Ionic Bonding

Ionic bonds are characterized by the complete transfer of electrons from one atom to another, resulting in the formation of two charged particles known as ions, which are held together with the help of electrostatic forces.

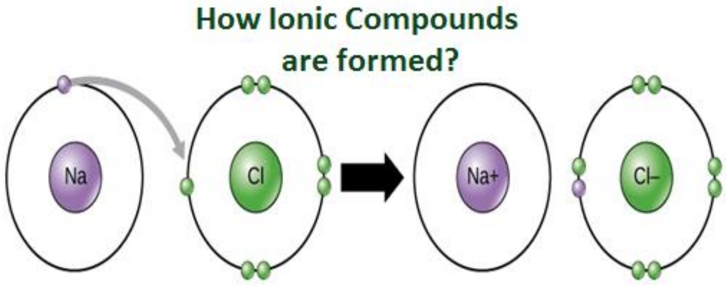
An Ionic bond is formed when one of the atoms can donate electrons to achieve the inert gas electron configuration and the other atom needs electrons to achieve the inert gas electron configuration. That is the chemical bond formed by the transfer of electrons from one atom to another. Ionic bond is also known as electrovalent bond and compounds composed of Ionic bonds are called ionic compounds. Therefore, it will not be wrong to say that ions form ionic compounds.
When a metal reacts with a non-metal, then they form ionic bond and the compound is called the ionic compound. As a result of reaction between metal and non-metal, they are bonded with electrostatic force of attraction with each other; such bonds are called chemical bonds.

For an example:

Formation of Sodium Chloride

Sodium is a metal whereas chlorine is a non-metal. Sodium metal reacts with chlorine to form an ionic compound, sodium chloride. Now we will see how sodium chloride is formed and what changes takes place in the electronic arrangements of sodium and chlorine atoms in the formation of this compound.

The atomic number of sodium is 11, so its *electronic configuration is* $1s^2,2s^2,2p^6,3s^1$. Sodium has only one electron in its outermost shell. So, sodium atom will donate one electron to chlorine atom and forms a sodium ion i.e. Na^+.
On the other side **chlorine atomic number is 17**, its *electronic configuration is* $1s^2,2s^2,2p^6,3s^2, 3p^5$. Therefore, chlorine atom has 7 electrons in the outermost shell and needs one more electron to achieve stable electronic configuration or inert gas configuration. So, a chlorine atom takes one electron from sodium atom and forms a negatively charged chloride ion i.e. Cl-.



Physical Properties of Ionic Compounds

Melting Points

Because of the many simultaneous attractions between cations and anions that occur, ionic crystal lattices are very strong. The process of melting an ionic compound requires the addition of large amounts of energy in order to break all of the ionic bonds in the crystal. For example, sodium chloride has a melting temperature of about $800^{o}C$.

Shattering

Ionic compounds are generally hard, but brittle. Why? It takes a large amount of mechanical force, such as striking a crystal with a hammer, to force one layer of ions to shift relative to its neighbor. However, when that happens, it brings ions of the same charge next to each other. The repulsive forces between like-charged ions cause the crystal to shatter. When an ionic crystal breaks, it tends to do so along smooth planes because of the regular arrangement of the ions.

Conductivity

The ionic bonded molecules in their aqueous solutions or in the molten state are good conductors of electricity. This is due to the presence of ions which acts as charge carriers.

Ionic Bonding and Lattice Energy

Ions are atoms or molecules which are electrically charged. **Cations** are positively charged and **anions** are negatively charged. Ions form when atoms gain or lose valence electrons. Since electrons are negatively charged, an atom that loses one or more electrons will become positively charged; an atom that gains one or more electrons becomes negatively charged. **Ionic bonding** is the attraction between positively- and negatively-charged ions. These oppositely charged ions attract each other to form ionic networks, or **lattices**. Electrostatics explains why this happens: opposite charges attract and like charges repel. When many ions attract each other, they form large, ordered, crystal lattices in which each ion is surrounded by ions of the opposite charge. Generally, when metals react with non-metals, electrons are transferred from the metals to the non-metals. The metals form positively-charged ions and the non-metals form negatively-charged ions.

The properties of ionic compounds follow from the orderly crystal lattice arrangement of tightly bonded charged particles that make them up. Ionic compounds tend to have high melting and boiling points, because the attraction between ions in the lattice is very strong. Moving ions out of the lattice disrupts the structure, so ionic compounds tend to be brittle rather than malleable. Ionic compounds do not conduct electricity in the solid state because ions are not free to move around the lattice; however, when ionic compounds are dissolved, they may *dissociate* into individual ions which move freely through the solution and therefore conduct electricity well.

Generating Ionic Bonds

Ionic bonds form when metals and non-metals chemically react. By definition, a metal is relatively stable if it loses electrons to form a complete valence shell and becomes positively charged. Likewise, a non-metal becomes stable by gaining electrons to complete its valence shell and become negatively charged. When metals and non-metals react, the metals lose electrons by transferring them to the non-metals, which gain them. Consequently, ions are formed, which instantly attract each other—ionic bonding. In the overall ionic compound, positive and negative charges must be balanced, because electrons cannot be created or destroyed, only transferred. Thus, the total number of electrons lost by the cationic species must equal the total number of electrons gained by the anionic species.

Ionic compounds are held together by electrostatic forces, which are described in classical physics by **Coulomb's Law**. According to this law, the energy of the electrostatic attraction (E) between two charged particles is proportional to the magnitude of the charges Q1 and Q2 and inversely proportional to the internuclear distance between the particles (r):

$E \propto Q_1 Q_2 / r$

The energy of attraction (E) is a type of *potential energy*, since it is based on the position of the charged particles relative to each other. If the two particles have opposite charges (as in ionic compounds), the value of (EE) will be negative, meaning that energy is *released* by bringing the particles together—that is, the particles naturally *attract* each other. According to Coulomb's Law, the larger the magnitude of the charges on each particle, the stronger the attraction will be. So, for example, Mg^{2+} and O^{2-} will have a stronger attraction than Na^+ and Cl^-, because of the larger charges. Also, the closer together the charges are, the stronger the attraction. Therefore, smaller ions also form stronger ionic bonds.

In an ionic lattice, many more than two charged particles interact simultaneously, releasing an amount of energy known as the **lattice energy**. The lattice energy is not exactly the same as that predicted by Coulomb's Law, but the same general principles of electrostatic attraction apply. *In an ionic compound, the value of the lattice energy corresponds to the strength of the ionic bonding.*

Electron Configuration of Ions

If ionic bonding becomes stronger for compounds with more highly charged ions, why does sodium only lose one electron to form Na^+ rather than, say, Na^{2+}? The number of electrons transferred between ions depends not only on the energy released in lattice formation but also on the energy required to strip away electrons from one atom and add them to another. In other words, *the lattice energy released by ionic compound formation must be balanced against the required ionization energy and electron affinity of forming the ions.* Since the Na^+ ion has a noble gas electron configuration, stripping away the next electron from this stable arrangement would require more energy than what is released during lattice formation (Sodium I_2 = 4,560 kJ/mol). Thus, sodium is present in ionic compounds as Na^+ and not Na^{2+}. Likewise, adding an electron to fill a valence shell (and achieve noble gas electron configuration) is exothermic or only slightly endothermic. To add an additional electron into a ***new*** subshell requires tremendous energy - more than the lattice energy. Thus, we find Cl^- in ionic compounds, but not Cl^{2-}. As a general rule, main group elements only form ions with the nearest noble gas electron configuration - otherwise, the lattice energy would not be enough to compensate for the ionization energy / electron affinity

Typical values of lattice energy can compensate for values as large as I_3 for valence electrons (i.e. can strip away up to 3 valence electrons from cations). Because most transition metals would require the removal of more than 3 electrons to attain a noble gas core, they are not found in ionic compounds with a noble gas core. A transition metal always loses electrons first from the higher 's' subshell, before losing from the underlying 'd' subshell. (The remaining electrons in the unfilled d subshell are the reason for the bright colors observed in many transition metal compounds!) For example, iron ions will **not** form a noble gas core:

- Fe: $[Ar]4s^2 3d^6$
- Fe^{2+}: $[Ar]\ 3d^6$
- Fe^{3+}: $[Ar]\ 3d^5$

Some metal ions can form a pseudo noble gas core (and be colorless), for example:

- Ag: $[Kr]5s^1 4d^{10}$ Ag^+ $[Kr]4d^{10}$ Compound: AgCl
- Cd: $[Kr]5s^2 4d^{10}$ Cd^{2+} $[Kr]4d^{10}$ Compound: CdS

Note: The silver and cadmium atoms lost the 5s electrons in achieving the ionic state. Remember that atoms always lost electrons from the subshell with the highest *n* quantum number first (i.e. 5s before 4d).

When a positive ion is formed from an atom, electrons are **always** lost first from the subshell with the largest principle quantum number.

Polyatomic Ions

Not all ionic compounds are formed from only two elements. Many **polyatomic ions** exist, in which two or more atoms are bound together by covalent bonds. They form a stable grouping which carries a charge (positive or negative). The group of atoms as a whole acts as a charged species in forming an ionic compound with an oppositely charged ion. Polyatomic ions may be either positive or negative, for example:

- NH_4^+ (ammonium) = cation
- SO_4^{2-} (sulfate) = anion

The principles of ionic bonding with polyatomic ions are the same as those with monatomic ions. Oppositely charged ions come together to form a crystalline lattice, releasing a lattice energy. Based on the shapes and charges of the polyatomic ions, these compounds may form crystalline lattices with interesting and complex structures.

