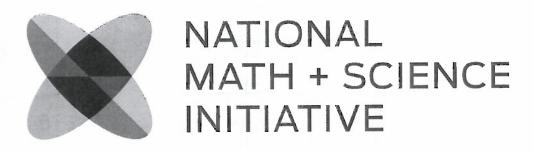


PES-diggnins on page 3



AP CHEMISTRY

Atomic Structure and Periodicity

2016 EDITION

Click on the following link or scan the QR code to complete the evaluation for the Study Session https://www.surveymonkey.com/r/S\_SSS



# Periodic Table of the Elements

	_	I		_		1
2 He 4.0026	10 Ne 20.179	18 Ar 39.948	36 Kr 83.80	54 Xe 131.29	86 Rn (222)	
	9 F 19.00	17 Cl 35.453	35 Br 79.90	53      126.91	85 At (210)	
	8 O 16.00	16 S 32.06	34 Se 78.96	52 Te 127.60	84 Po (209)	
	7 N 14.007	15 P 30.974	33 As 74.92	51 Sb 121.75	83 Bi 208.98	pəı
	6 C 12.011	14 Si 28.09	32 Ge 72.59	50 Sn 118.71	82 Pb 207.2	§Not yet named
	5 B 10.811	13 Al 26.98	31 Ga 69.72	49 In 114.82	81 Tl 204.38	§Not
			30 Zn 65.39	48 Cd 112.41	80 Hg 200.59	112 § (277)
			29 Cu 63.55	47 Ag 107.87	79 Au 196.97	111 § (272)
			28 Ni 58.69	46 Pd 106.42	78 Pt 195.08	110 § (269)
			27 Co 58.93	45 Rh 102.91	77 Ir 192.2	109 Mt (266)
			26 Fe 55.85	44 Ru 101.1	76 Os 190.2	108 Hs (265)
			25 Mn 54.938	43 Tc (98)	75 Re 186.21	107 Bh (262)
			24 Cr 52.00	42 Mo 93.94	74 W 183.85	106 Sg (263)
			23 V 50.94	41 Nb 92.91	73 Ta 180.95	105 Db (262)
			22 Ti 47.90	40 Zr 91.22	72 Hf 178.49	104 Rf (261)
_			21 Sc 44.96	39 Y 88.91	, 57 La 138.91	88 89 Ra <sup>†</sup> Ac 226.02 227.03
	4 Be 9.012	12 Mg 24.30	20 Ca 40.08	38 Sr 87.62	56 Ba 137.33	88 Ra 226.02
1 H 1.0079	3 Li 6.941	11 Na 22.99	19 K 39.10	37 Rb 85.47	55 Cs 132.91	87 Fr (223)

			_		
71	Γn	174.97	103	۲	(260)
20	Υb	173.04	102	%	(259)
69	T	168.93	101	Md	(258)
89	ш	167.26	100	Б	(257)
29	운	164.93	66	Es	(252)
99	DÀ	162.50	86	ర	(251)
65	Тр	158.93	26	簽	(247)
64	gg	157.25	96	Cm	(247)
63	Eu	151.97	96	Am	(243)
62	Sm	150.4	94	Pu	(244)
61	Pm	(145)	93	Ν	2.5
09	PN	144.24	62	_	238.03
29	ሏ	140.12 140.91 144.24	91	Ра	232.04 231.04 238.03 2
28	Ce	140.12	06	Ļ	232.04
	*Lanthanide Series:			†Actinide Series:	

# **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

$$E = h\nu$$

$$c = \lambda v$$

E = energy

v = frequency

 $\lambda$  = wavelength

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

Speed of light,  $c = 2.998 \times 10^8 \,\text{m s}^{-1}$ 

Avogadro's number =  $6.022 \times 10^{23} \text{ mol}^{-1}$ 

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

#### **EOUILIBRIUM**

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

$$K_p = \frac{(P_{\rm C})^c (P_D)^d}{(P_{\rm A})^a (P_{\rm B})^b}$$

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

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

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

$$= K_a \times K_b$$

$$pH = -log[H^+], pOH = -log[OH^-]$$

$$14 = pH + pOH$$

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

$$pK_a = -\log K_a, pK_b = -\log K_b$$

### **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

$$PV = nRT$$

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

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

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

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

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

$$KE$$
 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 torr

STP = 0.00 °C and 1.000 atm

#### THERMOCHEMISTRY/ ELECTROCHEMISTRY

$$q = mc\Delta T$$

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

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

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

$$\Delta G^{\circ} = \Delta H^{\circ} \quad T \Delta S^{\circ}$$

$$= -RT \ln K$$

$$= -n F E^{\circ}$$

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

q = heat

m = mass

c =specific heat capacity

T = temperature

 $S^{\circ}$  = standard entropy

 $H^{\circ}$  = standard enthalpy

 $G^{\circ}$  = standard free energy

n = number of moles

 $E^{\circ}$  = standard reduction potential

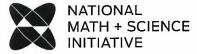
I = current (amperes)

