"A" students work (without solutions manual) ~ 10 problems/night.

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FITCH Rules

General

G1: Suzuki is Success
G2. Slow me down
G3. Scientific Knowledge is Referential
G4. Watch out for Red Herrings
G5. Chemists are Lazy

Chemistry

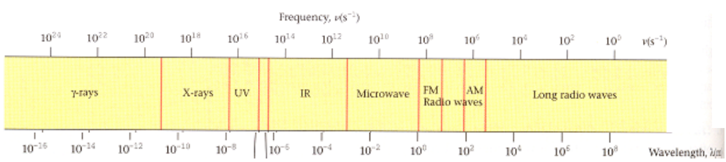
C1. It's all about charge
C2. Everybody wants to "be like Mike"
C3. Size Matters
C4. Still Waters Run Deep
C5. Alpha Dogs eat first

$$E_{el} = k\left(\frac{q_1 q_2}{r_1 + r_2}\right)$$

$$E = h\nu$$

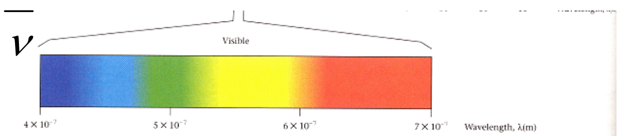
Note that we can measure the light either by frequency (energy) or by wavelength.

$$\nu\lambda = c$$



Expand this region

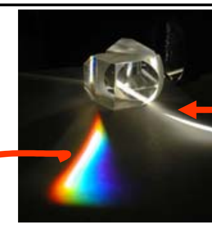
$$\lambda = \frac{c}{\nu}$$



Region our "eyes" sense

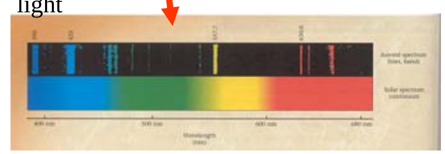
Visible

Split light



Aurora

Measure light

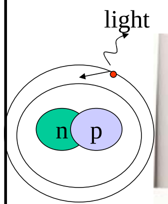


Allows us to Measure energy Of electrons and Identify elements In a gas phase

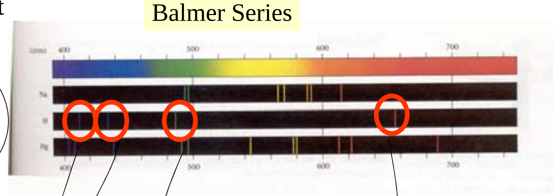
How we know solar system composition

Observe – that the light is in discrete "lines" or is **quantized** into discrete energies, related to specific Electron transitions.

The hydrogen atom, analyzed by Bohr (**The Bohr Model**)



Balmer Series



These four wavelengths measured for the hydrogen atom tell us Something about what electrostatic energy states with respect to Positive nucleus the electron occupy.

TABLE 6.1 Wavelengths (nm) of Lines in the Atomic Spectrum of Hydrogen

Ultraviolet (Lyman Series)	Visible (Balmer Series)	Infrared (Paschen Series)
121.53	656.28	1875.09
102.54	486.13	1281.80
97.23	434.05	1093.80
94.95	410.18	1004.93
93.75	397.01	
93.05		

1825-1898
Johann Balmer
Swiss mathematician

Niels Bohr
Physicist
1885-1962
Denmark

The Bohr Model

Based on an electrostatic model

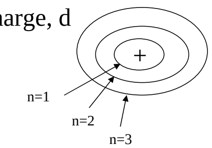
1. Protons in the nucleus
   Z = atomic number = # of protons in nucleus

$$q_+ = \left(+Z_{electric\ charge}\right)\left(\frac{1.6022x10^{-19}\,Coulomb}{electric\,charge}\right)$$

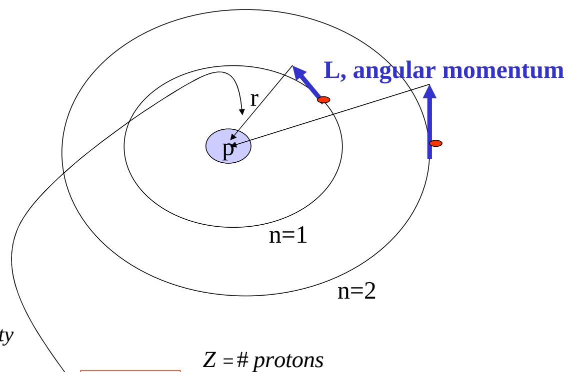
2. Electrons (Z) in orbit at some

$$q_- = \left(Z_{electric\ charge}\right)\left(\frac{-1.6022x10^{-19}\,Coulomb}{electric\,charge}\right)$$

3. Distance between + and – charge, d
   d related to orbit, n



$$Energy_{electrostatic} = k\left(\frac{q_1 q_2}{d}\right)$$



$\mu \propto mass$

$u = velocity$

$r = radius$

$Z = \#\,protons$

$e = charge\,of\ proton\,or\,electron$

$\pi\varepsilon_o = term\,related\,to\,resistance\,of\ vacuum$

$$\frac{\mu u^2}{r} = \frac{(Ze)e}{4\pi\varepsilon_o r^2}$$

Centripetal force = Electrostatic attraction

Bohr inferred that only certain angular momenta, L, were allowed which meant that only certain radii orbitals were allowed

$angular\ momentum \equiv L = mur$

Bohr said angular momentum Has to have fixed multiple values:

$$L = n_{=1,2,3,4,5....}\left(\frac{h}{2\pi}\right) = mur$$

$$\frac{n\left(\frac{h}{2\pi}\right)}{\mu r} = u$$

Solve the centripetal force (electrostatic attraction) with Bohr's Constraint on angular momentum

$$\frac{\mu u^2}{r} = \left|\frac{(Ze)(-e)}{4\pi\varepsilon_o r^2}\right|$$

$$\frac{\mu\left(\frac{n\left(\frac{h}{2\pi}\right)}{\mu r}\right)^2}{r} = \frac{(Ze)e}{4\pi\varepsilon_o r^2}$$

$$\frac{\mu n^2 h^2}{\mu^2 4\pi^2 r^3} = \frac{(Ze)e}{4\pi\varepsilon_o r^2}$$

$$\frac{n^2 h^2}{\mu\pi r} = \frac{(Ze)e}{\varepsilon_o}$$

$$\frac{\varepsilon_o n^2 h^2}{(Ze)e\mu\pi} = r = \frac{n^2 h^2 \varepsilon_o}{(Ze)e\mu\pi} = \left(\frac{n^2_{1,2,3....}}{Z}\right)a_o$$

a_o=Bohr radius=52.92pm

n can only have positive interger values

$$Energy_{electrostatic} = \frac{(Ze)(-e)}{4\pi\varepsilon_o r}$$

Just solved for r

$$r = \left(\frac{n^2_{1,2,3...}}{Z}\right)a_o$$

Combine

$$Energy_{electrostatic} = -\frac{Ze^2}{4\pi\varepsilon_o\left(\left(\frac{n^2}{Z}\right)a_o\right)}$$

$$Energy_{electrostatic} = -\frac{e^2}{4\pi\varepsilon_o a_o}\left(\frac{Z^2}{n^2}\right)$$

For the hydrogen nucleus Z=1

$$Energy_{electrostatic} = -\frac{(1.6022x10^{-19}C)^2}{4\pi\left(8.854x10^{-12}\frac{C^2}{Nm^2}\right)(52.92x10^{-12}m)}\left(\frac{1}{n^2}\right)$$

$$Energy_{electrostatic} = -4.359x10^{-18}N\cdot m\left(\frac{1}{n^2}\right)$$

$$Energy_{electrostatic} = -4.359x10^{-18}J\left(\frac{1}{n^2}\right)$$

$$Energy_{electrostatic} = -4.359x10^{-18}J\left(\frac{1}{n^2}\right)$$

1854-1919
Johannes Rydberg
Swedish mathematical physicist

$$Energy_{total} = \frac{-4.359x10^{-18}J\left(\frac{1}{n^2}\right)}{2} = -2.17x10^{-18}\left(\frac{1}{n^2}\right)$$

$$Energy_{total} = -2.17x10^{-18}\left(\frac{1}{n^2_{1,2,3...}}\right)$$

Rydberg Constant

I hate derivations

So what's the bottom line?
What do you need to know?
That this model is based on
The electrostatic attraction of an
Electron orbiting (circular) a
Proton. Only discrete orbits allowed

TABLE 6.1 Wavelengths (nm) of Lines in the Atomic Spectrum of Hydrogen

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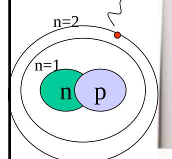
93.75	397.01	
93.05		