Energetics of Ionic Bond Formation

Ionic bonds are formed when positively and negatively charged ions are attracted by electrostatic forces. Consider a single pair of ions, one cation and one anion. How strong will the force of their attraction be? We can rewrite **Coulomb's Law** quantitatively for any two charged particles:

E=kQ1Q2/r

where each ion's charge is represented by the symbol *Q* and the internuclear distance between the particles is represented by (rr). The proportionality constant *k* is equal to 2.31×10^{-28} J·m. This value of *k* includes the charge of a single electron (1.6022×10^{-19} C) for each ion. The equation can also be written using the charge of each ion, expressed in coulombs (C), incorporated in the constant. In this case, the proportionality constant, *k*, equals 8.999 × 109 J·m/C^2. In the example given, $Q_1 = +1(1.6022 \times 10^{-19}$ C) and $Q_2 = -1(1.6022 \times 10^{-19}$ C). If Q1 and Q2 have opposite signs (as in NaCl, for example, where Q_1 is +1 for Na^+ and Q_2 is −1 for Cl^-), then *E* is negative, which means that energy is *released* when oppositely charged ions are brought together from an infinite distance to form an isolated ion pair.

Energy is always released when a bond is formed and correspondingly, it always requires energy to break a bond.

As shown by the green curve in the lower half of below Figure , the maximum energy would be released when the ions are infinitely close to each other, at $r = 0$. Because ions occupy space and have a structure with the positive nucleus being surrounded by electrons, however, they cannot be infinitely close together. At very short distances, repulsive electron–electron interactions between electrons on adjacent ions become stronger than the attractive interactions between ions with opposite charges, as shown by the red curve in the upper half of Figure . The total energy of the system is a balance between the attractive and repulsive interactions. The purple curve in Figure shows that the total energy of the system reaches a minimum at r_0, the point where the electrostatic repulsions and attractions are exactly balanced. This distance is the same as the experimentally measured **bond distance**.

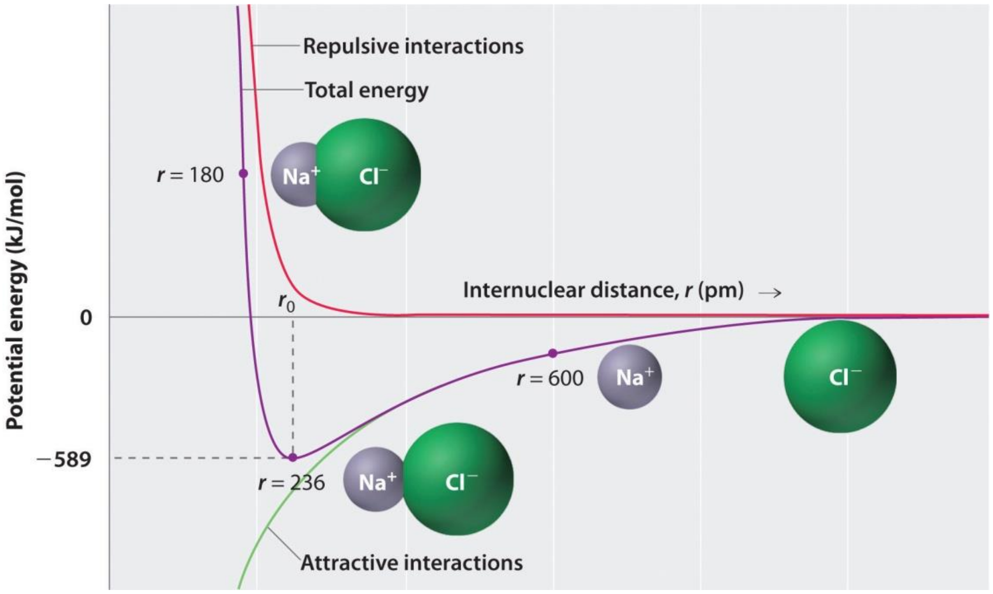


Figure: Plot of Potential Energy versus Internuclear Distance for the Interaction between a Gaseous Na^+ Ion and a Gaseous Cl^- Ion. The energy of the system reaches a minimum at a particular distance (r_0) when the attractive and repulsive interactions are balanced.

Consider the energy released when a gaseous Na^+ ion and a gaseous Cl^- ion are brought together from $r = \infty$ to $r = r_0$. Given that the observed gas-phase internuclear distance is 236 pm, the energy change associated with the formation of an ion pair from an $Na^+(g)$ ion and a $Cl^-(g)$ ion is as follows:

$E = kQ1Q2/r_0$

$= (2.31\times10^{-28} J\cdot m)[(+1)(-1)/236 pm\times10^{-12} m/pm] = -9.79\times10^{-19}$ J/ionpair

The negative value indicates that energy is released. Our convention is that if a chemical process provides energy to the outside world, the energy change is negative. If it requires energy, the energy change is positive. To calculate the energy change in the formation of a mole of NaCl pairs, we need to multiply the energy per ion pair by Avogadro’s number:

$E = (-9.79\times10^{-19}\ \text{J/ionpair})\ (6.022\times10^{23}\ \text{ionpair/mol}) = -589\text{kJ/mol}$

This is the energy released when 1 mol of gaseous ion pairs is formed, *not* when 1 mol of positive and negative ions condenses to form a crystalline lattice. Because of long-range interactions in the lattice structure, this energy does not correspond directly to the **lattice energy** of the crystalline solid.

Born–Landé equation

The **Born–Landé equation** is a mean of calculating the lattice energy of a crystalline ionic compound. In 1918 Max Born and Alfred Landé proposed that the lattice energy could be derived from the electrostatic potential of the ionic lattice and a repulsive potential energy term.

$$\Delta U(0K)= -N_AM|Z^+||Z^-|e^2\ (1-1/n)/4\pi\epsilon_o r_o$$

where:

- N_A = Avogadro constant;
- M = Madelung constant, relating to the geometry of the crystal;
- z^+ = numeric charge number of cation
- z^- = numeric charge number of anion
- e = elementary charge, 1.6022×10^{-19} C
- ε_0 = permittivity of free space

$4\pi\varepsilon_0 = 1.112\times10^{-10}\ C^2/(J\cdot m)$

Derivation

The ionic lattice is modeled as an assembly of hard elastic spheres which are compressed together by the mutual attraction of the electrostatic charges on the ions. They achieve the observed equilibrium distance apart due to a balancing short range repulsion.

Electrostatic potential

The electrostatic potential energy, E_{pair}, between a pair of ions of equal and opposite charge is:

$\Delta U = -Z^2 e^2 / 4\pi\epsilon_o r$

where

z = magnitude of charge on one ion

e = elementary charge, 1.6022×10^{-19} C

ε_0 = permittivity of free space

$4\pi\varepsilon_0 = 1.112\times10^{-10}\ C^2/(J\cdot m)$

r = distance separating the ion centers

For a simple lattice consisting ions with equal and opposite charge in a 1:1 ratio, interactions between one ion and all other lattice ions need to be summed to calculate E_M, sometimes called the Madelung or lattice energy:

$\Delta U = - N_A M Z^2 e^2 / 4\pi\epsilon_o r$

where

M = Madelung constant, which is related to the geometry of the crystal

r = closest distance between two ions of opposite charge

Repulsive term

Born and Lande suggested that a repulsive interaction between the lattice ions would be proportional to $1/r^n$ so that the repulsive energy term, E_R, would be expressed:

$\Delta U = N_A B / r^n$

where

B = constant scaling the strength of the repulsive interaction

r = closest distance between two ions of opposite charge

n = Born exponent, a number between 5 and 12 expressing the steepness of the repulsive barrier

The total intensive potential energy of an ion in the lattice can therefore be expressed as the sum of the Madelung and repulsive potentials:

$$\Delta U = -M\, N_A Z^2 e^2 / 4\pi\epsilon_o r \;+\; N_A B / r^n$$

Minimizing this energy with respect to r yields the equilibrium separation r_0 in terms of the unknown constant B

$$B = -\, N_A M Z^2 e^2 r_0^{(n-1)} / 4\pi\epsilon_o n$$

Evaluating the minimum intensive potential energy and substituting the expression for B in terms of r_0 yields the Born–Landé equation:

$$E(r_o) = -M N_A Z^2 e^2 (1 - 1/n) / 4\pi\epsilon_o r_o$$

Solvation energy

The change in Gibbs energy when an ion or molecule is transferred from a vacuum (or the gas phase) to a solvent. The main contributions to the solvation energy come from:

1. the cavitation energy of formation of the hole which preserves the dissolved species in the solvent;
2. the orientation energy of partial orientation of the dipoles;
3. the isotropic interaction energy of electrostatic and dispersion origin; and
4. the anisotropic energy of specific interactions, *e.g.* hydrogen bonds, donor-acceptor interactions *etc.*

Lattice Energy

Lattice Energy is a type of potential energy that may be defined in two ways. In one definition, the lattice energy is the energy required to break apart an ionic solid and convert its component atoms into gaseous ions. This definition causes the value for the lattice energy to always be positive, since this will always be an endothermic reaction. The other definition says that lattice energy is the reverse process, meaning it is the energy released when gaseous ions bind to form an ionic solid. As implied in the definition, this process will always be exothermic, and thus the value for lattice energy will be negative. Its values are usually expressed with the units kJ/mol.