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 is 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 = hv, where h is Planck's constant and v 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 = hv, where h is Planck's constant and v 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:
  - $c = \lambda v$  so we can also note  $E = hv = \frac{hc}{\lambda}$
  - $c = \text{speed of light} = 3.0 \times 10^8 \text{ m/s}$  ALERT! Be prepared to see wavelengths in "nm" therefore you must convert the c from m to nm or remember  $c = 3.0 \times 10^{17} \text{ nm/s}$

1

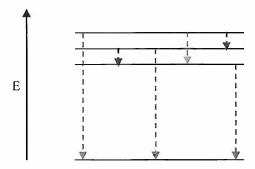
#### It's Spectral!

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.

$$\Delta E = hv = \frac{hc}{\lambda}$$



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.

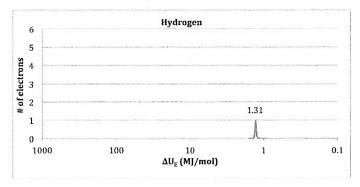
# Photoelectron Spectroscopy - Eject, Eject, Eject!

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**: 
$$U_E \propto \frac{q_1 q_2}{d}$$

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:

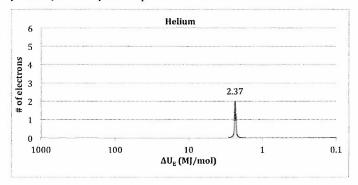
 $\Delta U_E = (U_E \text{ at an infinite distance from the nucleus}) - (U_E \text{ for the electron in its ground state})$ 

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

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.

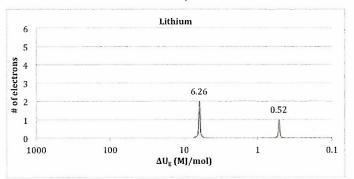


Notice that the energy is slightly greater than that for hydrogen. Why?

• 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.



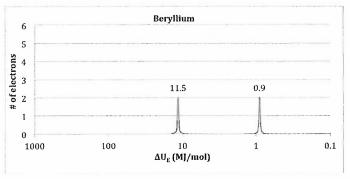
Let's move to the 2<sup>nd</sup> Period and look at lithium's PES; Li has 3 electrons.



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 (1<sup>st</sup> 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 it takes less energy to remove it i.e. it's 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.

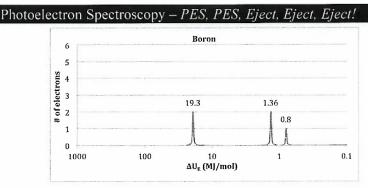
Both peaks in Be are closer to the nucleus than in Li. Why?

• 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.

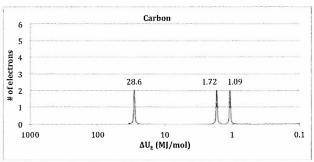
What do you expect?

Con't



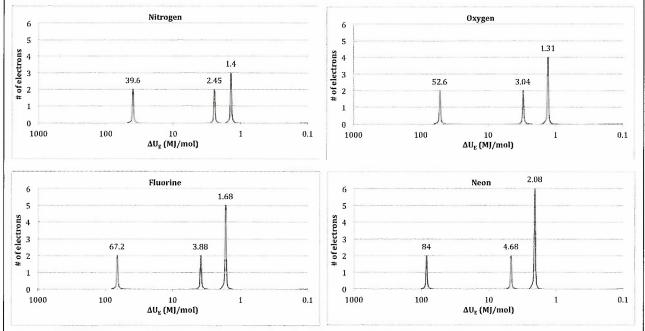
Why is there another peak, we didn't move to Period 3, we are still in Period 2?

• The electron in the 0.8 MJ/mol peak is a new "sublevel" of electrons within the 2<sup>nd</sup> energy level.

