# Lecture 3 CH131 Summer 1

Thursday, May 23, 2019

- Complete ch2: Chemical formulas, equations, and reaction yields

Begin ch3: Chemical bonding: The classical description

- Successive ionization energies, $IE_n$, and shell structure

Next lecture: Continue ch3: Electron affinity (EA), electronegativity (EN), ionic character. Lewis diagrams and shapes of molecules

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## General limiting reagent recipe

2 A + 3 B → C + 2 D, 7.00 mol of A and 10.00 mol of B react with 52 % yield. How much A, B, C, and D at the end of the reaction?

| | 2A | 3B | C | 2D |
|---|---|---|---|---|
| I | 7.00 | 10.00 | 0 | 0 |
| C | −6.67 | −10.00 | +3.33 | +6.67 |
| F | 0.33 | 0 | 3.33 | 6.67 |

−6.67*0.52 −10.00*0.52 3.33*0.52 6.67*0.52

① limiting reagent

$7.00\text{ A} * \frac{C}{2A} = 3.50\text{ C}$

$10.00\text{ B} * \frac{C}{3B} = 3.33\text{ C}$

$10.00\text{ B} * \frac{2D}{3B} = 6.67\text{ D}$

$10.00\text{ B} * \frac{2A}{3B} = 6.67\text{ A}$

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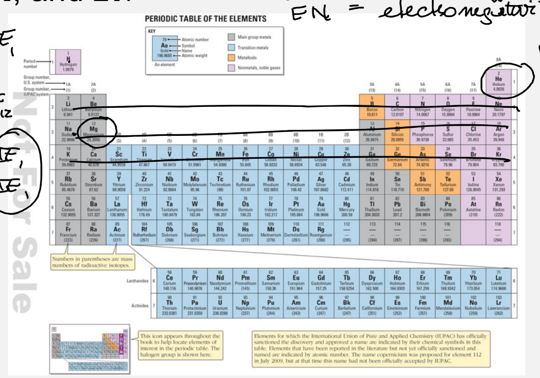
## $IE$, $EA$, and $EN$

IE = ionization energy
EA = electron affinity
EN = electronegativity

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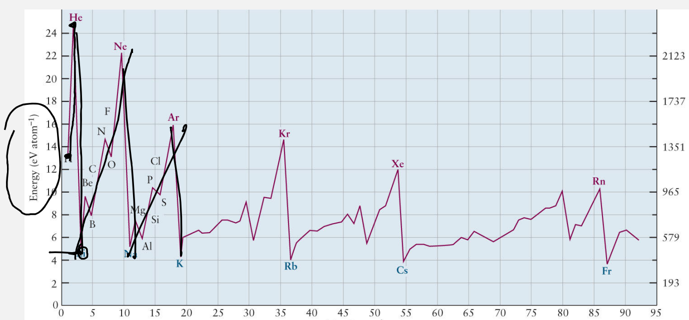
## First ionization energy, $IE_1$

$Li \rightarrow Li^+ + e^-$

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## eV/atom and kJ/mol

1 eV is the energy of 1 electron charge in a potential of 1 V = I J/C

$e^- = 1.6022 \times 10^{-19}$ C

1 eV = $1.6022 \times 10^{-19}$ C × 1 J/C = $1.6022 \times 10^{-19}$ J

For H atoms,

$IE_1 = 13.6 \frac{\text{eV}}{\text{atom}} = 13.6 \frac{\text{eV}}{\text{atom}} \times 1.6022 \times 10^{-19} \frac{\text{J}}{\text{eV}} = 21.8 \times 10^{-19} \frac{\text{J}}{\text{atom}}$

$IE_1 = 21.8 \times 10^{-19} \frac{\text{J}}{\text{atom}} \times \frac{N_A \text{ atom}}{\text{mol}} = 21.8 \times 10^{-19} \times 6.022 \times 10^{23}$ J/mol

$= 1.31 \times 10^6 \frac{\text{J}}{\text{mol}} = 1310 \frac{\text{kJ}}{\text{mol}}$

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[Quiz] Ionization energy can be expressed as kJ/mol and as eV/atom. The first ionization energy of Na atom is 5.14 eV. How many kJ are required to ionize one mole of Na atoms? Remember: electron charge is $1.60 \times 10^{-19}$ C and I V = 1 J/C.

