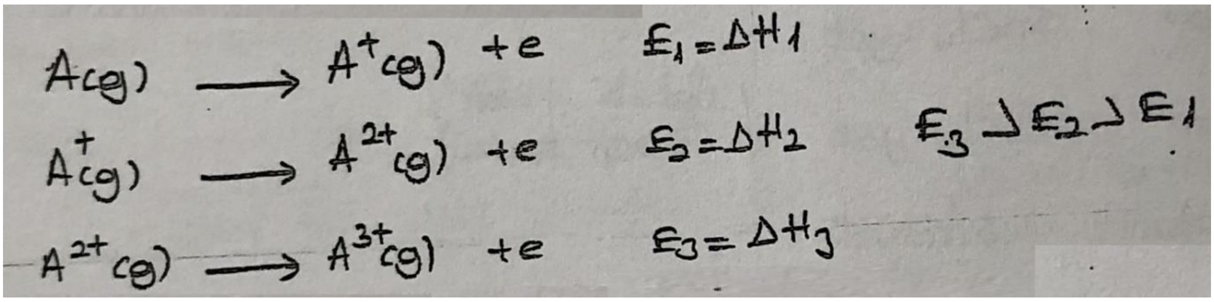
PERIODIC PROPERTIES OF ATOMS

IONIZATION ENERGY

Ionization energy is an energy needed to remove one electron from a neutral or gaseous atom. The energy needed to remove an electron from the atom is defined as the 1st ionization energy. The energy needed to remove an electron from the resulting cation is defined as the 2nd ionization energy.

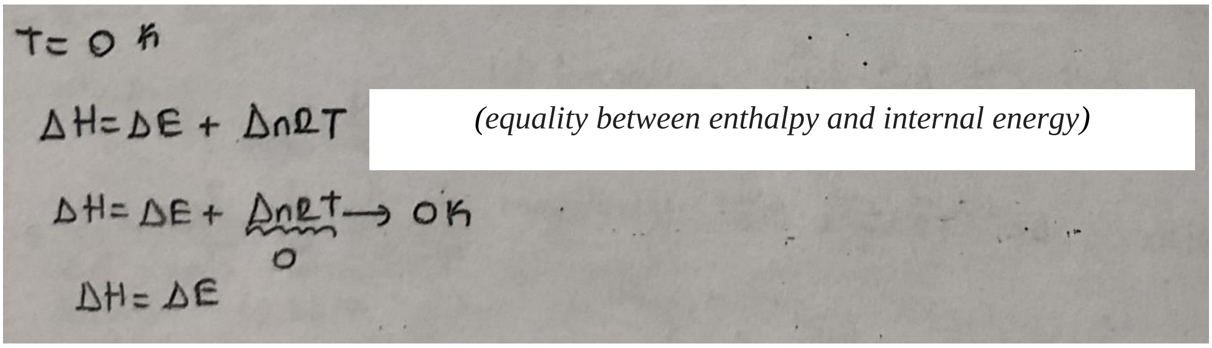


$$A_{(g)} \longrightarrow A^{+}_{(g)} + e \qquad E_1 = \Delta H_1$$

$$A^{+}_{(g)} \longrightarrow A^{2+}_{(g)} + e \qquad E_2 = \Delta H_2 \qquad E_3 > E_2 > E_1$$

$$A^{2+}_{(g)} \longrightarrow A^{3+}_{(g)} + e \qquad E_3 = \Delta H_3$$

Ionization energy is endothermic because we give the energy from the outside. Thermodynamically it is the molar energy change at the absolute zero point. The ionization energy must be measured at the absolute zero point.



