



NATIONAL MATH + SCIENCE INITIATIVE

AP CHEMISTRY

Atomic Structure and Periodicity

2016 EDITION
PRESENTER

Periodic Table of the Elements

1 H 1.0079																	2 He 4.0026	
3 Li 6.941	4 Be 9.012																9 F 19.00	10 Ne 20.179
11 Na 22.99	12 Mg 24.30																17 Cl 35.453	18 Ar 39.948
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.938	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80	
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 93.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.91	54 Xe 131.29	
55 Cs 132.91	56 Ba 137.33	57 *La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.2	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)	
87 Fr (223)	88 Ra 226.02	89 †Ac 227.03	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 § (269)	111 § (272)	112 § (277)	§Not yet named						

*Lanthanide Series:		58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.4	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
†Actinide Series:		90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

AP Chemistry Equations & Constants

Throughout the test the following symbols have the definitions specified unless otherwise noted.

L, mL = liter(s), milliliter(s)

g = gram(s)

nm = nanometer(s)

atm = atmosphere(s)

mm Hg = millimeters of mercury

J, kJ = joule(s), kilojoule(s)

V = volt(s)

mol = mole(s)

ATOMIC STRUCTURE

$$E = h\nu$$

$$c = \lambda\nu$$

E = energy

ν = frequency

λ = wavelength

Planck's constant, $h = 6.626 \times 10^{-34}$ J s

Speed of light, $c = 2.998 \times 10^8$ m s⁻¹

Avogadro's number = 6.022×10^{23} mol⁻¹

Electron charge, $e = -1.602 \times 10^{-19}$ coulomb

EQUILIBRIUM

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}, \text{ where } a A + b B \rightleftharpoons c C + d D$$

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_b = \frac{[OH^-][HB^+]}{[B]}$$

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$
$$= K_a \times K_b$$

$$\text{pH} = -\log [H^+], \text{ pOH} = -\log [OH^-]$$

$$14 = \text{pH} + \text{pOH}$$

$$\text{pH} = \text{p}K_a + \log \frac{[A^-]}{[HA]}$$

$$\text{p}K_a = -\log K_a, \text{ p}K_b = -\log K_b$$

Equilibrium Constants

K_c (molar concentrations)

K_p (gas pressures)

K_a (weak acid)

K_b (weak base)

K_w (water)

KINETICS

$$\ln[A]_t - \ln[A]_0 = -kt$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$t_{1/2} = \frac{0.693}{k}$$

k = rate constant

t = time

$t_{1/2}$ = half-life

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

$$P_A = P_{\text{total}} \times X_A, \text{ where } X_A = \frac{\text{moles A}}{\text{total moles}}$$

$$P_{\text{total}} = P_A + P_B + P_C + \dots$$

$$n = \frac{m}{M}$$

$$K = ^\circ\text{C} + 273$$

$$D = \frac{m}{V}$$

$$KE \text{ per molecule} = \frac{1}{2}mv^2$$

Molarity, M = moles of solute per liter of solution

$$A = abc$$

P = pressure

V = volume

T = temperature

n = number of moles

m = mass

M = molar mass

D = density

KE = kinetic energy

v = velocity

A = absorbance

a = molar absorptivity

b = path length

c = concentration

Gas constant, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

$$= 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$= 62.36 \text{ L torr mol}^{-1} \text{ K}^{-1}$$

1 atm = 760 mm Hg

$$= 760 \text{ torr}$$

STP = 0.00°C and 1.000 atm

THERMOCHEMISTRY/ ELECTROCHEMISTRY

$$q = mc\Delta T$$

$$\Delta S^\circ = \sum S^\circ \text{ products} - \sum S^\circ \text{ reactants}$$

$$\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= -RT \ln K$$

$$= -nFE^\circ$$

$$I = \frac{q}{t}$$

q = heat

m = mass

c = specific heat capacity

T = temperature

S° = standard entropy

H° = standard enthalpy

G° = standard free energy

n = number of moles

E° = standard reduction potential

I = current (amperes)

q = charge (coulombs)

t = time (seconds)

Faraday's constant, $F = 96,485$ coulombs per mole of electrons

$$1 \text{ volt} = \frac{1 \text{ joule}}{1 \text{ coulomb}}$$



ATOMIC STRUCTURE AND PERIODICITY

PES, Electron Configurations, and Trends

What I Absolutely Have to Know to Survive the AP Exam

The following might indicate that the question deals with atomic structure and periodicity: Wavelength, frequency, energy spectrum, quantum mechanics, orbitals, energy levels, electron clouds, electron configurations, Coulomb's Law, electrostatic potential energy, ionization energy, atomic and ionic radius, electronegativity, ionic charges, etc...

THE ATOM – *How Attractive!*

The atom is composed of negatively charged electrons, which can leave the atom, and a positively charged nucleus that is made of protons and neutrons.

- The attraction of the electrons to the nucleus is the basis of the structure of the atom.
- Coulomb's law is qualitatively useful for understanding the structure of the atom.

An electron in an atom remains in its lowest energy state (lowest shell allowed) unless it is energized

- Electrons in the first shell have the most negative electrostatic potential energy and are the most strongly attracted to the nucleus
- Electrons in shells farther from the nucleus have less negative electrostatic potential energies and are not as strongly attracted.

Why negative potential energies?

Think **Coulomb's Law**: $U_E \propto \frac{q_1 q_2}{d}$

- U_E is the electrostatic potential energy
- " q_1 " and " q_2 " are the charges
- d is the distance between the charges
- If the charges are opposite the force between the charges is attractive.
 - The attractive force between the positively charged nucleus and the negatively charged electron means the electrostatic potential energy is NEGATIVE.
 - Thus the more negative the U_E the stronger the attraction between the electron and the nucleus.

The Photoelectric Effect – *Uncle Albert's "Nobel" Contribution*

Light consists of photons, little "packets" of energy defined by $E = h\nu$, where h is Planck's constant and ν is the frequency of the light.

Albert Einstein discovered that when certain photons of light are shown directly on a substance, the electrons from the atoms of that material could be ejected – this is known as the Photoelectric Effect

- The removal of the electron depends not upon the intensity of the light, but on the photon having enough energy to eject the electron – i.e. overcome that electron's attraction to the nucleus, i.e. its electrostatic potential energy.
- $E = h\nu$, where h is Planck's constant and ν is the frequency of the light.
- Often light is measured based on the length of its wave (wavelength), so it is important to also know:

- $c = \lambda\nu$ so we can also note $E = h\nu = \frac{hc}{\lambda}$

- $c = \text{speed of light} = 3.0 \times 10^8 \text{ m/s}$ ALERT! Be prepared to see wavelengths in "nm" therefore you must convert the c from m to nm or remember $c = 3.0 \times 10^{17} \text{ nm/s}$

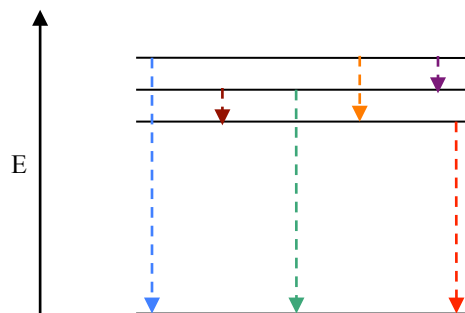
It's Spectral!