0% 1. 300 kJ
100% 2. 500 kJ
0% 3. 700 kJ
0% 4. 900 kJ

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## Successive ionization energies

TABLE 3.1

Successive Ionization Energies of the Elements Hydrogen through Argon (in eV Atom$^{-1}$)

| Z | Element | $IE_1$ | $IE_2$ | $IE_3$ | $IE_4$ | $IE_5$ | $IE_6$ | $IE_7$ | $IE_8$ | $IE_9$ | $IE_{10}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | H | 13.60 | | | | | | | | | |
| 2 | He | 24.59 | 54.42 | | | | | | | | |
| 3 | Li | 5.39 | 75.64 | 122.45 | | | | | | | |
| 4 | Be | 9.32 | 18.21 | 153.89 | 217.71 | | | | | | |
| 5 | B | 8.30 | 25.15 | 37.93 | 259.37 | 340.22 | | | | | |
| 6 | C | 11.26 | 24.38 | 47.89 | 64.49 | 392.08 | 489.99 | | | | |
| 7 | N | 14.53 | 29.60 | 47.45 | 77.47 | 97.89 | 552.06 | 667.03 | | | |
| 8 | 0 | 13.62 | 35.12 | 54.93 | 77.41 | 113.90 | 138.12 | 739.32 | 871.39 | | |
| 9 | F | 17.42 | 34.97 | 62.71 | 87.14 | 114.24 | 157.16 | 185.18 | 953.89 | 1103.08 | |
| 10 | Ne | 21.56 | 40.96 | 63.45 | 97.11 | 126.21 | 157.93 | 207.27 | 239.09 | 1195.79 | 1362.16 |
| 11 | Na | 5.14 | 47.29 | 71.64 | 98.91 | 138.39 | 172.15 | 208.47 | 264.18 | 299.87 | 1465.10 |
| 12 | Mg | 7.65 | 15.04 | 80.14 | 109.24 | 141.26 | 186.50 | 224.94 | 265.90 | 327.94 | 367.53 |
| 13 | Al | 5.99 | 18.83 | 28.45 | 119.99 | 153.71 | 190.47 | 241.43 | 284.59 | 330.21 | 398.57 |
| 14 | Si | 8.15 | 16.35 | 33.49 | 45.14 | 166.77 | 205.05 | 246.52 | 303.17 | 351.10 | 401.43 |
| 15 | P | 10.49 | 19.73 | 30.18 | 51.37 | 65.02 | 220.43 | 263.22 | 309.41 | 371.73 | 424.50 |
| 16 | S | 10.36 | 23.33 | 34.83 | 47.30 | 72.68 | 88.05 | 280.93 | 328.23 | 379.10 | 447.10 |
| 17 | Cl | 12.97 | 23.81 | 39.61 | 53.46 | 67.8 | 97.03 | 114.19 | 348.28 | 400.03 | 455.62 |
| 18 | Ar | 15.76 | 27.63 | 40.74 | 59.81 | 75.02 | 91.01 | 124.32 | 143.46 | 422.43 | 478.68 |
| 19 | K | 4.34 | 31.63 | 45.72 | 60.91 | 82.66 | 100.0 | 117.56 | 154.86 | 175.82 | 503.44 |
| 20 | Ca | 6.11 | 11.87 | 50.91 | 67.10 | 84.41 | 108.78 | 127.7 | 147.24 | 188.54 | 211.27 |
| 21 | Sc | 6.54 | 12.80 | 24.76 | 73.47 | 91.66 | 111.1 | 138.0 | 158.7 | 180.02 | 225.32 |

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## Plot log($IE_n$) versus $n$ for Mg

You will need the final two ionization energies, $IE_{11}$ and $IE_{12}$.

https://en.wikipedia.org/wiki/Ionization_energies_of_the_elements_(data_page)

