# WS 1: Ionic Bonds[1]

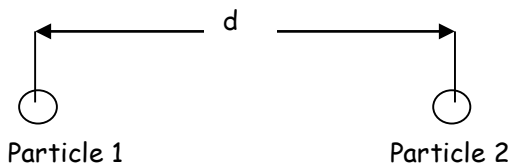
## Part I: The Ionic Bonding Model, Electrostatic attractions:[i]

Trends in ionization energies and electron affinities indicate that some elements for ions more readily than others. We know that ions with opposite charges attract each other. Ionic compounds form when the stabilization gained through ionic attraction exceeds the energy required to create ions from neutral atoms. In this handout, we will explore the concepts of ionic bonding starting with electrostatic attraction.[2]

Electrostatic attraction:[3]

With electrostatic attraction, we consider two charged particles (Q) separated by a distance of 'd', where d in this case represents the sum of the radii. Coulomb's law describes the attraction between them.

$$E_{El} = \frac{kQ_1Q_2}{d}$$




Charge on particle 1= Q1
Charge on particle 2 = Q2

Ionic bond strength can be directly related to the net strength of attractions and repulsions between the cations and anions in the ionic compound. This is described by Coulomb's law[4], which can be expressed as, "the energy of attraction (or repulsion) (electrostatic or $\Delta E_{el}$) between two particles is directly proportional to the product of the charges and inversely proportional to the distances between the centers."

[1] This information is covered in Brown and LeMay sections 8.2-8.3.
[2] Olmsted & Williams page 313
[3] See Moog & Farrell chem. Activity #3a
[4] Page 58, Silberberg, Martin S; Chemistry: The Molecular Nature Of Matter And Change.

## Questions to Help You Think About the Concept

1 If the charges ($Q_1$ & $Q_2$) remain constant, what happens to the magnitude of the electrostatic energy if the particles are moved farther apart?

2 If the particles are moved so far apart that they no longer feel an attractive force, what happens to the magnitude or value of the $\Delta E_{el}$?

3 If d is a small, finite value, and $Q_1 = Q_2$, is the $|\Delta E_{el}|$ a large value or a small value?

4 According to the electrostatic equation: if a particle with a charge of –1 is really, really close to a particle with a charge of 2+, the potential energy to separate the ions is: a) large and positive, b)large and negative, c)small and negative, or d) small and positive.

## Part II: Ionic Bonds and Coulomb' Law

The size of the lattice energy depends on the charges of the ion, their sizes and their arrangement in the solid. The behavior of ions can be generalized by the following observations:

- Within a family, ionic radii increase as the atomic number increases, that is, as the number of electron shells increases.
- The radii of cations with the same number of electrons (an isoelectronic series) decrease from left to right across a period.
    - The electronic charge cloud of these isoelectronic cations is pulled closer to the nucleus as the number of protons in the nucleus increase.
- For transition metal ions with the same charge, both the nuclear charge and the number of electrons increase from left to right across a period, and the size of the ions does not change by a large amount.
- Cations are significantly smaller than anions with the same electronic configurations.
    - For ions with the same number of electrons, the larger the nuclear charge, the more closely the electrons are pulled in toward the nucleus and the smaller the ion.
    - This translates to the larger the positive charge, the smaller the ion and the larger the negative charge, the larger the ion.
- When the same element forms two cations, the one with the higher charge is always smaller in size.
    - The radii of iron(II) and iron(III) are 75 and 64 pm, of chromium (II) and chromium (III) ions are 89 and 61 pm, and those of copper (I) and copper(II) are 96 pm and 70 pm respectively.

- The attractive interactions between two oppositely charged ions increases as the magnitude of their charges increase and as the distance between their centers decrease.

