Exercises 5

Exercise 5.1

a) How do atomic radii change across a period in the periodic table?
b) And within a group?
c) For the same atomic nucleus, what happens to the radius if an electron is removed? And if an electron is added? Why?
d) Without looking up their radii, rank the following atoms in order of increasing atomic radii:Se, Sr, Te, F, Br and Cs.
e) Indicate which is the largest in each of the following pairs: B/F, Cs/Cl, O/Te, B^{3+}/F^{-}, Cs^{+}/Cl^{-}, O^{2-}/Te^{2-} ?

Solution:

a) As the effective nuclear charge Z_{eff} grows from left to right in a period (we can verify this by Slater's rules) the electrons are more attracted towards the nuclei and therefore the atomic radii decrease.
b) The atomic radii grow going down a group.
c) If we remove an electron, the radius decreases (fewer electrons, larger Z_{eff}). If an electron is added, the radius increases (more electrons, Z_{eff} decreases).
d) With rules a) and b) :
   F (2, 17) < Br (4, 17) < Se (4, 16) < Te (5, 16) < Sr (5, 2) < Cs (6, 1)
e) B > F (rule a);
   Cs > Cl (Cs has many more electrons, since it is in a lower period of the periodic table);
   Te > O (rule b);
   $F^{-} > B^{3+}$ (rule a and c);
   $Cl^{-} > Cs^{+}$ (rule c for each atom; $r(Cs^{+})$ = 170 pm and $r(Cl^{-})$ = 181 pm);
   $Te^{2-} > O^{2-}$ (rule b is valid as long as the atoms have the same charge).

Exercise 5.2

Is the size of the Cl^{-} anion closer to the size of the Li^{+}, Na^{+} or K^{+} cation ? Why ?

Solution:

By taking an extra electron, chlorine will have the same number of electrons as argon, which is also the case for potassium when it loses an electron. Cl^{-} is therefore closer to the size of the K^{+} cation.

Exercise 5.3

Without looking up numerical values, rank the following atoms in ascending order of their first ionization energy: Se, Sr, Te, F, Br and Cs.

Solution:

The trends for the first ionization energies are the inverse of the trends for the atomic radii. The reason is purely electrostatic: a larger radius means that the electron with the highest energy is farther from the nucleus. The electrostatic force that holds it is therefore weaker than for an electron in a smaller atom.
So we find: Cs (6, 1) < Sr (5, 2) < Te (5, 16) < Se (4, 16) < Br (4, 17) < F (2, 17)

Exercise 5.4

Do we have to supply energy to a sulfur atom in the gas phase for it to capture an electron? And for it to capture a second one?

Solution:

According to the electron affinity table, the formation of the monocharged anion S^- releases energy since its electron affinity is positive.

On the other hand, the E_a of sulfur for the formation of the dicharged anion is −532 kJ/mol (negative). So the sulfur releases energy when it captures its first electron, but it must be supplied with energy for it to capture a second.

Exercise 5.5

What are the most probable ions formed by Li, Br, Ca, Ti? Why are these ions the most likely?

Solution:

The most probable ions here are those which have the electronic configuration of the closest noble gas, therefore: Li^+ ([He]) ; Br^- ([Kr]) ; Ca^{2+} ([Ar]) ; Ti^{4+} ([Ar])

Exercise 5.6

What charge do aluminum, sulfur and iodine atoms preferably have?

Solution:

These atoms seek to gain or lose electrons in order to satisfy the octet rule.

So the aluminum tends to lose three electrons, sulfur to gain two and iodine to gain one. The most probable loads are therefore: Al^{3+}, S^{2-} and I^-.

Exercise 5.7

How many bonds do the sodium, magnesium, carbon and chlorine atoms preferably form?

Solution:

– the valence shell of sodium is $3s^1$ ⇒ prefers 1 bond.

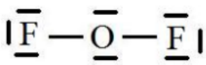
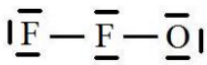
– the valence shell of magnesium is $3s^2$ ⇒ can adopt a $3s^1 3p^1$ configuration with 2 single electrons ⇒ can form 2 sp orbitals ⇒ prefers 2 bonds.

– the valence shell of carbon is $2s^2 2p^2$ ⇒ can adopt a $2s^1 2p^3$ configuration with 4 single electrons ⇒ can form 4 sp^3 orbitals ⇒ prefers 4 bonds.

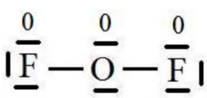
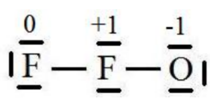
– the valence shell of chlorine is $3s^2 3p^5$ ⇒ 1 single electron ⇒ prefers to form 1 bond.

Exercise 5.8

Which of the two Lewis structures of OF_2 (or F_2O) is more likely?

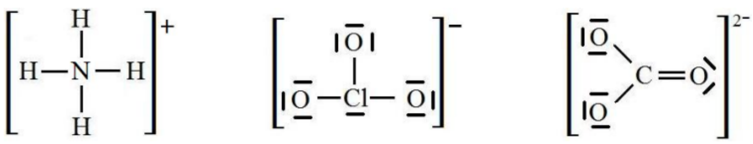
Solution:

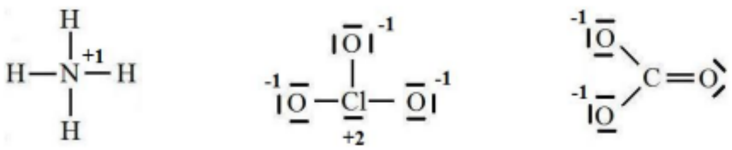
The first structure is privileged, since the sum of the absolute values of the formal loads is minimal.

Exercise 5.9

Indicate the formal charges of the atoms of the following ionic structures:



Solution:



When the charge is zero, no charge is indicated.

Exercise 5.10

Compare the magnitudes of the lattice energies of the following pairs of ionic compounds using the symbols '>' or '<'.

a) CaO BaO
b) NaI NaCl
c) LiF MgO

Solution:

Lattice energy (U) increases as the ionic radii decrease. Lattice energy is also influenced by the charges of the ions involved; a higher product of the charges results in higher lattice energy.

a) U(CaO) > U(BaO), because $r_{\mathrm{Ca}^{2+}} < r_{\mathrm{Ba}^{2+}}$
b) U(NaI) < U(NaCl), because $r_{\mathrm{I}^-} > r_{\mathrm{Cl}^-}$
c) U(LiF) < U(MgO), because $Z_{\mathrm{Li}^+} \cdot Z_{\mathrm{F}^-} < Z_{\mathrm{Mg}^{2+}} \cdot Z_{\mathrm{O}^{2-}}$

Exercise 5.11

Arrange the following ionic compounds NaCl, NaI, MgO, BaO a) in increasing order of lattice energy, b) in increasing order of melting point.

Solution:

As lattice energy increases, the melting point of ionic crystals also increases. Therefore, both properties increase in the order: NaI < NaCl < BaO < MgO.