Based on these discoveries by Einstein and others, we know that certain amounts of energy must be applied to move an electron(s) in an atom from its ground state to a higher energy state (or to eject it).

If the electron is not ejected, it will return to its ground state (lowest energy state). To do so it releases energy equal to the energy absorbed moving it to the excited state – *what goes in must come out!!!*

- The energy released is detectable by measuring the specific wavelengths of Electromagnetic (EM) Radiation (light – often, visible light) emitted as the electron returns to the ground state. This is called the atom's *emission spectrum*.
- Ever seen a neon light? Fireworks? Put something with Cu in it in a flame? The colors you see in the form of light are the specific wavelengths of light emitted as the electron(s) transition to lower energy states.
- When you pass the energy (light) of a hydrogen atom's *emission spectrum* through a prism (diffraction) a resulting *line spectrum* can be observed.
- A line spectrum for an element is unique for that element since has a unique number of electrons, based on all of the possible transitions as an excited electron moves back to a lower energy state (not just the ground state). Some might not be in the visible range (think UV or IR) so we might not seem them – but they exist and can be measured.

$$\Delta E = h\nu = \frac{hc}{\lambda}$$



These changes in energy can be calculated, but become very complex for multi-electron atoms and this is also outside the scope of the AP Chemistry course.

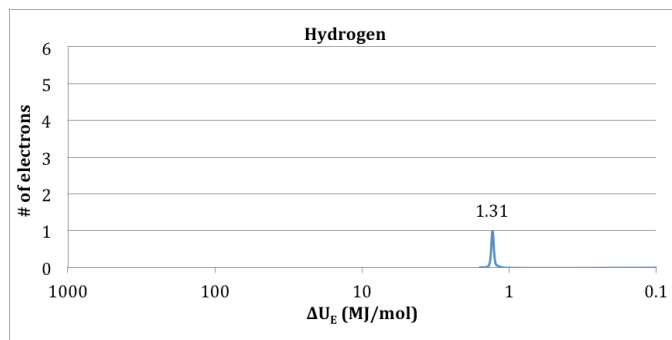
Photoelectron Spectroscopy – Eject, Eject, Eject!

The minimum energy needed to remove an electron from an atom or ion is defined as **ionization energy** and the energy required to remove the *least tightly held electron* is the **first ionization energy**.

Think back to **Coulomb's Law**: $U_E \propto \frac{q_1 q_2}{r}$

The farther an electron is from the nucleus, the less negative its electrostatic potential energy, the less energy required to remove it, the lower its ionization energy.

Photoelectron spectroscopy (PES) is used to measure these energies and provide a method to deduce the shell structure of the atom. Below is the PES spectrum for Hydrogen



Each peak represents the change in electrostatic potential energy that was required to move the electron from its ground state to some distance infinitely far from the nucleus (where it is no longer attracted) – we will call this ejecting the electron.

The intensity of the photoelectron signal is a measure of the number of electrons in that energy level.

Hydrogen only has **one electron**, so it has **one peak** with a **change** in electrostatic potential energy of:

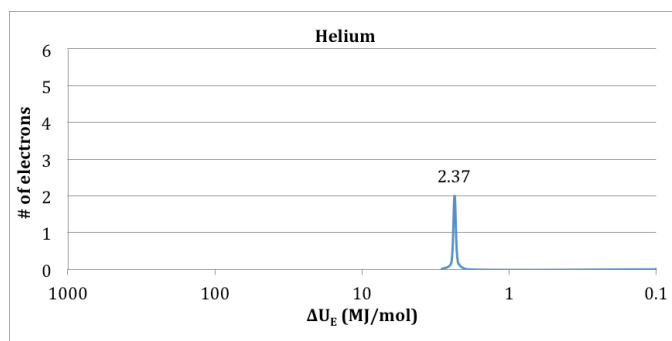
$$\Delta U_E = (U_E \text{ at an infinite distance from the nucleus}) - (U_E \text{ for the electron in its ground state})$$

$$\Delta U_E = 0 \text{ MJ/mol} - (-1.31 \text{ MJ/mol}) = 1.31 \text{ MJ/mol}$$

The intensity signal (amplitude) of the peak represents one electron.

Look at the PES data for Helium: Both electrons in He are considered to be identical, thus the **change** in electrostatic potential energy for *either of them (singularly)* is the same, 2.37 MJ/mol.

The intensity signal (amplitude) of the peak represents two electrons.

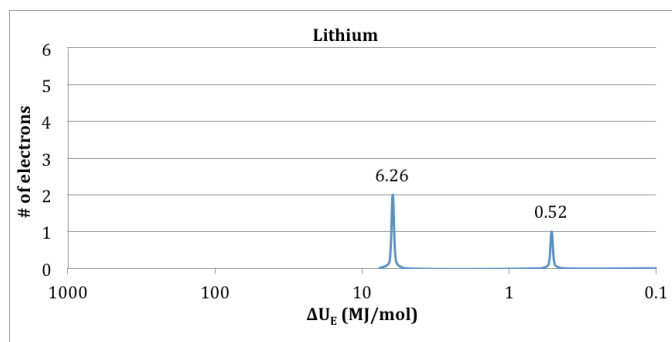


Notice that the energy is slightly greater than that for hydrogen. Why?

- It is all about the nucleus! He has 2 protons and there is only one in H. The higher the nuclear charge, the higher the ionization energy of an electron within a given energy shell.

Photoelectron Spectroscopy – PES, PES, Eject, Eject, Eject! Con't

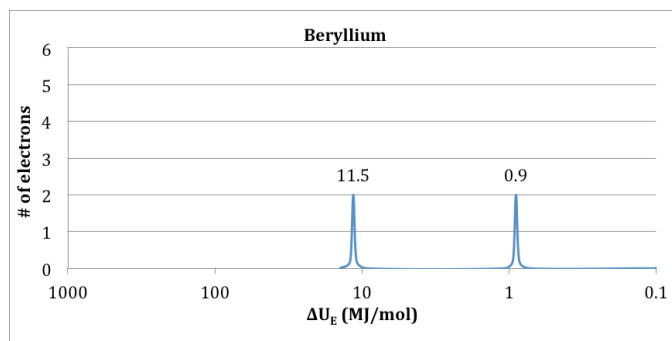
Let's move to the 2nd Period and look at lithium's PES; Li has 3 electrons.



We now see 2 different energy peaks. The one most attracted to the nucleus (6.36 MJ/mol) has 2 electrons and the other has 1. Why the difference?

- There are two shells of electrons in Li – H and He (1st Period elements) have only one shell (energy level) of electrons
- Also notice, the outermost electron (0.52 MJ/mol) is further from the nucleus than the outermost electron(s) in H or He (1.31 MJ/mol and 2.37 MJ/mol)
 - It takes less energy to remove it – i.e. its ionization energy is less than that of H or He.

