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Periodicity and Bonding

Name: _____

AP Chemistry Lecture Outline

valence orbitals:

- elements in the same group have the same valence-shell electron configuration
- since v. e^- are involved in bonding, elements in a group have similar properties

Development of the Periodic Table

- few elements appear in elemental form in nature
- most are in combined forms with other elements
- In 19th century, advances in chemistry allowed more elements to be identified.

1869: Independently, Dmitri Mendeleev (Russia) and Lothar Meyer (Germany) published classification schemes based on similarities in element properties.

** Mendeleev used his scheme to predict the existence of undiscovered elements, and so is given credit for inventing the first periodic table.

** D.M.'s guiding principle was...

- 1913: Henry Moseley bombarded atoms with high-energy electrons and measured the frequency of the X rays given off. X ray frequency *generally* increased as atomic mass increased, but *VERY nicely* increased as _____ increased.

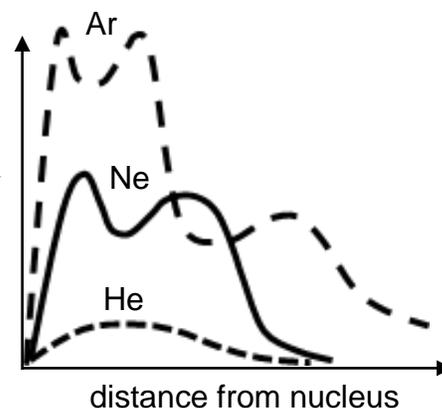
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Electron Shells

Even before Bohr, the American Gilbert Lewis had suggested that e^- are arranged in shells.

- Experiments show that e^- density is a maximum at certain distances from nucleus.
- no clearly defined boundaries between shells

e^- density



Approximate bonding atomic radii for the elements have been tabulated.

The distance between bonded nuclei can be approximated by adding bonding radii from both atoms.

e.g., Bonding atomic radii are as follows: C = 0.77 Å, Br = 1.14 Å

So the approximate bond length between bonded C and Br nuclei =

bond length: the center-to-center distance between two bonded atoms

- fairly constant for a given bond (e.g., the C–H bond), no matter the compound
e.g., C–H bonds in CH₄ are about the same length as those in CH₃CH₂CH₃
- Average bond lengths have been tabulated for many bonds.

- As the number of bonds between two atoms increases,
bond length... and bond enthalpy...

e.g., C–C

C=C

C≡C

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Trends in Atomic Radius

As we go down a group, atomic radius...

--

As we go from left to right across the Table, atomic radius...

-- effective nuclear charge on each subshell tends to...

EX. Arrange these atoms in order of increasing atomic radius: Sr, Ba, Cs.

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Trends in Ionic Radius

Cations are _____ than the neutral atoms from which they are derived.

e.g., Li 1s² 2s¹

Li⁺ 1s²

--

--

Fe

Fe²⁺

Fe³⁺

Anions are _____ than the neutral atoms from which they are derived.

--

Cl

Cl⁻

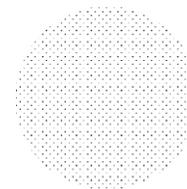
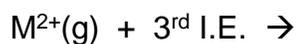
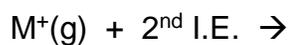
An isoelectronic series is a list of species having an identical electron configuration.

e.g.,

EX. Which has the largest radius? Rb^+ Sr^{2+} Y^{3+}

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Ionization Energy: the minimum energy needed to remove an e^- from an atom or ion



Successive ionization energies are larger than previous ones.

--

The ionization energy increases sharply when we try to remove an inner-shell electron.

e.g.,

As we go down a group, 1st IE...

--

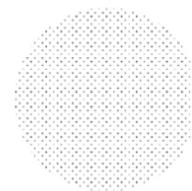
Generally, as we go from left to right, 1st IE...