Lattice Energy is used to explain the stability of ionic solids. Some might expect such an ordered structure to be less stable because the entropy of the system would be low. However, the crystalline structure allows each ion to interact with multiple oppositely charge ions, which causes a highly favorable change in the enthalpy of the system. A lot of energy is released as the oppositely charged ions interact. It is this that causes ionic solids to have such high melting and boiling points. Some require such high temperatures that they decompose before they can reach a melting and/or boiling point.

Born-Haber Cycle

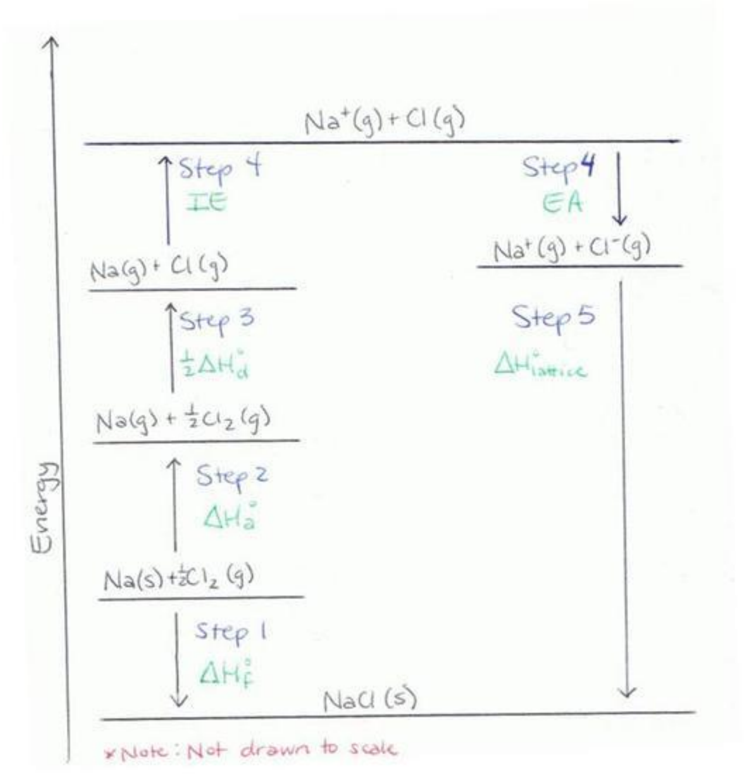
There are several important concept to understand before the Born-Haber Cycle can be applied to determine the lattice energy of an ionic solid; ionization energy, electron affinity, dissociation energy, sublimation energy, heat of formation, and Hess's Law.

- **Ionization Energy** is the energy required to remove an electron from a neutral atom or an ion. This process always requires an input of energy, and thus will always have a positive value. In general, ionization energy increases across the periodic table from left to right, and decreases from top to bottom. There are some excepts, usually due to the stability of half-filled and completely filled orbitals.
- **Electron Affinity** is the energy released when an electron is added to a neutral atom or an ion. Usually, energy released would have a negative value, but due to the definition of electron affinity, it is written as a positive value in most tables. Therefore, when used in calculating the lattice energy, we must remember to subtract the electron affinity, not add it. In general, electron affinity increases from left to right across the periodic table and decreases from top to bottom.
- **Dissociation energy** is the energy required to break apart a compound. The dissociation of a compound is always an endothermic process, meaning it will always require an input of energy. Therefore, the change in energy is always positive. The magnitude of the dissociation energy depends on the electronegativity of the atoms involved.
- **Sublimation energy** is the energy required to cause a change of phase from solid to gas, bypassing the liquid phase. This is an input of energy, and thus has a positive value. It may also be referred to as the energy of atomization.
- **The heat of formation** is the change in energy when forming a compound from its elements. This may be positive or negative, depending on the atoms involved and how they interact.

- **Hess's Law** states that the overall change in energy of a process can be determined by breaking the process down into steps, then adding the changes in energy of each step. The Born-Haber Cycle is essentially Hess's Law applied to an ionic solid.

Using the Born-Haber Cycle

The values used in the Born-Haber Cycle are all predetermined changes in enthalpy for the processes described in the section above. Hess' Law allows us to add or subtract these values, which allows us to determine the lattice energy.



Step 1

Determine the energy of the metal and nonmetal in their elemental forms. (Elements in their natural state have an energy level of zero.) Subtract from this the heat of formation of the ionic solid that would be formed from combining these elements in the appropriate ration. This is the energy of the ionic solid, and will be used at the end of the process to determine the lattice energy.

Step 2

The Born-Haber Cycle requires that the elements involved in the reaction are in their gaseous forms. Add the changes in enthalpy to turn one of the elements into its gaseous state, and then do the same for the other element.

Step 3

Metals exist in nature as single atoms and thus no dissociation energy needs to be added for this element. However, many nonmetals will exist as polyatomic species. For example, Cl exists as Cl_2 in its elemental state. The energy required to change Cl_2 into 2Cl atoms must be added to the value obtained in Step 2.

Step 4

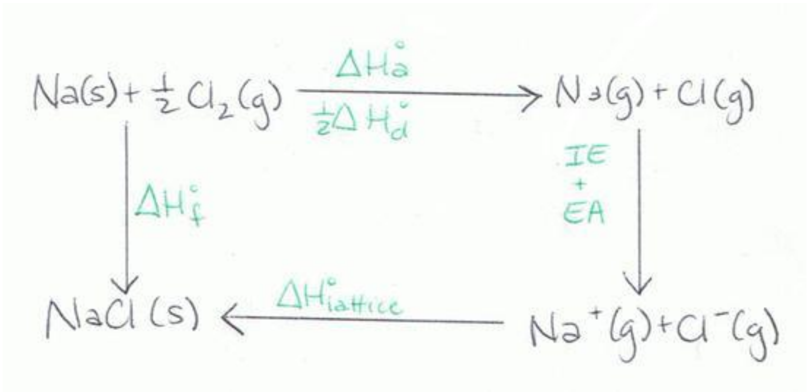
Both the metal and nonmetal now need to be changed into their ionic forms, as they would exist in the ionic solid. To do this, the ionization energy of the metal will be added to the value from Step 3. Next, the electron affinity of the nonmetal will be subtracted from the previous value. It is subtracted because it is a release of energy associated with the addition of an electron.

*This is a common error due to confusion caused by the definition of electron affinity, so be careful when doing this calculation.

Step 5

Now the metal and nonmetal will be combined to form the ionic solid. This will cause a release of energy, which is called the lattice energy. The value for the lattice energy is the difference between the value from Step 1 and the value from Step 4.

The diagram below is another representation of the Born-Haber Cycle.



Equation

The Born-Haber Cycle can be reduced to a single equation:

Heat of formation= Heat of atomization+ Dissociation energy+ (sum of Ionization energies)+ (sum of Electron affinities)+ Lattice energy

*Note: In this general equation, the electron affinity is added. However, when plugging in a value, determine whether energy is released (exothermic reaction) or absorbed (endothermic reaction) for each electron affinity. If energy is released, put a negative sign in front of the value; if energy is absorbed, the value should be positive.

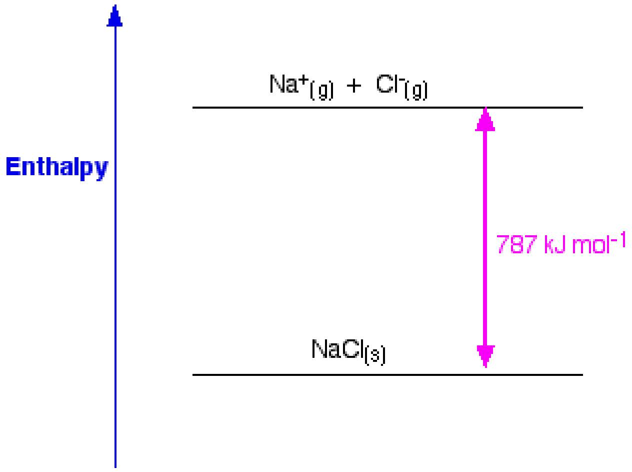
Rearrangement to solve for lattice energy gives the equation:

Lattice energy= Heat of formation- Heat of atomization- Dissociation energy- (sum of Ionization energies)- (sum of Electron Affinities)

Lattice enthalpy is a measure of the strength of the forces between the ions in an ionic solid. The greater the **lattice enthalpy**, the stronger the forces.

Defining Lattice Enthalpy

There are two different ways of defining lattice enthalpy which directly contradict each other, and you will find both in common use. In fact, there is a simple way of sorting this out, but many sources do not use it. Lattice enthalpy is a measure of the strength of the forces between the ions in an ionic solid. The greater the lattice enthalpy, the stronger the forces. Those forces are only completely broken when the ions are present as gaseous ions, scattered so far apart that there is negligible attraction between them. You can show this on a simple enthalpy diagram.



For sodium chloride, the solid is more stable than the gaseous ions by 787 kJ mol^{-1}, and that is a measure of the strength of the attractions between the ions in the solid. Remember that energy (in this case heat energy) is released when bonds are made, and is required to break bonds.

So lattice enthalpy could be described in either of two ways.

- It could be described as the enthalpy change when 1 mole of sodium chloride (or whatever) was formed from its scattered gaseous ions. In other words, you are looking at a downward arrow on the diagram.
- Or, it could be described as the enthalpy change when 1 mole of sodium chloride (or whatever) is broken up to form its scattered gaseous ions. In other words, you are looking at an upward arrow on the diagram.

