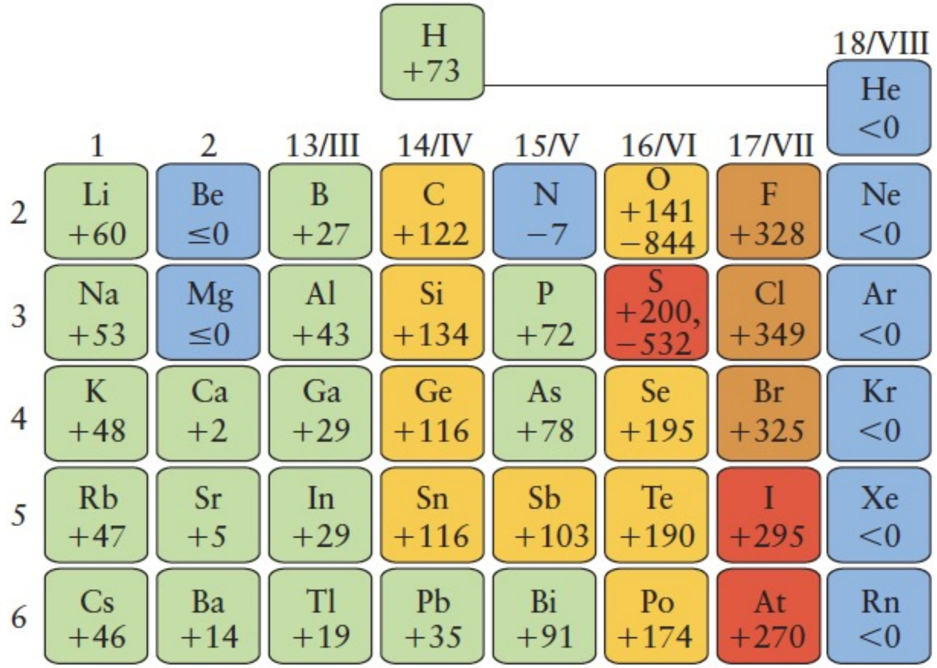
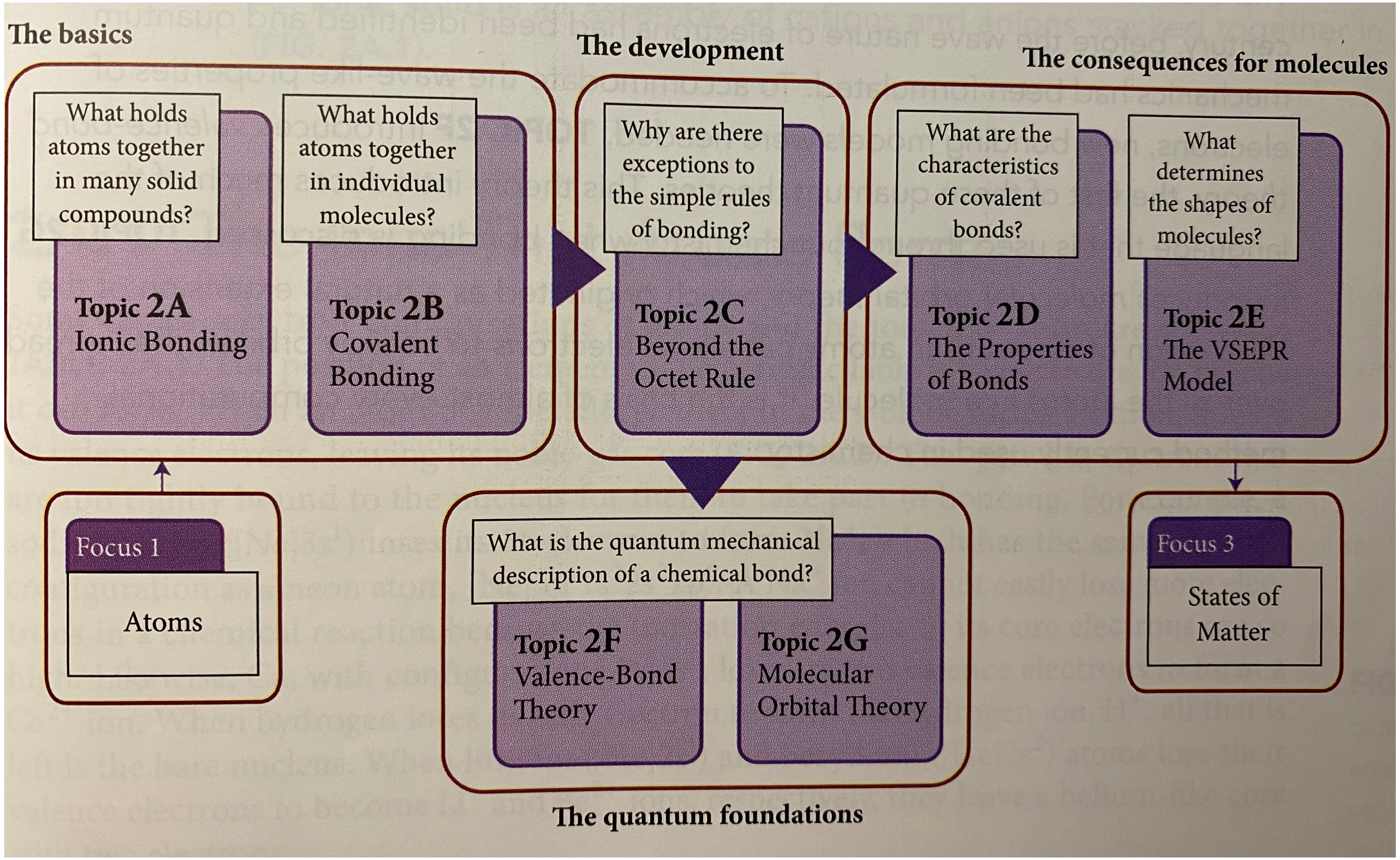
CH-110 Advanced General Chemistry I

