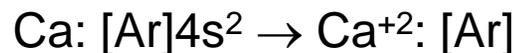


# Ionic Bonding

Whereas the term covalent implies sharing of electrons between atoms, the term ionic indicates that electrons are taken from one atom by another. The nature of ionic bonding is very different than that of covalent bonding and must be considered using different approaches.

Some aspects to remember:

1. Electronegative atoms will generally gain enough electrons to fill their valence shell and more electropositive atoms will lose enough electrons to empty their valence shell.

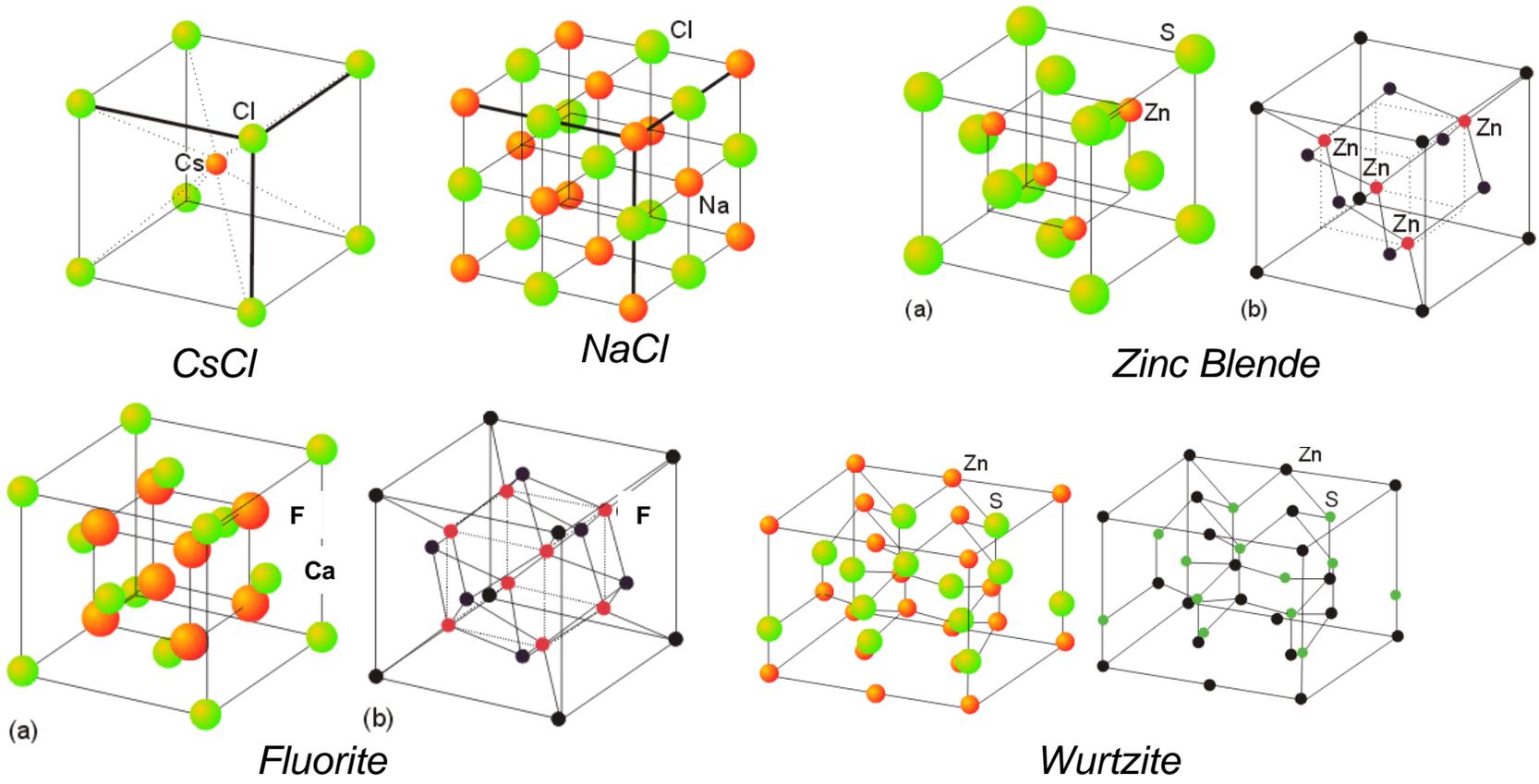


2. Ions are considered to be spherical and their size is given by the ionic radii that have been defined for most elements (there is a table in the notes on Atomic Structure). The structures of the salts formed from ions is based on the close packing of spheres.

