k, on Temp.,
T, in degrees Kelvin follows the Arrhenius Law

$$K = A\, e^{-Ea/RT}$$

E_a is the activation energy
A is called the "frequency factor"

- The higher the activation energy, the slower the reaction

- A plot of log K versus T allows for E_a to be determined

Q <u>Reaction Profile</u>   What is it?
<u>A</u> It is a graph of free energy, G, versus the pathway of the reaction.
(The pathway is the change in bond distances during the conversion from reactants to products)

ex. Decomposition of formic acid
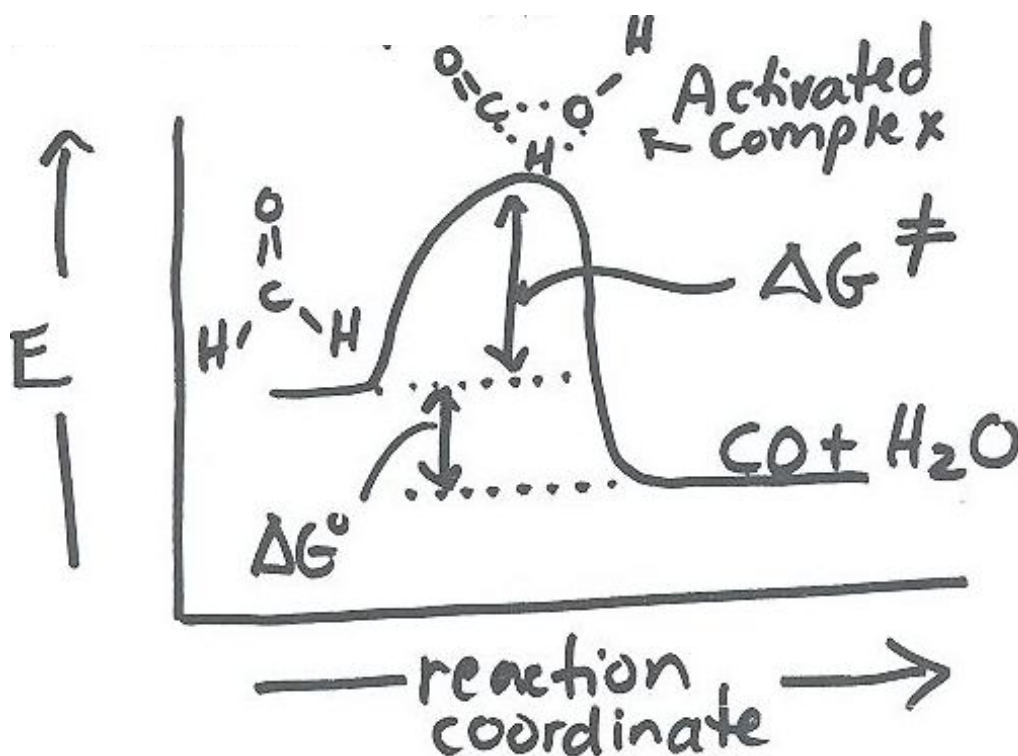
<u>Q</u> Based on the reaction profile, how can one increase the rate of a reaction?

<u>A</u> For one thing, we cannot change the value of the Equilibrium constant, K, unless we change the reaction conditions (temp., pressure, solvent etc.,) but we can alter the rate without changing the reaction conditions by adding a catalyst.
<u>A Catalyst lowers the $\Delta G^{\neq}$, Activation Energy</u>

<u>Two Ways:</u>
  1. catalysts can assist in forming the activated complex
  2. catalysts can provide an entirely different pathway by <u>temporarily</u> binding to the reactants.

            Continuing with the review…..

Electronic Structure
Chapter 2

Atomic Electronic Structure

The (a) number and (b) distribution of electrons around an atom.

These two features essentially dictate the properties of the atom.

First hints about the electronic structure of atoms came from experimental work carried out in late 1800's & early 1900's.

Absorption and Emission of radiation from atoms was well-documented but not at all understood.

- Not until 1913, were any theories advanced that could even explain the emission spectrum of Hydrogen.

This was when Rydberg realized that the emission lines had specific wave numbers, but he could not reconcile this relationship with classical physics which said: the e⁻ would spiral into the nucleus and emit a continuum of energies.

- In 1913, Bohr broke from classical physics and said there are <u>Discrete</u>, <u>Quantized Levels</u> where an electron can reside in an atom. He related the angular momentum mvr to an integer value (Quantized Value)

$$mvr = \frac{nh}{2\pi}$$

m is the mass
v is velocity
r is radius
h is Planck's const.
n is an integer value