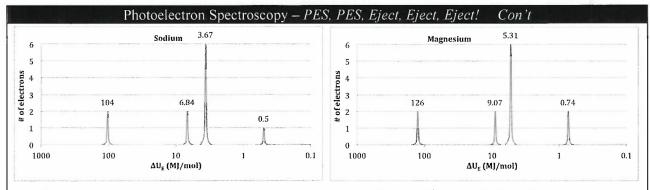


Carbon is similar to boron, it has 2 electrons in the first shell, and in the second shell (energy level) it has 2 electrons in the  $1^{st}$  peak (subshell). In the  $2^{nd}$  peak (subshell) it has 2 electrons where B has 1.

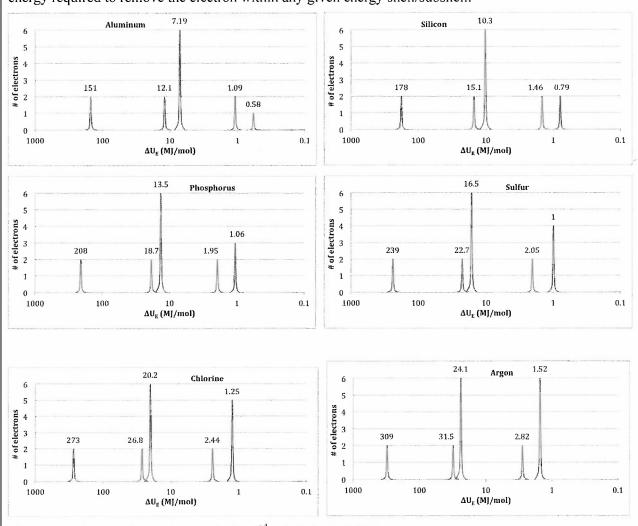
As you move through the rest of the Period 2 elements you will see 1 additional electron added to the 2<sup>nd</sup> subshell of the 2<sup>nd</sup> shell



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.



The first 2 elements of Period 3 have electron(s) in a new peak – the 1<sup>st</sup> 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  $2^{nd}$  subshell of shell 3.

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

#### Electron Arrangements - The Data Says So!

The pattern from the PES Data is clear...

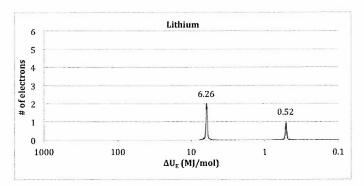
- Each electron in an atom has a specific ionization energy, thus it is located in a specific place
- The electrons can be thought of as being located in shells and subshells that make up the electron cloud
  - Inner shell electrons are called core electrons
  - Outer shell electrons are called valence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

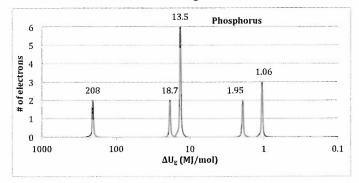
- This "configuration" is based on Schrodinger's Quantum Model, based on the wave functions that determine the allowed energy states of an electron.
- These allowed states called "atomic orbitals" reflect the quantum numbers that describe the different quantized energy states of an electron.

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



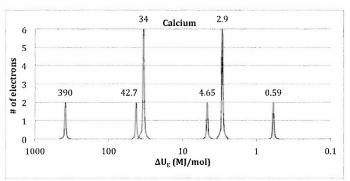
Look again at lithium, Li: It has 2 energy shells – each shell has one "peak" or subshell. The  $1^{st}$  subshell has 2 electrons and the  $2^{nd}$  has 1, thus its electron configuration is:  $1s^2 2s^1$ 



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

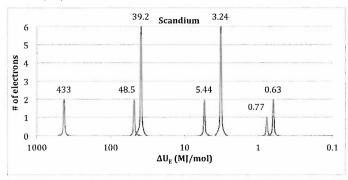
Electron Arrangements - The Data Says So! Con't

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 3<sup>rd</sup> energy shell, although it isn't until the 4<sup>th</sup> period until you see it actually describe electrons.
  - The 4<sup>th</sup> period elements known as the "transition elements" are the first to describe "d orbitals"

Scandium's electron configuration is:

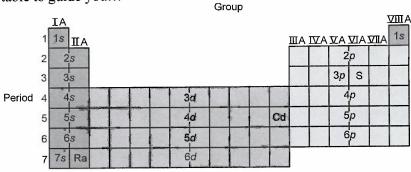
•  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$ 

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).