3. The cations and anions are held together by electrostatic attraction.

# Ionic Bonding

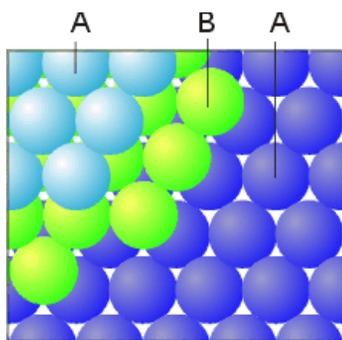
Because electrostatic attraction is not directional in the same way as is covalent bonding, there are many more possible structural types. However, in the solid state, all ionic structures are based on *infinite lattices of cations and anions*. There are some important classes that are common and that you should be able to identify, including:



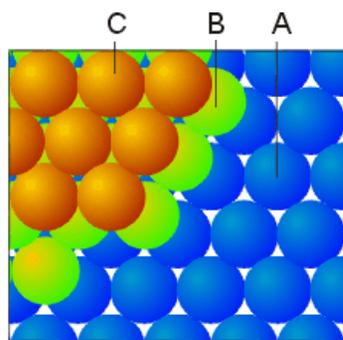
And others... Fortunately, we can use the size of the ions to find out what kind of structure an ionic solid should adopt and we will use the structural arrangement to determine the energy that holds the solid together - the crystal lattice energy,  $U_0$ .

# Ionic Bonding

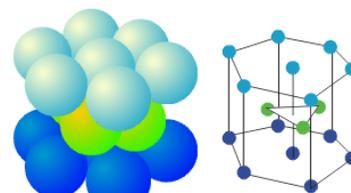
Most ionic (and metal) structures are based on the “close packing” of spheres - meaning that the spheres are packed together so as to leave as little empty space as possible - this is because *nature tries to avoid empty space*. The two most common close packed arrangements are hexagonal close-packed (hcp) and cubic close packed (ccp). Both of these arrangements are composed of layers of close packed spheres however hcp differs from ccp in how the layers repeat (ABA vs. ABC). In both cases, the spheres occupy 74% of the available space. Because anions are usually bigger than cations, it is generally the anions that dominate the packing arrangement.



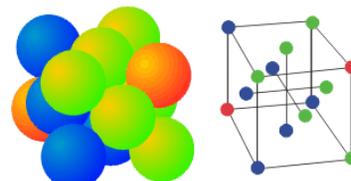
(a)



(b)



(a)

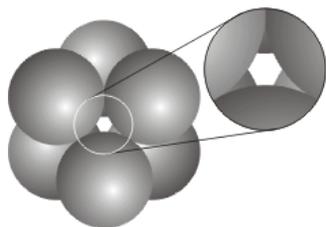


(b)

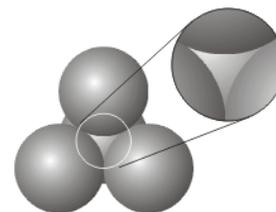
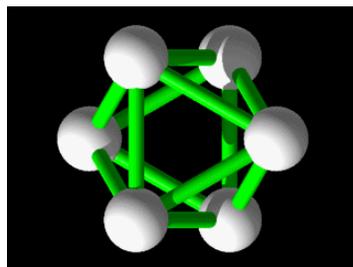
hcp

ccp

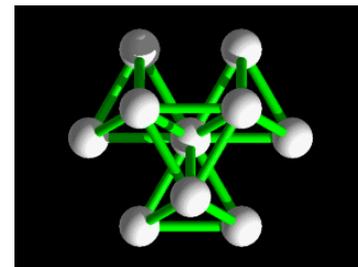
Usually, the smaller cations will be found in the holes in the anionic lattice, which are named after the local symmetry of the hole (i.e. six equivalent anions around the hole makes it octahedral, four equivalent anions makes the hole tetrahedral).



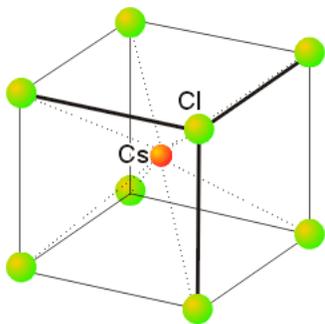
2 Octahedral hole



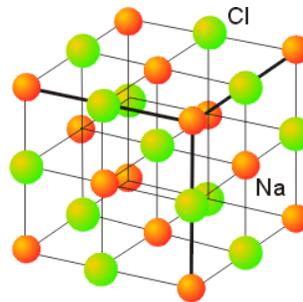
5 Tetrahedral hole



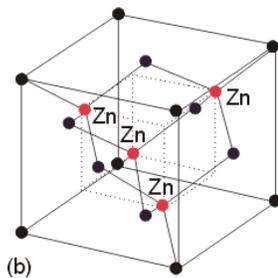
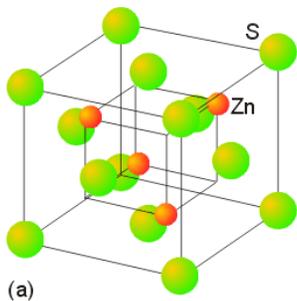
Some common arrangements for simple ionic salts:



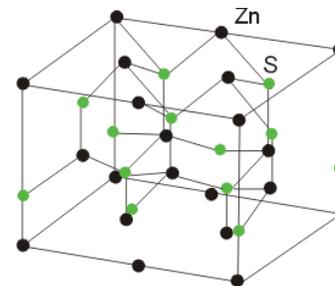
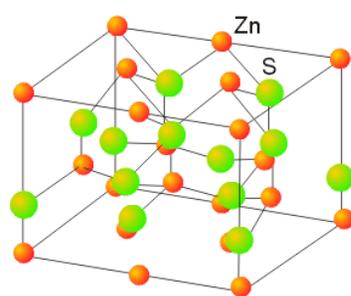
*Cesium chloride structure*  
8:8 coordination  
Primitive Cubic (52% filled)  
e.g. CsCl, CsBr, CsI, CaS



*Rock Salt structure*  
6:6 coordination  
Face-centered cubic (fcc)  
e.g. NaCl, LiCl, MgO, AgCl



*Zinc Blende structure*  
4:4 coordination  
fcc  
e.g. ZnS, CuCl, GaP, InAs



*Wurtzite structure*  
4:4 coordination  
hcp  
e.g. ZnS, AlN, SiC, BeO

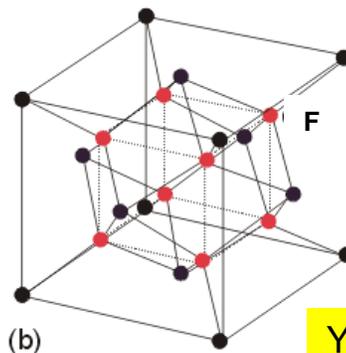
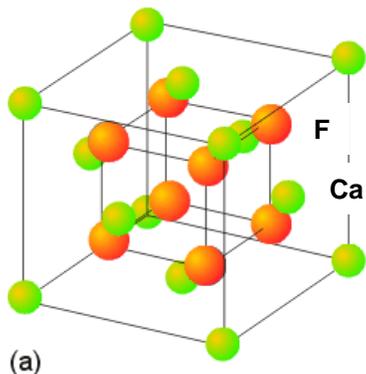
# Ionic Bonding

## Fluorite structure

8:4 coordination

fcc

e.g.  $\text{CaF}_2$ ,  $\text{BaCl}_2$ ,  $\text{UO}_2$ ,  $\text{SrF}_2$



## Anti-fluorite structure

4:8 coordination

e.g.  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{Se}$ ,  $\text{K}_2\text{S}$ ,  $\text{Na}_2\text{S}$

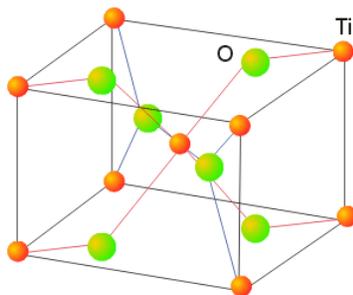
## Rutile structure

6:3 coordination

Body-centered cubic (bcc)

(68% filled)

e.g.  $\text{TiO}_2$ ,  $\text{GeO}_2$ ,  $\text{SnO}_2$ ,  $\text{NiF}_2$

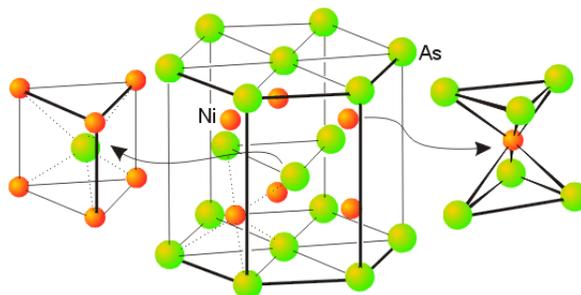


## Nickel arsenide structure

6:6 coordination

hcp

e.g.  $\text{NiAs}$ ,  $\text{NiS}$ ,  $\text{FeS}$ ,  $\text{PtSn}$



You can determine empirical formula for a structure by counting the atoms and partial atoms within the boundary of the unit cell (the box). E.g. in the rutile structure, two of the O ions (green) are fully within the box and there are four half atoms on the faces for a total of 4 O ions. Ti (orange) one ion is completely in the box and there are 8 eighth ions at the corners; this gives a total of 2 Ti ions in the cell. This means the empirical formula is  $\text{TiO}_2$ ; the 6:3 ratio is determined by looking at the number of closest neighbours around each cation and anion.