Look at beryllium's PES; Be has 4 electrons.



Just as expected we see 2 different energy peaks with 2 electrons in each peak.

Which electron requires the least amount of energy to remove?

- Either of the two electrons in the 0.9 MJ/mol peak.

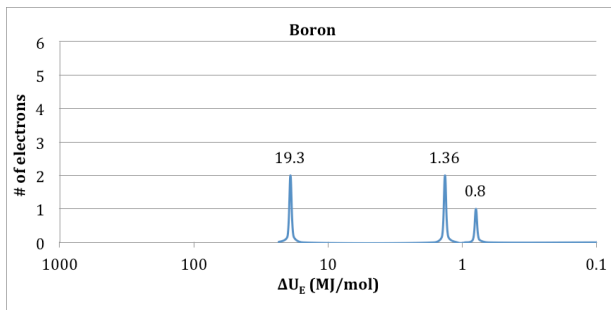
Both peaks in Be are closer to the nucleus than in Li. Why?

- It is all about the nucleus! Li has 3 protons and Be has 4. The higher the nuclear charge, the more energy required to remove the electron within any given energy shell, i.e. in Be, the electrons are more tightly held and are closer to the nucleus.

Next comes boron; B has 5 electrons.

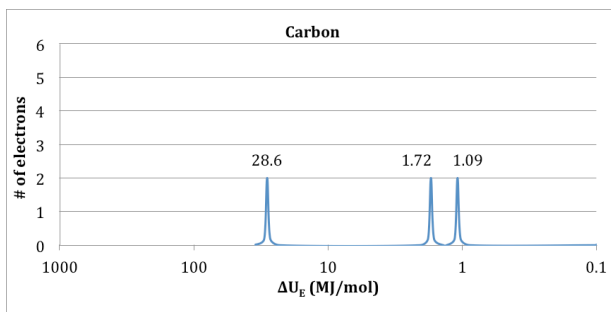
What do you expect?

Photoelectron Spectroscopy – PES, PES, Eject, Eject, Eject! Con't



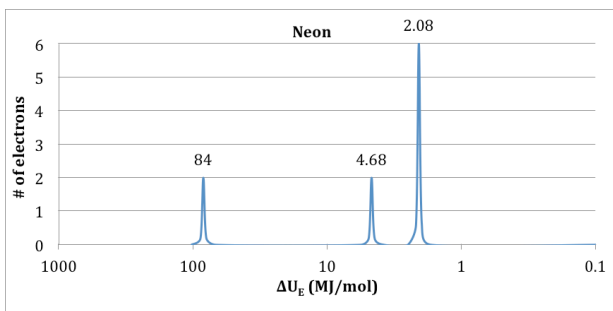
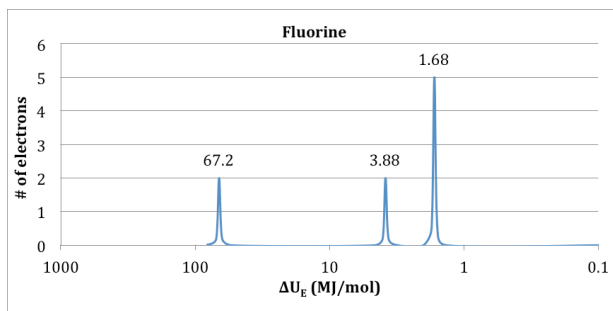
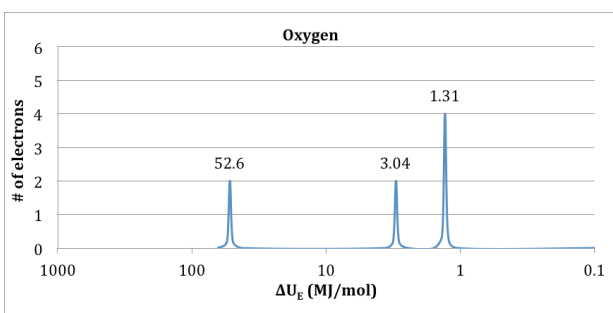
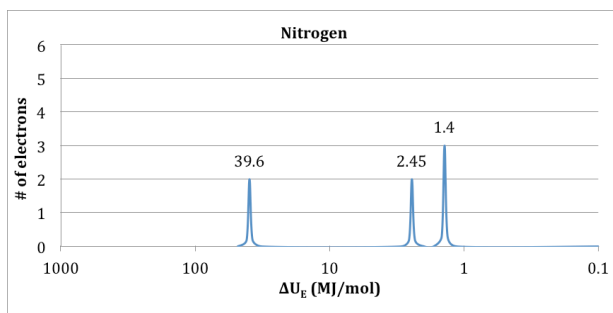
Why is there another peak, we didn't move to Period 3, we are still in Period 2?

- The electron in the 0.8 MJ/mol peak is a new “sublevel” of electrons within the 2nd energy level.



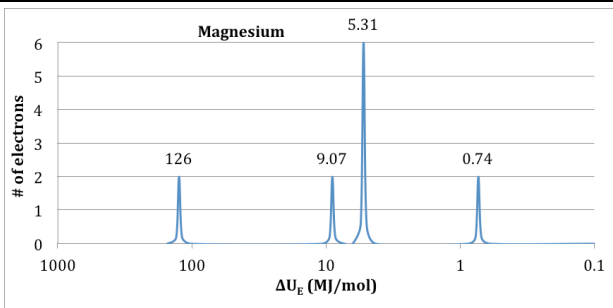
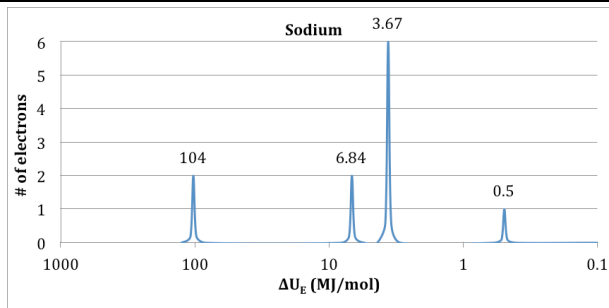
Carbon is similar to boron, it has 2 electrons in the first shell, and in the second shell (energy level) it has 2 electrons in the 1st peak (subshell). In the 2nd peak (subshell) it has 2 electrons where B has 1.