#### More on Electron Arrangements

REALIZE – the structure of the Periodic Table is a consequence of the pattern of electron configurations and the presence of shells and subshells of electrons.

Use the periodic table to guide you...





Ignoring a "few exceptions" the electron configuration can be deduced from the element's position on the periodic table.

Cadmium's (Cd) electron configuration is:

• 
$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2 4d^{10}$$

Sulfur's (S) electron configuration is:

• 
$$1s^2 2s^2 2p^6 3s^2 3p^4$$

Exceptions, you say, what about the exceptions..?

Certain elements' electron configurations "buck the trend" of what you would predict. You DO NOT have to know these, but be able to justify your reasoning if asked to explain one.

Look at Chromium:

Its electron configuration would be predicted to be:  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^4 4s^2$ 

Its actual configuration is:  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ 

Why do you think this happens?

- Electron electron repulsions are the culprit. Think back to the PES for Scandium and how close in energy the 3d and the 4s orbitals are (0.77 MJ/mol and 0.63 MJ/mol). This is true for all of the transition elements some much closer even!
- Since these are so close in energy (their energies are said to be degenerate) there are instances when the added electron electron repulsions of 2 electrons in the s orbital create a situation where the electron is at lower energy in the d orbital. This isn't always the case so we can't predict when these exceptions occurs, we would need to see the PES data to make those determinations.

Just be aware there are exceptions and be ready to justify why they occur if you are give one on the AP Exam.

#### 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 qualatatively 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:

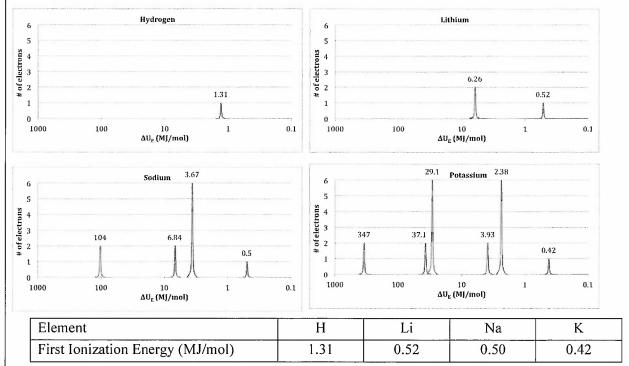
- 1. First ionization energy
- 2. Atomic and ionic radii
- 3. Electronegativity
- 4. Typical ionic charges

#### **IONIZATION ENERGY**

As discused 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*.

$$X(g) + \text{energy} \rightarrow X^{+}(g) + e^{-}$$

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*?



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

• Think back to **Coulomb's Law**:  $U_E \propto \frac{q_1q_2}{d}$  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 Fluroine what trend is developing with the *FIRST IONIZATION ENERGY*?

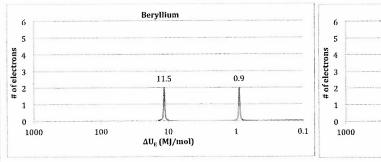
Element	Li	Be	В	С	N	О	F
First Ionization Energy (MJ/mol)	0.52	0.9	0.80	1.09	1.40	1.31	1.68

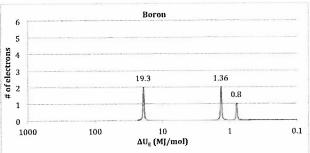
Generally, the *first ionization energy* **INCREASES** as you move ACROSS a Period in the Periodic Table. Why?

- 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 <u>within a given</u> energy shell.

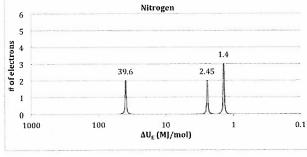
There are 2 obvious exceptions to this trend

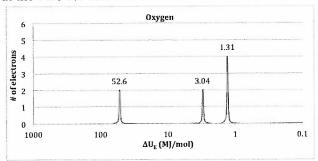
- Be to B (group III to group IV)
  - What is happening here? Look at the PES for these 2 elements





- 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 4<sup>th</sup> electron is paried), whereas N's 3 electrons are all unpaired. The added electron – electron repulsion with the paried 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	Н	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 Fluroine what trend is developing with the *ATOMIC RADII*?

Element	Li	Be	В	C	N	О	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 <u>within a given</u> <u>energy shell</u> 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<sup>+</sup>, F<sup>-</sup>, and O<sup>2-</sup>, what has happened?
  - Na<sup>+</sup> 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.  $O^{2-} > F^- > Na^+$

#### 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:  $U_E \propto \frac{q_1q_2}{d}$  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 Fluroine 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<sub>eff</sub>
  - 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!