Dr. Milena Schuhmacher



A Group 16/VI atom, such as O or S, has two vacancies in its valence-shell p-orbitals and can accommodate two additional electrons. The first electron affinity is positive because energy is released when an electron attaches to O or S. However, attachment of the second electron *requires* energy because of the repulsion by the negative charge already present in O^- or S^-. Unlike that of a halide ion, however, the valence shell of the O^- anion has only seven electrons and thus can accommodate an additional electron. Therefore, we expect that less energy will be needed to make O^{2-} from O^- than to make F^{2-} from F^-, where no such vacancy exists. In fact, 141 kJ·mol^{-1} is released when the first electron adds to the neutral atom to form O^-, but 844 kJ·mol^{-1} must be supplied to add a second electron to form O^{2-}; so the total energy required to make O^{2-} from O is +703 kJ·mol^{-1}. As we shall see in Chapter 2, this energy can be achieved in chemical reactions, and O^{2-} ions are common in metal oxides.

Overview Chapter 2 (Focus 2: Bonds Between Atoms)



Bonds Between Atoms

Focus 2

Vale!

- "Vale!" ("Be strong!") was what the Romans said on parting. **Valence is all about strength of links between atoms.**
- A *chemical bond* is the link between atoms that occurs when the valence electrons of two or more atoms move to new locations and settle into lower-energy arrangements.

Overview over focus 2

- **Complete transfer of electrons between atoms**: formation of ions and **ionic** compounds (Topic 2A).
- **Incomplete transfer of electrons**: formation of **covalent** bonds (Topic 2B).
- Exceptions to the octet rule (Topic 2C).
- Topic 2D explores how the **properties of bonds can be explained**.
- Topic 2E shows how the **shapes of molecules** can be predicted.
- To accommodate the wave-like properties of electrons, a new bonding model, the **valence-bond theory** was developed (Topic 2F).
- Topic 2G introduces the **molecular orbital theory**, a theory that explains how electrons occupy orbitals in molecules.

Ionic Bonding

Topic 2A

Topic 2A.1 The ions that atoms form
Topic 2A.2 Lewis symbols
Topic 2A.3 The energetics of ionic bond formation
Topic 2A.4 Interactions between ions

WHY DO YOU NEED TO KNOW THIS MATERIAL?

- One of the principal kinds of bonding in compounds.

WHAT DO YOU NEED TO KNOW ALREADY?

- Electron configurations of many-electron atoms (Topic 1E)
- Potential energy, nature of Coulomb interaction between charges (Fundamentals A)
- Ionic radius, ionization energy, and electron affinity (Topic 1F)