As you move through the rest of the Period 2 elements you will see 1 additional electron added to the 2nd subshell of the 2nd shell

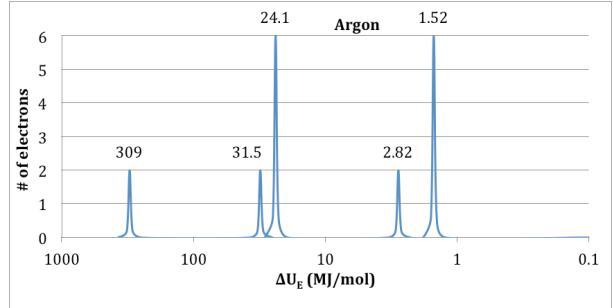
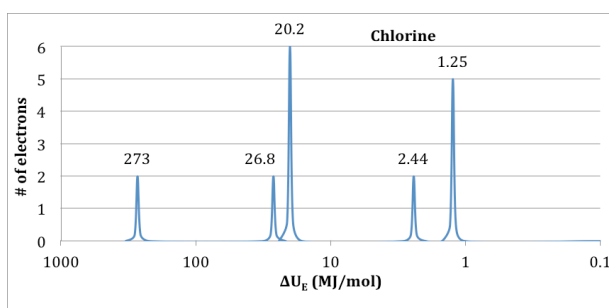
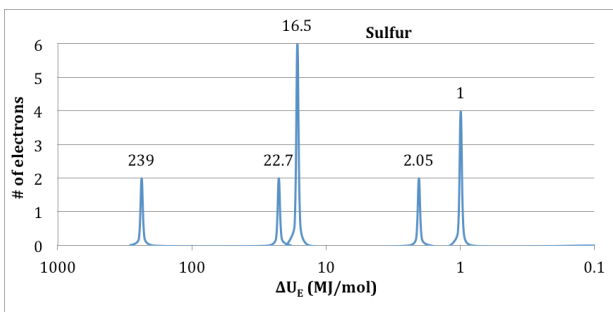
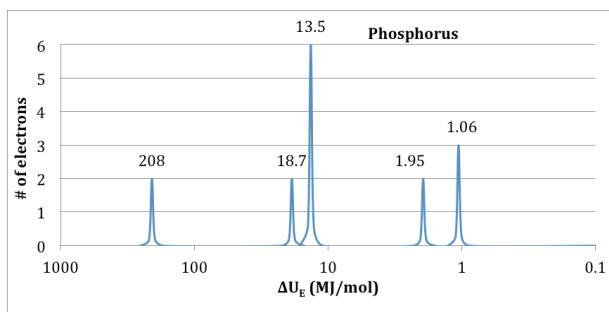
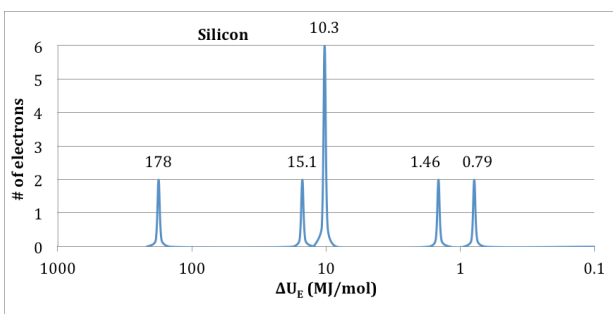
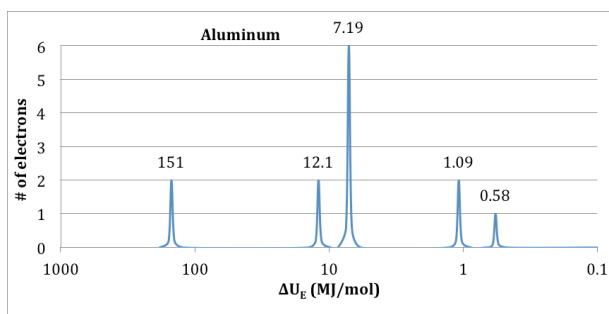


Notice again, the least tightly held electron in Ne requires less energy to remove than the least tightly held electron in Li. Same reason as before – Li has 3 protons and Ne has 10. The higher the nuclear charge, the more energy required to remove the electron within any given energy shell/subshell (and the closer they are to the nucleus).

Photoelectron Spectroscopy – PES, PES, Eject, Eject, Eject! Con't



The first 2 elements of Period 3 have electron(s) in a new peak – the 1st subshell of shell 3. Notice again, the least tightly held electron in Na requires less energy to remove than the least tightly held electron in Mg. Same reason as before – Na has 11 protons and Mg has 12. The higher the nuclear charge, the more energy required to remove the electron within any given energy shell/subshell.



The next 6 elements have electron in the 2nd subshell of shell 3.

Do you see a pattern? The first peak in the 1st energy shell has a maximum of 2 electrons; the 1st peak in the 2nd energy shell has a max of 2 electrons and the 2nd peak has a max of 6 electrons; the 1st peak in the 3rd energy shell has a maximum of 2 electrons and the 2nd peak has a maximum of 6 electrons.

Electron Arrangements – *The Data Says So!*

The pattern from the PES Data is clear...

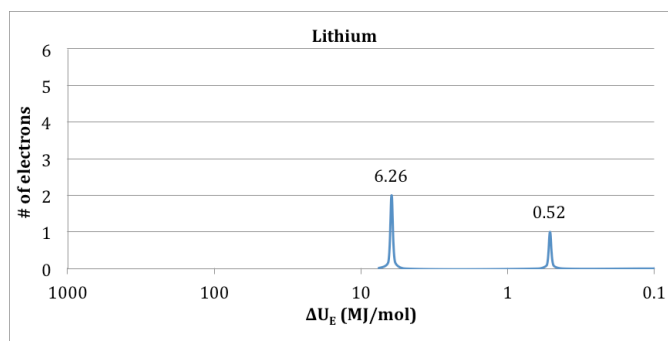
- Each electron in an atom has a specific ionization energy, thus it is located in a specific place
- The electrons can be thought of as being located in shells and subshells that make up the electron cloud
 - Inner shell electrons are called core electrons
 - Outer shell electrons are called valence electrons

Based on the PES Data each shell is comprised of 1 or more subshells. Using this concept, the electronic arrangement of an atom can be described using an **electron configuration**

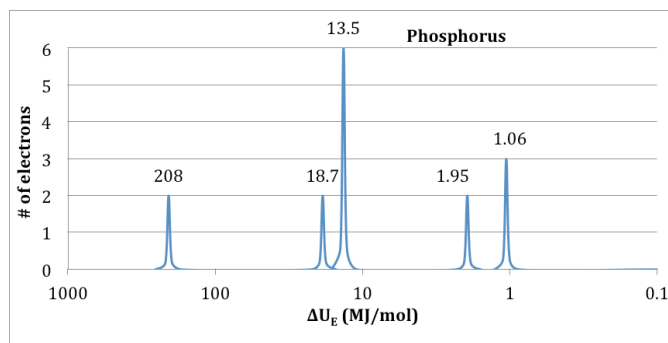
- This “configuration” is based on Schrodinger’s Quantum Model, based on the wave functions that determine the allowed energy states of an electron.
- These allowed states called “atomic orbitals” reflect the quantum numbers that describe the different quantized energy states of an electron.