There are many other common forms of ionic structures but it is more important to be able to understand the reason that a salt adopts the particular structure that it does and to be able to predict the type structure a salt might have.



The ratio of the radii of the ions in a salt can allow us to predict the type of arrangement that will be adopted. The underlying theory can be attributed to the problem of trying to pack spheres of different sizes together while leaving the least amount of empty space and minimizing the contact between the negatively charged anions. The size of a cation (the smaller sphere) that can fill the hole between close packed anions (the larger spheres) can be calculated using simple geometry. The ratio of the radii can give a rough estimate of the coordination number of the ions which can then be used to predict the structural arrangement of the salt.

E.g. for a 3-coordinate arrangement where A is at the center of the hole (of radius  $r^+$ ) and B is at the center of the large sphere (of radius  $r^-$ ), one can define the right triangle ABC where the angle CAB must be  $60^\circ$ .

$$\sin(60^\circ) = 0.866 = BC/AB = r^-/(r^++r^-)$$

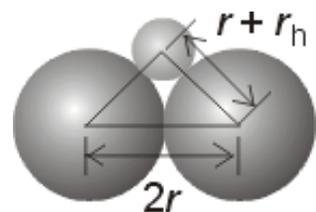
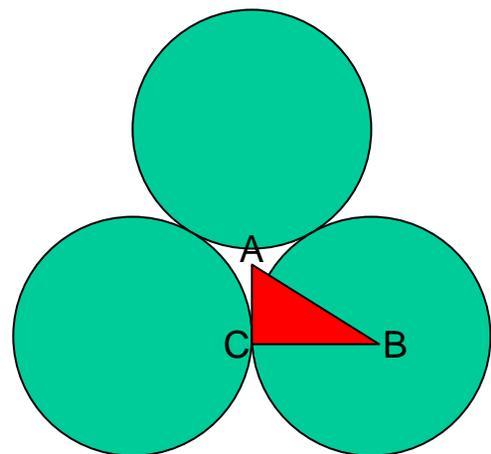
$$0.866 (r^++r^-) = r^-$$

$$0.866 r^+ + 0.866 r^- = r^-$$

$$0.866 r^+ = r^- - 0.866 r^-$$

$$0.866 r^+ = (1 - 0.866) r^- = (0.134) r^-$$

So:  $r^+/r^- = 0.134/0.866 = 0.155$  This means that the smallest cation that will fill in the hole must have a radius that is at least 15.5% of the radii of the anions.



3

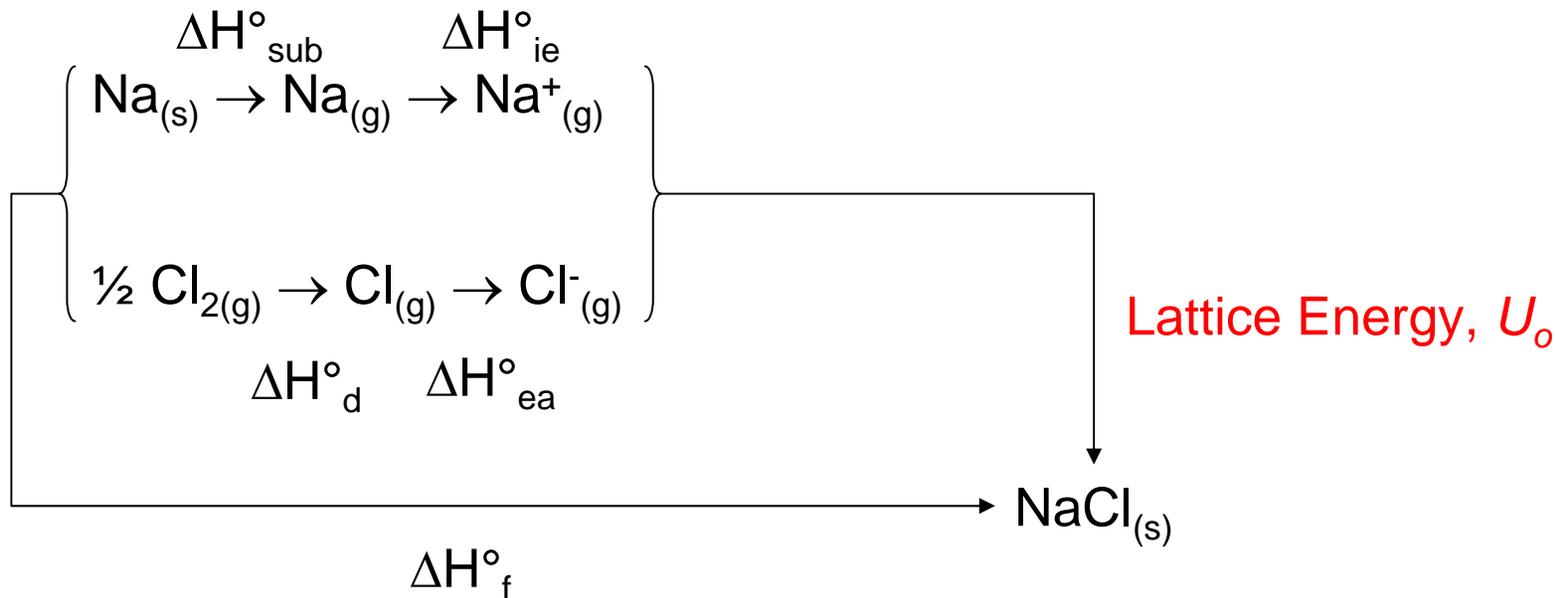
Coordination number	2	3	4	6	8
$r^+/r^-$	< 0.155	0.155 - 0.225	0.225 - 0.414	0.414 - 0.732	> 0.732
structure	"covalent"	"covalent"	ZnS	NaCl	CsCl