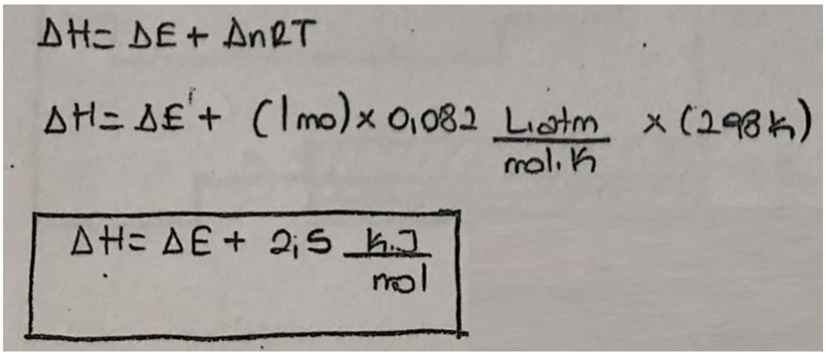
$T = 0\,K$

$\Delta H = \Delta E + \Delta nRT$ *(equality between enthalpy and internal energy)*

$$\Delta H = \Delta E + \underbrace{\Delta nRT}_{0} \rightarrow 0K$$

$$\Delta H = \Delta E$$

Under normal conditions 25°C→298K



$$\Delta H = \Delta E + \Delta nRT$$

$$\Delta H = \Delta E + (1\,mo) \times 0{,}082\,\frac{L.atm}{mol.K} \times (298\,K)$$

$$\boxed{\Delta H = \Delta E + 2{,}5\,\frac{kJ}{mol}}$$

- ✓ *When we move right on the periodic table, the atomic radius becomes smaller, the ionization energy is generally increased. But, there are exceptions to the general pattern of first ionization energies. The exceptions in the ionization energy when going from left to right are due to the global symmetrical properties of atoms.*
- ✓ *When we move down a group on the periodic table, the atomic radius increases, the ionization energy decreases.*
- ✓ *In the periodic table, while the alkali metals have the lowest ionization energy, the noble gases have the highest ionization energy. Because the 1^{st} ionization energy of the noble gases is very high because it requires a lot of energy to remove an electron from a fully charged stable layer. The element with the highest ionization energy in the periodic table is Ne, the lowest is Fr. When the 1^{st} and 2^{nd} ionization energies of the IA group elements are compared, more energy is required for the removal of a second electron from the resulting IA group element cation (ranging from 7 to 14 times). Therefore, a second electron cannot be removed from the IA group elements. This difference between the 1st and 2nd ionization energies relates to the increased effective nuclear chargeaafter the electron is removed and the electronic structure of the IA group elements.*
- ✓ *The 2^{nd} ionization energy of the IIA group elements is twice that of the 1^{st} ionization energy. That the 3th ionization energy of the IIA group elements is very high due to the fact that the energy required to break down the full internal orbitals is big.*
- ✓ *The 1st ionization energy of Be and Mg is greater than the ionization energy of the next element. Because the orbitals of these elements are full.*
- ✓ *Ionization energy depends on the type of electron removed (s>p>d>f).*
- ✓ *The ionization event begins with removing an electron in the orbital of the largest quantum number. In the transition elements, the electrons are removed from ns first and after (n-1)d. In the lanthanides and actinides, the electrons are removed from ns first and after (n-2)f.*
- ✓ *Since the radius of Al and Ga is the same, the ionization energies of them are the same ($Z^*=1.8$ for Al; $Z^*=5$ for Ga).*
- ✓ *The ionization energy of the 3^{rd} row transition elements (contrary to the general tendency) is higher than the 2^{nd} row transition elements. The reason is lanthanide contraction.*

Methods for Calculating the Ionization Energy

1. Finding ionization energy of a single-electron system

$$İE' = B.Z^2 \qquad B = 13{,}6\ \text{eV}$$

$$\sqrt{İE} = \sqrt{B}.Z$$

2. Finding ionization energy for isoelectronic systems

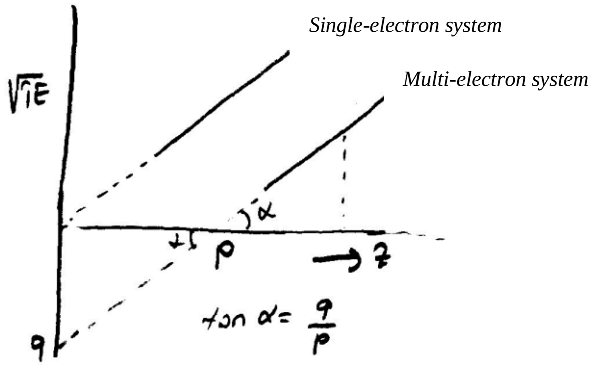
${}_{2}He$, ${}_{3}Li^{+}$, ${}_{4}Be^{2+}$, ${}_{5}B^{3+}$,${}_{6}C^{4+}$,… $2e^{-}$ $(1s^{2})$