Both refer to the same enthalpy diagram, but one looks at it from the point of view of making the lattice, and the other from the point of view of breaking it up. Unfortunately, both of these are often described as "lattice enthalpy".

DEFINITIONS

- The *lattice dissociation enthalpy* is the enthalpy change needed to convert 1 mole of solid crystal into its scattered gaseous ions. Lattice dissociation enthalpies are **always positive**.
- The *lattice formation enthalpy* is the enthalpy change when 1 mole of solid crystal is formed from its separated gaseous ions. Lattice formation enthalpies are **always negative**.

This is an absurdly confusing situation which is easily resolved by never using the term "lattice enthalpy" without qualifying it.

- You should talk about "lattice dissociation enthalpy" if you want to talk about the amount of energy needed to split up a lattice into its scattered gaseous ions. For NaCl, the lattice dissociation enthalpy is +787 kJ mol^{-1}.
- You should talk about "lattice formation enthalpy" if you want to talk about the amount of energy released when a lattice is formed from its scattered gaseous ions. For NaCl, the lattice formation enthalpy is -787 kJ mol^{-1}.

That immediately removes any possibility of confusion.

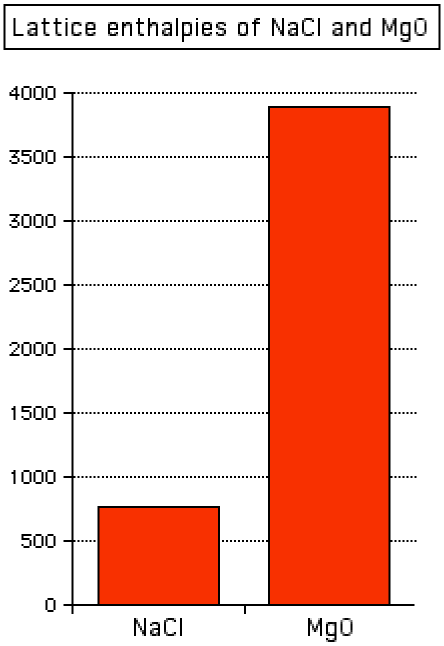
Factors affecting Lattice Enthalpy

The two main factors affecting lattice enthalpy are

- The charges on the ions and
- The ionic radii (which affects the distance between the ions).

The charges on the ions

Sodium chloride and magnesium oxide have exactly the same arrangements of ions in the crystal lattice, but the lattice enthalpies are very different.

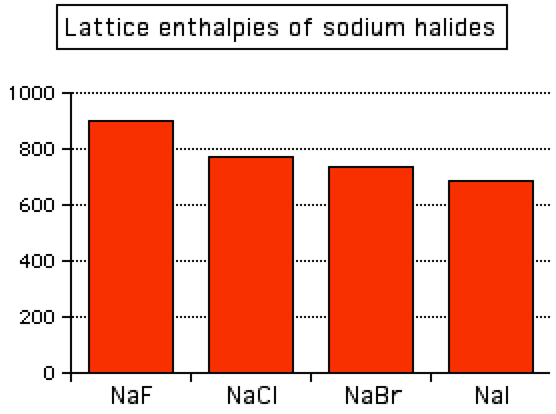


ou can see that the lattice enthalpy of magnesium oxide is much greater than that of sodium chloride. That's because in magnesium oxide, 2+ ions are attracting 2- ions; in sodium chloride, the attraction is only between 1+ and 1- ions.

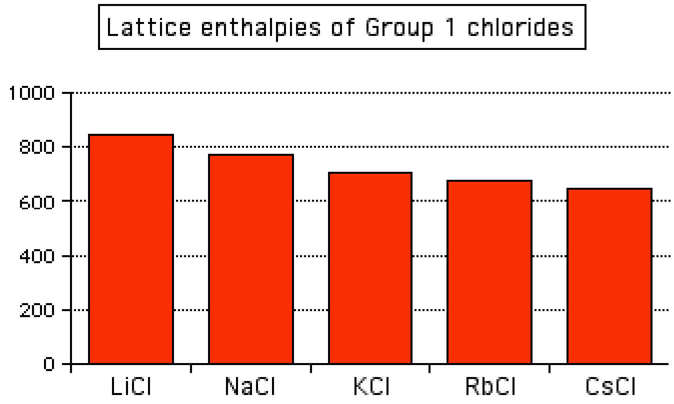
The Radius of the Ions

The lattice enthalpy of magnesium oxide is also increased relative to sodium chloride because magnesium ions are smaller than sodium ions, and oxide ions are smaller than chloride ions. That means that the ions are closer together in the lattice, and that increases the strength of the attractions.

This effect of ion size on lattice enthalpy is clearly observed as you go down a Group in the Periodic Table. For example, as you go down Group 7 of the Periodic Table from fluorine to iodine, you would expect the lattice enthalpies of their sodium salts to fall as the negative ions get bigger - and that is the case:



Attractions are governed by the distances between the centers of the oppositely charged ions, and that distance is obviously greater as the negative ion gets bigger. And you can see exactly the same effect if as you go down Group 1. The next bar chart shows the lattice enthalpies of the Group 1 chlorides.



Calculating Lattice Enthalpy

It is impossible to measure the enthalpy change starting from a solid crystal and converting it into its scattered gaseous ions. It is even more difficult to imagine how you could do the reverse - start with scattered gaseous ions and measure the enthalpy change when these convert to a solid crystal. Instead, lattice enthalpies always have to be calculated, and there are two entirely different ways in which this can be done.

1. You can can use a Hess's Law cycle (in this case called a Born-Haber cycle) involving enthalpy changes which can be measured. Lattice enthalpies calculated in this way are described as experimental values.
2. Or you can do physics-style calculations working out how much energy would be released, for example, when ions considered as point charges come together to make a lattice. These are described as theoretical values. In fact, in this case, what you are actually calculating are properly described as lattice energies.

Born-Haber Cycles

Standard Atomization Enthalpies

Before we start talking about Born-Haber cycles, we need to define the atomization enthalpy, ΔHoa . The standard atomization enthalpy is the enthalpy change when 1 mole of gaseous atoms is formed from the element in its standard state. Enthalpy change of atomization is always positive. You are always going to have to supply energy to break an element into its separate gaseous atoms. All of the following equations represent changes involving atomization enthalpy:

$1/2Cl_2(g) \rightarrow Cl(g)\ \Delta H^o_a = +122kJmol^{-1}$ (1)

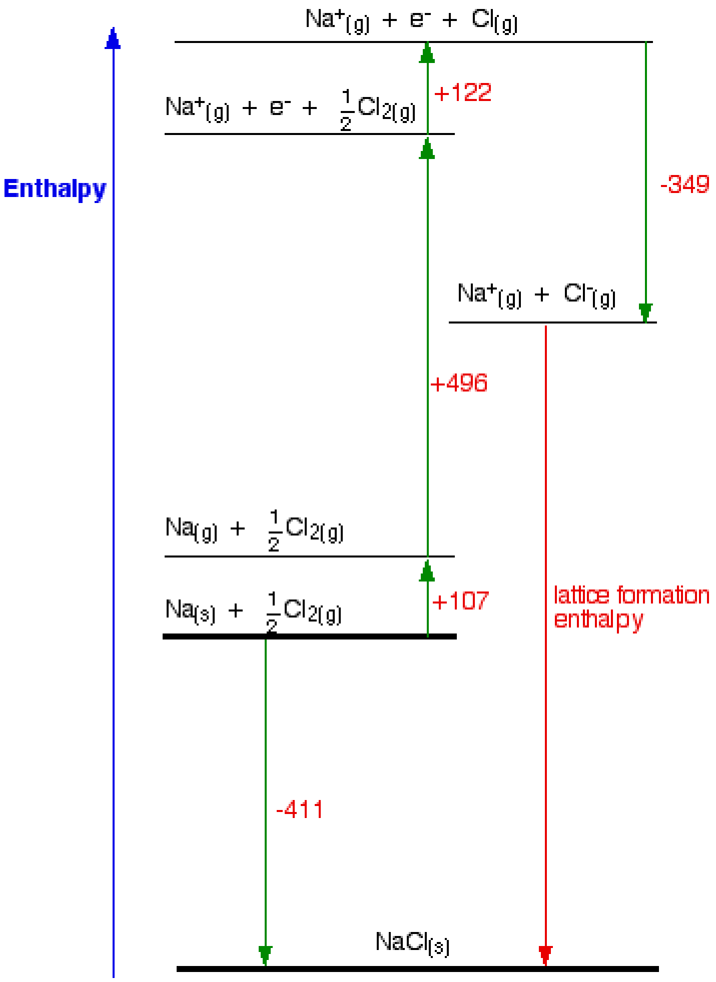
$12Br_2(l) \rightarrow Br(g)\ \Delta H^o_a = +122kJmol^{-1}$ (2)

$Na(s) \rightarrow Na(g)\ \Delta H^o_a = +107kJmol^{-1}$ (3)

Notice particularly that the "mol^{-1}" is per mole of atoms formed - NOT per mole of element that you start with. You will quite commonly have to write fractions into the left-hand side of the equation. Getting this wrong is a common mistake.

BORN-HABER CYCLE FOR NaCl

Consider a Born-Haber cycle for sodium chloride, and then talk it through carefully afterwards. You will see that I have arbitrarily decided to draw this for lattice formation enthalpy. If you wanted to draw it for lattice dissociation enthalpy, the red arrow would be reversed - pointing upwards.