Here is what we know:

- The FIRST “energy peak” or subshell in a given energy shell is called an “s subshell”
 - Made up of 1 “orbital” thus describes a maximum of 2 electrons
- The SECOND “energy peak” or subshell in a given energy shell is called a “p subshell”
 - Made up of 3 “orbitals” thus describes a maximum of 6 electrons



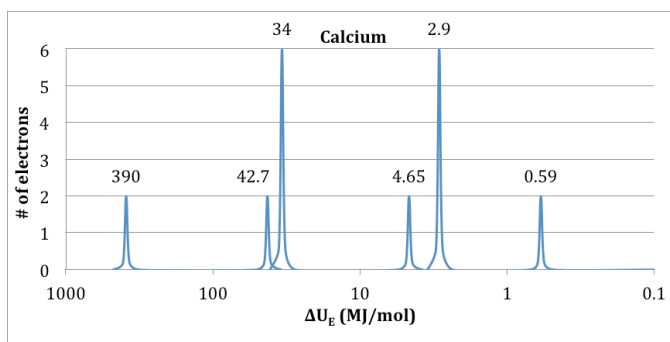
Look again at lithium, Li: It has 2 energy shells – each shell has one “peak” or subshell. The 1st subshell has 2 electrons and the 2nd has 1, thus its electron configuration is: $1s^2 2s^1$



Look at phosphorus, P: It has 3 energy shells – the 1st shell has one “peak” or subshell, the 2nd shell has 2 subshells, one with 2 electrons and one with 6. The 3rd shell has 2 subshells, one with 2 electrons and one with 3. Its electron configuration is: $1s^2 2s^2 2p^6 3s^2 3p^3$

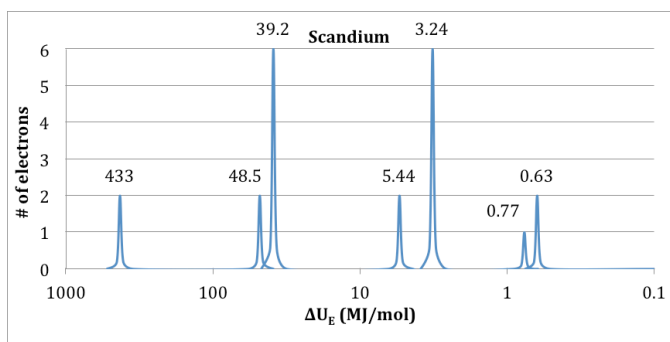
Electron Arrangements – *The Data Says So!* Con't

Look at the PES Data for Calcium:



Calcium's electron configuration is: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

Now let's consider Scandium (Sc)



- WHOA, what is that 0.77 MJ/mol peak doing right in front of the peak we would “label” $4s^2$?
- That is the 3rd “energy peak” or sublevel found within shells 3 and greater.
 - It is called a “d subshell”
 - Made up of 5 “orbitals” thus describes a maximum of 10 electrons
 - Belongs to the 3rd energy shell, although it isn't until the 4th period until you see it actually describe electrons.
 - The 4th period elements known as the “transition elements” are the first to describe “d orbitals”

Scandium's electron configuration is:

- $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$

While you won't always have PES Data to look at it is important to see that these configurations aren't some “made up labeling” or just something to memorize – they are based on the wave functions of the electrons in each specific atom and can be experimentally verified looking at the ionization energy for each electron in an atom (the PES data).

Periodicity – It is All About the Trends

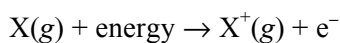
Elements display periodicity in their properties when organized as they are in the periodic table (which is really based on their electronic structure). This periodicity is useful in understanding properties and predicting properties of different elements.

These trends can be qualitatively understood and explained using Coulomb's Law, the shell model, and the concept of effective nuclear charge. The properties that we most often explain are:

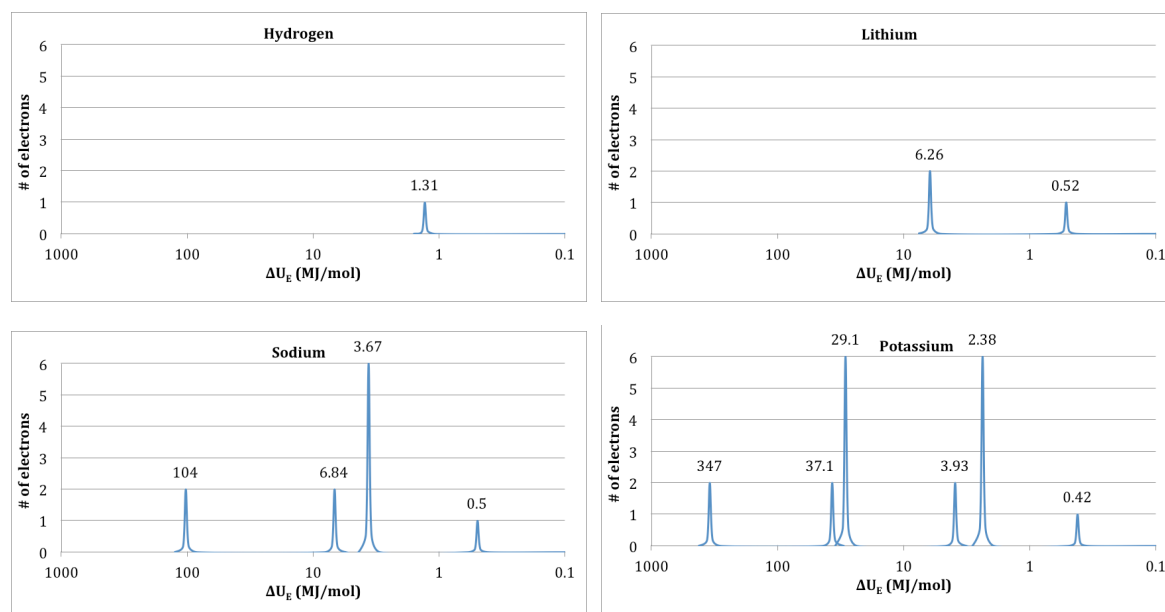
1. First ionization energy
2. Atomic and ionic radii
3. Electronegativity
4. Typical ionic charges

IONIZATION ENERGY

As discussed in the PES section, The minimum energy needed to remove an electron from an atom or ion is defined as **ionization energy** and the energy required to remove the *least tightly held electron* is the **first ionization energy**.



As you move from Hydrogen to Lithium to Sodium to Potassium (i.e. down Group I) what trend is developing with the **FIRST IONIZATION ENERGY**?



Element	H	Li	Na	K
First Ionization Energy (MJ/mol)	1.31	0.52	0.50	0.42

The **first ionization energy DECREASES** as you move down a Group in the Periodic Table. Why?

- Think back to **Coulomb's Law**: $U_E \propto \frac{q_1 q_2}{d}$ As the distance (d) increases (when you add shells the electrons are further from the positive nucleus and are further shielded by the inner electrons) their electrostatic potential energy decreases, thus it takes less energy (or is easier) to remove the electron.

Periodicity – It is All About the Trends con't

As you move from Lithium **ACROSS PERIOD 2** to Fluorine what trend is developing with the **FIRST IONIZATION ENERGY**?

