General Chemistry I
Tutorial 06

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Outline

Quiz 6.1

In the following, IE_1 = first ionization energy, EA = electron affinity, and χ = electronegativity.
(a) Why is there a diagonal relationship between Li and Mg, but Zr and Hf have almost the same atomic radius?
(b) Why does Au have the highest EA in all metal elements?

Quiz 6.2

(a) Can you name an element that has a relatively high IE1 and a relatively low EA?
(b) An element that has a relatively low IE1 and a relatively high EA?

Quiz 7.1

Sort the following oxides from the least acidic to the most acidic in water, and explain the order.

$$CO_2 \quad CrO_3 \quad Mn_2O_7 \quad P_2O_5$$

Quiz 7.2

What is Born-Oppenheimer approximation?

PS 4.1

Without consulting any tables, arrange the following substances in order and explain your choice of order:

(a) Mg^{2+}, Ar, Br^{-}, Ca^{2+} in order of increasing radius;
(b) Na, Na^{+}, O, Ne in order of increasing ionization energy;
(c) H, F, Al, O in order of increasing electronegativity.

PS 4.2

In the periodic table, the halogens include Cl, Br, and I, and the alkali metals include Na, K, and Rb. These elements within each group exhibit similar but not identical chemical properties.

(a) Find out (in the textbook) the ionic radii r and electronegativities χ of all six elements;
(b) For each trio, determine whether the middle one (Br, K) is more different from the lighter one (Cl, Na) or the heavier one (I, Rb) in terms of their chemical properties;
(c) Give arguments to support your conclusion in (b). For instance, if you consider Br is more different from I, then give an example of the difference between the chemical properties of Br and I.

	Na	K	Rb	Cl	Br	I
r(Å)	0.98	1.33	1.48	1.81	1.96	2.20
χ	0.93	0.82	0.82	3.16	2.96	2.66

Table 1: Table of radius and electronegativity

PS 4.3

Consider the group IVA elements C, Si, Ge, Sn, and Pb, as well as the group IVB elements Ti, Zr, and Hf. For each of the elements, their tetrachlorides and dioxides, draw a table to list its melting point (or sublimation/decomposition point).
(a) Which group IVB element(s) shows similar properties to which group IVA element(s)?
(b) How can the group IVA and IVB elements be divided into subgroups according to their properties? Explain your reason according to the element's position in the Periodic Table.

	CCl_4	$SiCl_4$	$GeCl_4$	$SnCl_4$	$PbCl_4$	$TiCl_4$	$ZrCl_4$	$HfCl_4$
Melting Point(°C)	-22.92	-70	-49.5	-34	-15	-24	437	432
	CO_2	SiO_2	GeO_2	Sn_2	PbO_2	TiO_2	ZrO_2	HfO_2
Melting Point(°C)	-56.65	1713	1115	1630	290	1843	2715	2758
	C	Si	Ge	Sn	Pb	Ti	Zr	Hf
Melting Point(°C)	3642	1414	938	232	327	1668	1855	2233

Table 2: Table of melting point

PS 4.4

The MO of the ground state of a heteronuclear diatomic molecule AB is:

$$\psi_{mol} = C_A\varphi_A + C_B\varphi_B$$

If a bonding electron spends 90% of its time in an orbital φ_A on atom A and 10% of its time in φ_B on atom B, what are the values of C_A and C_B? (Neglect the overlap of the two orbitals.)

PS 4.5

The stable molecular ion H^{3+} is triangular, with H-H distances of 0.87 Å. Sketch the molecule and indicate the region of greatest electron density of the lowest energy MO.