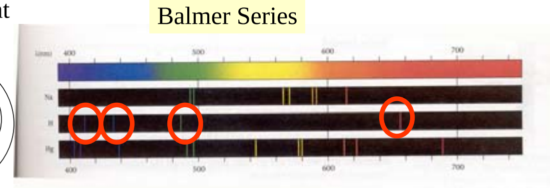
Only discrete, quantized,
(**n=unit values**) of energy
are allowed for electrons.
This accounts for lines as opposed
To range of energy

$$E = \left.\frac{-R_H}{n^2}\right|_{n=1,2,3........}$$

$$R_H = 2.180x10^{-18}J$$ Rydberg constant



Balmer Series



n=1 is the ground state
Where electron really wants to be

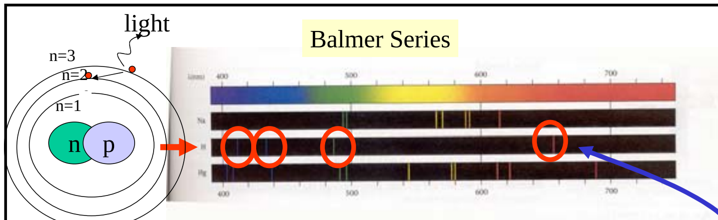
n=2,3,…. Are excited states

Energy in the form of light
is released when an
electron drops from
n=2,3…..to n=1 state

$$\Delta E = h\nu = E_{hi} - E_{low}$$

$$\Delta E = h\nu = \left[\frac{-R_H}{(n_{hi})^2}\right] - \left[\frac{-R_H}{(n_{low})^2}\right]$$

$$\Delta E = h\nu = -R_H\left[\frac{1}{(n_{hi})^2} - \frac{1}{(n_{low})^2}\right]$$



Example: Prove that the Bohr model works by calculating the wavelength associated with an electron dropping from n=3 to n=2 and comparing that value to wavelengths in the Balmer series.

$$\Delta E = h\nu = -R_H\left[\frac{1}{(n_{hi})^2} - \frac{1}{(n_{low})^2}\right]$$

$$\nu = \frac{-R_H}{h}\left[\frac{1}{(3)^2} - \frac{1}{(2)^2}\right]$$

$$\nu = \frac{-R_H}{h}[-0.1388]$$

$$\nu = \left[\frac{-2.180x10^{-18}\,J}{6.626x10^{-34}\,Js}\right][-0.1388]$$

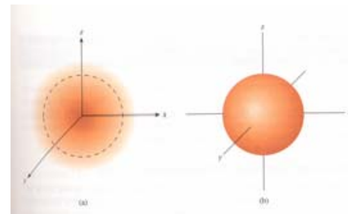
$$\nu = 4.569x10^{14}\,\frac{1}{s}$$

$$\lambda = \frac{c}{\nu}$$

$$\lambda = \frac{\left[2.998x10^{8}\,\frac{m}{s}\right]\left[\frac{10^{9}\,nm}{m}\right]}{4.569x10^{14}\,\frac{1}{s}} = 656.08nm$$

The fly in the ointment
Indicates there is a problem

The "fly in the ointment" of Bohr's successful model of the Hydrogen model is that it does Not account for any other element!



The reason is that the electron Does not really occupy a specific Orbital around the nucleus. It Has a "probability" of being in that Space that is high, but with some Probability of not being in that space.

Math Phobic
Can sleep → Just keep track of ideas

Louis de Broglie (1892-1987)
French Mathematical physicist
Proposed wave like properties of particles

Relate the kinetic energy of
The motion of the electron

$$E_k = \frac{1}{2}mv^2 \qquad E = h\nu = \frac{hc}{\lambda}$$

Remember c is velocity of light

$$m\upsilon^2 = \frac{h\upsilon}{\lambda}$$

$$\lambda = \frac{h\upsilon}{m\upsilon^2}$$

$$\lambda = \frac{h}{m\upsilon}$$

λ Characteristic wavelength of a mass

h Planck's constant $h = 6.626x10^{-34}\,J\cdot s$

m Mass

υ velocity

Example: What is the wavelength of an electron (mass of 9.11×10^{-28} g) moving at 5.97×10^{6} m/s?

$$\lambda = \frac{h}{m\upsilon} \qquad h = 6.626x10^{-34}\ J \cdot s$$

$$\lambda = \frac{6.63x10^{-34}\ J - s}{(9.11x10^{-28}\ g)\left(5.97x10^{6}\ \frac{m}{s}\right)}\left[\frac{\frac{1kg - m^2}{s^2}}{J}\right]\left(\frac{10^3\ g}{kg}\right)$$

(%&*! Conversions!)

$$\lambda = 1.22x10^{-10}\ m$$

$$\lambda = 0.122nm$$

1. Electron is a particle
2. Electron is a wave

Mutually contradictory statements Which are resolved by saying:

A particle which has probability Of occupying different locations simultaneously

Werner Heisenberg (1901-1976) formulated the **Uncertainty Principle**

$$(\Delta x)(\Delta mv) \geq \frac{h}{4\pi} \quad \text{OR} \quad (\Delta x) \geq \frac{h}{4\pi(\Delta mv)}$$

Can we measure where a 57 g tennis ball moving at 60 m/s is?

$$\Delta x \geq \frac{6.63x10^{-34}\ J - s}{4(3.14)(57g)\left(60\frac{m}{s}\right)}\left[\frac{\frac{1kg - m^2}{s^2}}{J}\right]\left(\frac{10^3\ g}{kg}\right)$$

$$\Delta x \geq 1.54x10^{-35}$$

We can know the position of the ball to within 10^{-35} m

Werner Karl Heisenberg
1901-1976
German theoretical physicist

$$(\Delta x) \geq \frac{h}{4\pi(\Delta mv)}$$

9.11×10^{-31}kg mass of an electron
5×10^{6}m/s average velocity of an electron
1% uncertainity in the velocity

Can we measure where an electron around the nucleus is?

$$\Delta x \geq \frac{6.63x10^{-34}\ J - s}{4(3.14)(9.11x10^{-31}\ kg)(0.01)\left(5x10^{6}\ \frac{m}{s}\right)}\left[\frac{\frac{1kg - m^2}{s^2}}{J}\right]$$

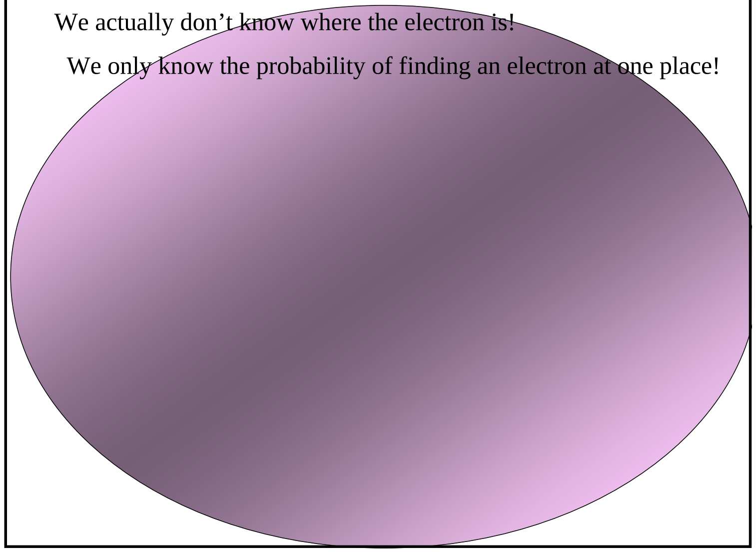
$$\Delta x \geq 1x10^{-9}$$

We can know the position of the electron to within 10^{-9} m=1nm

Radius of hydrogen = 200 pm =0.2 nm

We actually don't know where the electron is!

We only know the probability of finding an electron at one place!



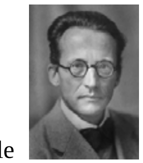
Electron has Light-like properties
Electron has a probability of occupying a certain volume

Snork,
Bst, huh? Math Phobic wake up here

Quantum mechanical models describe the probability of electron density; from these we get possible energy states for the electron "Cloud"

Quantum mechanical models postulate several **quantum Numbers**

1. describe the allowed energy levels of the electrons
2. Energy levels are related to **probability** of finding electron **density** (SHAPE of orbital) ψ



1. **Look at math**
2. Look at shapes
3. See relationship to periodic table

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m(E-V)}{h^2}\psi = 0$$

An equation to inhabit your worst Nightmares

Erwin Schodinger
Austrian 1887-1961

Schrodinger equation is solved by the physical Chemists and physicists to give us **allowed** orbitals governed by Principal **quantum numers**

Principal n	Azimuthal $\ell = 0,1,2....(n-1)$	Magnetic $m_\ell = \ell,......+1,0,-1.......-\ell$	Spin $m_s = +\frac{1}{2};-\frac{1}{2}$	Total Allowed e
1	$\ell = 0$; $\ell_0 = s$	$m_{\ell=0} = 0$	$m_s = +\frac{1}{2};-\frac{1}{2}$	2x1
2	$\ell = 0, 1$; $\ell_0 = s$	$m_{\ell=0} = 0$	$m_s = +\frac{1}{2};-\frac{1}{2}$	2x1
	$\ell_1 = p$	$m_{\ell=1} = +1, 0, -1$	$m_s = +\frac{1}{2};-\frac{1}{2}$	2 x 3; 8
3	$\ell = 0, 1, 2$; $\ell_0 = s$; $\ell_1 = p$; $\ell_2 = d$	$m_{\ell=2} = 2, 1, 0, -1, -2$	$m_s = +\frac{1}{2};-\frac{1}{2}$; $m_s = +\frac{1}{2};-\frac{1}{2}$; $m_s = +\frac{1}{2};-\frac{1}{2}$	2x1; 2x3; 2x5; 18
distance	Orbital shape	Orientation in space	Electron spin	

Quantum mechanical models describe the probability of electron density; from these we get possible energy states for the electron "Cloud"