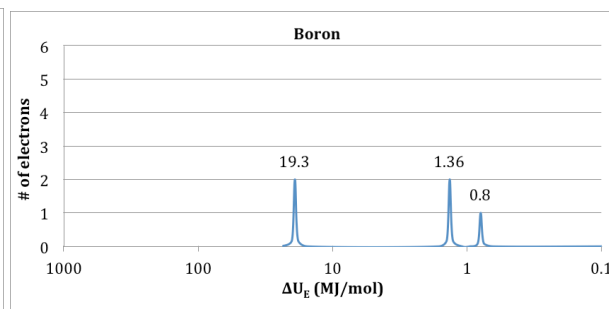
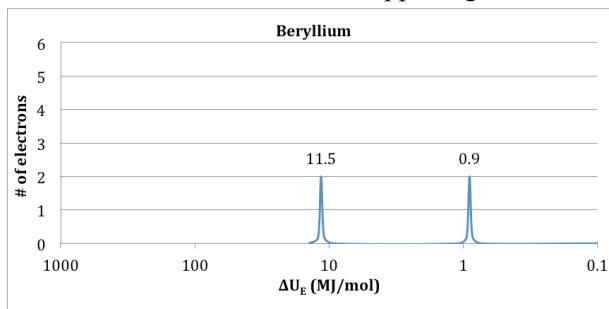
Element	Li	Be	B	C	N	O	F
First Ionization Energy (MJ/mol)	0.52	0.9	0.80	1.09	1.40	1.31	1.68

Generally, the *first ionization energy* **INCREASES** as you move **ACROSS** a Period in the Periodic Table. Why?

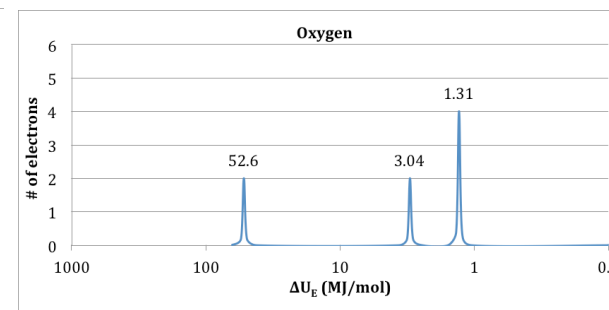
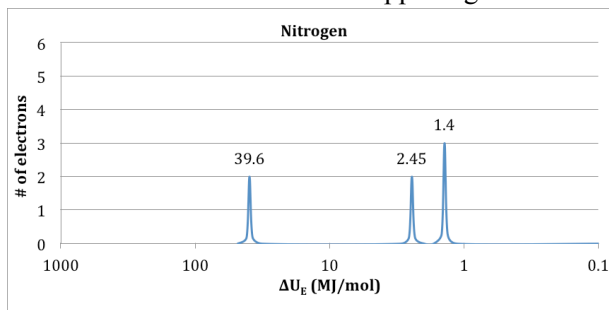
- As explained earlier... It is all about the nucleus! All of the elements in Period 2 have their valence electrons in the same energy shell. However, Li has 3 protons, Be 4, B 5, and so on up to F, which has 9.
- The higher the nuclear charge (the more effective the nuclear charge Z_{eff}), the more tightly held the electron, the more energy required to remove the electron *within a given energy shell*.

There are 2 obvious exceptions to this trend

- Be to B (group III to group IV)
 - What is happening here? Look at the PES for these 2 elements



- It takes less energy to remove the first electron in B than in Be because the electron being removed from B is the first electron in the “p orbital” whereas the electron removed from Be is in the “s” orbital. The electrons in the “p orbital” penetrate the nucleus less than those of the “s orbital” thus they are typically not as attracted to the nucleus and require less energy to remove. You see this “glitch in the trend” between all Group III and Group IV elements.
- N to O (group 5 to group VI)
 - What is happening here? Look at the PES for these 2 elements



- It takes less energy to remove the least tightly held electron in O than in N because the electron being removed in O is the first electron in the “p orbital” that is paired with another electron (there are 3 ‘orbitals’ so the 4th electron is paired), whereas N’s 3 electrons are all unpaired. The added electron – electron repulsion with the paired electron means this electron will require less energy to remove it.

Periodicity – It is All About the Trends con't

ATOMIC and IONIC RADII

The atomic and ionic radius can be described as a boundary beyond which the electron rarely strays. The “size” of the atom or ion is affected by two things; the attraction the protons in the nucleus have towards the electron cloud and the number of energy levels of electrons (n) in the cloud. Think effective nuclear charge and Coulomb’s Law.

As you move from Hydrogen to Lithium to Sodium to Potassium (i.e. down Group I or any group) what trend is developing with the *ATOMIC RADII*?

Element	H	Li	Na	K
Atomic Radius (Å)	0.37	1.52	1.86	2.31

The *atomic radius* **INCREASES** as you move down a group in the periodic table. Why?

- Think back to **Coulomb’s Law**: $U_E \propto \frac{q_1 q_2}{d}$ As the distance (d) increases, (when you add more shells), the electrostatic potential energy of the electrons decreases. So, the electrons are further from the positive nucleus and are further shielded by the inner electrons from the nucleus. As this increases so does the size of the atom.

As you move from Lithium **ACROSS PERIOD 2** to Fluorine what trend is developing with the *ATOMIC RADII*?

Element	Li	Be	B	C	N	O	F
Atomic Radius (Å)	1.52	1.11	0.88	0.77	0.70	0.66	0.64

Generally, the *atomic radius* **DECREASES** as you move **ACROSS** a Period in the Periodic Table. Why?

- As explained earlier... It is all about the nucleus! All of the elements in Period 2 have their valence electrons in the same energy shell – i.e. they are essentially the same distance from the nucleus. However, Li has 3 protons, Be 4, B 5, and so on up to F, which has 9.
- The higher the nuclear charge (the more effective the nuclear charge Z_{eff}), the more tightly held the electron, the more energy required to remove the electron within a given energy shell thus the electrons are pulled in closer – they are getting smaller!

The same “size trends” found with atomic radii apply when comparing cations to cations and anions to anions. However be cautious when comparing cations to anions. Think about what has happened to form those particular ions... They often are isoelectronic (same electron configuration)

- Comparing Na^+ , F^- , and O^{2-} , what has happened?
 - Na^+ lost an electron – and its $3s$ subshell its configuration is now: $1s^2 2s^2 2p^6$
 - F^- gained an electron – to its $2p$ subshell. Its configuration is now: $1s^2 2s^2 2p^6$
 - O^{2-} gained 2 electrons – to its $2p$ subshell. Its configuration is now: $1s^2 2s^2 2p^6$
 - All three ions have their outer electrons in the same shell/subshells; however the number of protons hasn’t changed: Na has 11, F, 9, and O 8. It is all about the effective nuclear charge.
 - The higher the nuclear charge (the more effective the nuclear charge Z_{eff}), the more tightly held the electron, the more energy required to remove the electron within a given energy shell thus the electrons are pulled in closer and the ions are smaller. $\text{O}^{2-} > \text{F}^- > \text{Na}^+$

Periodicity – *It is All About the Trends con't*ELECTRONEGATIVITY

This can be thought of as the ability of atoms to attract a shared electron pair in a covalent bond. Think tug of war! Again, use effective nuclear charge and Coulomb's Law to guide your thinking!