Absorption Spectrum of Hydrogen
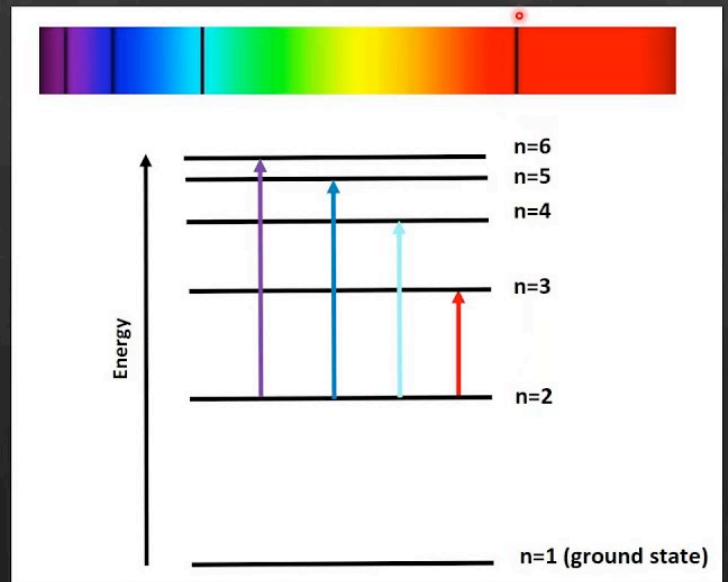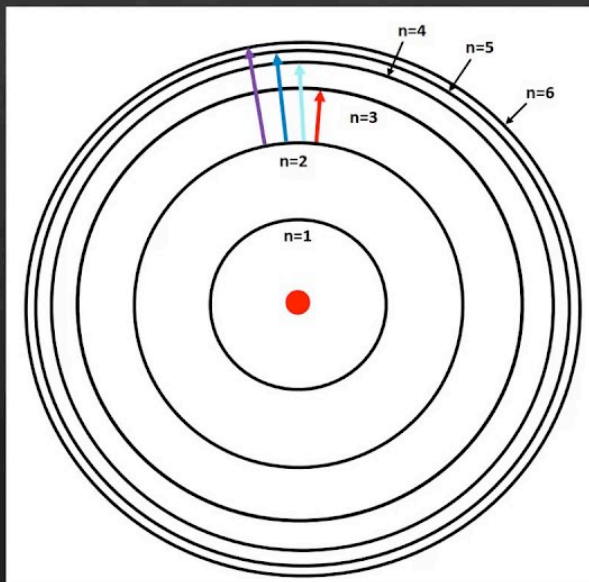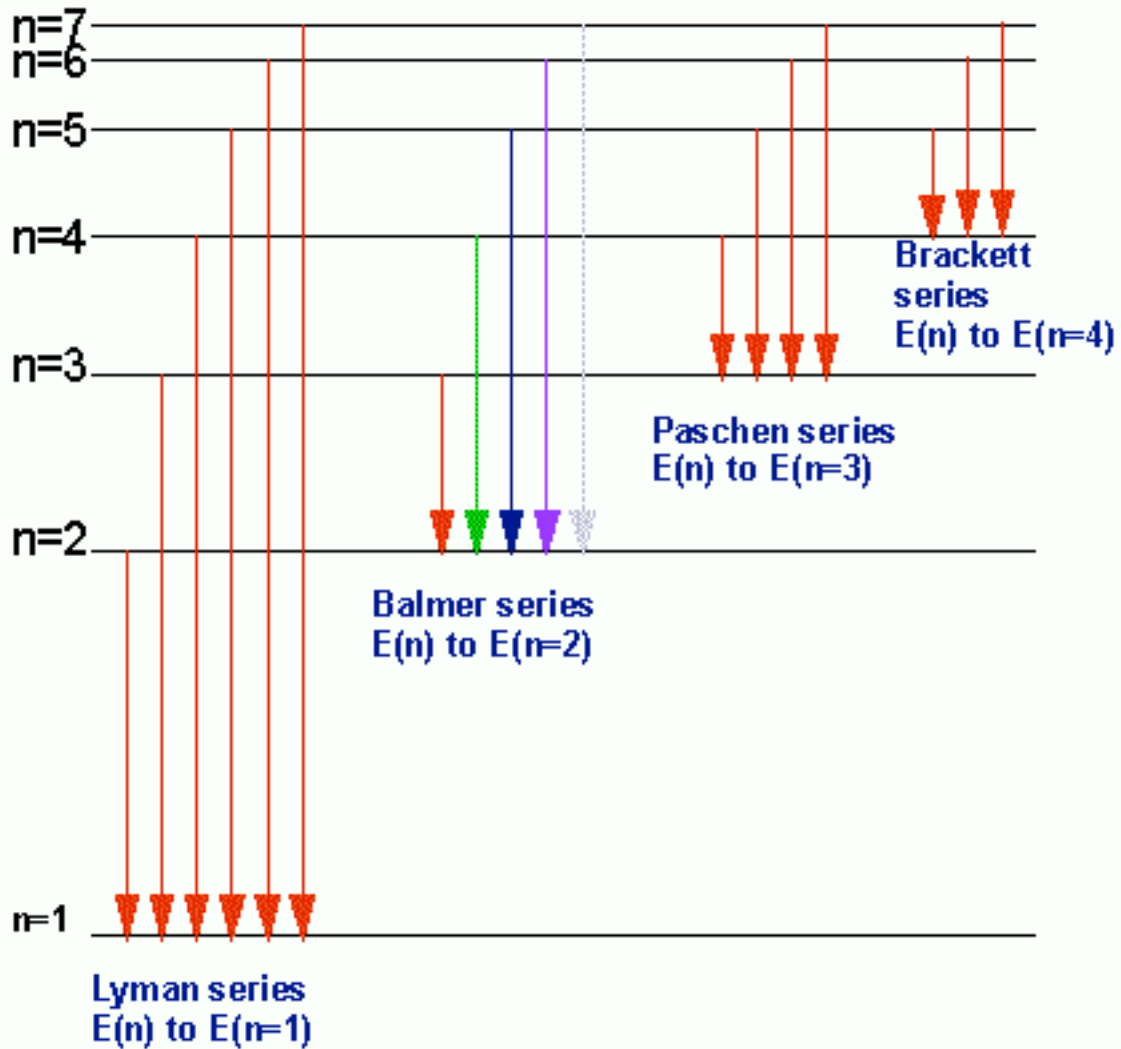
Bohr orbits and the transitions associated with Emissions from higher orbits to orbits n = 1, n = 2, n = 3.