Exceptions: e.g., $\text{B} < \text{Be}$ $\left. \begin{array}{l} \text{Be: } 1s^2 2s^2 \\ \text{B: } 1s^2 2s^2 2p^1 \end{array} \right\}$

e.g., $\text{O} < \text{N}$ $\left. \begin{array}{l} \text{N: } 1s^2 2s^2 2p^3 \\ \text{O: } 1s^2 2s^2 2p^4 \end{array} \right\}$

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Electron affinity: the energy change that occurs when
an e^- is added to a gaseous atom



For most atoms, adding an e^- causes energy to be...

Exceptions:

the added e^- must go into a new, higher energy level

the added e^- must go into a higher-energy p orbital

the added e^- is the first one to double-up a p orbital

The halogens have the most ($-$) e^- affinities; i.e.,
they become very stable when they accept e^- s.

Electron affinities don't vary much going down a group.

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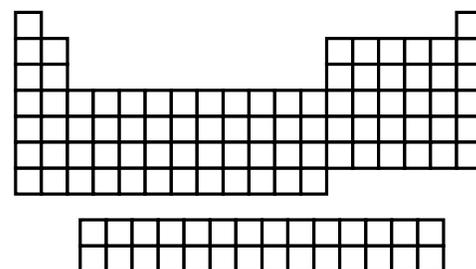
Regions of the Table

metals: left side of Table; form cations

properties:

-- Because of their low ionization energies,
they are often oxidized in reactions.

-- Metallic character of the elements increases as we go down-and-to-the-left.



nonmetals: right side of Table; form anions

properties:

-- memorize the HOB rFINCl twins

metalloids (semimetals): "stair" between metals and nonmetals

properties:

Si and Ge →

alkali metals:

alkaline earth metals:

transition elements:

chalcogens:

halogens:

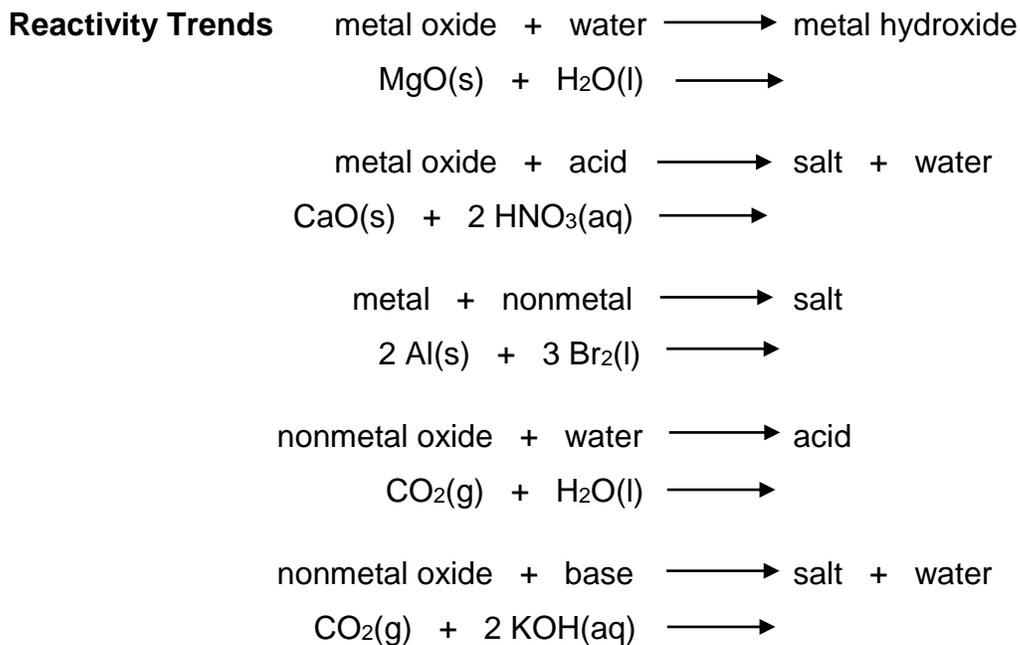
noble gases:

lanthanides:

actinides:

main block (representative) elements:

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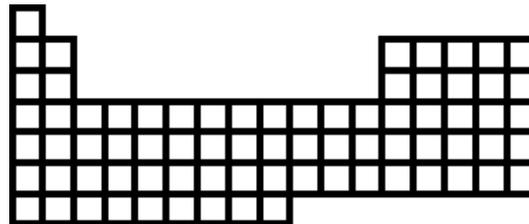
Group Trends

- Alkali Metals*
- the most reactive metals (one e^- to lose)
 - obtained by electrolysis of a molten salt
 - e.g., chloride ion is oxidized and sodium ion is reduced
 - react with hydrogen to form metal hydrides:
 - react with water to form metal hydroxides:
 - react $^w/\text{O}_2$: Li yields Li_2O , others yield (mostly) peroxides (M_2O_2)
- Alkaline-Earths*
- not as reactive as alkalis (two e^- to lose)
 - Ca and heavier ones react $^w/\text{H}_2\text{O}$ to form metal hydroxides
 - MgO is a protective oxide coating around substrate Mg
- Hydrogen*
- a nonmetal, but belongs to no family
 - reacts $^w/\text{other nonmetals}$ to form molecular (i.e., covalent) compounds
- Halogens*
- At isn't considered to be a halogen; little is known about it
 - at 25°C , F_2 and Cl_2 are gases, Br_2 is a liquid, I_2 is a solid
 - their exo. reactivity is dominated by their tendency to gain e^-
 - Cl_2 is added to water; the HOCl produced acts as a disinfectant
 - HF(aq) = weak acid; HCl(aq) , HBr(aq) , HI(aq) = strong acids
- Noble Gases*
- all are monatomic; have completely-filled s and p orbitals
 - He, Ne, and Ar have no known compounds; Rn is radioactive
 - Kr has one known compound (KrF_2); Xe has a few (XeF_2 , XeF_4 , XeF_6)

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Electronegativity

electronegativity:



Electronegativity increases going...

Most electronegative element is...

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Basics of Chemical Bonding

Properties of substances are largely dependent on the bonds holding the material together.

Basics of Bonding

A chemical bond occurs when atoms or ions are **strongly** attached to each other.

Ionic bonds involve the transfer of e^- and the subsequent electrostatic attractions.

--

Covalent bonds involve the sharing of e^- between two atoms.

--

metallic bonds: each metal atom is bonded to several neighboring atoms

--

Lewis symbols show ONLY the valence e^- (i.e., the ones involved in bonding).

octet rule:

--

With transition-metal ions, the first e^- lost come from the subshell with the largest value of n .



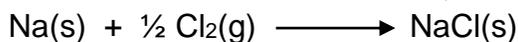
Recall that polyatomic ions are groups of atoms that stay together and have a net charge.



-- their atoms are held to each other by...

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Ionic Bonding



↓ "Salts" are brittle solids with high melting points.

$$\Delta H_f^\circ = -410.9 \text{ kJ/mol}$$

lattice energy: the energy required to separate 1 mole of solid ionic compound into gaseous ions

--



In general, ionically bonded substances have...

Because lattice energies are electrostatic in nature, two variables are involved in how big they are:

- 1.
- 2.

When comparing lattice energies, always look at...

EX. Put the following in order of increasing lattice energy:

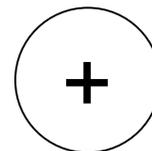
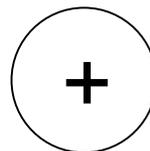
LiBr, FeN, CdO

Now these: MgS, MgCl₂, MgO

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Covalent Bonding

- atoms share e⁻
- covalent (molecular) compounds tend to be solids with low melting points, or liquids or gases



- one shared pair of e⁻ (i.e., 2 e⁻) = a single covalent bond
- two shared pairs of e⁻ (i.e., 4 e⁻) = a double covalent bond
- three shared pairs of e⁻ (i.e., 6 e⁻) = a triple covalent bond

bond polarity:

nonpolar covalent bond:

polar covalent bond:

electronegativity (EN): the ability of an atom in a molecule to attract e⁻ to itself

- A bonded atom w/a large EN has a great ability to attract e⁻.
- A bonded atom w/a small EN does not attract e⁻ very well.
- EN values have been tabulated.