As you move from Hydrogen to Lithium to Sodium to Potassium (i.e. down Group I or any group) the atoms electronegativity is **DECREASING**. Why?

- Think back to **Coulomb's Law**: $U_E \propto \frac{q_1 q_2}{d}$ As the distance (d) increases, (when you add more shells), the electrostatic potential energy of the electrons decreases. So, the ability of that atom's nucleus to attract electrons from another atom in a covalent bond **DECREASES** as well since the electrons being attracted are further from the positive nucleus and are further shielded by the inner electrons from the nucleus.

As you move from Lithium **ACROSS PERIOD 2** to Fluorine the *electronegativity* **INCREASES**. Why?

- As explained earlier... It is all about the nucleus! All of the elements in Period 2 have their valence electrons in the same energy shell. However, Li has 3 protons, Be 4, B 5, and so on up to F, which has 9.
- The higher the nuclear charge (the more effective the nuclear charge Z_{eff}), the more tightly held the electron, the more attraction the nucleus will have on electrons in another atom in a covalent bond.

Trendy Thoughts

First recognize what the question is asking, i.e. what property is in question and what elements are being compared.

To best answer the question use the following 3 steps...

1. Locate both elements on the periodic table and note the energy shell and subshell of their valence electrons.
2. Compare their values!
 - If same *energy shell*: argue with Z_{eff}
 - If different *energy shell*: argue based on distance from the nucleus – for Pete's sake it is all about Coulomb's Law!
3. **ENERGY!** Comment of whether the electrons are more attracted or less attracted; or whether it takes more energy or less energy to remove the electron, etc... **NEVER FORGET the ENERGY relationship!** Again – Coulomb's Law!

Be careful when comparing isoelectronic species – those that have the same electron configurations, such as Ca^{2+} , K^+ , and Cl^- . If they all have the same number of electrons in the same energy shell then the property differences can be explained using effective nuclear charge! Determine the number of protons and answer accordingly.

NMSI SUPER PROBLEM

Answer the following questions about hydrogen atoms, H, hydrogen molecules, H₂, and hydrogen compounds.

- (a) An atom of hydrogen emits a discrete wavelength of electromagnetic radiation at 486 nm as the electron transitions from a higher energy level back to the second energy level $n = 2$. Calculate the energy change, in Joules, associated with this transition.

$\Delta E = h\nu = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J s})(3.0 \times 10^8 \frac{\text{nm}}{\text{s}})}{486 \text{ nm}} = 4.09 \times 10^{-19} \text{ J}$	<p>1 point for correct substitution</p> <p>1 point for the correct number of joules (or kJ); unit must be shown to receive credit</p>
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- (b) A second discrete emission line in an atom of hydrogen has a wavelength of 434 nm as the electron transitions from a higher energy level back to the second energy level ($n = 2$).

- (i) Would the change in energy associated with the 434 nm spectral line be greater than, less than, or equal to, that of the 486 nm spectral line? Justify your answer.

<p>The energy change for the 434 nm emission will be greater than that of the 486 nm.</p> $\Delta E = h\nu = \frac{hc}{\lambda}$ <p>Since ΔE and λ are inversely related a decrease in wavelength corresponds to an increase in energy.</p>	<p>1 point for correct answer with justification</p>
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- (ii) Would the energy level (n) of the electronic transition responsible for the 434 nm spectral line be at a higher energy level or a lower energy level than that of the 486 nm spectral line? Justify your answer.

<p>If the energy change is greater for the 434 nm spectral line then the electron must be at a higher initial energy level since both return to the same energy level, $n = 2$.</p>	<p>1 point for correct answer with justification</p>
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In a separate experiment a molecule of hydrogen, H₂, absorbs a photon of electromagnetic radiation with a wavelength of 300 nm. The energy required to break the bond in H₂ gas is 432 kJ mol⁻¹.

- (c) Calculate the frequency of the photons with a 300 nm wavelength.

$\nu = \frac{c}{\lambda} = \frac{(3.0 \times 10^8 \text{ nm s}^{-1})}{300 \text{ nm}} = 1.00 \times 10^{15} \text{ s}^{-1}$	<p>1 point for correct calculation</p>
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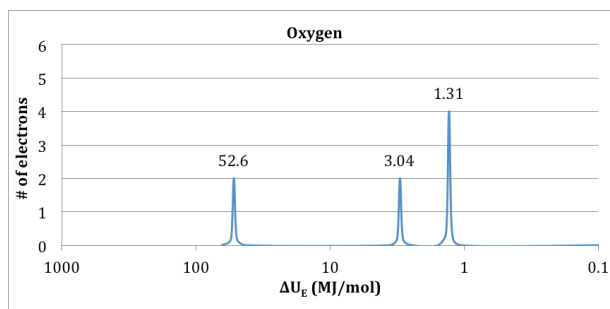
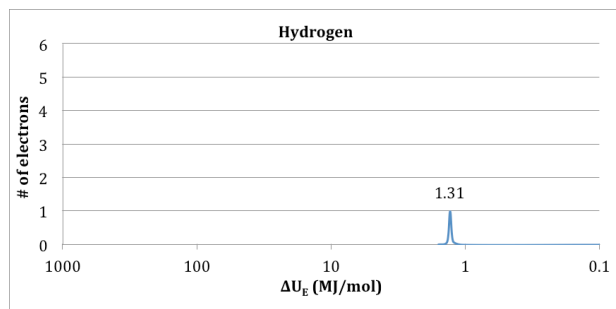
- (d) Calculate the number of joules required to break the bond in a single molecule of H₂ gas.

$432 \text{ kJ mol}^{-1} \times \frac{1000 \text{ J}}{\text{kJ}} \times \frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ molecules}} = 7.18 \times 10^{-19} \text{ J for each molecule}$	<p>1 point for the correct answer</p>
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- (e) Does the photon have enough energy to break the bond in a molecule of H_2 gas? Mathematically justify your answer.

$E = h\nu = (6.63 \times 10^{-34})(1.00 \times 10^{15}) = 6.63 \times 10^{-19} \text{ J}$ $6.63 \times 10^{-19} \text{ J} < 7.18 \times 10^{-19} \text{ J}$ <p>Therefore the photon does not have enough energy to break the bond.</p>	<p>1 point for calculating the energy of the photon</p> <p>1 point for comparing the energy of the photon to the energy of the single molecule of H_2 and stating the correct answer</p>
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The photoelectron spectrographs for both hydrogen and oxygen are shown below.



- (f) Using evidence from the PES data, explain why two atoms of hydrogen and one atom of oxygen are required to form water, H_2O .