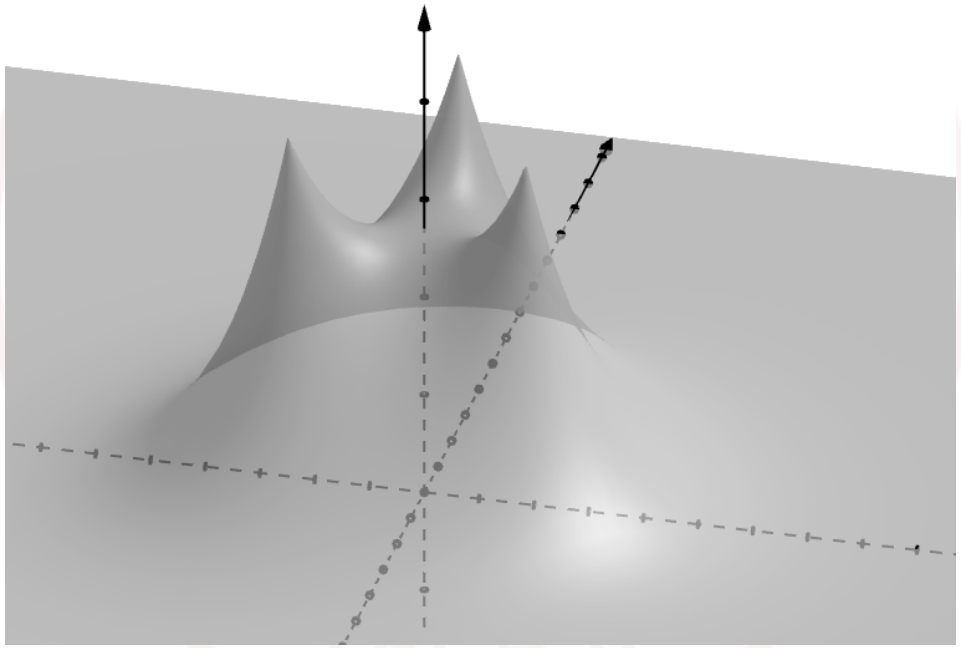

Figure 1: Electron density(ψ^2) of H_3^+

Atomic Radius

Remark 2.1

Outermost electron determines atomic radius, not electrons that're filled in last.

$$r^* = \frac{n^2}{Z_{eff}} a_0$$

For main group elements:
Increasing of atomic number by one within the same period leads to addition of an electron to s or p orbitals. Effective charge increases by 0.65. (shielding constant is 0.35 within the same group)

For transition metals:
Increasing of atomic number by one within the same period usually leads to addition of an electron to $(n-1)d$ or $(n-2)f$ orbitals.

- For d block element:
  Effective charge increases by 0.15.
- For f block element:
  Effective charge almost stays the same.