The ΔEN between bonded atoms approximates the type of bond between them.

$\Delta EN < 0.5 \rightarrow$

$0.5 \leq \Delta EN < 2.0 \rightarrow$

$\Delta EN \geq 2.0 \rightarrow$

As ΔEN increases, bond polarity...

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Bond Dipoles and Dipole Moments

The bond dipoles of a molecule's bonds can lead to a molecule having a permanent dipole moment.



Polar molecules tend to align themselves with each other and with ions.



** Nomenclature tip: For binary compounds, the less electronegative element comes first.

-- Compounds of metals w/high ox. #'s (e.g., 4+ or higher) tend to be molecular rather than ionic.
e.g.,

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Lewis Structures

1. Sum the valence e^- for all atoms. If the species is an ion, add one e^- for every (-); subtract one e^- for every (+).
2. Write the element symbols and connect the symbols with single bonds.
3. Complete octets for the atoms on the exterior of the structure, but NOT for H.
4. Count up the valence e^- on your L.S. and compare that to the # from Step 1.
 - If your LS doesn't have enough e^- , place as many e^- as needed on central atom.
 - If LS has too many e^- OR if central atom doesn't have an octet, use multiple bonds.

EX. Draw Lewis structures for the following species.





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formal charge: the charge a bonded atom would have if all the atoms had the same electronegativity; to find it, you must first draw the Lewis structure

$$\text{formal charge} = \begin{array}{l} \# \text{ of v.e}^- \text{ in} \\ \text{the isolated} \\ \text{atom} \end{array} - \begin{array}{l} \# \text{ of e}^- \text{ assigned} \\ \text{to the atom in the} \\ \text{Lewis structure} \end{array}$$

When several Lewis structures are possible, the most stable is the one in which:

- (1) the atoms have the smallest formal charges, and
- (2) the (-) charges reside on the most electronegative atoms

EX. Find the formal charge on each atom in the following species



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resonance structures: the two or more Lewis structures that are equally correct for a species
e.g., For NO_3^- ...

Resonance structures are a blending of two or more Lewis structures.

Aromatic compounds are based on resonance structures of the benzene molecule.

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Exceptions to the Octet Rule

There are a few cases (other than for H) in which the octet rule is violated. These are:

1. particles with an odd number of valence e^-
 - e.g.,
2. atoms with less than an octet
 - e.g.,
3. atoms with more than an octet
 - this occurs when an atom gains an expanded valence shell
 - other e.g.,

Expanded valence shells occur only for atoms in periods ≥ 3 .

-
- large central atom =
- small exterior atoms =

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The strengths of a molecule's covalent bonds are related to the molecule's stability and the amount of energy required to break the bonds.

bond enthalpy: the ΔH req'd to break 1 mol of a particular bond in a gaseous substance

-
- big ΔH =
- e.g.,

atomization: the process of breaking a molecule into its individual atoms

- ΔH for a given bond (e.g., the C–H bond) varies little between compounds.
 - e.g., C–H bonds in CH_4 vs. those in $\text{CH}_3\text{CH}_2\text{CH}_3$ have about the same ΔH
- Typical values of bond enthalpies for specific bonds have been tabulated.

-- To find bond enthalpy for atomization, add up bond enthalpies for each bond broken.

EX. Calculate the bond enthalpy for the atomization of dichloromethane.

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You can approximate reaction enthalpy using Hess's law and tabulated bond enthalpies.

EX. Approximate the reaction enthalpy for the combustion of propane.