Q Is the Bohr atom model capable of being extended to other atoms besides H?
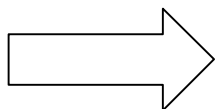
A NO

Q Why?

A Electrons are not discrete particles with precisely defined positions and velocities.

Bohr himself used the idea put forth by Max Planck that electromagnetic energy (photons or any wave) is quantized:

$$E = h\nu$$

Planck's constant

$\Longrightarrow$ Electrons have the same wave-like properties that photons have.

Dawn of Dual Particle-Wave Theories
$\Longrightarrow$ **Wave Mechanics**

Two important players:

De Broglie

$\lambda = $ h/mv

Particle-Wave
Equation

$\left.\begin{array}{c} \\ \\ \\ \end{array}\right\}$ All particles with velocities, v, and mass, m can be described by a wavelength

Schrödinger

$H\Psi = E\Psi$
Wave equation

$\left.\begin{array}{c} \\ \\ \\ \end{array}\right\}$ Proposed a general mathematical expression for an electron

The Theory of Wave Mechanics is the method of operator algebra

H - Hamiltonian operator defines a series of operations to perform

Ψ - Wave function describes the e⁻ in terms of its wave properties

$\Psi = R(r) \quad \Theta(\theta) \quad \Phi(\varphi)$

Radial   angular

Wave functions have two components:
The physical manifestation of Ψ is what we call an orbital. Orbitals have:
   1) <u>shape</u> determined by angular part
    2) <u>extension</u> determined by radial part
       <u>or size</u>

The most simplistic way that these two are depicted is in the form of boundary surface diagrams (our usual meaning of an orbital)

p_x

z

x

y

p_y

z

x

y

p_z

z

x

y
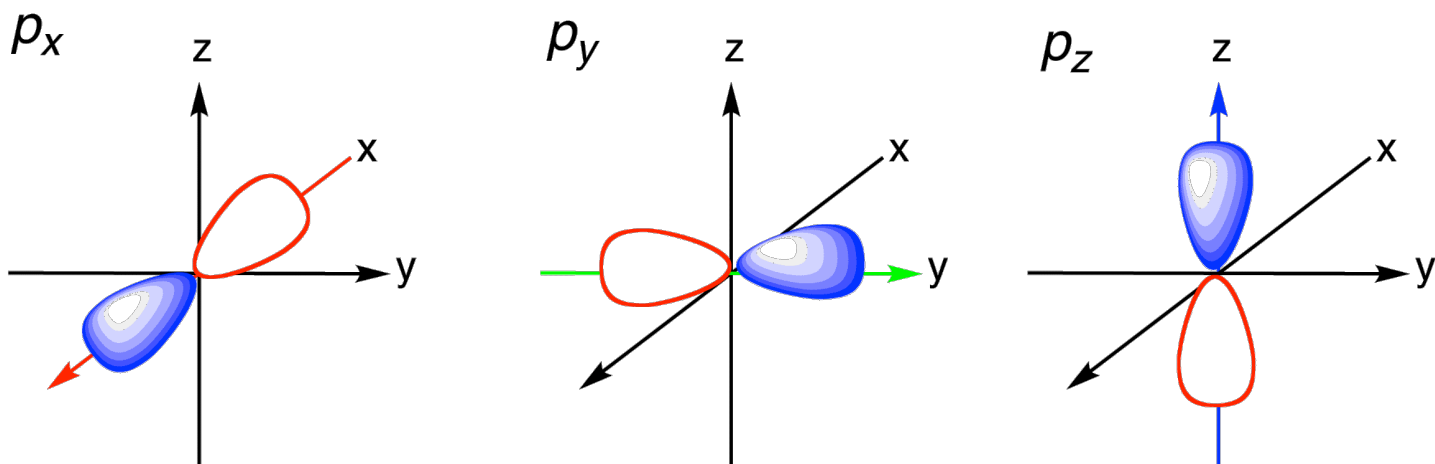
The three p orbitals are aligned along perpendicular axes