Focus to start with on the higher of the two thicker horizontal lines. We are starting here with the elements sodium and chlorine in their standard states. Notice that we only need half a mole of chlorine gas in order to end up with 1 mole of NaCl. The arrow pointing down from this to the lower thick line represents the enthalpy change of formation of sodium chloride.

The Born-Haber cycle now imagines this formation of sodium chloride as happening in a whole set of small changes, most of which we know the enthalpy changes for - except, of course, for the lattice enthalpy that we want to calculate.

- The +107 is the atomization enthalpy of sodium. We have to produce gaseous atoms so that we can use the next stage in the cycle.
- The +496 is the first ionization energy of sodium. Remember that first ionization energies go from gaseous atoms to gaseous singly charged positive ions.

- The +122 is the atomization enthalpy of chlorine. Again, we have to produce gaseous atoms so that we can use the next stage in the cycle.
- The -349 is the first electron affinity of chlorine. Remember that first electron affinities go from gaseous atoms to gaseous singly charged negative ions.
- And finally, we have the positive and negative gaseous ions that we can convert into the solid sodium chloride using the lattice formation enthalpy.

Now we can use Hess' Law and find two different routes around the diagram which we can equate. As drawn, the two routes are obvious. The diagram is set up to provide two different routes between the thick lines. So, from the cycle we get the calculations directly underneath it . . .

-411 = +107 + 496 + 122 - 349 + LE

LE = -411 - 107 - 496 - 122 + 349

LE = -787 kJ mol^{-1}

How would this be different if you had drawn a lattice dissociation enthalpy in your diagram? Your diagram would now look like this:

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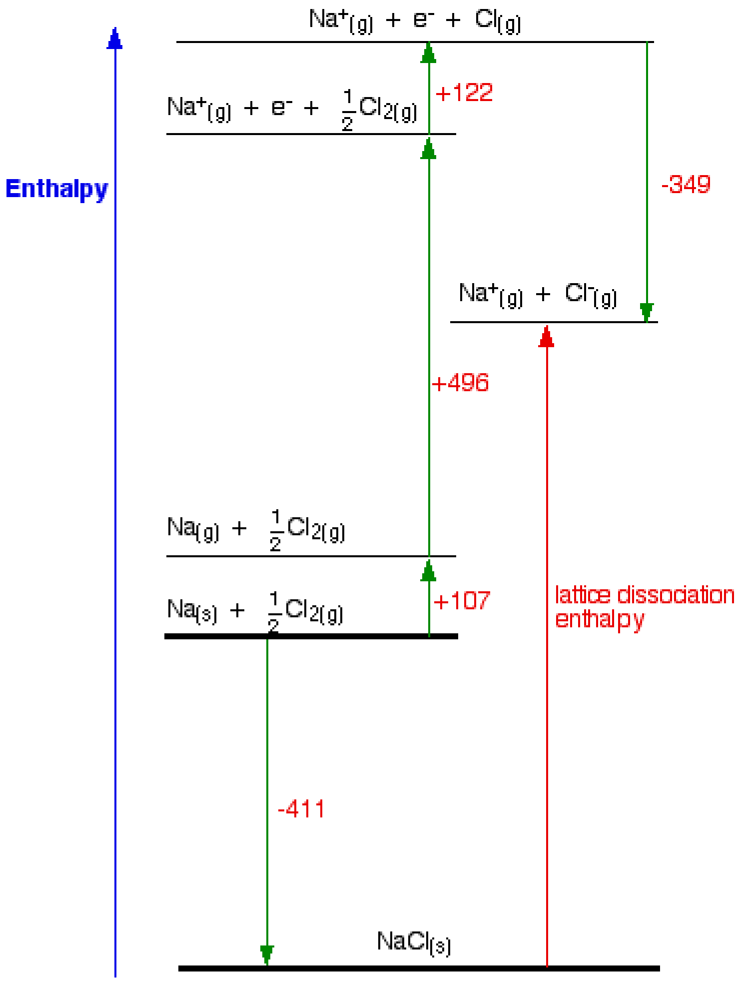


The only difference in the diagram is the direction the lattice enthalpy arrow is pointing. It does, of course, mean that you have to find two new routes. You cannot use the original one, because that would go against the flow of the lattice enthalpy arrow. This time both routes would start from the elements in their standard states, and finish at the gaseous ions.

-411 + LE = +107 + 496 + 122 - 349

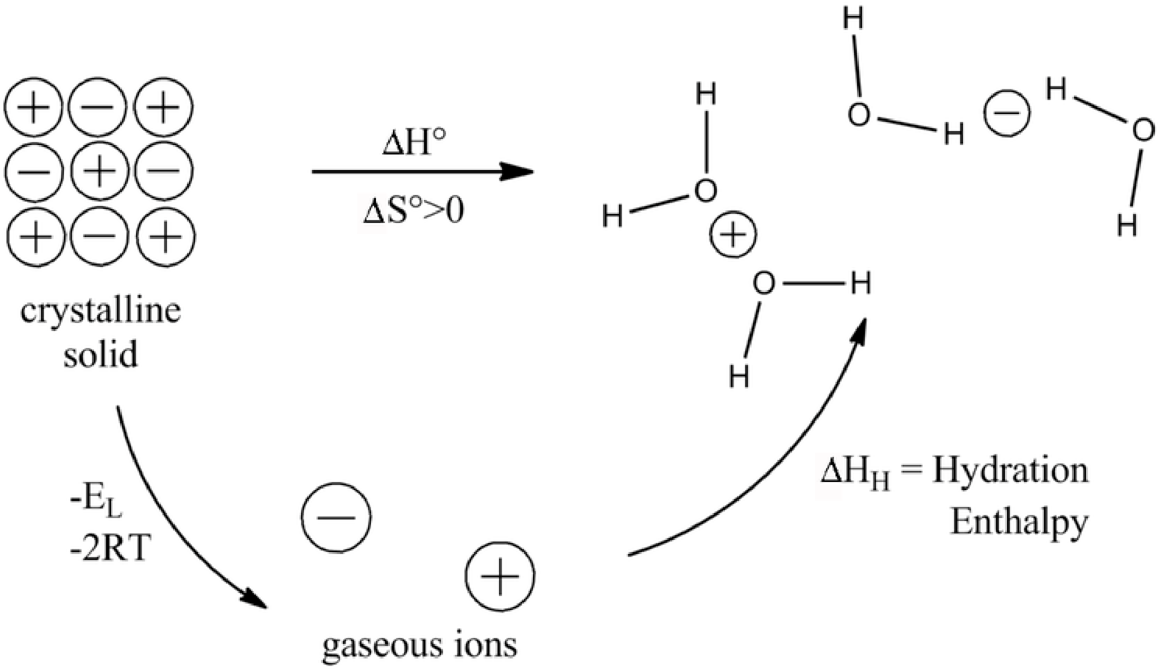
LE = +107 + 496 + 122 - 349 + 411

LE = +787 kJ mol^{-1}

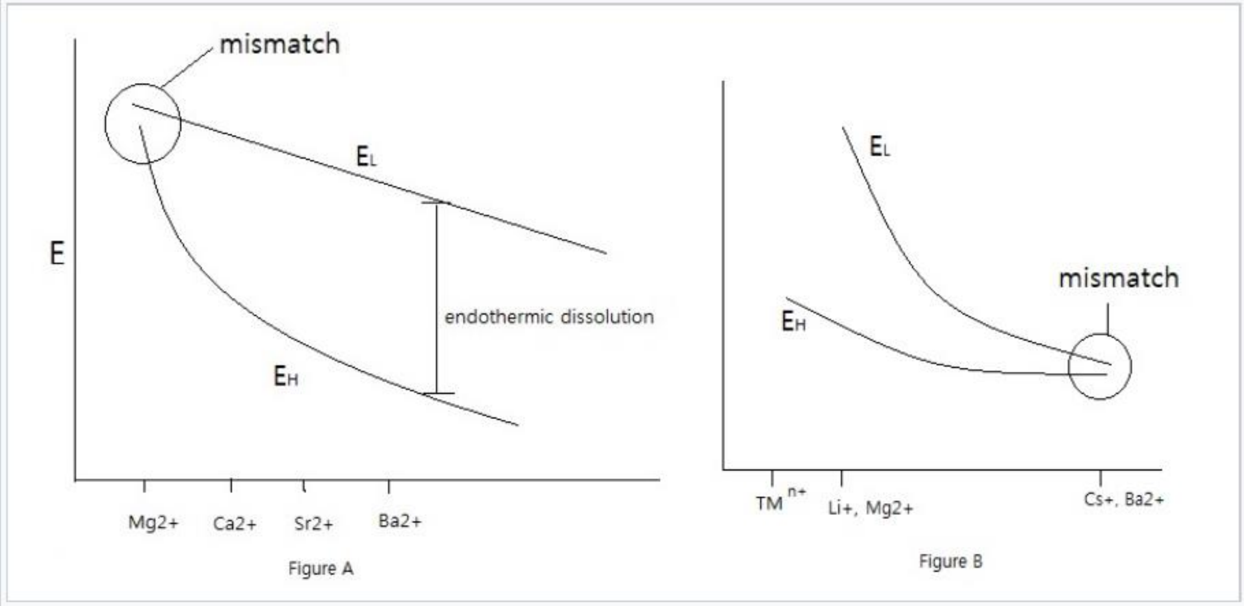
Once again, the cycle sorts out the sign of the lattice enthalpy.