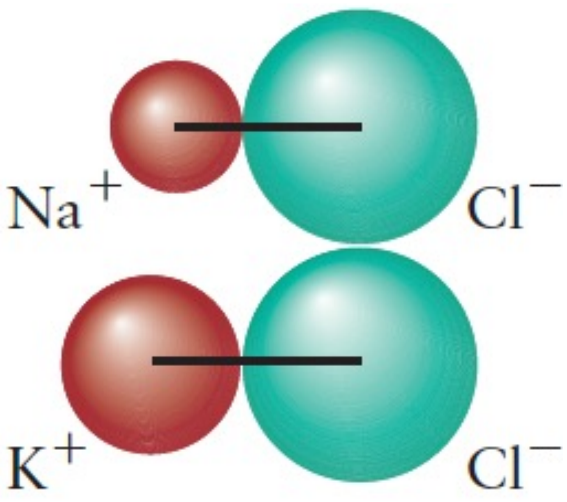
The Ions that Atoms Form

Topic 2A.1

2A.1: The ions that atoms form

Ionic solids

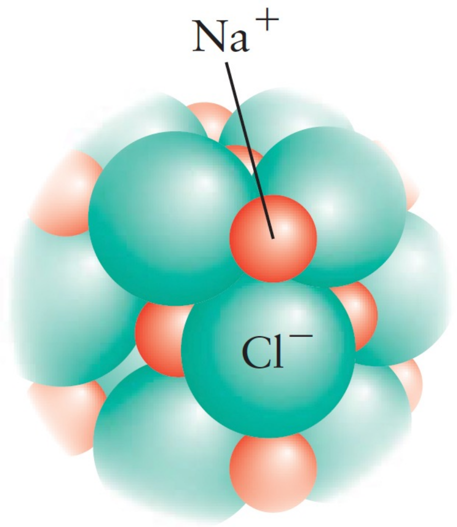
- The **ionic model** is a description of chemical bonding in terms of **electrostatic interactions** between ions.
- It is particularly appropriate for describing binary compounds formed between **metallic and nonmetallic** elements, such as sodium chloride (NaCl).