Boundary surface Diagrams
The orbitals are identical in shape
(probabilities) and energies

d_{xy} d_{yz} d_{xz} $d_{x^2-y^2}$ d_{z^2}
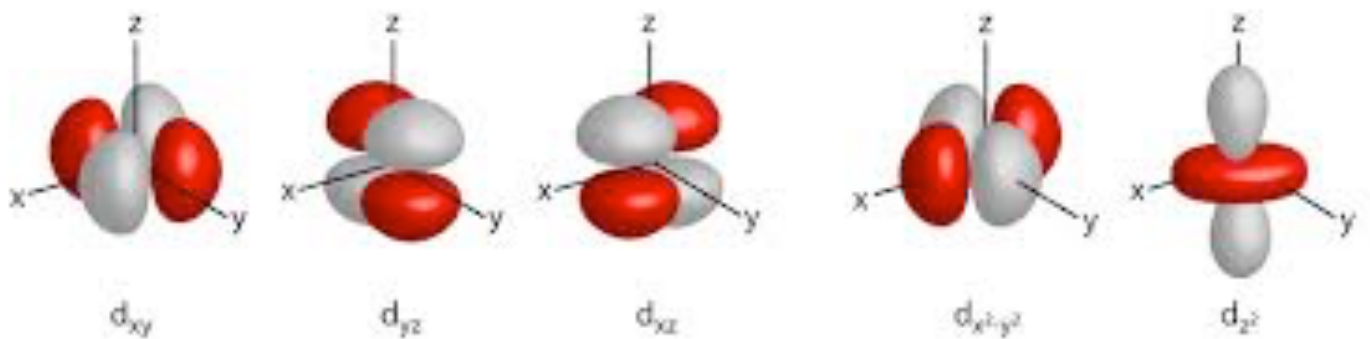
Boundary Surface Diagrams for d-orbitals

Although the dz^2 orbital looks different, it is identical in all aspects to the other orbitals

The square of Ψ, Ψ^2, gives a measure of the e⁻ density in various regions.