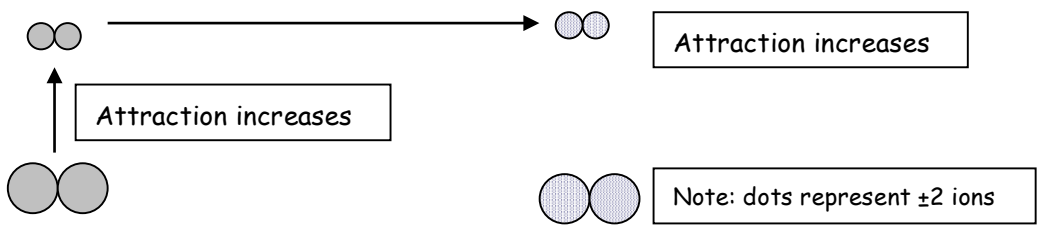
**Thus, for a given arrangement of ions, the lattice energy increases as the charges on the ions increase and as their radii decrease.**

The magnitude of lattice energies depends mostly on the ion charges because ionic radii do no vary over a very wide range. Potential energy is expressed as where Q is the charge on the particles (charge of electron (e) $=1.602\times10^{-19}$C), k is a constant ($8.99\times10^{9}$J/m•$C^{2-}$), and d (sum of radii) is the distance between their centers. By this equation, the attraction between the particles increases as the charge increases, and the distance between the ions decrease.

$$Eel = \frac{kQ_1Q_2}{d}$$

The nature of the bond between ions gives ionic compounds their characteristic behaviors of crystalline solids, with high melting and boiling points. When dissolved in a solvent (usually water), melted or vaporized into gas phase ions, the ions conduct electricity. Ionic compounds exist in huge networks. This is different from molecular compounds, which are discrete units.

Factors that influence the strength of ionic bonding: for ions of an given size, strength of attraction increases with higher ionic charge. For ions of a given charge, strength of attraction increases with smaller ionic size.[5]




For example: let's look at the attractions between LiCl and CaO. When comparing the sum of the two radii (which gives us d) for each ion pair, $d_{(LiCl)}$ = 241 ppm and $d_{(CaO)}$= 239 ppm. The 'd' for each pair is essentially the same, but when we compare the charges, there is a <u>HUGE</u> difference. The lithium and chloride ions are singly charged while the ions of CaO are ±2. the lattice energy for CaO should be 4 times greater than the lattice energy for LiCl. The observed values are 845 for LiCl and 3460 for CaO. Calcium oxide is harder and has a much higher melting point (2580°C) than LiCl (614°C), because of the stronger forces of attraction between the doubly charged ions. calcium oxide is also very much less soluble than LiCl.[6]

[5] Page 58, Silberberg, Martin S; chemistry: the molecular nature eof matter and change.
[6] Silberg, Bernice page 824-830

## Questions To Start You Thinking:

1. In LiCl, what are the charges on the ions?

2. Looking at the picture of sodium chloride in your textbook or on the internet; the two different types of ions are represented by spheres of different sizes.
   a) Which spheres represent the sodium ions and which spheres represent the chloride ions?

3. Now imagine the compound magnesium oxide.

   a) What is the charge on the cation formed from Mg?
   b) What is the charge on the anion formed from O?
   c) What is the formula for the ionic compound containing magnesium ions and oxide ions?
   d) Which compound should have the largest lattice energy, magnesium oxide or sodium chloride?

4. Which is larger a fluoride ion or a chloride ion? Explain your answer.

5. Account for the following variation in lattice energies (in kJ/mol) observed for the potassium halides:

   KF [817], KCl [718], KBr [688], KI [636].

## Problems and Exploration:

1. When Na(s) and $Cl_2$(g) react, the ionic compound NaCl(s) forms. Predict the formula of ionic compounds formed from the following combinations of elements:

   a) Sodium metal and liquid bromine _____
   b) Lithium metal and oxygen gas _____
   c) Aluminum metal and nitrogen gas _____
   d) Magnesium metal and liquid bromine _____
   e) Calcium metal and oxygen gas _____

2. A representative group metal reacts with chlorine and with oxygen to form ionic compounds with the formulas $MCl_4$ and $MO_2$. Propose a possible identity for the metal M. Explain your reasoning.

3. One measure of the strength of the bonds holding the ions together is the melting point: the more strongly the ions are held together, the higher the melting point.