Quantum mechanical models postulate several **quantum Numbers**

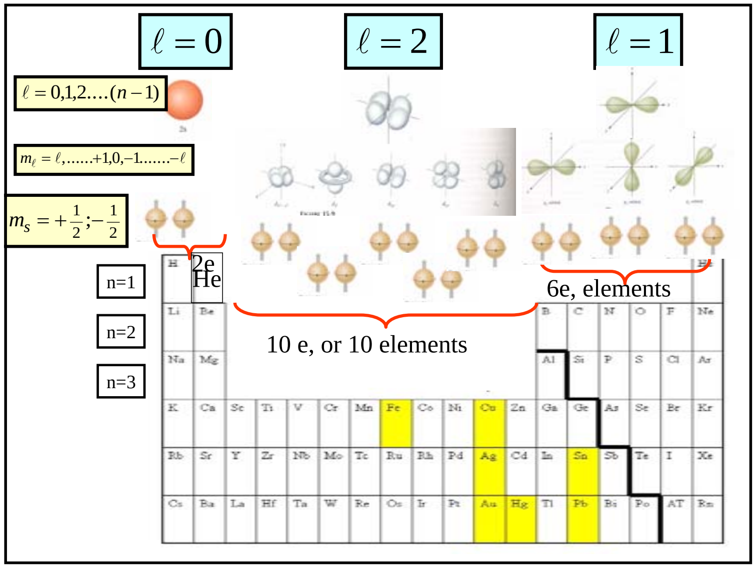
1. describe the allowed energy levels of the electrons
2. Energy levels are related to **probability** of finding electron **density** (SHAPE of orbital) ψ

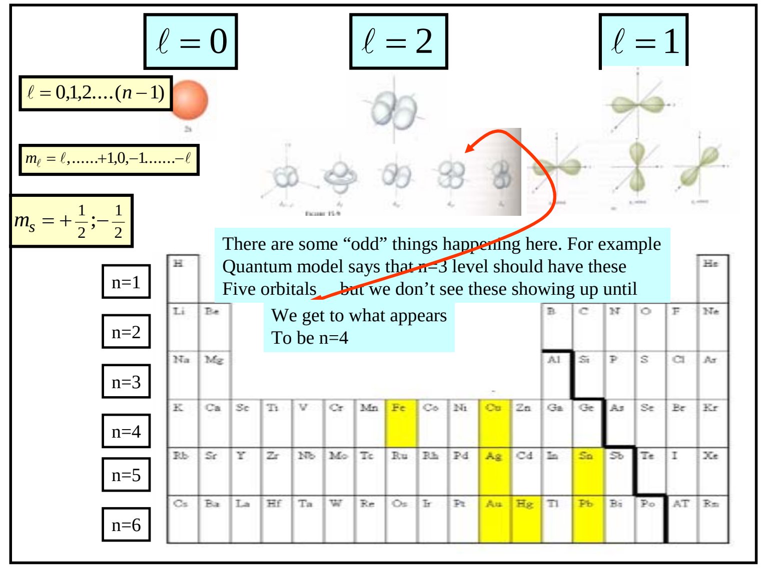
1. Look at math
2. Look at shapes
3. **See relationship to periodic table**

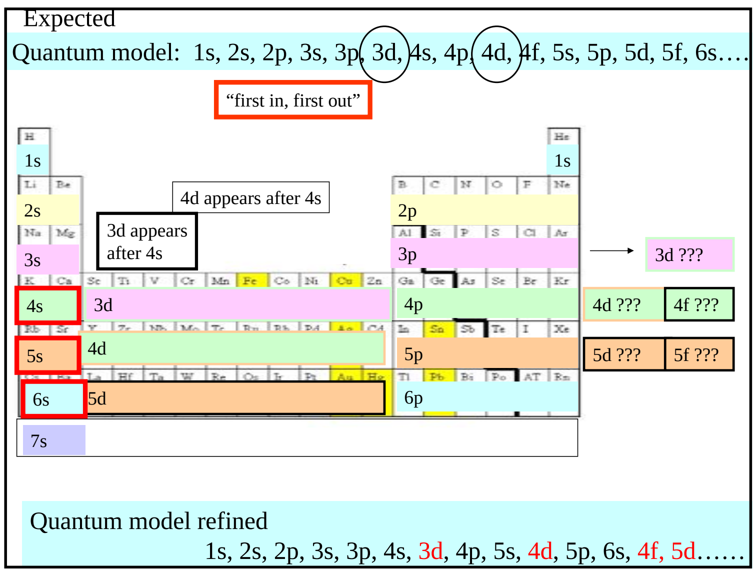
Each element is described by a unique set of quantum numbers

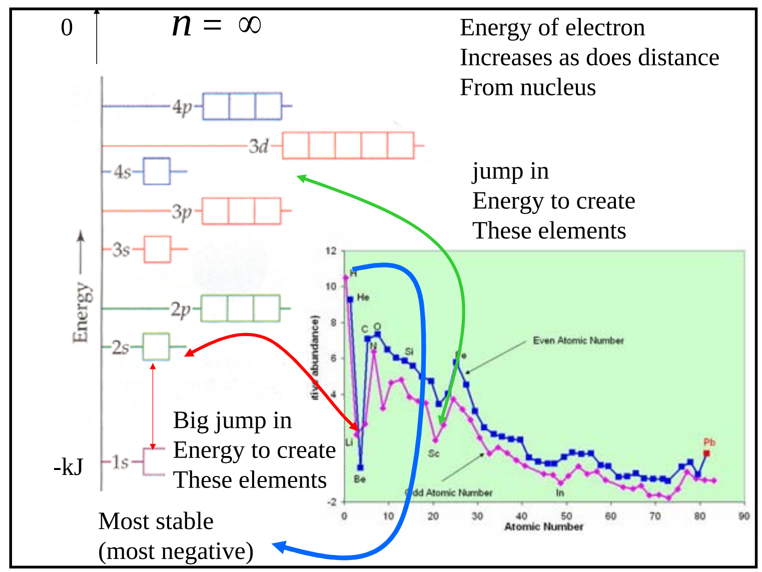
the **Pauli Exclusion Rule** (no two electrons can have the same quantum mechanical numbers

Wolfgang Pauli
1900-1958
Vienna, theoretical physicist


$\ell = 0$
$\ell = 2$
$\ell = 1$
$\ell = 0,1,2....(n-1)$
$m_\ell = \ell,......+1,0,-1.......-\ell$
$m_s = +\frac{1}{2};-\frac{1}{2}$
2e
He
n=1
n=2
n=3
10 e, or 10 elements
6e, elements


$\ell = 0$
$\ell = 2$
$\ell = 1$
$\ell = 0,1,2....(n-1)$
$m_\ell = \ell,......+1,0,-1.......-\ell$
$m_s = +\frac{1}{2};-\frac{1}{2}$
There are some "odd" things happening here. For example
Quantum model says that n=3 level should have these
Five orbitals but we don't see these showing up until
We get to what appears
To be n=4
n=1
n=2
n=3
n=4
n=5
n=6


Expected
Quantum model: 1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f, 5s, 5p, 5d, 5f, 6s….
"first in, first out"
4d appears after 4s
3d appears after 4s
1s
2s
3s
4s
5s
6s
7s
3d
4d
5d
2p
3p
4p
5p
6p
3d ???
4d ???
4f ???
5d ???
5f ???
Quantum model refined
1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d…..


0
$n = \infty$
Energy of electron
Increases as does distance
From nucleus
4p
3d
4s
3p
3s
2p
2s
1s
Energy
-kJ
jump in
Energy to create
These elements
Big jump in
Energy to create
These elements
Most stable
(most negative)
Even Atomic Number
Odd Atomic Number
Atomic Number

Writing electron Configurations

$n\ell^{\#e}$ ....

Number of electrons within those shaped orbitals

Numerical value of principle quantum number
(row in periodic table= distance from nucleus of orbit)

letter of azimuthal quantum number
(shape of orbital)

$\ell = 1 = s$

$\ell = 2 = p$

$\ell = 3 = d$

$\ell = 4 = f$

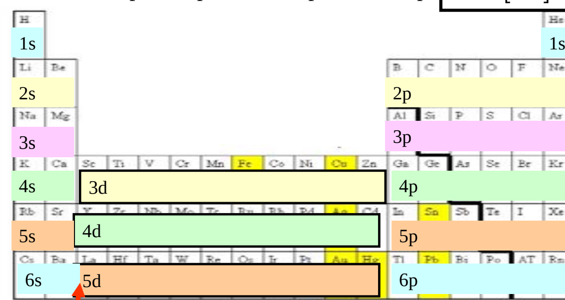
Example: Write the electron configuration of the atoms carbon, iron, and lead.