Lattice Energies and Solubility

Lattice energies can also help predict compound solubilities. Let's consider a Born-Haber cycle for dissolving a salt in water. We can imagine this as the sum of two processes: (1) the vaporization of the salt to produce gaseous ions, characterized by the lattice enthalpy, and (2) the hydration of those ions to produce the solution. The enthalpy change for the overall process is the sum of those two steps. We know that the entropy change for dissolution of a solid is positive, so the solubility depends on the enthalpy change for the overall process.



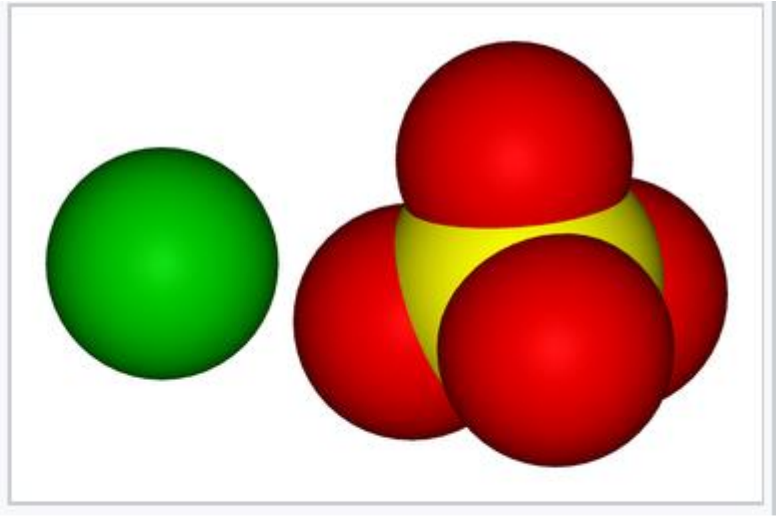
Here we need to consider the trends in both the lattice energy E_L and the hydration energy E_H. The lattice energy depends on the sum of the anion and cation radii ($r_+ + r_-$), whereas the hydration energy has separate anion and cation terms. Generally the solvation of small ions (typically cations) dominates the hydration energy because of the $1/r^2$ dependence.



Left: E_L diagram for sulfate salts. The large SO_4^{2-} ion is size-mismatched to small cations such as Mg^{2+}, which have large h
soluble salts. With larger cations such as Ba^{2+}, which have lower E_H, the lattice energy exceeds the solvation enthalpy and
the case of small anions such as F^- and OH^-, the lattice energy dominates with small cations such as transition metal ions (T
cation size mismatch occurs with larger cations, such as Cs^+ and Ba^{2+}, which make soluble fluoride salts.

For small anions, E_L is more sensitive to r_+, whereas E_H does not depend on r_+ as strongly. For fluorides and hydroxides, LiF is slightly soluble whereas CsF is very soluble, and $Mg(OH)_2$ is insoluble whereas $Ba(OH)_2$ is very soluble.

Putting both trends together, we see that **low solubility** is most often encountered when the **anion and cation match well in their sizes**, especially when one or both are **multiply charged**.



Space-filling models showing the van der Waals surfaces of Ba^{2+} and SO_4^{2-} of $BaSO_4$ in water.

Combining all our conclusions about solubility, we note the following trends:

1) Increasing **size mismatch** between the anion and cation leads to greater solubility, so CsF and LiI are the most soluble alkali halides.

2) Increasing **covalency** leads to lower solubility in the salts (due to larger E_L. For example, AgF, AgCl, AgBr, and AgI exhibit progressively lower solubility because of increasing covalency.

AgF>AgCl>AgBr>AgIAgF>AgCl>AgBr>AgI

3) Increasing the **charge on the anion** lowers the solubility because the increase in E_L is large relative to the increase in E_H.

4) Small, polyvalent cations (having large E_H) make **soluble salts with large, univalent anions** such as I^-, NO_3^-, ClO_4^-, PF_6^-, and acetate.

Examples: Salts of transition metal and lanthanide ions

- Ln^{3+}: Nitrate salts are soluble, but oxides and hydroxides are insoluble.
- Fe^{3+}: Perchlorate is soluble, but sulfate is insoluble.

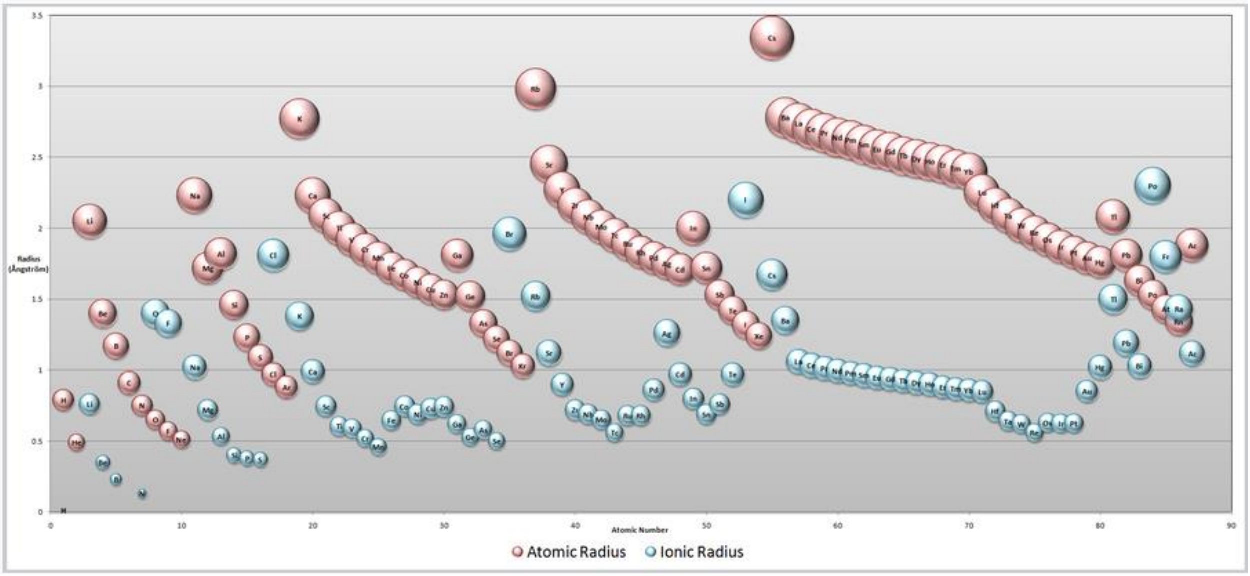
5) Multiple charged anions such as O^{2-}, S^{2-}, PO_4^{3-}, and SO_4^{2-} make insoluble salts with most M^{2+}, M^{3+}, and M^{4+} metals.

Ionic Radii and Radius Ratios

Atoms in crystals are held together by electrostatic forces, van der Waals interactions, and covalent bonding. It follows that arrangements of atoms that can maximize the strength of these attractive interactions should be most favorable and lead to the most commonly observed crystal structures.

Radius ratio rules

Early crystallographers had trouble solving the structures of inorganic solids using X-ray diffraction because some of the mathematical tools for analyzing the data had not yet been developed. Once a trial structure was proposed, it was relatively easy to calculate the diffraction pattern, but it was difficult to go the other way (from the diffraction pattern to the structure) if nothing was known *a priori* about the arrangement of atoms in the unit cell. It was (and still is!) important to develop some guidelines for guessing the coordination numbers and bonding geometries of atoms in crystals. The first such rules were proposed by Linus Pauling, who considered how one might pack together oppositely charged spheres of different radii. Pauling proposed from geometric considerations that the quality of the "fit" depended on the **radius ratio** of the anion and the cation.

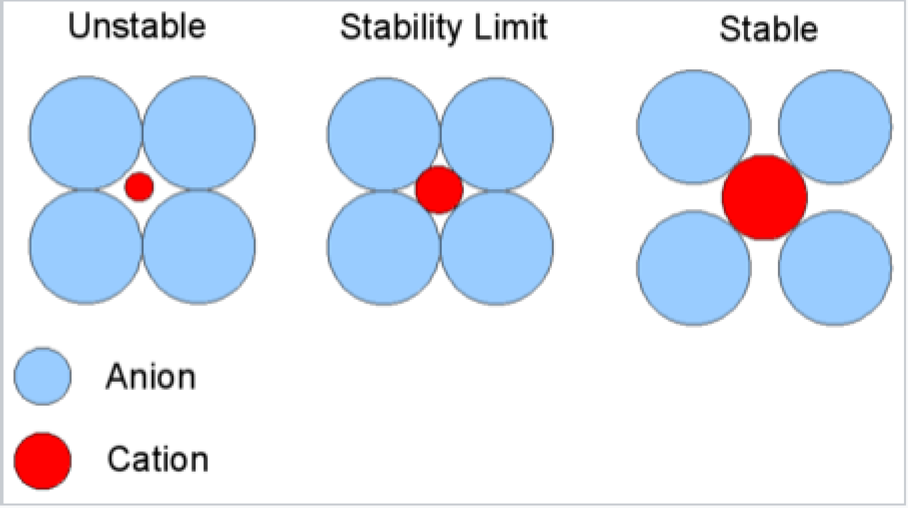


Atomic and Ionic Radii.

Note that cations are always smaller than the neutral atom (pink) of the same element, whereas anions are larger.

Going from left to right across any row of the periodic table, neutral atoms and cations contract in size because of increasing nuclear charge.