The energy that holds the arrangement of ions together is called the *lattice energy*,  $U_o$ , and this may be determined experimentally or calculated.

$U_o$  is a measure of the energy released as the **gas phase ions** are assembled into a crystalline lattice. A lattice energy must always be exothermic.

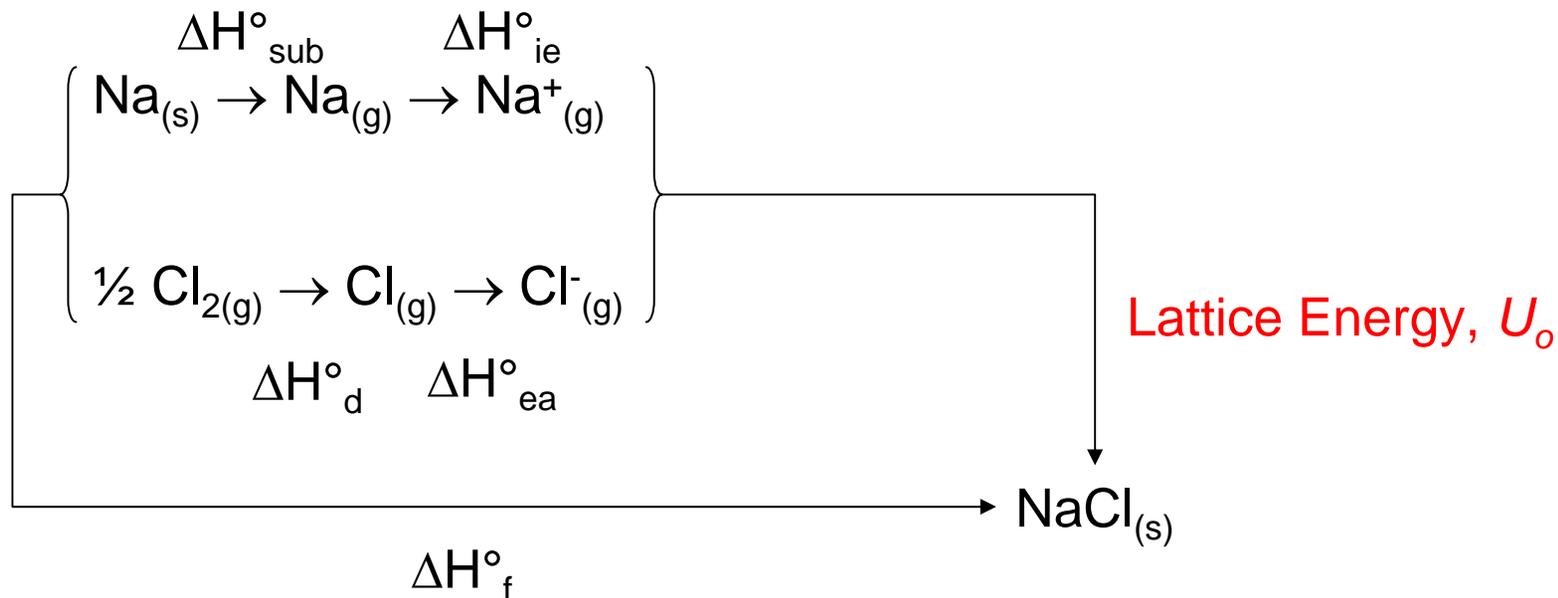


Lattice energies are determined experimentally using a Born-Haber cycle such as this one for NaCl. This approach is based on Hess' law and can be used to determine the unknown lattice energy from known thermodynamic values.