Q How does the Bohr model compare to the wave function model?
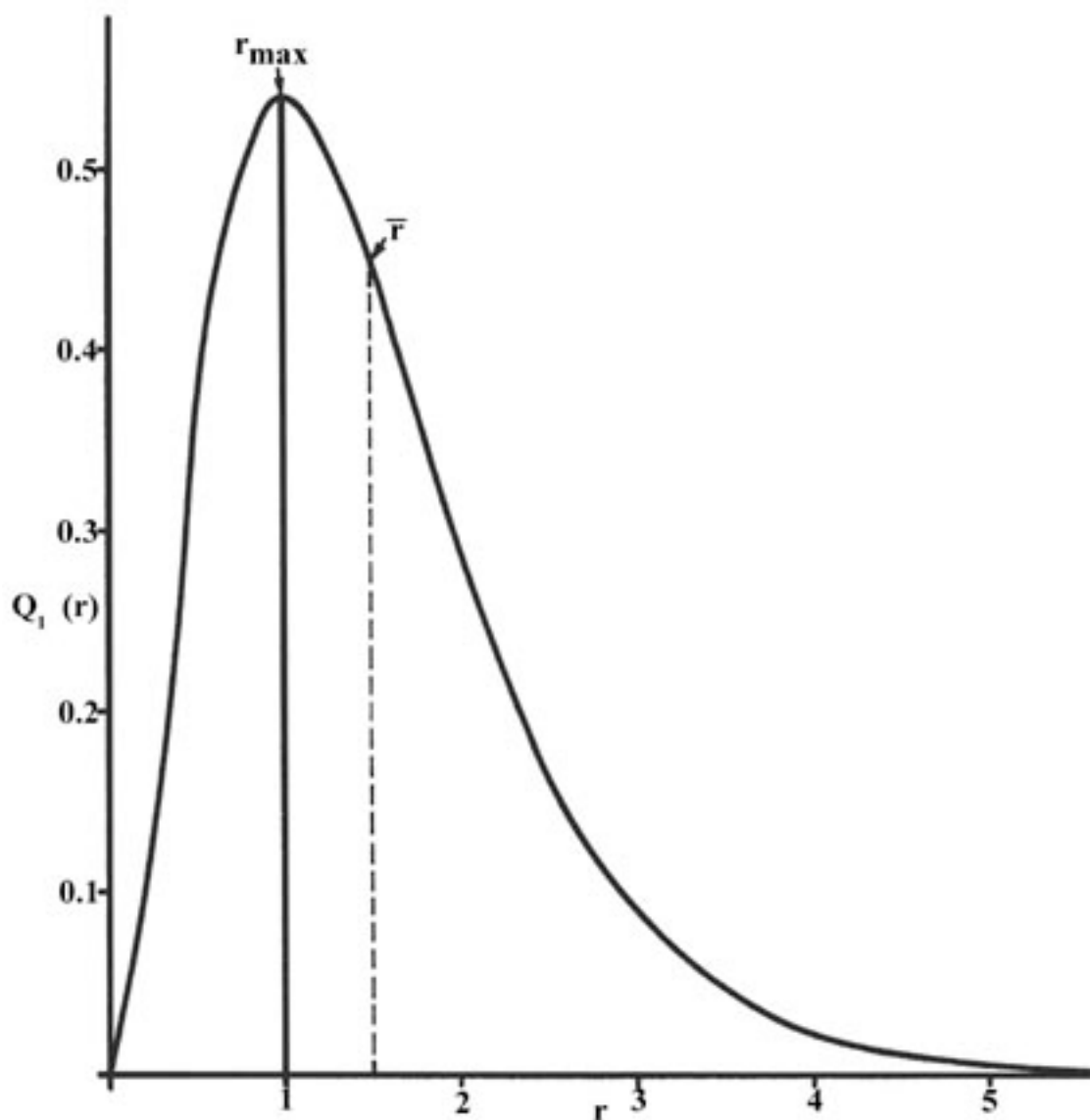
A The precise orbit of an e⁻ in a Bohr orbit is the place where the e⁻ density probability is the highest:
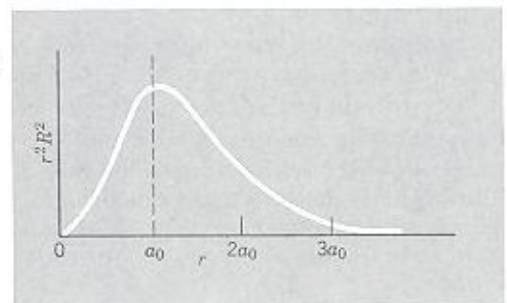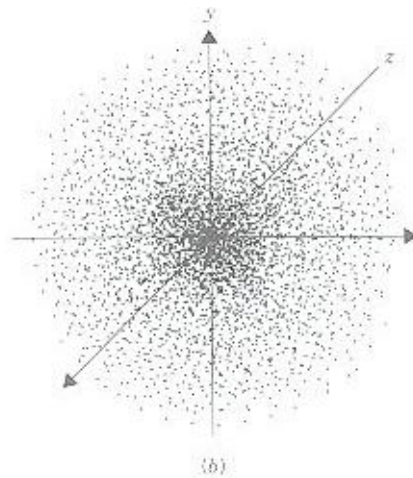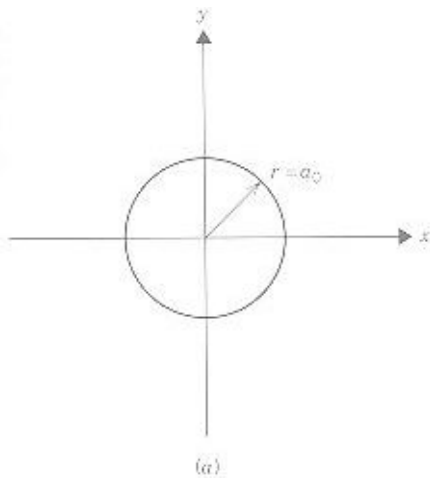
Bohr model   dot density   e⁻ density
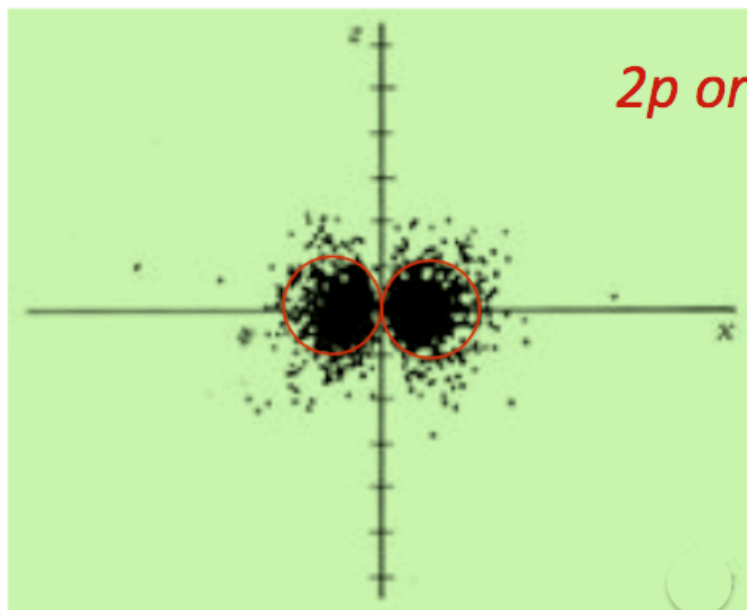   diagram   probability
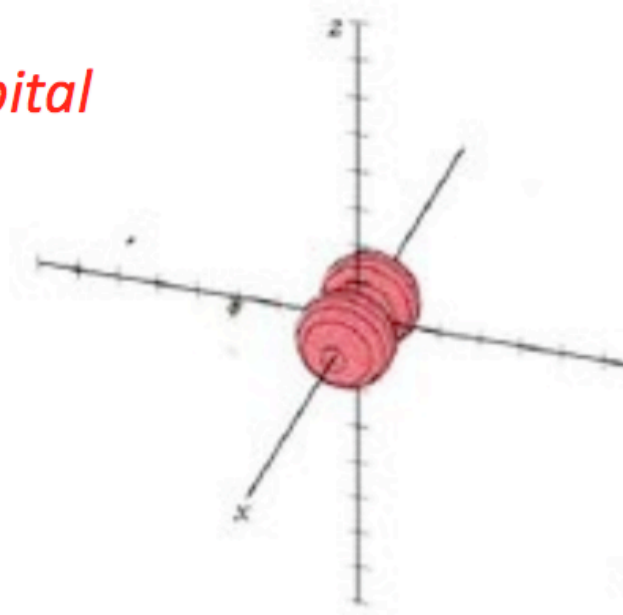   function