<p>The PES data shows that H has one electron in its valence shell and oxygen has 4 – so it can form 2 single bonds, one with each of the 2 atoms of hydrogen.</p>	<p>1 point for the correct answer referencing the data provided</p>
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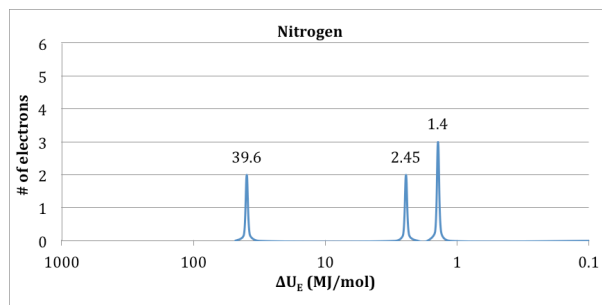
- (g) Look at the photoelectron spectrum for oxygen. Circle the peak that contains the first electron that would be removed from an oxygen atom.

<p>The peak labeled 1.31 (the farthest to the right) should be circled as one of those 4 electrons would be the first removed.</p>	<p>1 point for correct peak</p>
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- (h) Give the value for the first ionization energy for an atom of oxygen.

<p>1.31 MJ/mol</p>	<p>1 point for the correct first ionization energy</p>
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- (i) Below is the photoelectron spectrum for nitrogen. Explain why oxygen has a lower first ionization energy than does nitrogen.



Although oxygen has a more effective nuclear charge than nitrogen, oxygen has 2 electrons paired in its *p* orbital. Nitrogen has all three of its *p* electrons unpaired. The pairing of oxygen's electrons causes an increase in electron – electron repulsion which decreases the electrostatic potential energy of those 2 paired electrons thus it takes less energy to remove the first one of them.

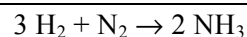
1 point for the correct explanation

- (j) Circle the peak in the photoelectron spectrum for nitrogen that represents the electrons in the 2*s* subshell.

The peak labeled 2.45 (the farthest to the right) should be circled.

1 point for the correct peak

- (k) When hydrogen and nitrogen react they form ammonia. Write the balanced equation for this reaction.



1 point for the balanced equation

- (l) Atoms of phosphorus and nitrogen are in the same group, or family, on the periodic table.

- (i) Predict the formula that results when hydrogen atoms form a compound with phosphorus atoms.



1 point for the correct formula

- (ii) Atoms of phosphorus are larger than atoms of nitrogen. Explain

Atoms of phosphorus have valence electrons in the 3rd shell whereas the valence electrons in nitrogen are in the 2nd shell. The more shells the less attracted the electrons are to the nucleus the further away they are from the nucleus.

1 point for the correct answer with justification

Modified AP[®] CHEMISTRY SCORING GUIDELINES

(4 points)

Answer the following questions related to sulfur and one of its compounds.

(a) Consider the two chemical species S and S²⁻.

(i) Write the electron configuration (e.g., 1s² 2s² . . .) of each species.

<p>S: 1s² 2s² 2p⁶ 3s² 3p⁴</p> <p>S²⁻: 1s² 2s² 2p⁶ 3s² 3p⁶</p> <p>Note: Replacement of 1s² 2s² 2p⁶ by [Ne] is acceptable.</p>	<p>One point is earned for the correct configuration for S.</p> <p>One point is earned for the correct configuration for S²⁻.</p>
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(ii) Explain why the radius of the S²⁻ ion is larger than the radius of the S atom.

<p>The nuclear charge is the same for both species, but the eight valence electrons in the sulfide ion experience a greater amount of electron-electron repulsion than do the six valence electrons in the neutral sulfur atom. This extra repulsion in the sulfide ion increases the average distance between the valence electrons, so the electron cloud around the sulfide ion has the greater radius.</p>	<p>One point is earned for a correct explanation.</p>
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(b) The S²⁻ ion is isoelectronic with the Ar atom. From which species, S²⁻ or Ar, is it easier to remove an electron? Explain.

<p>It requires less energy to remove an electron from a sulfide ion than from an argon atom. A valence electron in the sulfide ion is less attracted to the nucleus (charge +16) than is a valence electron in the argon atom (charge +18).</p>	<p>One point is earned for the correct answer with a correct explanation.</p>
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Modified AP[®] CHEMISTRY SCORING GUIDELINES

(3 Points)

Using principles of atomic and molecular structure and the information in the table below, answer the following questions about atomic fluorine, oxygen, and xenon, as well as some of their compounds.

Atom	First Ionization Energy (kJ mol ⁻¹)
F	1,681.0
O	1,313.9
Xe	?

(a) Write the equation for the ionization of atomic fluorine that requires 1,681.0 kJ mol⁻¹.

$\text{F}(g) \rightarrow \text{F}^+(g) + e^-$	One point is earned for the correct equation. (Phase designations are not required.)
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(b) Account for the fact that the first ionization energy of atomic fluorine is greater than that of atomic oxygen. (You must discuss both atoms in your response.)

In both cases the electron removed is from the same energy level ($2p$), but fluorine has a greater effective nuclear charge due to one more proton in its nucleus (the electrons are held more tightly and thus take more energy to remove).	One point is earned for recognizing that the effective nuclear charge of F is greater than that of O.
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(c) Predict whether the first ionization energy of atomic xenon is greater than, less than, or equal to the first ionization energy of atomic fluorine. Justify your prediction.

The first ionization energy of Xe should be less than the first ionization energy of F. To ionize the F atom, an electron is removed from a $2p$ orbital. To ionize the Xe atom, an electron must be removed from a $5p$ orbital. The $5p$ is a higher energy level and is farther from the nucleus than $2p$, hence it takes less energy to remove an electron from Xe.	One point is earned for a prediction based on size and/or energy level.
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AP[®] Chemistry — Scoring Standards Modified

(6 points)

- (a) The isotopes have the same number (34) of protons, but a different number of neutrons. **1 pt.**
1 pt.

- No comment about the number of electrons is necessary

- (b) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^4$
or
 $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^4$ **1 pt.**

- No point is earned for $[\text{Ar}] 4s^2 3d^{10} 4p^4$, because the question specifically asks for a complete electron configuration.

Since there are three different $4p$ orbitals, there must be two unpaired electrons. **1 pt.**



Notes: The second part should have some explanation of Hund's rule, and may include a diagram. The second point can still be earned even if the first point is not IF the electron configuration is incorrect, but the answer for the second part is consistent with the electron configuration given in the first part.

- (c) (i) The ionized electrons in both Se and Br are in the same energy level, but Br has more protons than Se, so the attraction to the nucleus is greater. **1 pt.**

Note: There should be two arguments in an acceptable answer -- the electrons removed are from the same ($4p$) orbital **and** Br has more protons (a greater nuclear charge) than Se.

- (ii) The electron removed from a Te atom is in a $5p$ orbital, while the electron removed from an Se atom is in a $4p$ orbital. The $5p$ orbital is at a higher energy than the $4p$ orbital, thus the removal of an electron in a $5p$ orbital requires less energy. **1 pt.**