${}_{4}Be$, ${}_{5}B^{+}$, ${}_{6}C^{2+}$, ${}_{7}N^{3+}$, ${}_{8}O^{4+}$, ${}_{9}F^{5+}$,…$4e^{-}$ $(1s^{2}\ 2s^{2})$

${}_{5}B$, ${}_{6}C^{+}$, ${}_{7}N^{2+}$, ${}_{8}O^{3+}$, ${}_{9}F^{4+}$,…$5e^{-}$ $(1s^{2}\ 2s^{2}2p^{1})$

${}_{6}C$, ${}_{7}N^{+}$, ${}_{8}O^{2+}$, ${}_{9}F^{3+}$, ${}_{10}Ne^{4+}$,…$6e^{-}$ $(1s^{2}\ 2s^{2}2p^{2})$

When plotted √IE values against atomic numbers of multi-electron isoelectronic systems, a linear trend is obtained.



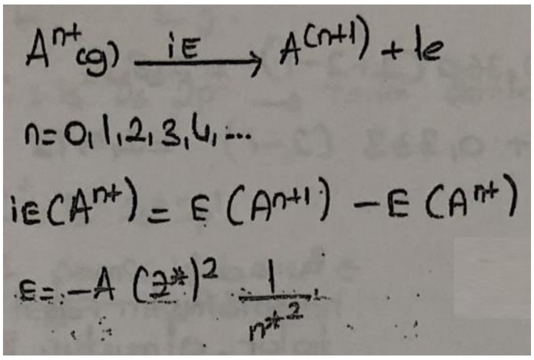
$$\sqrt{İE} = mZ + n$$

$$m = \frac{q}{p}\ ; \quad n = q$$

$$\sqrt{İE'} = \frac{q}{p}Z + q$$

Each isoelectronic series has its own p and q values. After determining these parameters for an isoelectronic sequence, the ionization energy of any one is calculated from this equation. p and q can be determined by the graphical method, and the values of two isoelectronic types are used and equation with two unknowns are formed.

3. Finding ionization energy by using Slater method



$$A^{n+}_{(g)} \xrightarrow{iE} A^{(n+1)} + 1e$$

$n = 0, 1, 2, 3, 4, \ldots$

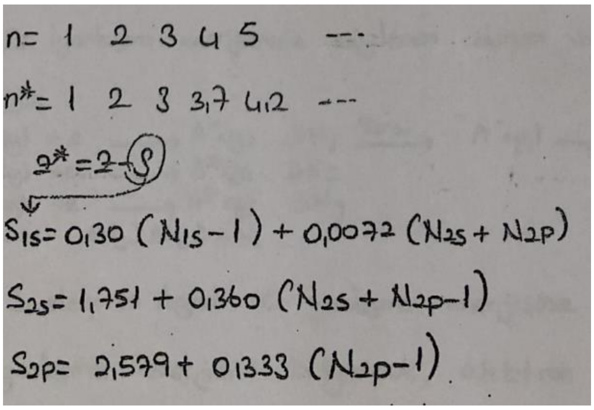
$$iE(A^{n+}) = E(A^{n+1}) - E(A^{n+})$$

$$E = -A\,(Z^*)^2\,\frac{1}{n^{*2}}$$

E formula is for single-electron system. For multi-electron systems, multiply the number of electrons. However, the Slater method does not work well after Z=20.