Another way to show how the e⁻ density (or probability for finding the e⁻) varies in an orbital is a contour map:
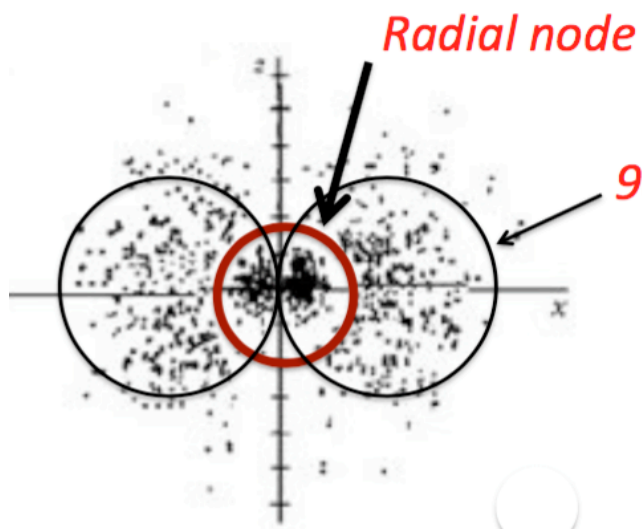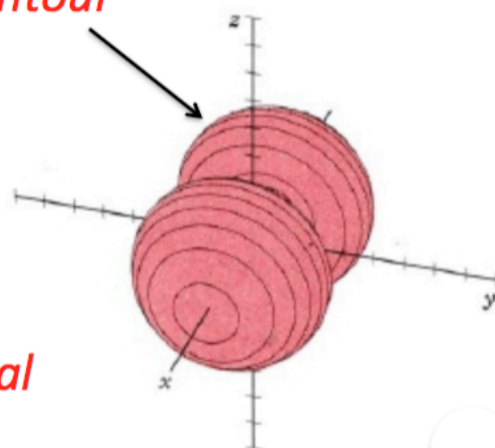
2p orbital

Dot diagram

Contour diagram

2p orbital

3p orbital

Dot diagram

Radial node

90% contour

Contour diagram

3p orbital

There are major differences that arise because of the function $4\pi r^2[R(r)]^2$ which is the e^- density probability function.

e⁻ density probability functions
$4\pi r^2[R(r)]^2$ ($r^2[R(r)]^2$ for short)
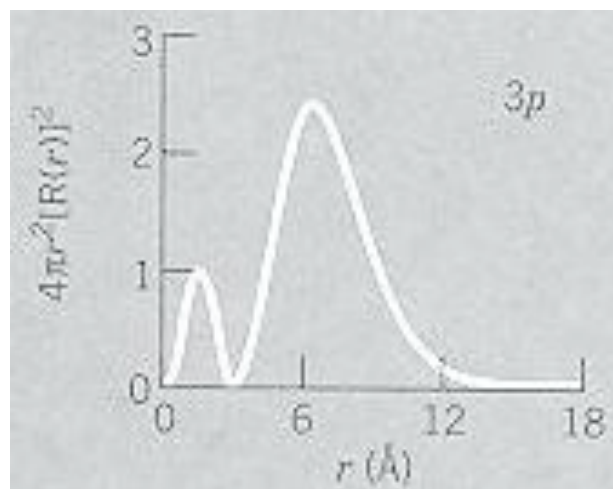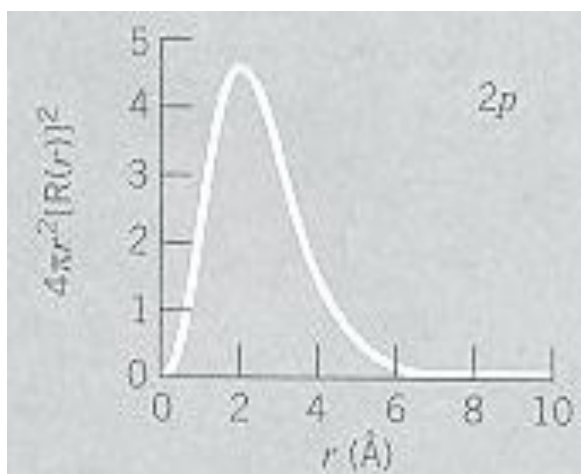1s   2s

no probability of the e⁻ at the nucleus

2p   3p

for a 2p orbital the e⁻ density increases to a maximum then drops off.   3p is different

<u>Summary of Quantum numbers for an electron:</u>

n   principal Q.N   n can be $0 \rightarrow \infty$
        n determines the **size** of the orbitals

ℓ orbital Q. N. $\ell = 0,1,2\ldots(n-1)$
        ℓ determines the **shape** of orbitals

m_ℓ $_+\ell\ldots o\ldots- \ell$ $\ell=1$ $m_\ell =_\pm 1, 0$ etc.,

m_s $_\pm$ ½ for each election

<u>Four Q.N.'s in all:</u>
n = 1 shell $\ell=0$ 1s
n = 2 shell $\ell=0$ 2s
                       $\ell=1$ 2p
n = 3 shell $\ell=0$ 3s
                       $\ell=1$ 3p
                       $\ell=2$ 3d