Invoke Rule G5: Chemists are Lazy

$C = 1s^2 2s^2 2p^2$ $\quad C = [He]2s^2 2p^2$

$Fe = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$ $\quad Fe = [Ar]4s^2 3d^6$

$Pb = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$ $\quad Pb = [Xe]6s^2 4f^{14} 5d^{10} 6p^2$



Abbreviated Electron configuration

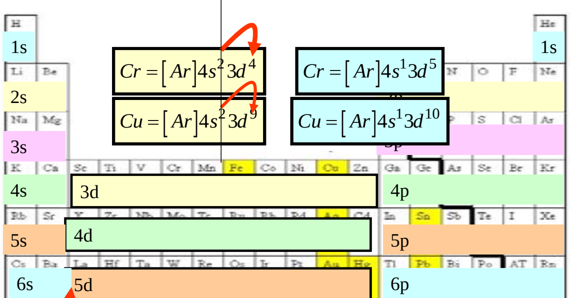
4f = lanthanides, 14 elements (7 m_l, 2 per orbital

Transition elements often have electron configurations
Different than we have predicted

they try to get to a stable ½ filled or fully filled d orbital
by shifting s electrons around

$Cr = [Ar]4s^2 3d^4$ $\quad Cr = [Ar]4s^1 3d^5$

$Cu = [Ar]4s^2 3d^9$ $\quad Cu = [Ar]4s^1 3d^{10}$



4f = lanthanides, 14 elements (7 m_l, 2 per orbital

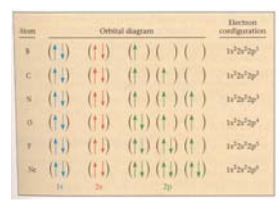
Orbital diagrams of Atoms

$C = [He]2s^2 2p^2$ → **Filled orbital** – follow Pauli exclusion Rule and give different spins (diff. direction arrows)

1s	2s	2p			
(↑↓)	(↑↓)	(↑↓)	( )	( )	**Is the correct one?**
(↑↓)	(↑↓)	(↑)	(↑)	( )	

Correct model

My daughter and son
Do not like to be in
The same room unless
Forced to be so

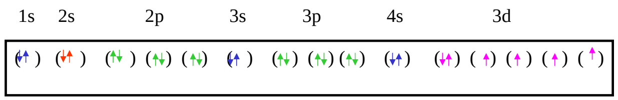


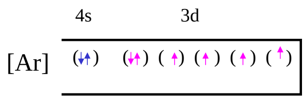
Unfilled orbitals
Hund's rule: when several orbitals of equal energy Are available, electrons enter singly with parallel Spins

1896-1997
German physicist
Friedrich Hermann Hund

Orbital diagrams of Atoms

$Fe = [Ar]4s^2 3d^6$



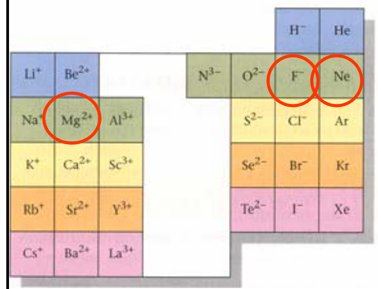


Monatomic Ions: Electronic Configurations

1. **Ions with Noble Gas Configuration**
2. Transition Metal Cations

Invoke Rule #C2

Everyone wants to be like Mike



$$F = [He]2s^2 2d^5$$

$$F^- = [He]2s^2 2d^6$$

$$Ne = [He]2s^2 2d^6 = [Ne]$$

All are ***isoelectronic*** with the noble gases.

$$Mg = [Ne]2s^2$$

$$Mg^{2+} = [Ne]2s^0 = [Ne]$$

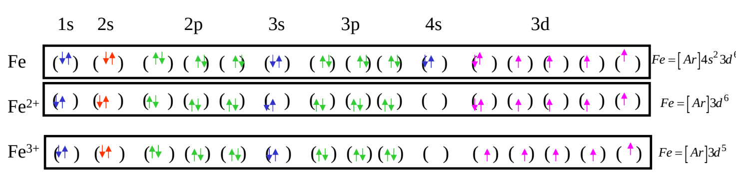
Be Like Mike ← Competing Rules → It's all about Charge

Transition Metal Cations

Atoms try to get to the noble gas configuration
every electron they lose/gain makes them charged and "unstable"
eventually the "cost" is too high and they no longer try to make it to the noble gas configuration – e.g. the transition metals.

"first in, first out"
electrons are removed from the sublevel of the highest "n"

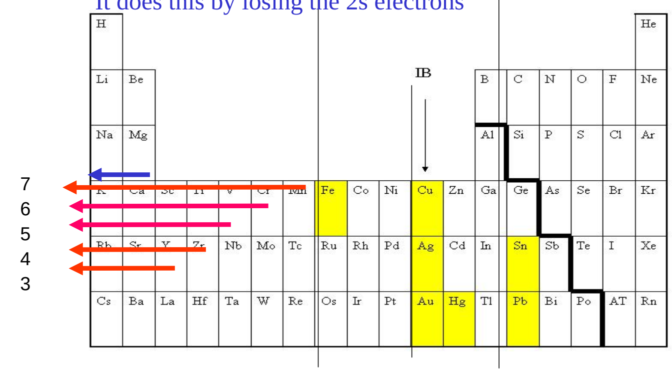
Example: Fe^{2+}, Fe^{3+}



For first half of transition metals
Most common oxidation state is to "be like Mike"

Mn can have +1, +2, +3, +4, +5, +6 oxidation states

To avoid the +6 state it will try and maintain a ½ filled d block
It does this by losing the 2s electrons



Predominate Charge States for 1st Row Transition Metals

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
VII					X					
VI				X	*	*				
V			X	*	*	*				
IV		X	X	*	X	*	*	*	*	
III	X	*	X	X	X	X	X	*	*	
II		*	X	*	X	X	X	X	X	
I			*	*	*	*	*	*	*	
0	*	*	*	*	*	*	*	*	*	
(-)I		*	*	*	*		*	*		
(-)II				*		*				
(-)III					*					
(-)IV										

a) 2+ Most preferred by Post Mn elements
b) Before Mn, wants to "be like Mike"

X = Preferred States

Can skip this slide

"A" students work (without solutions manual)
~ 10 problems/night.

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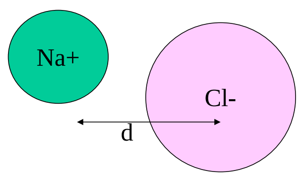
Periodic Properties of the Elements

$$E_{el} = \frac{\kappa Q_1 Q_2}{d}$$

$$k = \frac{8.99x10^9\ J-m}{(C_{oulomb})^2}$$



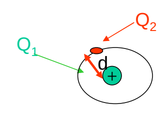
Chemistry Rule #1 = it's all about Charge and How To Balance Positive and Negative Charge

Nuclear Positive charge affects

1. Atomic size (pull on atom's own electrons)

Periodic Properties of the Elements: Pull on own electrons

$$E_{el} = \frac{\kappa Q_1 Q_2}{d}$$



$$+\frac{1.60x10^{-19}C}{proton} \quad -\frac{1.60x10^{-19}C}{electron}$$

$$\kappa = \frac{8.99x10^9\ Jm}{C^2}$$

We did a calculation of an electron moving from an electrostatic energy felt at the n =3 orbital to the n=2 orbital using the Bohr model and found a wavelength of 656.08 nm

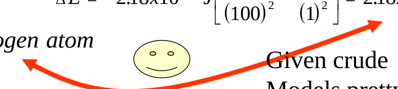
$$diameter_{hydrogen} = 52\,pm$$

$$E_{el} = \left(\frac{8.99x10^9\ Jm}{C^2}\right)\frac{(-1.60x10^{-19}C)(+1.60x10^{-19}C)}{\left(\frac{52x10^{-12}m}{2}\right)}$$

Do one from n=100 to 1

$$\Delta E = -2.18x10^{-18}J\left[\frac{1}{(100)^2} - \frac{1}{(1)^2}\right] = 2.18x10^{-18}J$$

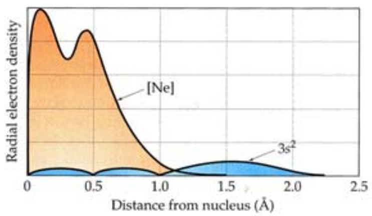
$$E_{el} = -4.48x10^{-18}\ J\ /\ hydrogen\ atom$$



Given crude Models pretty good

The thing that attracted me to science is the ability to come at a problem from a multitude of directions and get confirmation

Difference is electrostatic vs total energy)



Difficult to make a "real" calculation of Electron attraction to proton beyond Hydrogen

For Mg – $3s^2$ electrons "shielded" from positive charge by [Ne] core electrons

To deal with this a concept of

Effective nuclear charge is introduced

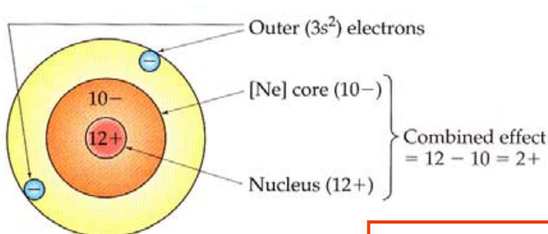
Charge experienced by added electrons is reduced by Inner electrons

Math Phobic Can sleep → Just keep track of ideas

Effective Nuclear Charge

$$Z_{eff} = Z - S$$ SIMPLE MODEL

Z = number of protons in nucleus
S = **average** number of electrons between nucleus and electron



$Mg = [Ne]3s^2$ $\quad Z_{eff} = 12 - 10_{Neon} = +2$

Do we expect Similar shielding From an s vs p orbital Electron?