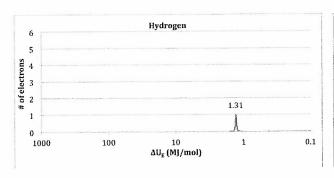
Be careful when comparing isoelectronic species – those that have the same electron configurations, such as Ca<sup>2+</sup>, K<sup>+</sup>, and Cl<sup>-</sup>. If they all have the same number of electrons in the same energy shell then the property differences can be explained using effective nuclear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

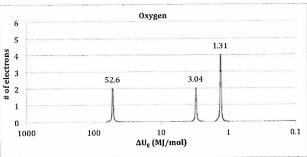
# NMSI SUPER PROBLEM

Answer the following questions about hydrogen atoms, H, hydrogen molecules, H <sub>2</sub> , 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.
(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 you answer.
(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 you answer.
In a separate experiment a molecule of hydrogen, $H_2$ , absorbs a photon of electromagnetic radiation with a wavelength of 300 nm. The energy required to break the bond in $H_2$ gas is 432 kJ mol <sup>-1</sup> .
(c) Calculate the frequency of the photons with a 300 nm wavelength.
(d) Calculate the number of joules required to break the bond in a single molecule of $H_2$ gas.

(e) Does the photon have enough energy to break the bond in a molecule of H<sub>2</sub> gas? Mathematically justify your answer.

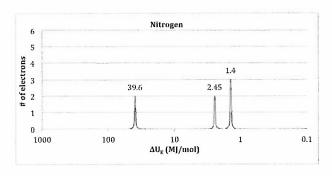
The photoelectron spectrographs for both hydrogen and oxygen are shown below.





- (f) Using evidence from the PES data, explain why two atoms of hydrogen and one atom of oxygen are required to form water, H<sub>2</sub>O.
- (g) Look at the photoelectron spectrum for oxygen. Circle the peak that contains the first electron that would be removed from an oxygen atom.
- (h) Give the value for the first ionization energy for an atom of oxygen.

(i) Below is the photoelectron spectrum for nitrogen. Explain why oxygen has a lower first ionization energy than does nitrogen.



- (j) Circle the peak in the photoelectron spectrum for nitrogen that represents the electrons in the 2s subshell.
- (k) When hydrogen and nitrogen react they form ammonia. Write the balanced equation for this reaction.
- (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.
  - (ii) Atoms of phosphorus are larger than atoms of nitrogen. Explain

# AP® CHEMISTRY FREE-RESPONSE QUESTIONS Modified for a Short Response

Answer	the	foll	owing	questions	related	to	sulfur.
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- (a) Consider the two chemical species S and  $S^{2-}$ .
  - (i) Write the electron configuration (e.g.,  $1s^2 2s^2 ...$ ) of each species.
  - (ii) Explain why the radius of the  $S^{2-}$  ion is larger than the radius of the S atom.
- (b) The  $S^{2-}$  ion is isoelectronic with the Ar atom. From which species,  $S^{2-}$  or Ar, is it easier to remove an electron? Explain.

#### **AP® CHEMISTRY FREE-RESPONSE QUESTIONS**

# Modified for a Short Response

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 <sup>-1</sup> )
F	1,681.0
0	1,313.9
Xe	?

- (a) Write the equation for the ionization of atomic fluorine that requires 1,681.0 kJ mol<sup>-1</sup>.
- (b) Account for the fact that the first ionization energy of atomic fluorine is greater than that of atomic oxygen. (You must discuss <u>both</u> atoms in your response.)
- (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.

# **AP® CHEMISTRY FREE-RESPONSE QUESTIONS**

# Modified for a Short Response

Answer the following questions about the element selenium, Se (atomic number 34).

- (a) Samples of natural selenium contain six stable isotopes. In terms of atomic structure, explain what these isotopes have in common, and how they differ.
- (b) Write the complete electron configuration (e.g.,  $1s^2 2s^2$ ... etc.) for a selenium atom in the ground state. Indicate the number of unpaired electrons in the ground-state atom, and explain your reasoning.
- (c) In terms of atomic structure, explain why the first ionization energy of selenium is
  - (i) less than that of bromine (atomic number 35), and
  - (ii) greater than that of tellurium (atomic number 52).