$IE_{11}$ = 1762 eV

$IE_{12}$ = 1962 eV


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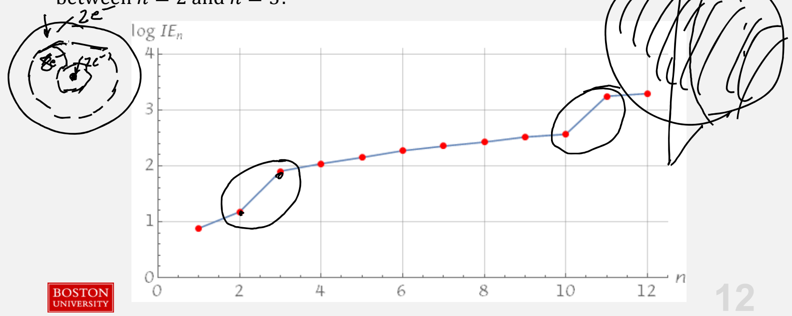
## Plot log($IE_n$) versus $n$ for Mg

Physically (in terms of Coulomb's law), what accounts for the discontinuity between $n = 2$ and $n = 3$?

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## Successive $IE_n$ → electron cloud contraction

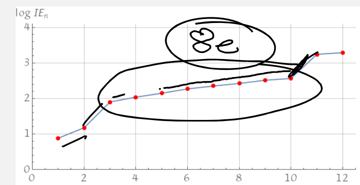
$IE_2 > IE_1$ : $Mg^{2+} > Mg^{+}$ increase in residual ion charge

$IE_3 \gg IE_2$ : $Mg^{3+} \gg Mg^{2+}$ large contraction of electron cloud

$IE_{10} > IIE_9 > \cdots > IE_3$ : increase in residual ion charge

$IE_{11} \gg IE_{10}$ : $Mg^{11+} \gg Mg^{10+}$ large contraction of electron cloud

$IE_{12} > IE_{11}$ : $Mg^{12+} > Mg^{11+}$ integer increase in residual ion charge



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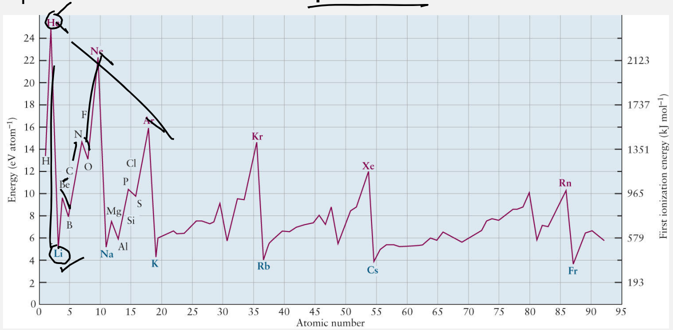
## $IE_1$ → electron cloud expansion

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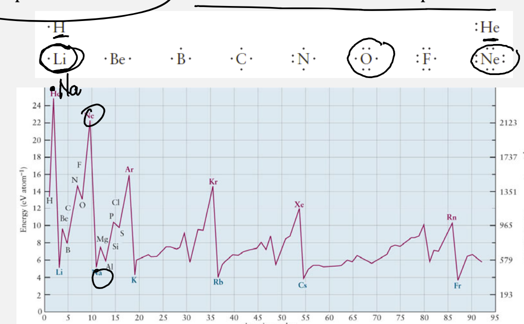
## $IE_1$ → electron cloud expansion

Lewis dot picture summarizes effect of electron cloud expansion.



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$IE_1$: $X \to X^+ + e^-$

Electron affinity, EA

Electronegativity, EN $\propto EA + IE$

Ionic character

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## Electron affinity, EA: $X^- \to X + e^-$

$F^- \to F + e^-$ 328 kJ/mol

**TABLE 3.2**

**Electron Affinity of Selected Atoms (in kJ mol$^{-1}$)**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H 73 | | | | | | | He * |
| Li 60 | Be * | B 27 | C 122 | N * | O 141 | F 328 | Ne * |
| Na 53 | Mg * | Al 42 | Si 134 | P 72 | S 200 | Cl 349 | Ar * |
| K 48 | Ca 2 | Ga 41 | Ge 119 | As 79 | Se 195 | Br 325 | Kr * |
| Rb 47 | Sr 5 | In 29 | Sn 107 | Sb 101 | Te 190 | I 295 | Xe * |
| Cs 46 | Ba 14 | Tl 19 | Pb 35 | Bi 91 | Po 183 | At 270 | Rn * |

*No stable anion A$^-$ exists for this element in the gas phase.