etc.,

Electronic Configuration

The term used to describe the manner in which electrons are arranged in an atom
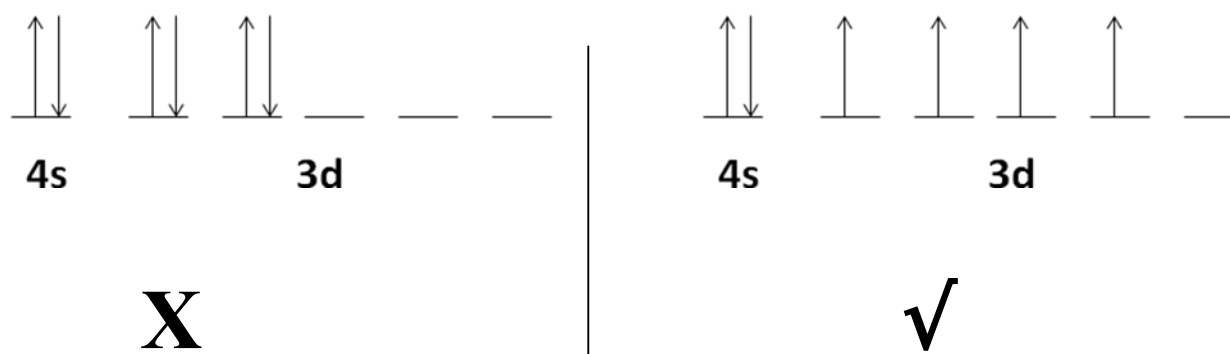
1.) <u>Aufbau Principle:</u>
Add electrons from the lowest to the highest levels

2.) <u>Hund's Rule of maximum multiplicity:</u>
Add electrons in orbitals of the same energy (degenerate set) with same spin before pairing spins.

e.g. $1s^2s^22p^63s^23p^64s^23d^4$ is:

4s   3d   4s   3d

X   **√**

Pauli Exclusion Principle:

No two electrons can have the same 4 Quantum numbers (in other words, if two electrons are in the same shell (n), same set of orbitals (ℓ), and same exact orbital (m_ℓ), then they would have different values of m_s (spins) + ½ for one and - ½ for the other

$$m_\ell = \quad \overline{} \; \overline{} \; \overline{}$$
$$ \quad -1 \quad 0 \quad +1$$
$$2p$$

Both electrons:

$$n=2$$
$$\ell=1$$
$$m_\ell = -1$$

but $m_s = + ½$ for one and $m_s = - ½$ for other

Orbital energies in the Hydrogen Atom

E

| 3s | 3p | 3d |
| 2s | 2p |
| 1s |
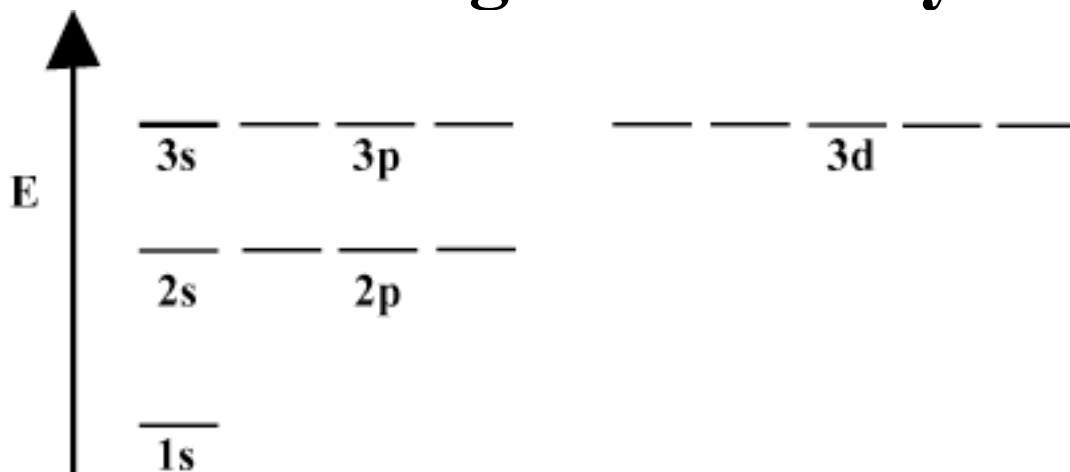
Orbital energies in the Multi-Electron Atom