# Ionic Bonding

## Born-Haber cycle



$$\Delta H^\circ_{\text{f}} = \Delta H^\circ_{\text{sub}} + \Delta H^\circ_{\text{ie}} + \frac{1}{2} \Delta H^\circ_{\text{d}} + \Delta H^\circ_{\text{ea}} + U_o$$

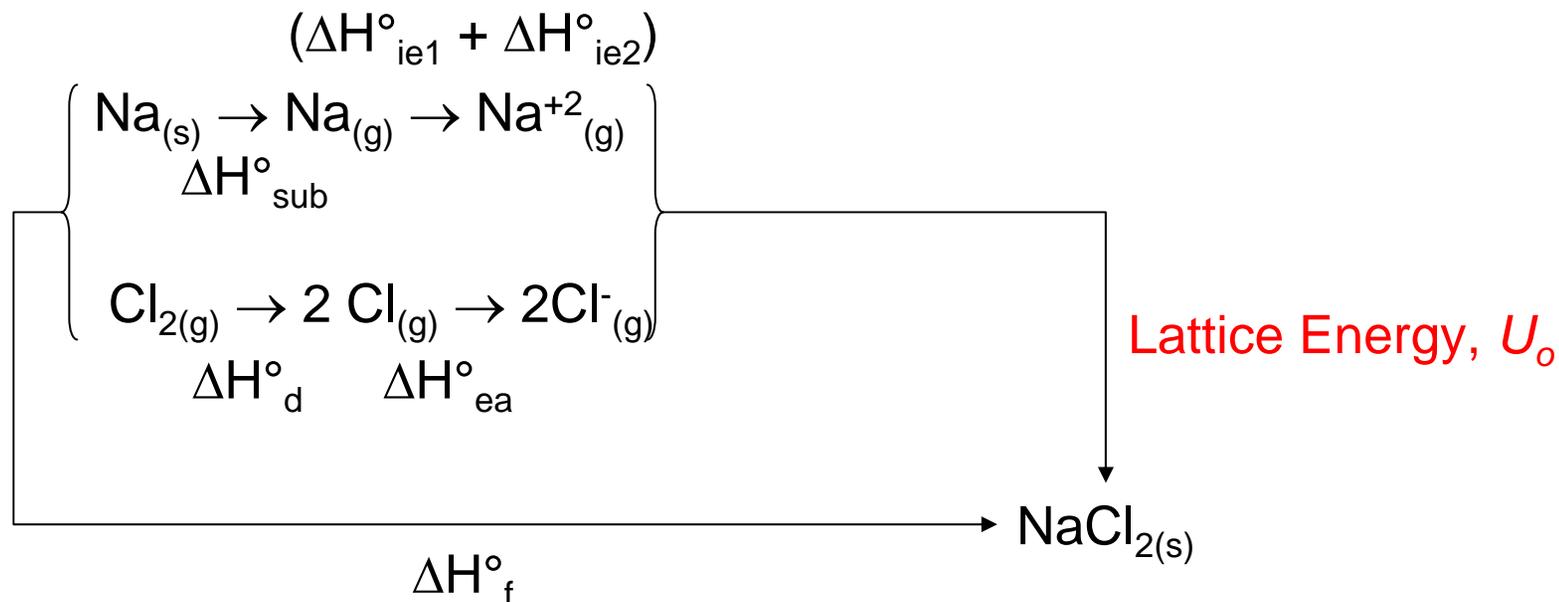
$$-411 = 109 + 496 + \frac{1}{2} (242) + (-349) + U_o$$

$$U_o = -788 \text{ kJ/mol}$$

You must use the correct stoichiometry and signs to obtain the correct lattice energy.



If we can predict the lattice energy, a Born-Haber cycle analysis can tell us why certain compounds do not form. E.g.  $\text{NaCl}_2$



$$\Delta H^\circ_{\text{f}} = \Delta H^\circ_{\text{sub}} + \Delta H^\circ_{\text{ie1}} + \Delta H^\circ_{\text{ie2}} + \Delta H^\circ_{\text{d}} + \Delta H^\circ_{\text{ea}} + U_o$$

$$\Delta H^\circ_{\text{f}} = 109 + 496 + 4562 + 242 + 2*(-349) + -2180$$

$$\Delta H^\circ_{\text{f}} = +2531 \text{ kJ/mol}$$

This shows us that the formation of  $\text{NaCl}_2$  would be highly endothermic and very unfavourable. Being able to predict lattice energies can help us to solve many problems so we must learn some simple ways to do this.