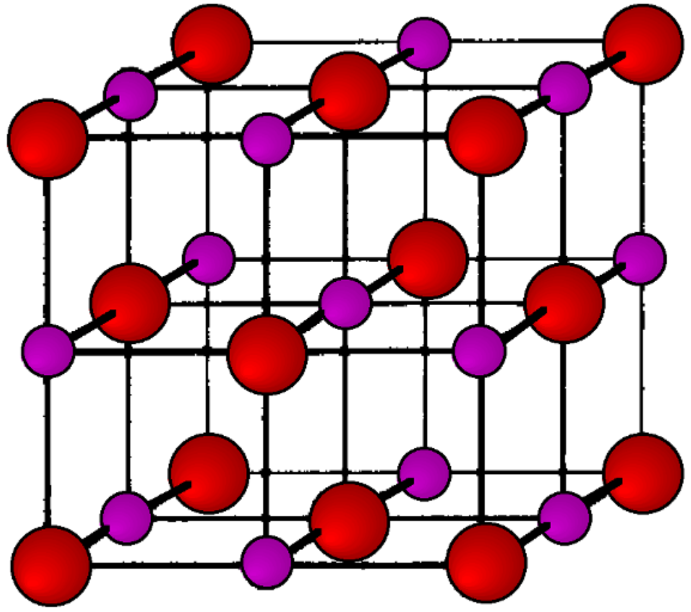


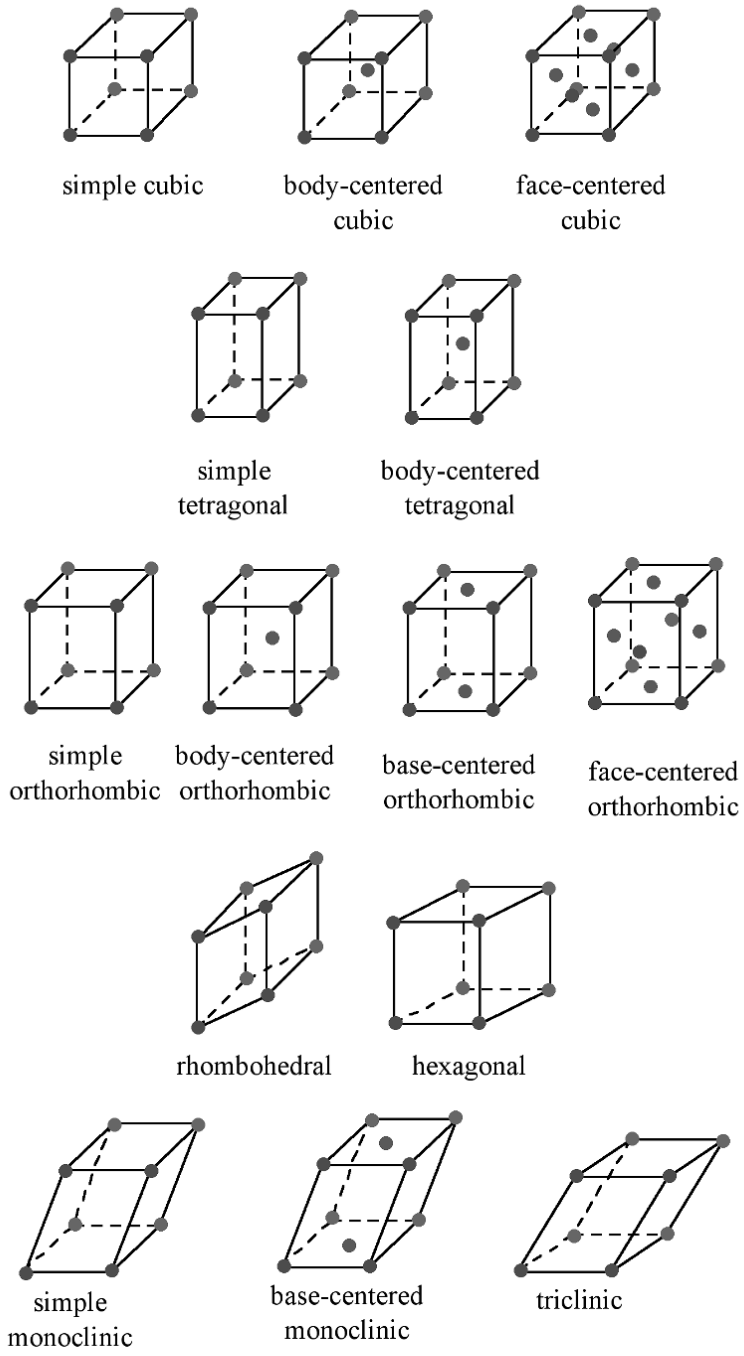
2A.1: The ions that atoms form

Different crystal structures:

An ionic solid is an assembly of cations and anions stacked together in a regular array







Typical electron configurations of atoms and the ions they form

TABLE 2.1 Some Typical Electron Configurations of Atoms and the Ions They Form

Atom	Configuration	Ion	Configuration
Li	$[He]2s^1$	Li^+	$[He]$ $(1s^2)$
Be	$[He]2s^2$	Be^{2+}	$[He]$
Na	$[Ne]3s^1$	Na^+	$[Ne]$ $([He]2s^22p^6)$
Mg	$[Ne]3s^2$	Mg^{2+}	$[Ne]$
Al	$[Ne]3s^23p^1$	Al^{3+}	$[Ne]$
N	$[He]2s^22p^3$	N^{3-}	$[Ne]$ $([He]2s^22p^6)$
O	$[He]2s^22p^4$	O^{2-}	$[Ne]$
F	$[He]2s^22p^5$	F^-	$[Ne]$
S	$[Ne]3s^23p^4$	S^{2-}	$[Ar]$ $([Ne]3s^23p^6)$
Cl	$[Ne]3s^23p^5$	Cl^-	$[Ar]$

2A.1: The ions that atoms form

s-block elements

- s-block elements lose their valence electrons to leave a noble gas core (Fig. 2A.2).
- Core has electrons that are **too tightly bound** to the nucleus for them to take part in bonding.
- Sodium ([Ne]$3s^1$) loses its 3s-electron to form Na^+
- Ca ([Ar]$4s^2$) loses ist two 4s-electrons to form Ca^{2+}
- Hydrogen loses its only 1s-electron to form H^+, a bare nucleus.