Atomic Radius

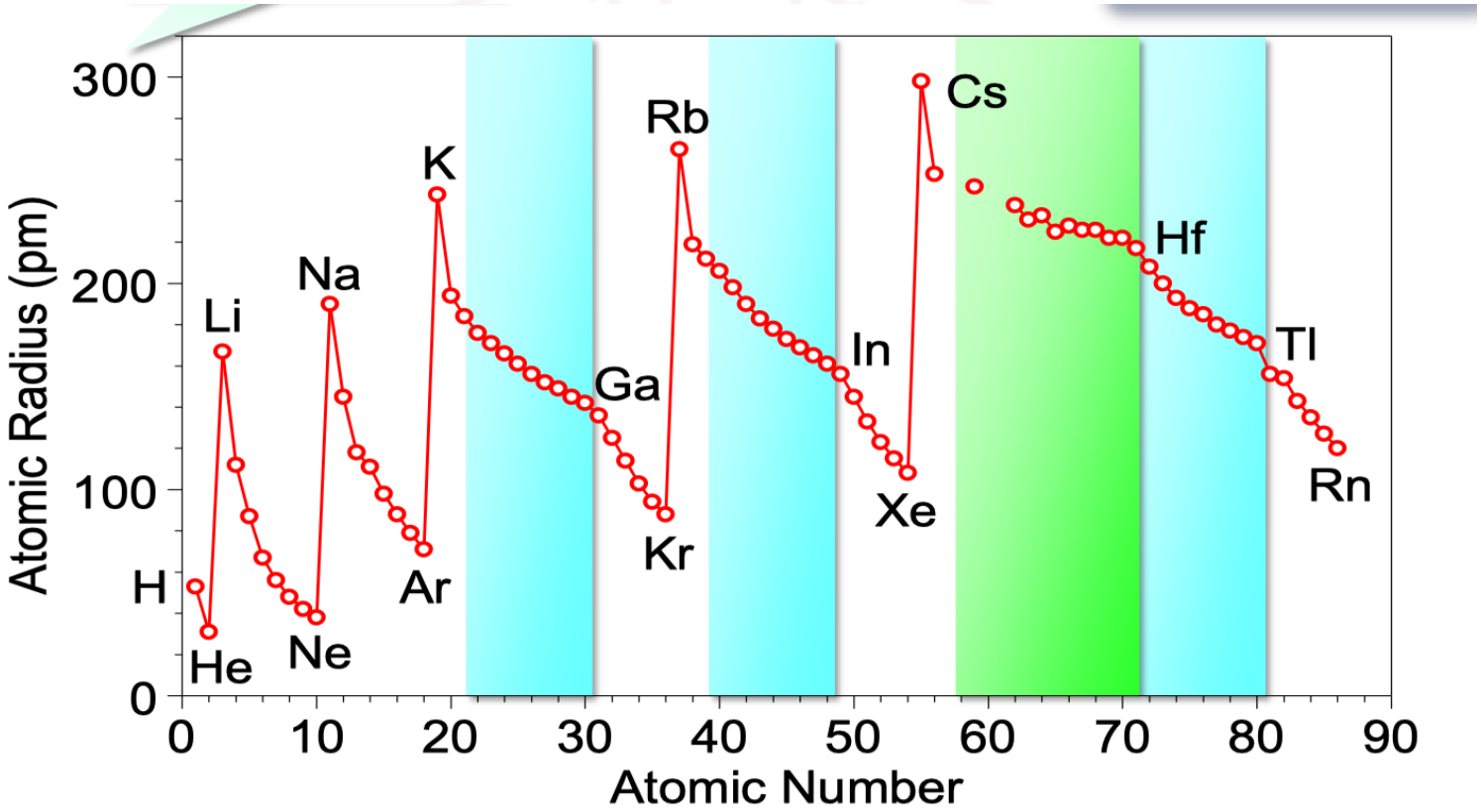

Figure 2: Atomic radius versus atomic number

Ionization Energy

$$A(g) \rightarrow A^+(g) + e^-(g) \qquad \Delta H = I_1 \approx -E_{n,z}$$

Remark 2.2

Outermost *electrons are always ionized first.*
Koopmans' theorem: We use orbital energy to estimate ionization energy.

$$E_{n,z} = -\frac{Z_{eff}^2}{n^2} Ry$$

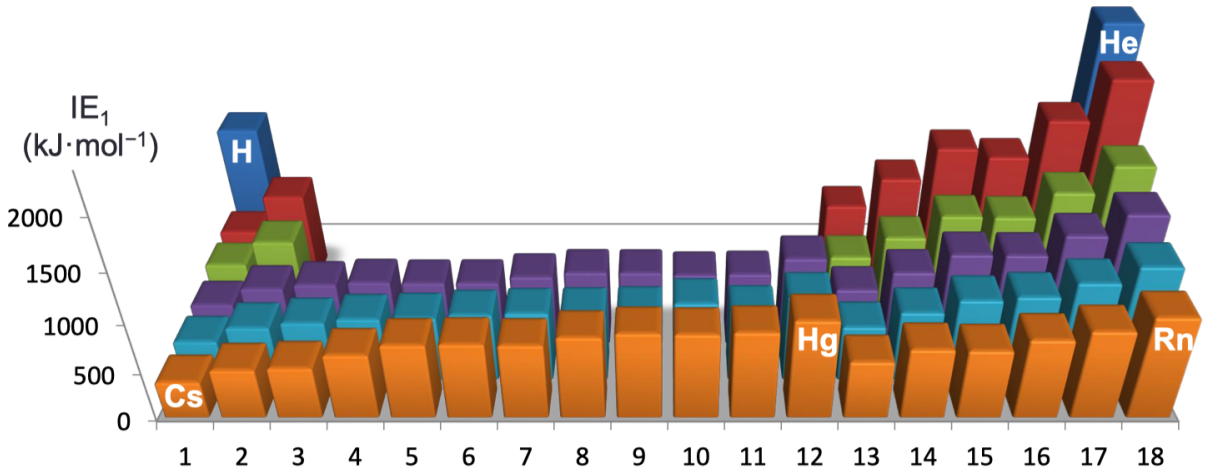

Figure 3: First ionization energy

Electron Affinity

$$A(g) + e^-(g) \rightarrow A^-(g) \qquad -\Delta H = Y$$

Remark 2.3

We use orbital energy of atom with (Z+1) electrons to approximate electron affinity.

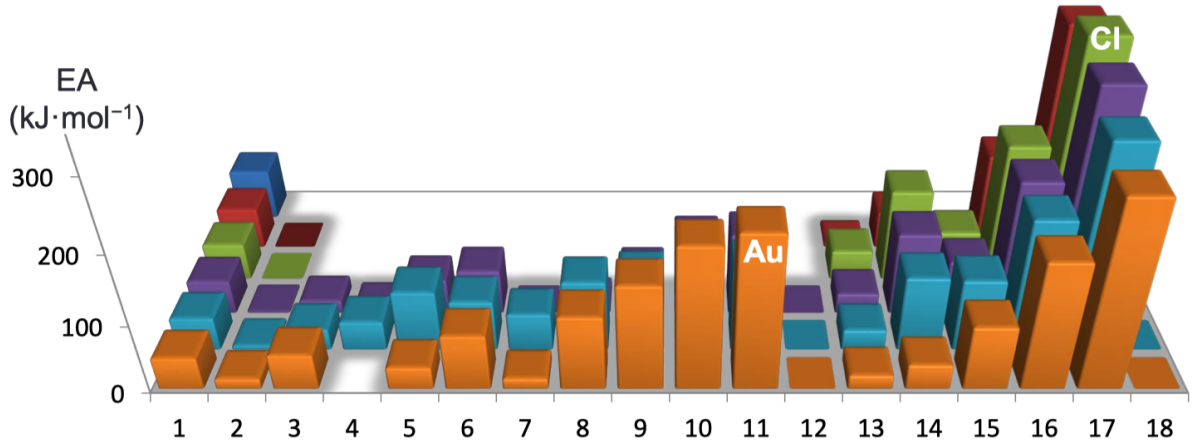

Figure 4: Electron affinity