The equations that we will use to predict lattice energies for crystalline solids are the Born-Mayer equation and the Kapustinskii equation, which are very similar to one another. These equations are simple models that calculate the attraction and repulsion for a given arrangement of ions.

**Born-Mayer Equation:**

$$U_0 = (e^2 / 4 \pi \epsilon_0) * (N z_A z_B / d_0) * A * (1 - (d^* / d_0))$$

$$U_0 = 1390 (z_A z_B / d_0) * A * (1 - (d^* / d_0)) \text{ in kJ/mol}$$

**Kapustinskii equation :**

$$U_0 = (1210 \text{ kJ } \text{\AA} / \text{mol}) * (n z_A z_B / d_0) * (1 - (d^* / d_0))$$

Where:

$e$  is the charge of the electron,  $\epsilon_0$  is the permittivity of a vacuum

$N$  is Avogadro's number

$z_A$  is the charge on ion "A",  $z_B$  is the charge on ion "B"

$d_0$  is the distance between the cations and anions (in  $\text{\AA}$ ) =  $r^+ + r^-$

**$A$  is a Madelung constant**

$d^*$  = exponential scaling factor for the repulsive term =  $0.345 \text{ \AA}$

$n$  = the number of ions in the formula unit

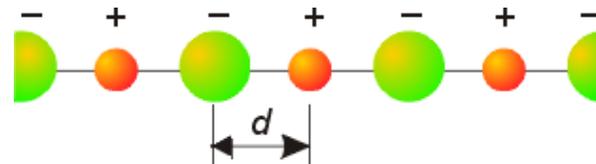


The origin of the equations for lattice energies.

$$U_0 = E_{\text{coul}} + E_{\text{rep}}$$

The lattice energy  $U_0$  is composed of both coulombic (electrostatic) energies and an additional close-range repulsion term - there is some repulsion even between cations and anions because of the electrons on these ions. Let us first consider the coulombic energy term:

For an Infinite Chain of Alternating Cations and Anions:



In this case the energy of coulombic forces (electrostatic attraction and repulsion) are:

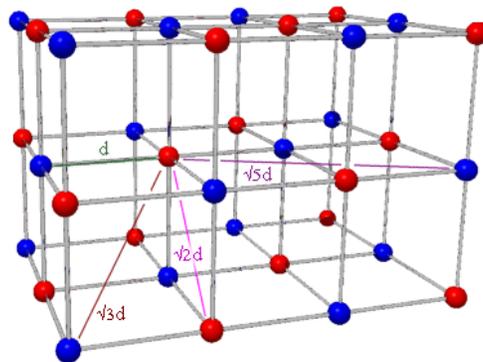
$$E_{\text{coul}} = (e^2 / 4 \pi \epsilon_0) * (z_A z_B / d) * [+2(1/1) - 2(1/2) + 2(1/3) - 2(1/4) + \dots]$$

because for any given ion, the two adjacent ions are each a distance of  $d$  away, the next two ions are  $2 \times d$ , then  $3 \times d$ , then  $4 \times d$  etc. The series in the square brackets can be summarized to give the expression:

$$E_{\text{coul}} = (e^2 / 4 \pi \epsilon_0) * (z_A z_B / d) * (2 \ln 2)$$

where  $(2 \ln 2)$  is a *geometric factor* that is adequate for describing the 1-D nature of the infinite alternating chain of cations and anions.

For a 3-dimensional arrangement, the geometric factor will be different for each different arrangement of ions. For example, in a NaCl-type structure:



$$E_{\text{coul}} = (e^2 / 4 \pi \epsilon_0) * (z_A z_B / d) * [6(1/1) - 12(1/\sqrt{2}) + 8(1/\sqrt{3}) - 6(1/\sqrt{4}) + 24(1/\sqrt{5}) \dots]$$

The geometric factor in the square brackets only works for the NaCl-type structure, but people have calculated these series for a large number of different types of structures and the value of the series for a given structural type is given by the **Madelung constant, A**.

This means that the general equation of coulombic energy for any 3-D ionic solids is:

$$E_{\text{coul}} = (e^2 / 4 \pi \epsilon_0) * (z_A z_B / d) * A$$

Note that the value of  $E_{\text{coul}}$  must be negative for a stable crystal lattice.



The numerical values of Madelung constants for a variety of different structures are listed in the following table. CN is the coordination number (cation,anion) and  $n$  is the total number of ions in the empirical formula e.g. in fluorite ( $\text{CaF}_2$ ) there is one cation and two anions so  $n = 1 + 2 = 3$ .

