

9.9.9D: Ionization Potentials

The energy it takes to remove an electron from an atom to infinity is called the ionization potential or the ionization energy. Ionization energy (IP) is the energy change of the following reaction, where the energy of the infinitely separated electron, called the free electron, is defined as zero.



with

$$\Delta E = E_f - E_i = IP_1 \quad (9.9.9D.2)$$

Since the chemical reaction of one element with another involves transferring or sharing electrons, the ionization energies of the electrons affect the chemical reactivity and bonding characteristics of the elements.

The first ionization energies of the elements are illustrated in Figure 9.9.9D.1 and available in tabulated form (Table A6). The table also includes the second ionization energies



with

$$\Delta E = E_f - E_i = IP_2 \quad (9.9.9D.4)$$

and third ionization energies



with

$$\Delta E = E_f - E_i = IP_3 \quad (9.9.9D.6)$$

for some elements.

In general, ionization energy increases across a period (a horizontal row of the periodic table) and decreases down a family (a vertical column of the periodic table.) These trends are often rationalized by assuming that the ionization energy is given by the negative of the orbital energy of the highest filled orbital. This assumption, called **Koopman's theorem**, correctly predicts most of the trends in ionization energy when the Hartree-Fock orbital energies are used. The extent to which ionization energies can be predicted by orbital energies is one measure of how well the product function approximates the true multi-electron wavefunction. The applicability of Koopman's theorem also depends on the similarity between the neutral atom and the positive ion. For example, the formation of a positive ion by removing an electron reduces the total electron-electron repulsion interactions, which in turn can change the relative ordering of energy levels in the neutral and positive ion. This effect can be seen for ions in the transition elements. The electron configurations of the first row transition element ions have electrons in the 3d orbitals and no electrons in the 4s orbital. The s and d orbitals are close in energy for the transition elements, and the effect of ionization is to lower the total energy of a configuration that contains occupied 3d orbitals relative to a configuration in which some of the electrons are in the 4s orbital.

When very careful values are required to explain discrepancies between theory and experiment in ionization energies, configuration interaction is used to calculate the total energy of the neutral and, in a separate calculation, the total energy of the positive ion. The two energies are then subtracted to give the ionization energy. This is akin to what we would do to calculate ionization energies if we were able to solve the multi-electron Schrödinger equation exactly. In that case, we would know the total energy eigenvalues of the multi-electron atom and ion and there would be no single-electron atomic orbital energies to worry about.

Exercise 9.9.9D.3

How can the data in Figure 9.9.9D.1 explain why the noble gases form few compounds?

Exercise 9.9.9D. 4

Use ionization energy data to explain why higher oxidation states of Mo might be found more readily than those of Cr.

Exercise 9.9.9D. 5

How can ionization energy data be used to explain why Cu^{2+} is common, but Ag^{2+} is not?

Exercise 9.9.9D. 6

Predict the relative first ionization potentials of Ba, Pb, At, Rn and Fr.

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