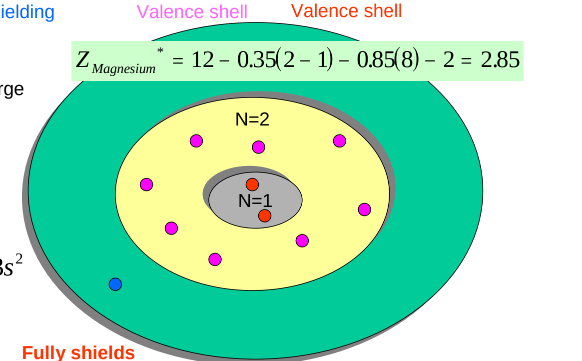
$$Z^* = Z - 0.35\left(\left(\sum_n s,p\right) - 1\right) - 0.85\sum_{n-1} s,p - \sum_0^{n-2} s,p,$$

Outer valence shielding — inner Valence shell — innermost Valence shell

Expanded model Effective Nuclear Charge

Effective Nuclear charge Felt by "last" electron

$$Z_{Magnesium}^* = 12 - 0.35(2-1) - 0.85(8) - 2 = 2.85$$



$Mg = [Ne]3s^2$

$Z = 12$

Fully shields

Mg: $2s^1 2s^2 2p^6 1s2$ ← Shields only a little (0.35)

Shields a lot (0.85)

Effective Nuclear Charge

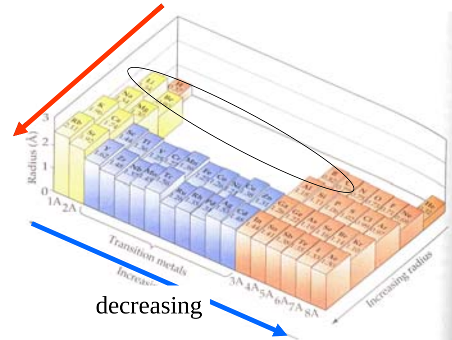
Snork,
Bst, huh? Math Phobic wake up here

1. Decreases with increased orbital distance from nucleus
2. Within a row (general orbital distance from nucleus) increases with electrons because they do not fully shield increasing positive charge of protons added.
3. Effect depends greatly on the orbital type so the rule (2) is not perfect

---

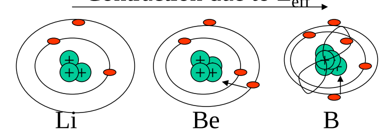
1. Size increases down table as we increase 'n' effective nuclear charge is lower

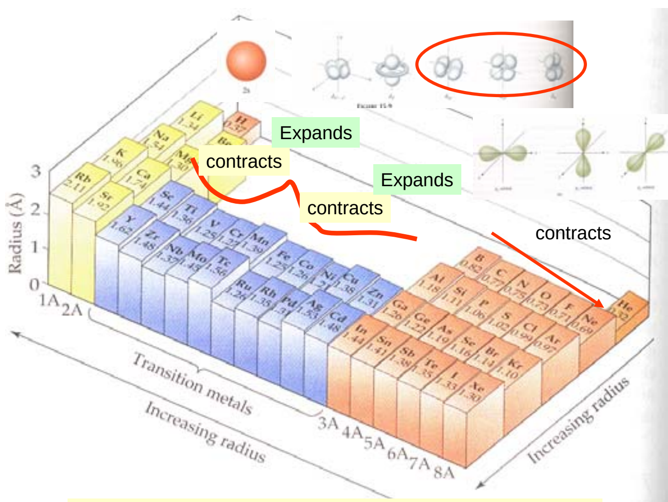
2. Size **decreases** as we move Across the periodic table. Effective nuclear charge increases due to incomplete electron shielding



Remember in any given row we are at some approximate orbit from the center of the positively charged nucleus. As we add more protons for each element we increase positive charge. This draws the electrons within that 'n' value in.

Contraction due to Z_{eff}





Adding 1e to each of any three d orbitals results in pretty good Shielding – next electron not held as tightly

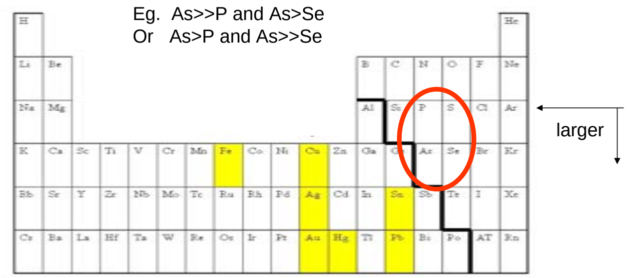
---

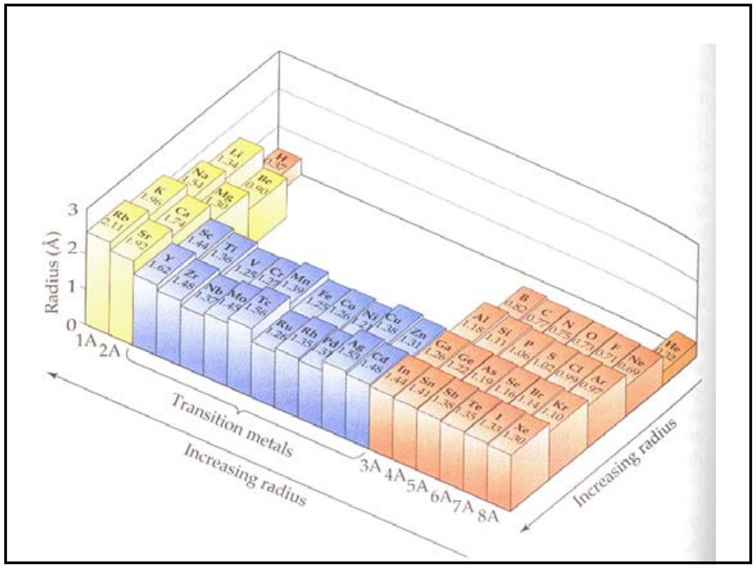
Organize the following atoms in order of increasing size by referring to the periodic table

P, S, As, Se

As>P, Se>S
As>Se
As>P,,Se>S
But P vs Se?
Eg. As>>P and As>Se
Or As>P and As>>Se

Question which trend is greater? Horizontal or Down?





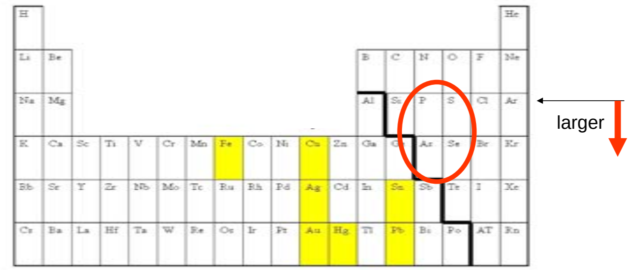
Organize the following atoms in order of increasing size by Referring to the periodic table

P, S, As, Se

As>P,,Se>S
Is As>>P and As>Se
Or As>P and As>>Se

Question which trend is greater?
Horizontal or Down (with exceptions)

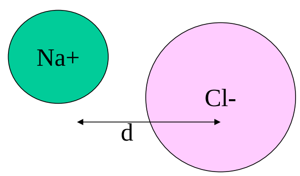
As>Se>P>S



Periodic Properties of the Elements

$$E_{el} = \frac{\kappa Q_1 Q_2}{d}$$

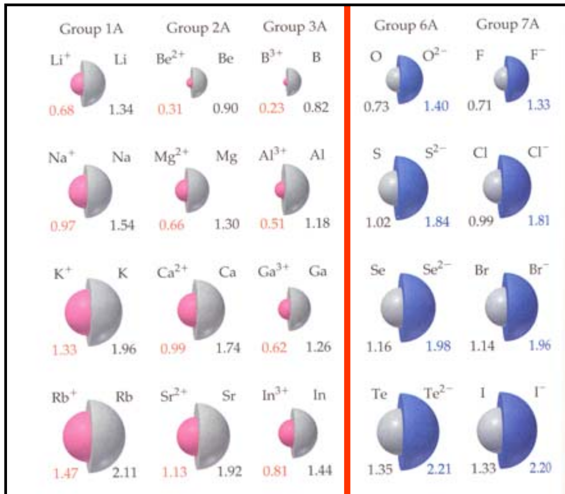
$$k = \frac{8.99x10^9\ J - m}{(C_{oulomb})^2}$$



Chemistry Rule #1 = it's all about Charge and How To Balance Positive and Negative Charge

Nuclear Positive charge affects

1. Atomic size (pull on atom's own electrons)
2. Ionic size (more pull on atom's remaining electrons)



Cations smaller than atoms (Lose electrons) WHY?

Anions larger than atoms (Gain electrons) WHY?

Arrange in order of decreasing size Mg^{2+}, Ca^{2+}, Ca

Cations smaller than their atoms: **Ca^{2+} <Ca**

Ca is lower in periodic table than Mg: **Mg<Ca and Mg^{2+} < Ca^{2+}**

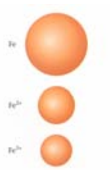
Ca > Ca^{2+} > Mg^{2+}

Order the size of the Following:

Fe, Fe^{2+}, Fe^{3+}

Order the size of the Following:

Fe, Fe^{2+}, Fe^{3+}

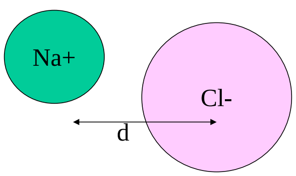


Fe> Fe^{2+} > Fe^{3+}

Periodic Properties of the Elements

$$E_{el} = \frac{\kappa Q_1 Q_2}{d}$$

$$k = \frac{8.99x10^9\ J-m}{\left(C_{oulomb}\right)^2}$$



Chemistry Rule #1 = it's all about Charge and How To Balance Positive and Negative Charge

Nuclear Positive charge affects

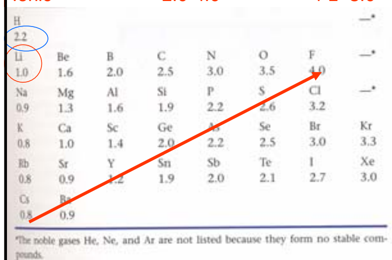
1. Atomic size (pull on atom's own electrons)
2. Ionic size (more pull on atom's remaining electrons)
3. Ability to attract somebody else's electrons into forming a covalent bond (electronegativity)
4. Ability to lose electrons (ionization potentials)