General Energy Ordering of Orbitals for Multi-electron Atoms

Energy

5s
4p 4p 4p   4d 4d 4d 4d 4d
4s   3d 3d 3d 3d 3d
3p 3p 3p
3s
2p 2p 2p
2s
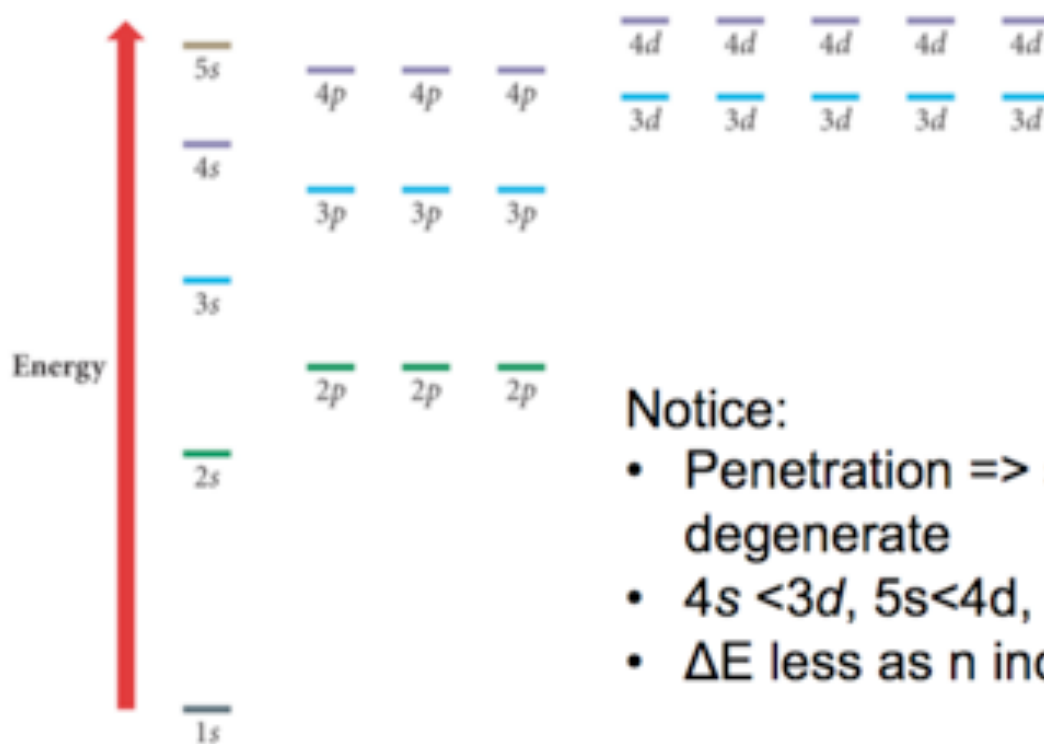
Notice:
- Penetration => sublevels are not degenerate
- 4s <3d, 5s<4d, etc
- ΔE less as n increases

1s

Knowledge of Atomic Structure **is so important**, because it allows us to understand the periodic relationships among elements.

Concepts that follow from Electronic Structure:
1. The interpenetrations of atomic orbitals which depends on size & shape (in other words, how they fit together)

2. Because of their interpenetration, we order the orbitals in the Aufbau way: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p…

3. Because of the different interpenetrations and orientations of the orbitals, the electrons experience different nuclear charges.

and finally….**MAIN POINT!!!**

4. Properties Such as:
    • Ionization Energies
    • Atomic & Ionic Sizes
    • Electron Affinities
    • Electronegativities

    Reflect on the Electronic Configuration of a group (column) and a period (row)

Ionization Energy or Enthalpy
ΔH_{ion} in kJ/mol – First Ionization Energy

   Three trends are noticeable:
   1. Maximum at Noble Gases
   2. Minimum at alkali metals (closed-shell is favored)
   3. The increase in going from alkali metal to noble gas. (e.g. Na to Ar for example) is not regular $\rightarrow$ there are two "dips

<u>Q.</u> Why?

<u>A.</u> Because of differences in shielding of s &
      p orbitals

<u>Shielding</u>
When you put electrons in orbitals with the
same Quantum number, n, (same shell), as you
keep adding more, they are less shielded from
the positive charge of the nucleus.

The leads to it being more difficult to remove
electrons (higher I.E.)
<u>in other words</u>…

The Effective Nuclear Charge increases as you
go across a row

Ar

Cl

P S

Si

$P^4 \rightarrow P^3$
half-filled

Mg

Al

Na

↑
first p
electron is
being added
(less shielded)
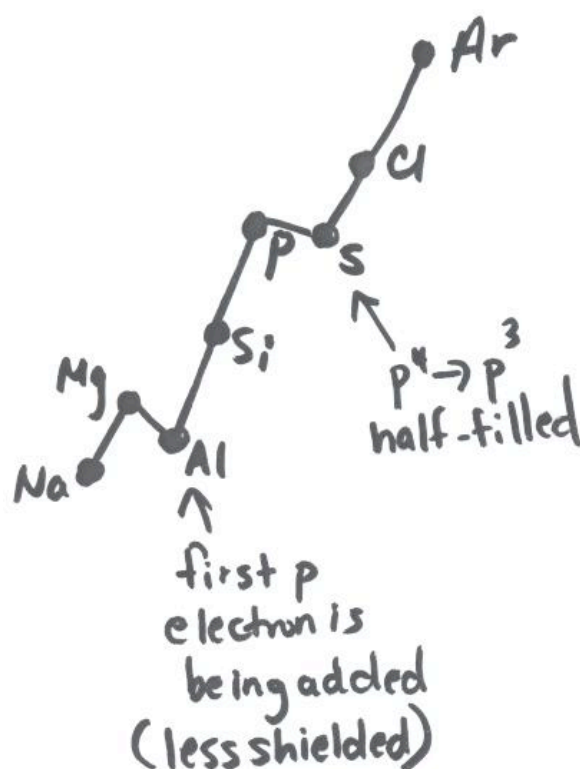
Q. Why do the changes at Al and S happen?

A. Because   Na is $2s^1$
             Mg is $2s^2$
- Al is $2s^2 2p^1$ - it is favored to lose the one p
electron to go back to a filled sub-shell
-S is $2s^2 2p^4$ - it is easier to lose an electron to
get it back to the stable half-filled sub-shell
$2s^2 2p^3$