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## Problem 3.23a

$Cl^- \to Cl + e^-$ +349 kJ

$IE_1$(K) = 4.34 eV/atom
$IE_1$(Cl) = 12.97 eV/atom
$EA$(K) = 48 kJ/mol
$EA$(Cl) = 349 kJ/mol

**23.** Use the data in Figure 3.7 and Table 3.2 to calculate the energy changes ($\Delta E$) for the following pairs of reactions:
(a) $K(g) + Cl(g) \longrightarrow K^+(g) + Cl^-(g)$
$K(g) + Cl(g) \longrightarrow K^-(g) + Cl^+(g)$
(b) $Na(g) + Cl(g) \longrightarrow Na^+(g) + Cl^-(g)$
$Na(g) + Cl(g) \longrightarrow Na^-(g) + Cl^+(g)$
Explain why $K^+Cl^-$ and $Na^+Cl^-$ form in preference to $K^-Cl^+$ and $Na^-Cl^+$.

$K \to K^+ + e^-$ 4.34 eV = $\Delta E_1$
$e^- + Cl \to Cl^-$ −349 kJ = $\Delta E_2$
$K + Cl \to K^+ + Cl^-$ $\Delta E_3 = \Delta E_1 + \Delta E_2$ = 70 kJ/mol
$K + Cl \to K^- + Cl^+$ $\Delta E_4 = \Delta E_5 + \Delta E_6$ = 1200 kJ/mol
$e^- + K \to K^-$ $\Delta E_5$ = −48 kJ/mol
$Cl \to Cl^+ + e^-$ $\Delta E_6$ = 12.97 eV/atom = 1250 kJ/mol

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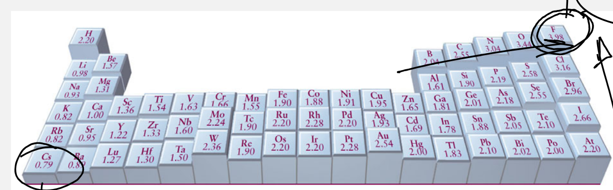
## Electronegativity: $EN \propto IE_1 + EA$

high



low

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Fig. 3-10, p. 90

## Dipole moment

$\mu$ = charge × separation

Dipole moment of charges $e^+$ and $e^-$ separated by $0.2082 \times 10^{-10}$ m is defined as one Debye,

$1 \text{ D} = 3.336 \times 10^{-30}$ C m





## Dipole moment

Typically, only a fraction, $\delta$, of an electron charge is displaced

$\pm q = \pm\delta\,|e|$

Where $\delta$ is the fractional ionic character.





## Ionic character

The internuclear distance of HF is $R_e = 0.917 \times 10^{-10}$ m and its dipole moment is 1.82 D.

Calculate dipole moment, assuming charge is |e|.

Answer: $1.602 \times 10^{-19}\text{C} \times 0.917 \times 10^{-10}\text{m} \times \frac{\text{D}}{3.336 \times 10^{-30}\text{C m}} = 4.40$ D





## Ionic character

The internuclear distance of HF is $R_e = 0.917 \times 10^{-10}$ m and its dipole moment is 1.82 D.

Calculate the fractional ionic character of HF.

Answer: $\delta = \frac{1.82 \text{ D}}{4.40 \text{ D}} = 0.41$



 

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## Ionic character

The internuclear distance of HF is $R_e = 0.917 \times 10^{-10}$ m and its dipole moment is 1.82 D. The fractional ionic character of HF is 0.41.

Percent ionic character is $\delta \times 100\ \% = 41\ \%$

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## Percent ionic character

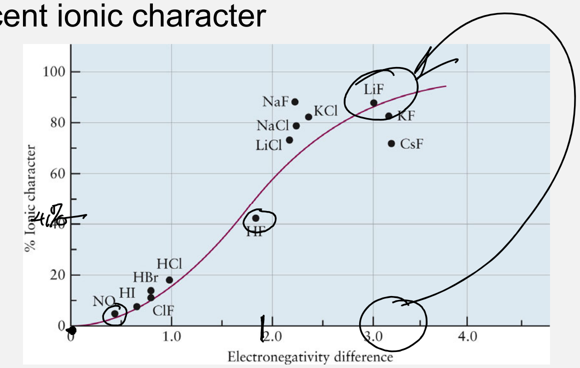


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Fig. 3-16, p. 107