The units for $\Delta E_{el}$ is kJ/mol, 1e = $1.602 \times 10^{-19}$C, d is the meter, and k = $8.99 \times 10^{9}$ J/m•$C^{2-}$.
<u>WATCH YOUR UNITS!</u>

<u>Example:</u> $Rb_2O$ we consider the charge between the $Rb^+$ and the $O^{2-}$

$$\frac{8.99x10^9 J}{mx\ C^2} x \frac{(1+)(2-)x(1.602\ x10^{-19}C)^2}{1.66\ x10^{-10}m + 1.26\ x10^{-10}m} x \frac{(6.022x10^{23}\ ion\ pair)}{mole} \frac{kJ}{1000J}$$
$$= 476\ kJ/mol$$

<u>Now you try!</u>
**Melting points are in the handout. You need to do the problems to find them.

| Ionic compound | Radius (in pm) | | D= $r_{cation}$ + $r_{anion\ in\ pm}$ | Charge | | $E_{El} = \frac{kQ_1Q_2}{d}$ (kJ/mol) | Melting point |
|---|---|---|---|---|---|---|---|
| | Cation | anion | | Cation | Anion | | |
| NaF | 102 | 133 | 235 | 1+ | 1– | 591 | |
| NaCl | 102 | 181 | 283 | 1+ | 1– | | |
| MgO | 72 | 140 | 212 | 2+ | 2– | | |
| MgS | 72 | 184 | 256 | 2+ | 2– | | |

Fill in the chart above before answering the questions below. Melting points are presented in problems below

Questions To Start You Thinking:

1. Consider the ionic compounds NaF and NaCl. In which compound is the columbic force of attraction greater? NaCl has a melting point of 801°C. Which of these would you predict is the melting point of NaF: 609°C, 800°C, 993°C? Explain your reasoning.

2. Consider the ionic compounds MgO and MgS: In which compound is the columbic force of attraction greater? MgO has a melting point of 2852°C. Which of these would you predict is the melting point of MgS: ≈2000°C, ≈2850°C, ≈ 4000°C? Explain your reasoning.

3. Based on your choices for the melting points, which factor, the size of the ions or the charge of the ions has the larger effect on the melting point?

## Problems and Exploration:

1. Predict which ionic compound has the higher melting point in each of the following pairs

   a) NaCl and NaBr

   b) NaCl and KCl

   c) MgO and CaO

   d) KCl and CaO

   e) NaCl and MgS

   f) NaCl and NaF

2. Rank the following compounds in order of increasing melting point and explain your reasoning:
   CaO CaS KCl $K_2S$

3. For each of the following, which compound is expected to have the highest melting point? Explain your choice in one or two sentences.

   a) LiF; LiCl; NaF; NaCl; KI

   b) NaF; NaCl; CaS; CaO

   c) $Na_2SO_4$; $K_2SO_4$; $CaSO_4$; $BaSO_4$

   d) LiF; CaO; BaO; $Al_2O_3$

   e) $H_2O$; $NH_3$; $N_2$; $CaSO_4$; $O_2$

## Part III: Ionic bonds

Ionic compounds are electrically neutral and consist of infinite arrays of positive and negative ions held together by electrostatic forces. These arrays are generally lower in energy then the isolated ions because of the electrostatic attraction between particles of opposite charge. No bond is purely ionic, but the ionic bond, the description of bonding in terms of ions, is a good starting point for the discussion of bonding in many compounds, particularly compounds containing cations that come from elements of the s block, such as sodium chloride and magnesium oxide,

When a cation and an anion come together, they form an ion pair and energy is released. This energy is the standard enthalpy change needed for the conversion of one mole of solid to a gas of ions, which is called The Lattice Energy.

Knowledge of the lattice energy is important for judging whether an ionic compound is likely to form. We see that the formation of an ion pair depends on the overall change in energy when ions are formed. A net input of energy is required to form the gas-phase ions from the atoms. The ion pair forms only because the interaction between two neighboring ions is so strong that the net outcome is a reduction in energy.

We can predict the charge of the ion by considering the Z-effective, electron affinity, ionization energy, and the electron configuration of the parent atom. Atoms that have loosely held electrons in outer orbitals tend to form cations. The ionization energy is low and the electron affinity is high. Atoms, which have tightly held electrons, have high ionization energies and large exothermic electron affinities. These atoms tend to gain electrons.

Questions To Start You Thinking:

1. Compounds that contain ions formed from group 1A atoms have a 1+ charge, rather than a 2+ charge. Explain this based on Z-effective, electron affinity, ionization energy, and/or electron configuration.

2. Compounds that contain ions formed from group 7A atoms are —1. Why would it not be 2–? Explain this based on Z-effective, electron affinity, ionization energy, and/or electron configuration.

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[i] This handout is based on the works of MOOG and Farrell. Moog, Richard & Farrell, John; Chemistry, A guided Inquiry; 3rd ed.;