The basic idea of radius ratio rules is illustrated at the right. We consider that the anion is the packing atom in the crystal and the smaller cation fills interstitial sites ("holes"). Cations will find arrangements in which they can contact the largest number of anions. If the cation can touch all of its nearest neighbor anions, as shown at the right for a small cation in contact with larger anions, then the fit is good. If the cation is too small for a given site, that coordination number will be unstable and it will prefer a lower coordination structure. The table below gives the ranges of cation/anion radius ratios that give the best fit for a given coordination geometry.



Critical Radius Ratio. This diagram is for coordination number six: 4 anions in the plane are shown, 1 is above the plane and 1 is below. The stability limit is at $r_C/r_A = 0.414$

Coordination number	Geometry	$\rho = r_{cation}/r_{anion}$
2	Linear	0 - 0.155
3	Triangular	0.155-0.225
4	Tetrahedral	0.225-0.414
4	Square Plannar	0.414-0.732
6	Octahedral	0.414-0.732
8	Cubic	0.732-1.000
12	Cubooctahedral	1.0

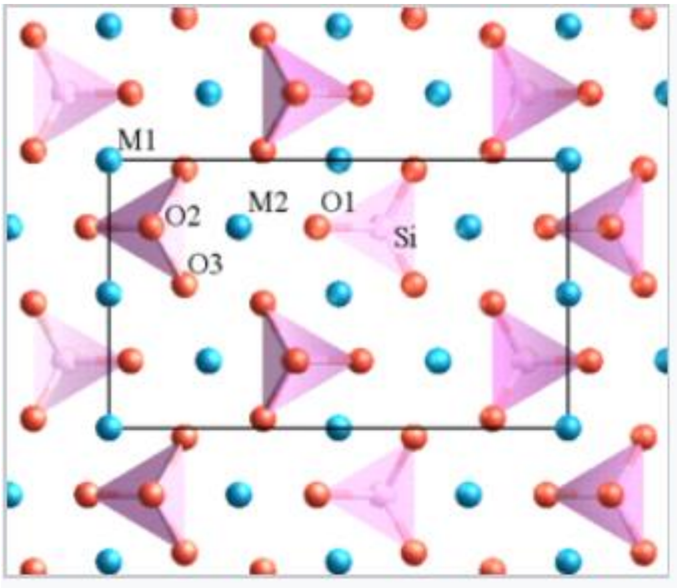
There are unfortunately several challenges with using this idea to predict crystal structures:

- We don't know the radii of individual ions
- Atoms in crystals are not really ions - there is a varying degree of covalency depending electronegativity differences
- Bond distances (and therefore ionic radii) depend on bond strength and coordination number (remember Pauling's rule D(n) = D(1) - 0.6 log n)
- Ionic radii depend on oxidation state (higher charge => smaller cation size, larger anion size)

What about the alkali halides NaCl, KBr, LiI, CsF, etc.? All of them have the NaCl structure except for CsCl, CsBr, and CsI, which have the CsCl (8-8) structure. In this case the radius ratio model fails rather badly. The Li^+ salts LiBr and LiI are predicted to have tetrahedral structures, and KF is predicted to have an 8-8 structure like CsCl. We can try adjusting the radii (e.g., making the cations larger and anions smaller), but the best we can do with the alkali halides is predict about half of their structures correctly. Since the alkali halides are clearly ionic compounds, this failure suggests that there is something very wrong with the radius ratio model, and its success with MO_2 compounds was coincidental.

- In addition to the radius ratio rule, Linus Pauling developed other useful rules that are helpful in rationalizing and also predicting the structures of inorganic compounds. Pauling's rules[1] state that:
- Stable structures are **locally electroneutral**. For example, in the structure of the double perovskite Sr_2FeMoO_6, MO_6 (M = Fe^{2+}, Mo^{6+}) octahedra share all their vertices, and Sr^{2+} ions fill the cubooctahedral cavities that are flanked by eight MO_6 octahedra.[2] Each O^{2-} ion is coordinated to one Fe^{2+} and one Mo^{6+} ion in order to achieve local electroneutrality, and thus the FeO_6 and MoO_6 octahedra alternate in the structure.
- **Cation-cation repulsion** should be minimized. Anion polyhedra can share vertices (as in the perovskite structure) without any energetic penalty. Shared polyhedral edges, and especially shared faces, cause cation-cation repulsion and should be avoided. For example, in rutile, the most stable polymorph of TiO_2, the TiO_6 octahedra share vertices and two opposite edges, forming ribbons in the structure. In anatase TiO_2, each octahedron shares four edges so the anatase polymorph is less thermodynamically stable.

- **Highly charged cations** in anion polyhedra tend not to share edges or even vertices, especially when the coordination number is low. For example, in orthosilicates such as olivine (M_2SiO_4), there are isolated SiO_4^{4-} tetrahedra.



Structure of olivine. M (Mg or Fe) = blue spheres, Si = pink tetrahedra, O = red spheres.

As we will soon see, all of Pauling's rules are justified on the basis of lattice energy considerations. In ionic compounds, the arrangement of atoms that maximizes anion-cation interactions while minimizing cation-cation and anion-anion contacts is energetically the best.

Polarizability

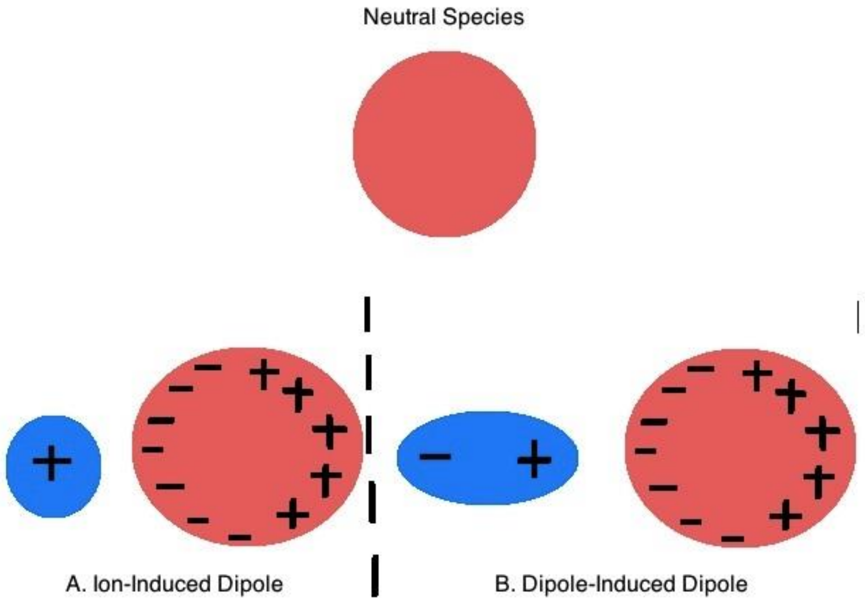
Polarizability allows us to better understand the interactions between nonpolar atoms and molecules and other electrically charged species, such as ions or polar molecules with dipole moments.

Introduction

Neutral nonpolar species have spherically symmetric arrangements of electrons in their electron clouds. When in the presence of an electric field, their electron clouds can be distorted. The ease of this distortion is defined as the **polarizability** of the atom or molecule. The created distortion of the electron cloud causes the originally nonpolar molecule or atom to acquire a dipole moment. This induced dipole moment is related to the polarizability of the molecule or atom and the strength of the electric field by the following equation:

$$\mu_{ind} = \alpha E \qquad (1)$$

where E denotes the strength of the electric field and α is the polarizability of the atom or molecule with units of C m^2V^{-1}.



In general, polarizability correlates with the interaction between electrons and the nucleus. The amount of electrons in a molecule affects how tight the nuclear charge can control the overall charge distribution. Atoms with fewer electrons will have smaller, denser electron clouds, as there is a strong interaction between the few electrons in the atoms' orbitals and the positively charged nucleus. There is also less shielding in atoms with fewer electrons contributing to the stronger interaction of the outer electrons and the nucleus. With the electrons held tightly in place in these smaller atoms, these atoms are typically not easily polarized by external electric fields. In contrast, large atoms with many electrons, such as negative ions with excess electrons, are easily polarized. These atoms typically have very diffuse electron clouds and large atomic radii that limit the interaction of their external electrons and the nucleus.

Factors that Influence Polarizability

The relationship between polarizability and the factors of electron density, atomic radii, and molecular orientation is as follows:

1. The greater the number of electrons, the less control the nuclear charge has on charge distribution, and thus the increased polarizability of the atom.

2. The greater the distance of electrons from nuclear charge, the less control the nuclear charge has on the charge distribution, and thus the increased polarizability of the atom.
3. Molecular orientation with respect to an electric field can affect polarizibility (labeled Orientation-dependent), except for molecules that are: tetrahedral, octahedral or icosahedral (labeled Orientation-independent). This factor is more important for unsaturated molecules that contain areas of electron-dense regions, such as 2,4-hexadiene. Greatest polarizability in these molecules is achieved when the electric field is applied parallel to the molecule rather than perpendicular to the molecule.

Polarizability Influences Dispersion Forces

The dispersion force is the weakest intermolecular force. It is an attractive force that arises from surrounding temporary dipole moments in nonpolar molecules or species. These temporary dipole moments arise when there are instantaneous deviations in the electron clouds of the nonpolar species. Surrounding molecules are influenced by these temporary dipole moments and a sort of chain reaction results in which subsequent weak, dipole-induced dipole interactions are created. These cumulative dipole- induced dipole interactions create attractive dispersion forces. Dispersion forces are the forces that make nonpolar substances condense to liquids and freeze into solids when the temperature is low enough.