Pauling's Electronegativity scale

A measure of ability of an element to attract via
Electrostatic charge the electrons of a second atom
And hence, engage in covalent bonding

$\Delta E.N. = (E.N._A - E.N._B) = measure \ \ of \ \ polarity$ Separation of charg

Covalent, non-polar	0 to 0.5	2.2-2.2=0	H-H	very high bond energy
Covalent, polar	0.5 to 2.0	4-2.2=1.7	HF	Weak Acid (F holds onto H)
Ionic	2.0-4.0	4-1=3.0	LiF	Electrolyte



H 2.2							
Li 1.0	Be 1.6	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	—*
Na 0.9	Mg 1.3	Al 1.6	Si 1.9	P 2.2	S 2.6	Cl 3.2	—*
K 0.8	Ca 1.0	Sc 1.4	Ge 2.0	As 2.2	Se 2.5	Br 3.0	Kr 3.3
Rb 0.8	Sr 0.9	Y 1.2	Sn 1.9	Sb 2.0	Te 2.1	I 2.7	Xe 3.0
Cs 0.8	Ba 0.9						

*The noble gases He, Ne, and Ar are not listed because they form no stable compounds.

Electronegativity increases across
And up towards F

Linus Pauling
U.S.A.
CalTec
1901-1994
Chemist
Electronegativity 1934

Properties and Measurements

Property	Unit	Reference State
Size	m	size of earth
Volume	cm^3	m
Weight	gram	mass of 1 cm^3 water at specified Temp (and Pressure)
Temperature	°C, K	boiling, freezing of water (specified Pressure)
$1.66053873 \times 10^{-24}$g	amu	(mass of 1C-12 atom)/12
quantity	mole	atomic mass of an element in grams
Pressure	atm, mm Hg	earth's atmosphere at sea level

$$P = \frac{F}{A} = \frac{ma}{A} = \frac{\frac{kg \cdot m}{s^2}}{m^2} = \frac{kg}{m s}$$

Energy, General

electronic states in atom **Energy of electron in vacuum**
Electronegativity **F**

Allred-Rochow method

Relate Pauling's Electronegativity to
Effective Nuclear Charge (It's all about charge!)

$$Bond \ \ Energy\big|_{AB} = Energy_{covalent} + Energy_{electronegativity}$$

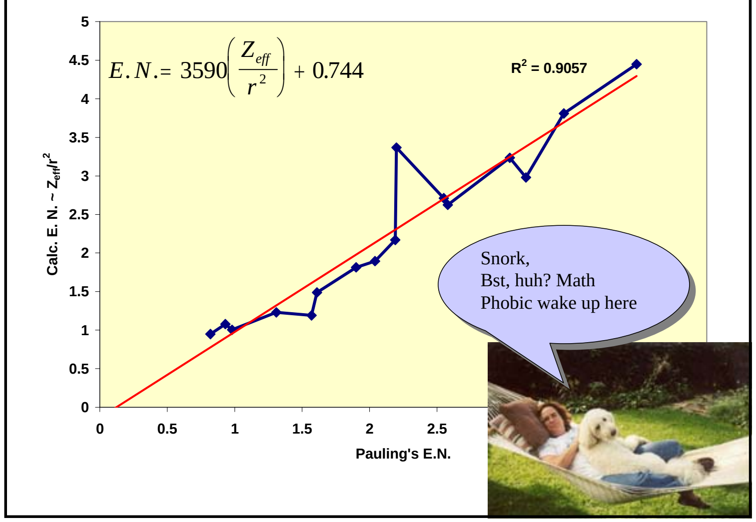
$$E_{el} = \frac{kQ_1Q_2}{d} \longleftrightarrow Energy_{ionic} \propto \frac{charge}{size}$$

$$Energy_{electronegativity} = 3590\left(\frac{Z^*}{r^2}\right) + 0.744$$

Z* = effective nuclear charge
R = covalent radius of atom in pm

$$Z^* = Z - 0.35\sum_{n} s,p - 0.85\sum_{n-1} s,p,d,f - \sum_{0}^{n-2} s,p,d,f$$

Outer valence shielding — First inner Valence shell — innermost Valence shells



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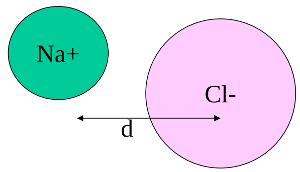

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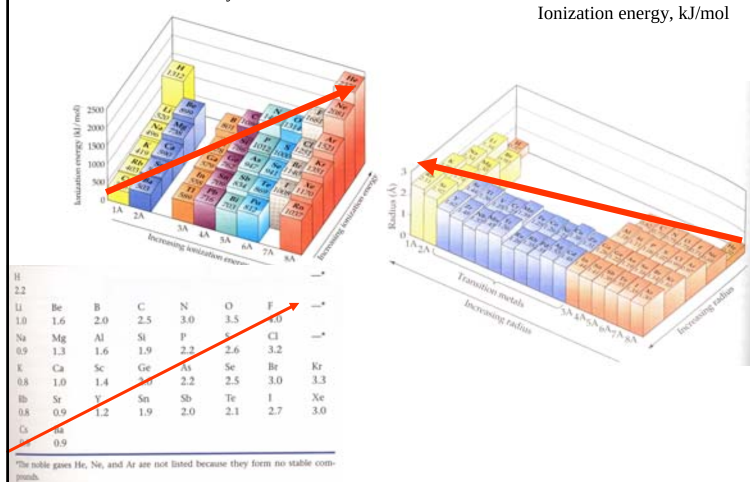
1. Atomic size (pull on atom's own electrons)
2. Ionic size (more pull on atom's remaining electrons)
3. Ability to attract somebody else's electrons into forming a covalent bond (electronegativity)
4. **Ability to lose electrons (ionization potentials)**

Who has the least ability to hold onto it's electrons?

$$M_{(g)} + energy \rightarrow M^{+}_{(g)} + 1e_{(g)}$$

Ionization energy, kJ/mol



Ionization energy follows size trends; which are a function of Z_{eff}

Ionization energies increase
a) with greater effective nuclear charge
b) $I_3 > I_2 > I_1$
c) **I_{inner} shell electrons > I_{outer} shell electrons**

I_1 $\quad M_{(g)} + energy \rightarrow M^{+}_{(g)} + 1e_{(g)}$

I_2 $\quad M^{+}_{(g)} + energy \rightarrow M^{2+}_{(g)} + 1e_{(g)}$

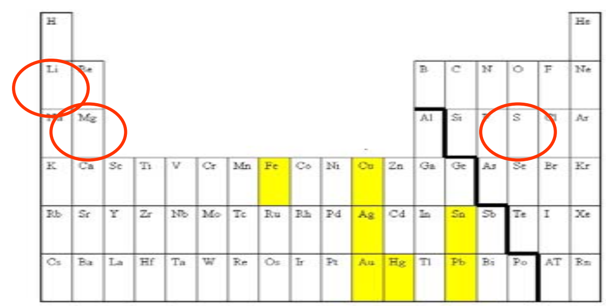
I_3 $\quad M^{2+}_{(g)} + energy \rightarrow M^{3+}_{(g)} + 1e_{(g)}$

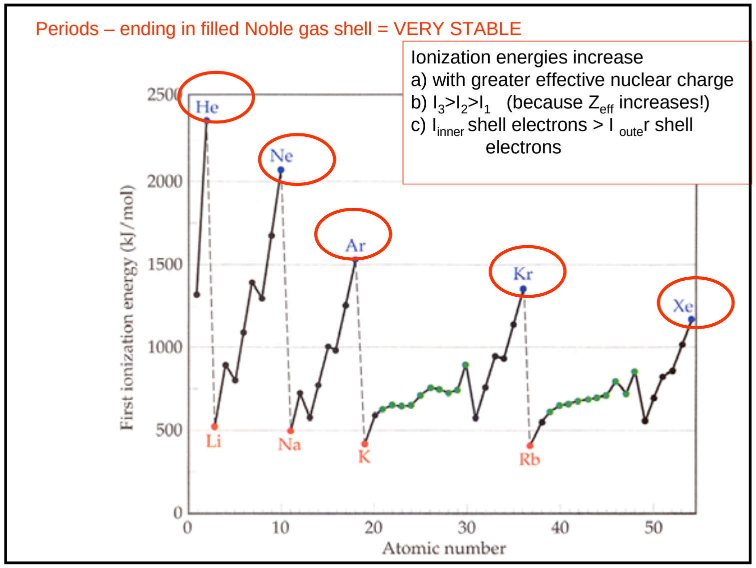
TABLE 7.2 Successive Values of Ionization Energies, I, for the Elements Sodium through Argon (kJ/mol)