4. Finding ionization energy by solution of Schrödinger equation (Clamenti Raimondi)

*The purpose of this method is to correct errors in the Z * calculation of Slater. According to this method, Z * is exactly found.*



$n = 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad \ldots$

$n^* = 1 \quad 2 \quad 3 \quad 3{,}7 \quad 4{,}2 \quad \ldots$

$Z^* = Z - S$

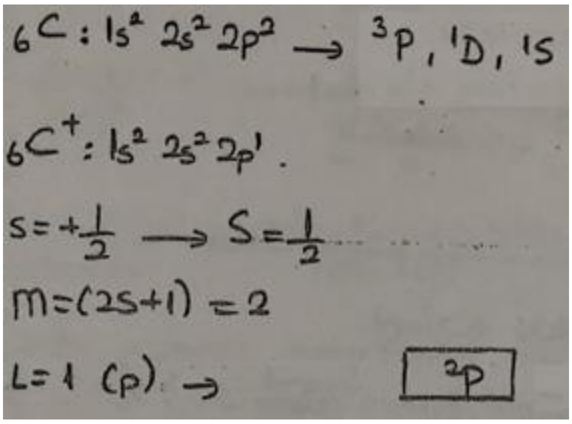
$S_{1s} = 0{,}30\,(N_{1s} - 1) + 0{,}0072\,(N_{2s} + N_{2p})$

$S_{2s} = 1{,}751 + 0{,}360\,(N_{2s} + N_{2p} - 1)$

$S_{2p} = 2{,}579 + 0{,}333\,(N_{2p} - 1)$

5. Finding ionization energy by the spectroscopic method (valence orbital ionization energy)

It is calculated from the difference in energy between the electronic states of the atom before and after ionization. For example, the spectroscopic states of C and C^+ *are used to find the ionization energy of the 2p orbital of the* $_6C$ *atom. The spectroscopic states of the C atom are determined by the orbital-orbital interaction terms (*^3P, $^1D_2$ *and* $^1S_0$*) and the spin-orbital interaction terms (*$^3P_0$, $^3P_1$, $^3P_2$, $^1D_2$ *and* $^1S_0$*). There are* ^2P *(orbital-orbital) and* $^2P_{1/2}$ *and* $^2P_{3/2}$ *(spin-orbital) terms for* C^+*. Only orbital-orbital interaction term symbols are considered for finding valence orbital ionization energy. Because the energies of* $^3P_0$, $^3P_1$, $^3P_2$ *are very close* *to each other. The spectroscopic conditions of C and C^+ and the energy differences between them are shown in the figure below.*



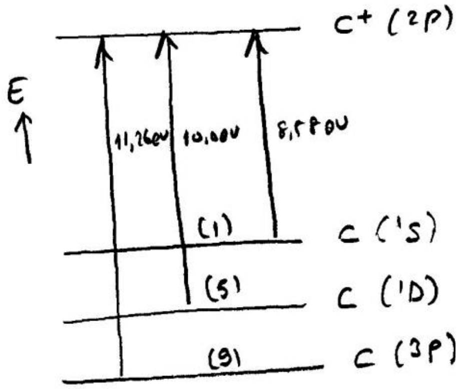
$_6C : 1s^2\,2s^2\,2p^2 \rightarrow {}^3P, {}^1D, {}^1S$

$_6C^+ : 1s^2\,2s^2\,2p^1$.

$s = +\frac{1}{2} \rightarrow S = \frac{1}{2}$

$m = (2S+1) = 2$

$L = 1\ (p) \rightarrow \boxed{{}^2P}$

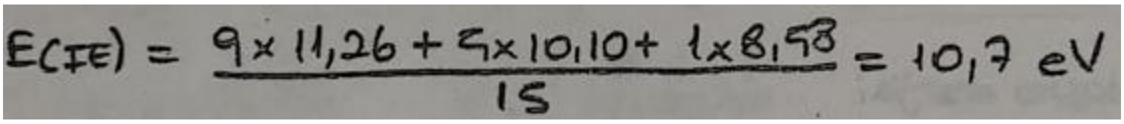


Microstate number=1

Microstate number=5

Microstate number=9

Microstate number of C atom=15



$$E(IE) = \frac{9 \times 11{,}26 + 5 \times 10{,}10 + 1 \times 8{,}58}{15} = 10{,}7\ eV$$