Polarizability affects dispersion forces in the following ways:

- As polarizability *increases*, the dispersion forces also become *stronger***.** Thus, molecules attract one another more *strongly* and melting and boiling points of covalent substances *increase* with *larger* molecular mass.
- Polarazibility also affects dispersion forces through the molecular shape of the affected molecules. Elongated molecules have electrons that are easily moved increasing their polarizability and thus strengthening the dispersion forces,. In contrast, small, compact, symmetrical molecules are less polarizable resulting in weaker dispersion forces.

The relationship between polarizability and dispersion forces can be seen in the following equation, which can be used to quantify the interaction between two like nonpolar atoms or molecules:

$V= -3\alpha^2 I/4r^6$ (2)

where

- r is the distance between the atoms or molecules,

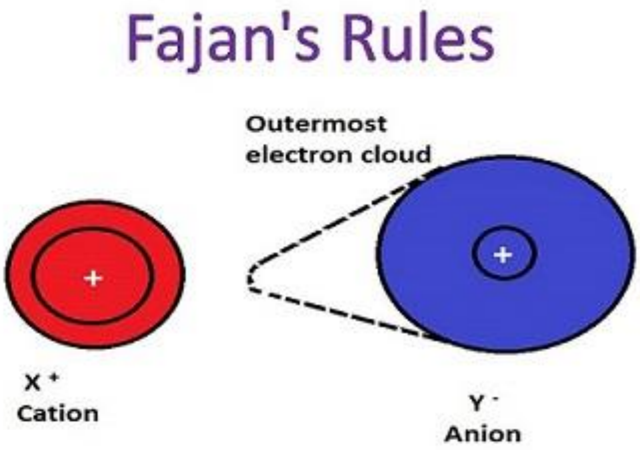
- I is the first ionization energy of the atom or molecule, and
- α is the polarizability constant expressed in units of m^3.

Fazan's Rule

Fajans' rule predicts whether a chemical bond will be covalent or ionic. Few ionic bonds have partial covalent characteristics which were first discussed by **Kazimierz Fajans** in **1923**. In the time with the help of X-ray crystallography, he was able to predict ionic or covalent bonding with the attributes like ionic and atomic radius.

What is Fajans' rule?

We classify certain compounds as ionic and other compounds as covalent. Now if we were to ask the question, amongst the alkali chlorides, which is the most ionic? To answer these kinds of questions, we employ Fajans' rules as a tool.



To understand the Fajans' rule, Let us first understand a few terms:

Polarising power

It is the extent to which a cation can polarise an anion. It is proportional to charge density. Charge density is the ratio of charge to volume. Polarising power α Charge density. More the charge density, greater is the polarising power for that cation.

Polarisability

It is the extent to which an ion can be polarised. It can also be called as the ease with which an ion can be polarised. Polarisation is the distortion of a spherically symmetric electron cloud to an unsymmetric cloud.

Postulates of Fajans' Rule

The rule can be stated on the basis of 3 factors, which are:

1. **Size of the ion:** Smaller the size of cation, the larger the size of the anion, greater is the covalent character of the ionic bond.
2. **The charge of Cation:** Greater the charge of cation, greater is the covalent character of the ionic bond.
3. **Electronic configuration:** For cations with same charge and size, the one, with $(n-1)d^n$ ns^o which is found in transition elements have greater covalent character than the cation with ns^2 np^6 electronic configuration, which is commonly found in alkali or alkaline earth metals.

Explanation of Fazans' Rule

Rule 1:

The **first rule** speaks about the polarising power of the cation. If the cation is smaller, then we can say that the volume of the ion is less. If the volume is less, we can conclude that the charge density of the ion would be high.

Since the charge density is high, the polarising power of the ion would be high. This makes the compound to be more covalent.

Rule 2:

The **second rule** speaks about the polarizability of the anion. Larger the anion, less is the effective nuclear charge that holds the valence electron of the ion in place. Since the last electron is loosely bound in large anions, it can easily be polarised by a cation, thereby making the compound more covalent.

Rule 3:

The **third rule** is a special case. Let us use an example to explain this point.

Example: If we want to find the more covalent compound among $HgCl_2$ and Calcium Chloride we cannot use size as a factor to conclude. This is because both Hg^{2+} and Ca^{2+} are of almost equal size. To explain this, we employ the **third rule**.

The electronic configuration of Hg^{2+} is $6s^0$ $5d^{10}$. This configuration is called pseudo-octet because d-orbital is fully filled, but the element does not have 8 electrons or an octet.

We know that d orbitals are not good at shielding, so we can say that the anion (Cl^-) would be more polarised because the d orbital is poor at shielding making $HgCl_2$ more covalent than $CaCl_2$ because Ca^{2+} ion has a noble gas configuration.

Now to answer the question that we asked first, amongst the alkali chlorides, which one is the most covalent?

Since the anion is the same, we have to compare the cations. According to **Fajans' rules**, smaller the cation, more is the covalency. Therefore, LiCl is the most covalent.

Let us Understand Fajans' Rule Using a Detailed Illustration:

Consider Aluminum Iodide (AlI_3)

This is an ionic bond which was formed by transfer of electrons.

- The iodine being bigger in size has a lesser effective nuclear charge. Thus, the bonding electrons are attracted lesser towards the Iodine nucleus.
- On the contrary, the aluminium having three positive charges attracts the shared pair of electron towards itself.
- This leads to insufficient charge separation for it to be ionic and so it results in the development of covalent character in AlI_3.

Consider Aluminium Fluoride (AlF_3)

This is an ionic bond which was also formed by transfer of electron. But here the fluorine being smaller in size attracts the shared pair of an electron more towards itself and so there is sufficient charge separation to make it ionic.

Examples on Fajans' rule

Illustration 1: Which compound should theoretically the most ionic and the most covalent amongst the metal halides?

Solution:

The smallest metal ion and the largest anion should technically be the most covalent

Therefore, LiI is the most covalent.

The largest cation and the smallest anion should be the most ionic. Therefore, CsF should be the most ionic.

Illustration 2: Arrange the following according to the increasing order of covalency:

- NaF, NaCl, NaBr, NaI
- LiF, NaF,KF,RbF,CsF

Solution:

1. Since the cation is the same, compare the anions. Amongst the anions, larger the size more would be the covalency. Therefore the order is: NaF < NaCl < NaBr < NaI

2. Here the anion is the same, so we compare with cations. Smaller the cation more is the covalency. Therefore the order is: CsF < RbF < KF < NaF < LiF

Illustration 3: The melting point of KCl is higher than that of AgCl though the crystal radii of Ag^+ and K^+ ions are almost the same.

Solution : Now whenever any comparison is asked about the melting point of the compounds which are fully ionic from the electron transfer concept it means that the compound having lower melting point has got lesser amount of ionic character than the other one. To analyse such a question first find out the difference between the 2 given compounds. Here in both the compounds the anion is the same. So the deciding factor would be the cation. Now if the anion is different, then the answer should be from the variation of the anion. Now in the above example, the difference of the cation is their electronic configuration. K^+ = [Ar]; Ag^+ = [Kr] $4d^{10}$. This is now a comparison between a noble gas core and pseudo noble gas core, the analysis of which we have already done. So try to finish off this answer.

Percentage of Ionic Character

Every ionic compound having some percentage of covalent character according to Fajan's rule. The percentage of ionic character in a compound having some covalent character can be calculated by the following equation.

The percent ionic character = Observed dipole moment/Calculated dipole moment assuming 100% ionic bond × 100

Example: Dipole moment of KCl is 3.336×10^{-29} coulomb metre which indicates that it is highly polar molecule. The interatomic distance between k^+ and Cl^- is 2.6×10^{-10} m. Calculate the dipole moment of KCl molecule if there were opposite charges of one fundamental unit located at each nucleus. Calculate the percentage ionic character of KCl.

Solution: Dipole moment $\mu = e \times d$ coulomb metre

For KCl $d = 2.6 \times 10^{-10}$ m

For complete separation of unit charge

$e = 1.602 \times 10^{-19}$ C

Hence $\mu = 1.602 \times 10^{-19} \times 2.6 \times 10^{-10} = 4.1652 \times 10^{-29}$ Cm

$\mu_{KCl} = 3.336 \times 10^{-29}$ Cm

$\therefore$ % ionic character of KCl = $3.336\times10^{-29}/4.165\times10^{-29}$ = 80.09%

Example. Calculate the % of ionic character of a bond having length = 0.83 Å and 1.82 D as it's observed dipole moment.

Solution: To calculate μ considering 100% ionic bond

$= 4.8 \times 10^{-10} \times 0.83 \times 10^{-8}$esu cm

$= 4.8 \times 0.83 \times 10^{-18}$ esu cm = 3.984 D

$\therefore$ % ionic character = 1.82/3.984 × 100 = 45.68

The example given above is of a very familiar compound called HF. The % ionic character is nearly 43.25%, so the % covalent character is (100 – 43.25) = 56.75%. But from the octet rule HF should have been a purely covalent compound but actually it has some amount of ionic character in it, which is due to the electronegativity difference of H and F. Similarly knowing the bond length and observed dipole moment of HCl, the % ionic character can be known. It was found that HCl has 17% ionic character. Thus it can be clearly seen that although we call HCl and HF as covalent compounds but it has got appreciable amount of ionic character. So from now onwards we should call a compound having more of ionic less of covalent and vice versa rather than fully ionic or covalent.