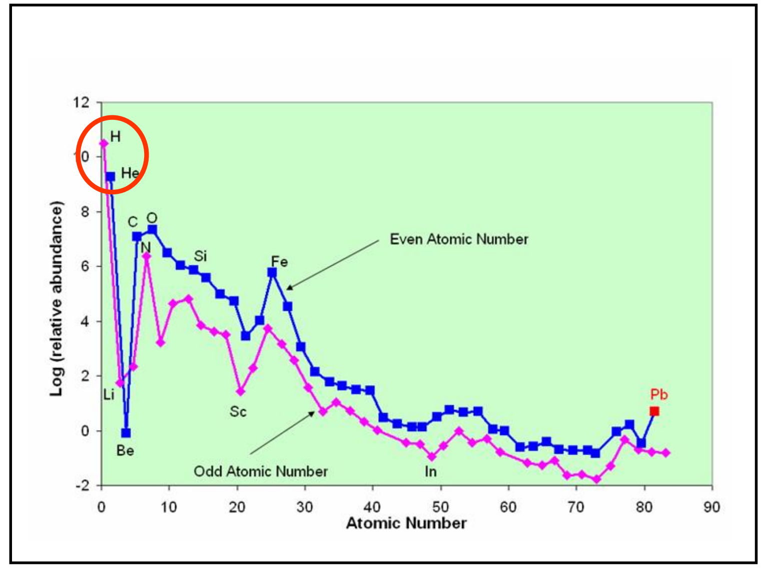
Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	496	4560			(inner-shell electrons)		
Mg	738	1450	7730				
Al	578	1820	2750	11,600			
Si	786	1580	3230	4360	16,100		
P	1012	1900	2910	4960	6270	22,200	
S	1000	2250	3360	4560	7010	8500	27,100
Cl	1251	2300	3820	5160	6540	9460	11,000
Ar	1521	2670	3930	5770	7240	8780	12,000

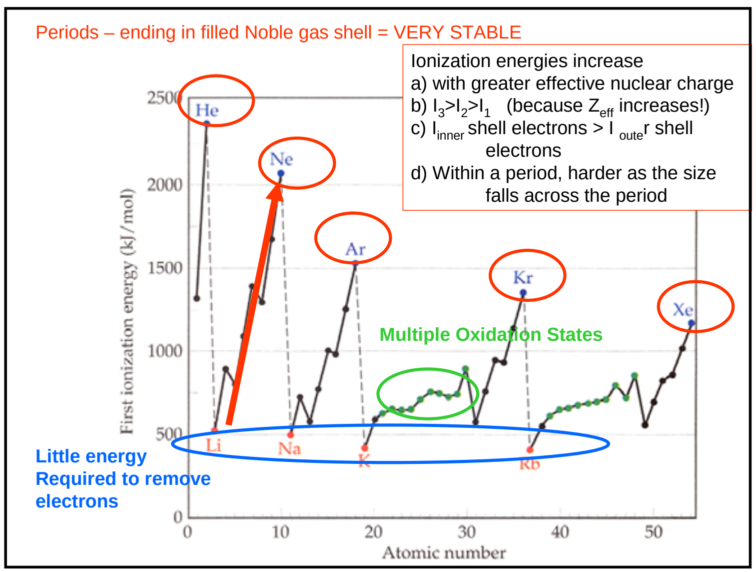
Predict the which of the circled elements has the largest **second ionization** energy

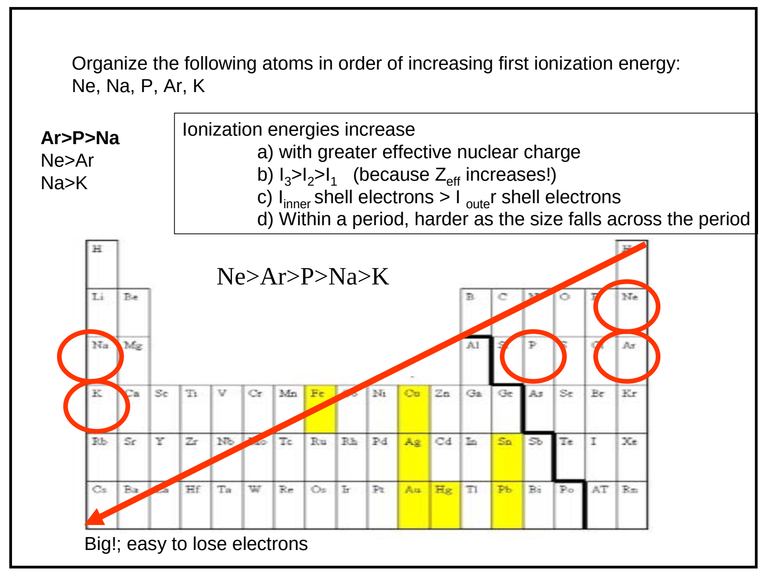
For Li to lose a second electron would have to come from an inner shell




Periods – ending in filled Noble gas shell = VERY STABLE
Ionization energies increase
a) with greater effective nuclear charge
b) $I_3 > I_2 > I_1$ (because Z_{eff} increases!)
c) I_{inner} shell electrons > I_{outer} shell electrons
He
Ne
Ar
Kr
Xe
Li
Na
K
Rb
First ionization energy (kJ/mol)
Atomic number


H
He
Li
Be
C
N
O
Si
Sc
Fe
Even Atomic Number
Odd Atomic Number
In
Pb
Log (relative abundance)
Atomic Number


Periods – ending in filled Noble gas shell = VERY STABLE
Ionization energies increase
a) with greater effective nuclear charge
b) $I_3 > I_2 > I_1$ (because Z_{eff} increases!)
c) I_{inner} shell electrons > I_{outer} shell electrons
d) Within a period, harder as the size falls across the period
Multiple Oxidation States
Little energy Required to remove electrons
He
Ne
Ar
Kr
Xe
Li
Na
K
Rb
First ionization energy (kJ/mol)
Atomic number


Organize the following atoms in order of increasing first ionization energy:
Ne, Na, P, Ar, K
Ar>P>Na
Ne>Ar
Na>K
Ionization energies increase
a) with greater effective nuclear charge
b) $I_3 > I_2 > I_1$ (because Z_{eff} increases!)
c) I_{inner} shell electrons > I_{outer} shell electrons
d) Within a period, harder as the size falls across the period
Ne>Ar>P>Na>K
Big!; easy to lose electrons

"A" students work (without solutions manual)

~ 10 problems/night.

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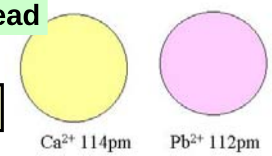
Why Size Matters! – Toxicity of Lead

$Ca = [Ar]4s^2$

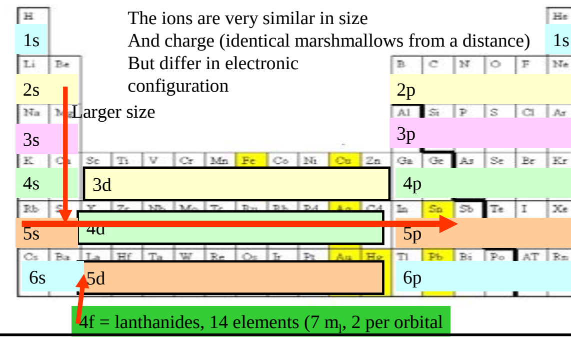
$Ca^{2+} = [Ar]$



$Pb = [Xe]6s^2 4f^{14} 5d^{10} 6p^2$

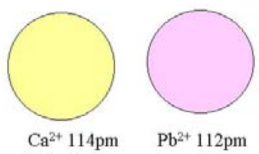
$Pb^{2+} = [Xe]6s^2 4f^{14} 5d^{10}$

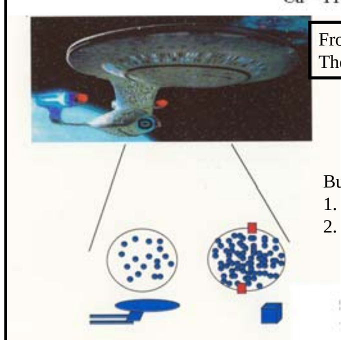
The ions are very similar in size
And charge (identical marshmallows from a distance)
But differ in electronic configuration



$Ca^{2+} = [Ar]$

$Pb^{2+} = [Xe]6s^2 5d^{10}$



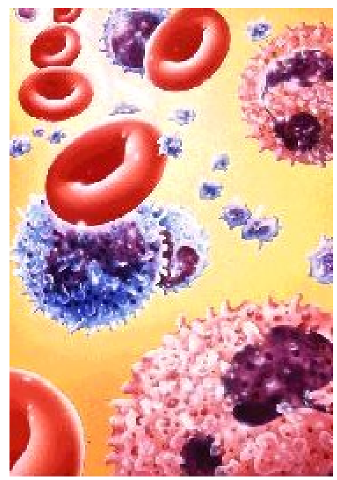


From a distance both Ca^{2+} and Pb^{2+} behave similarly. They both experience a similar electrostatic attraction.

$$E_{el} = \frac{\kappa Q_1 Q_2}{d}$$

But when they dock at the docking bay, Pb^{2+} has

1. more electrons, **and**
2. two lose cannons (the 2s electrons) which require space and orientation.