<b>lattice</b>	<b>A</b>	<b>CN</b>	<b>stoich</b>	<b>A / n</b>
CsCl	1.763	(8,8)	AB	0.882
NaCl	1.748	(6,6)	AB	0.874
Zinc blende	1.638	(4,4)	AB	0.819
wurtzite	1.641	(4,4)	AB	0.821
fluorite	2.519	(8,4)	$\text{AB}_2$	0.840
rutile	2.408	(6,3)	$\text{AB}_2$	0.803
$\text{CdI}_2$	2.355	(6,3)	$\text{AB}_2$	0.785
$\text{Al}_2\text{O}_3$	4.172	(6,4)	$\text{A}_2\text{B}_3$	0.834

Notice that the value of A is fairly constant for each given stoichiometry and that the value of  $A/n$  is very similar regardless of the type of lattice.

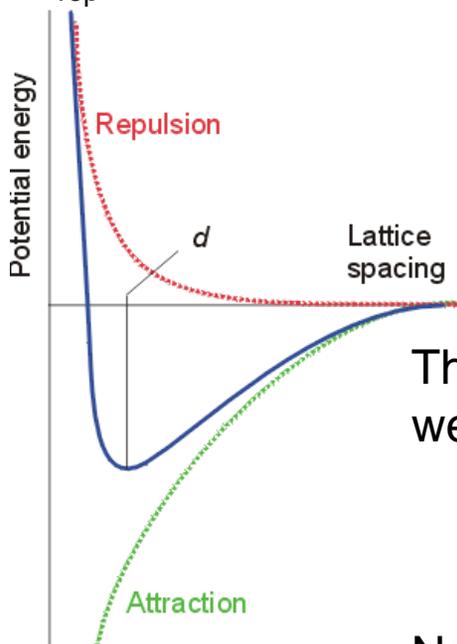


If only the point charge model for coulombic energy is used to estimate the lattice energy (i.e. if  $U_0 = E_{\text{coul}}$ ) the calculated values are much higher than the experimentally measured lattice energies.

E.g. for NaCl ( $r_{\text{Na}^+} = 0.97\text{\AA}$ ,  $r_{\text{Cl}^-} = 1.81\text{\AA}$ ):

$$U_0 = 1390 (z_A z_B / d_0) * A = 1390 ((1)(-1)/2.78) * (1.748) \text{ kJ/mol} = - 874 \text{ kJ/mol}$$

But the experimental energy is -788 kJ/mol. The difference in energy is caused by the repulsion between the electron clouds on each ion as they are forced close together. A correction factor,  $E_{\text{rep}}$ , was derived to account for this.



$$E_{\text{rep}} = - (e^2 / 4 \pi \epsilon_0) * (z_A z_B d^* / d^2) * A \quad \text{and since}$$

$$E_{\text{coul}} = (e^2 / 4 \pi \epsilon_0) * (z_A z_B / d) * A \quad \text{the total is given by}$$

$$U_0 = (e^2 / 4 \pi \epsilon_0) * (z_A z_B / d_0) * A * (1 - (d^* / d_0))$$

This is the Born-Mayer equation, when the constants are evaluated we get the form of the equation that we will use:

$$U_0 = 1390 (z_A z_B / d_0) * A * (1 - (d^* / d_0)) \text{ in kJ/mol}$$

Note:  $d^*$  is the exponential scaling factor for the repulsive term and a value that we will use for this is **0.345 Å**.



Using the Born-Mayer equation, for our example with NaCl.

$$U_0 = 1390 (z_A z_B / d_0) * A * (1 - (d^* / d_0))$$
$$= 1390 ((1)(-1)/2.78) * (1.748) * (1-(0.345/2.78)) \text{ kJ/mol} = - 765 \text{ kJ/mol}$$

Which is much closer to the experimental energy of -788 kJ/mol.

---

Kapustinskii observed that  $A/n$  is relatively constant but increases slightly with coordination number. Because coordination number also increases with  $d$ , the value of  $A/nd$  should also be relatively constant. From these (and a few other) assumptions he derived an equation that does not involve the Madelung constant:

Kapustinskii equation :

$$U_0 = (1210 \text{ kJ } \text{\AA} / \text{mol}) * (n z_A z_B / d_0) * (1 - (d^* / d_0))$$

One advantage of the Kapustinskii equation is that the type of crystal lattice is not important. This means that the equation can be used to determine ionic radii for non-spherical ions (e.g.  $\text{BF}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{OH}^-$ ,  $\text{SnCl}_6^{2-}$  etc.) from experimental lattice energies. The self-consistent set of radii obtained in this way are called *thermochemical radii*.