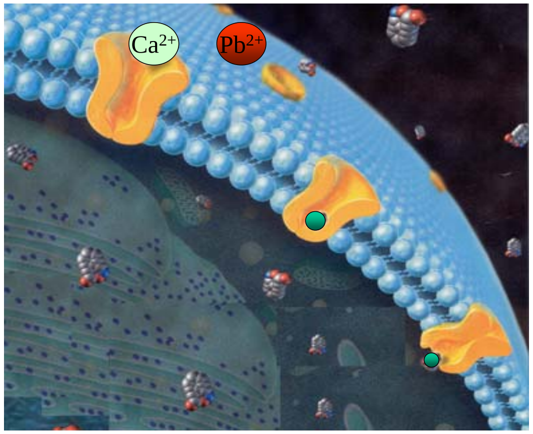
94-99% of lead attached to external surfaces of erythrocytes

1-6% lead in plasma, of which 99% attached to proteins

~0.1 to 0.6 % of lead is as the free cation

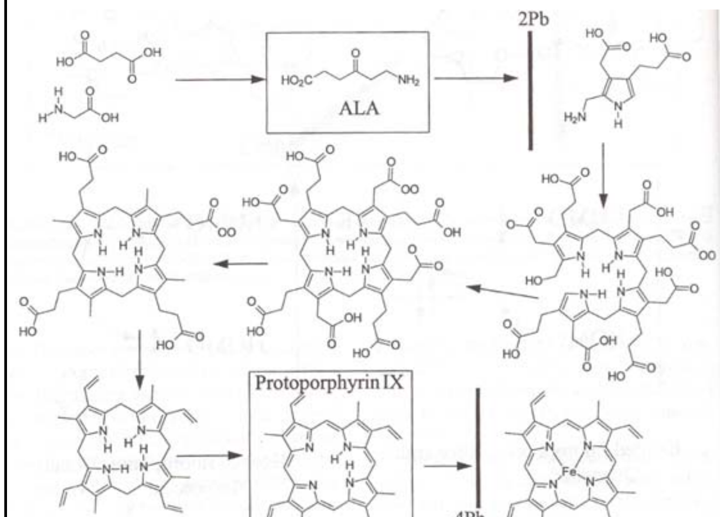
Passive Uptake from stomach to blood

Recognition will be similar for various species



Active uptake of calcium, apparently to lesser extent other divalent similar sized cations, including lead.

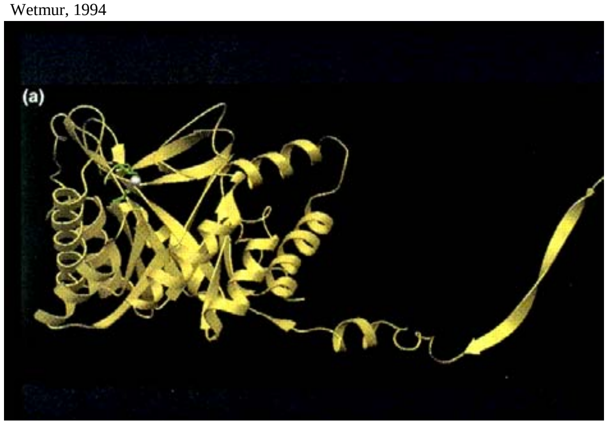
Calcium uptake is controlled by Vitamin D and growth regulators parathyroid hormone (PTH)



Warren et al, TIBS, 1998, 23, 217

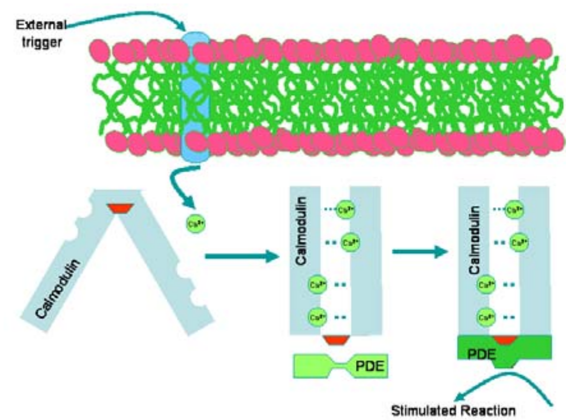
An estimated 40% of lead in blood plasma bound to ALAD

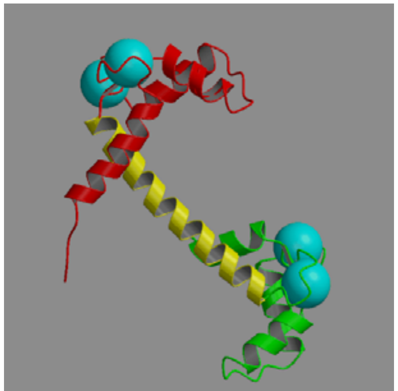
Wetmur, 1994



ALAD dehydratase with lead binding site

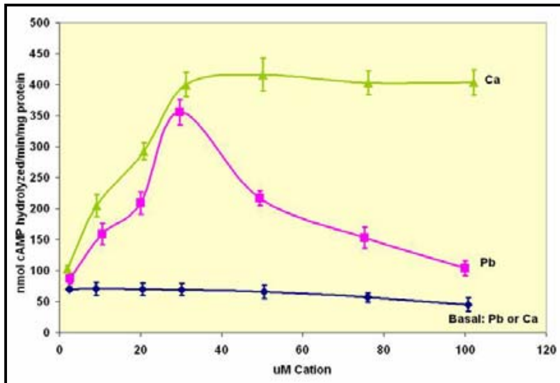
Calcium is closely monitored by kidney because it plays a large role in various signalling processes





Calcium bound to calmodulin

C. Yang, G. S. Jas, K. Kuczera, J. Biomolecular Structural Dynamics, 2001, 19,257-271

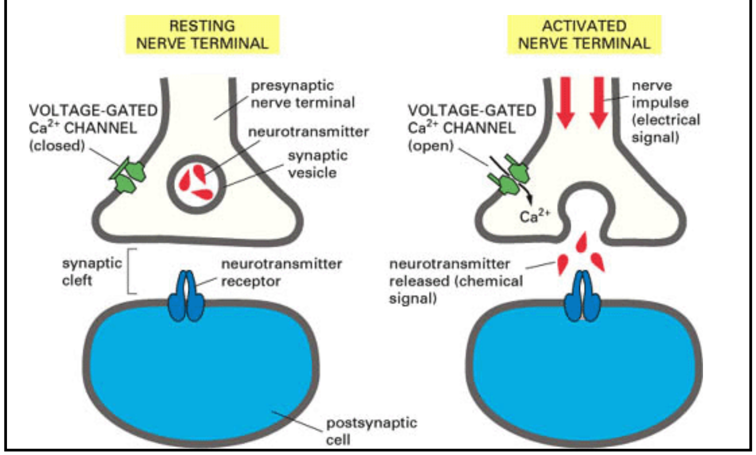


Lead double whammy

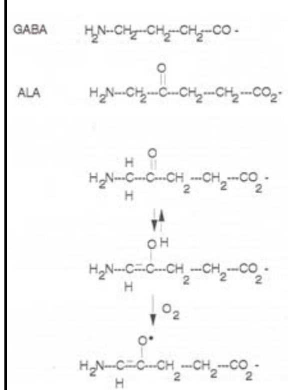
1. Low lead turns on triggers
2. Hi lead turns off triggers

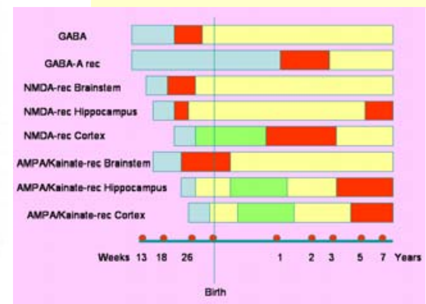
Calcium serves as a trigger for muscle contractions: troponin C

Seizures can result from lead due to Ca triggers of the synapses

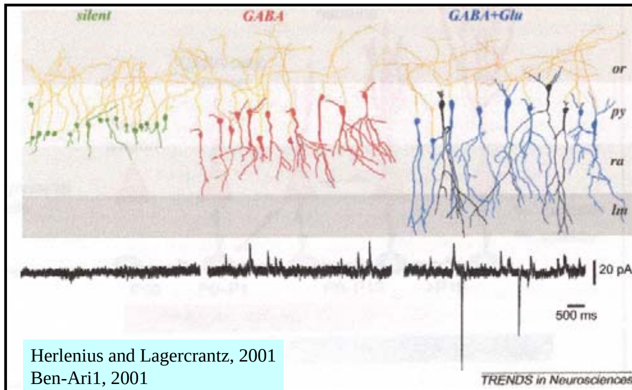


Because lead affected ALAD resulting in overproduction of ALA ALA may also affect the function of GABA but a close similarity in molecular structure



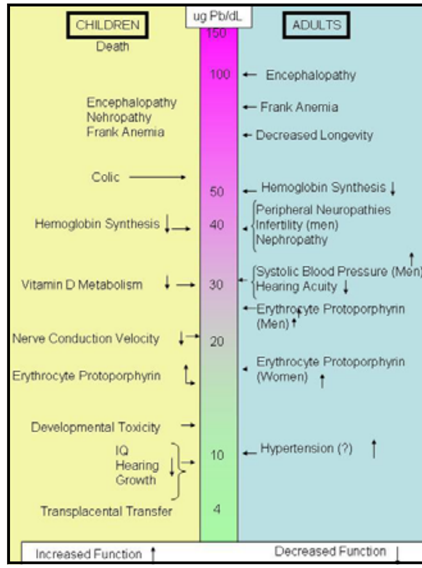


GABA controls leaf tip growth, and brain development. Function changes with time, so growing tips and infants differentially affected from adults



Herlenius and Lagercrantz, 2001
Ben-Ari1, 2001

<u>Certain portions of the brain more greatly affected</u>:
prefrontal cortex: problem solving
hippocampus (memory)
cerebellum (motor coordination, body movement, posture and balance)



"A" students work
(without solutions manual)
~ 10 problems/night.

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