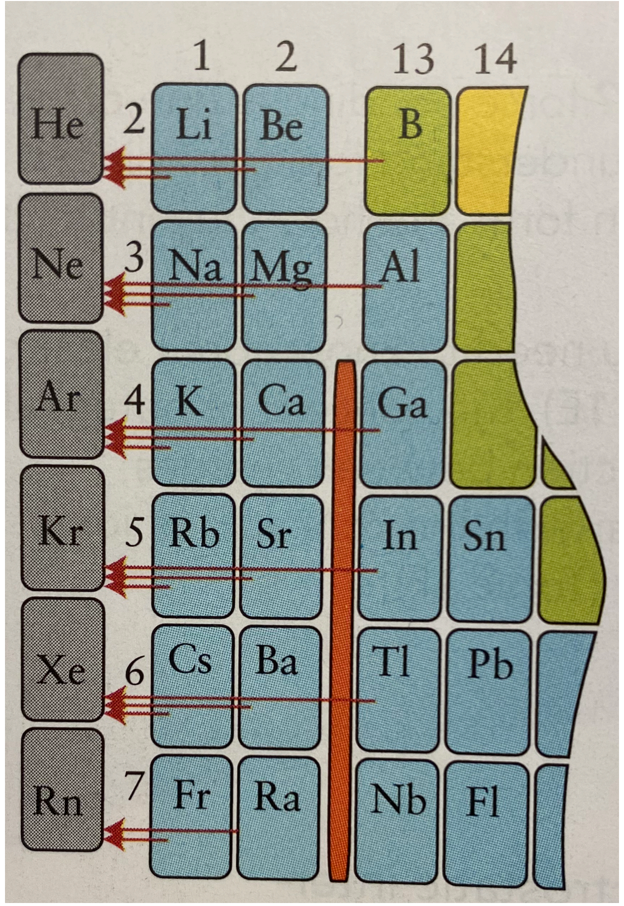


Figure 2A.2

p-block elements

Group 13, 14: on the left of p-block

- Period 3: Aluminum ([Ne]$3s^2 3p^1$) forms Al^{3+}
- Period 4: Gallium ([Ar]$3d^{10} 4s^2 4p^1$) forms Ga^{3+} with configuration [Ar]$3d^{10}$
- A complete d-shell is stabilized and not easy to remove.

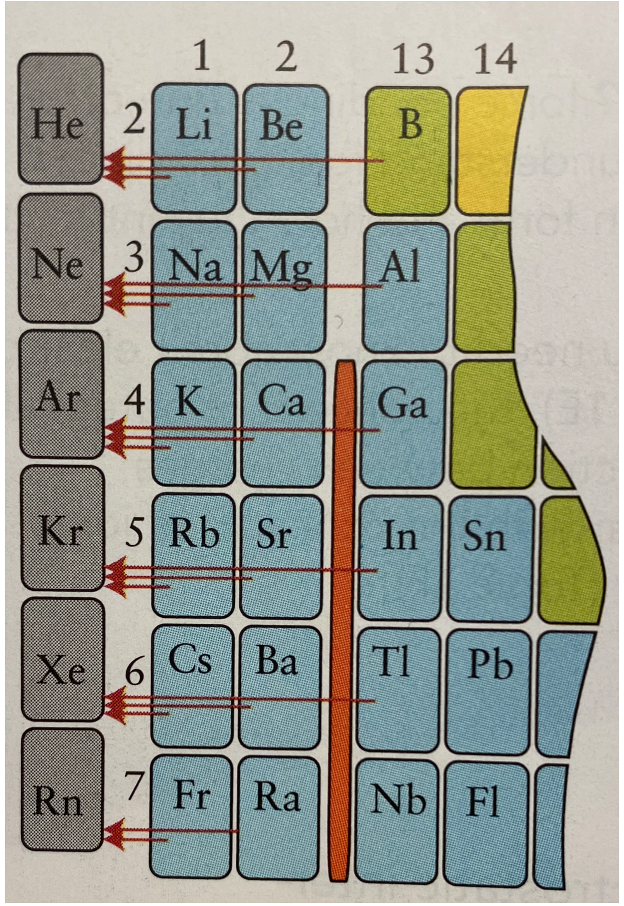


Figure 2A.2

d-block elements

- d-block elements can lose a variable number of electrons: **variable valence.**
- *n*s-electrons are lost first, followed by a variable number of (*n*-1)d-electrons

E.g. Fe ([Ar]$3d^6 4s^2$) → Fe^{2+} ([Ar]$3d^6$) → Fe^{3+} ([Ar]$3d^5$)

Iron ([Ar]$3d^6 4s^2$) rarely goes beyond losing three electrons to form cation Fe^{4+}

- d-block behavior **not always easy to predict**:

E.g. copper ([Ar]$3d^{10} 4s^1$) forms Cu^+ ([Ar]$3d^{10}$) and Cu^{2+} with configuration [Ar]$3d^9$, but not Cu^{3+} with [Ar]$3d^8$

Variable valence in the lower p-block: inert-pair effect

- Group 13: compare aluminum ([Ne]$3s^2p^1$) and indium ([Kr]$4d^{10}5s^25p^1$):
- Aluminum only forms Al^{3+}
- Indium forms In^+ and In^{3+} with [Kr]$4d^{10}5s^2$ and [Kr]$4d^{10}$, respectively.
- Starting in the 4th period: The ability of elements to form ions **two units lower in charge than expected** from the group number is called the **inert-pair effect.** Intervening d- (and f-) orbitals do not effectively shield the s-electrons of the valence shell. As a result, the *inert pair* of *ns* electrons remains more tightly held by the nucleus and hence participates less in bond formation.

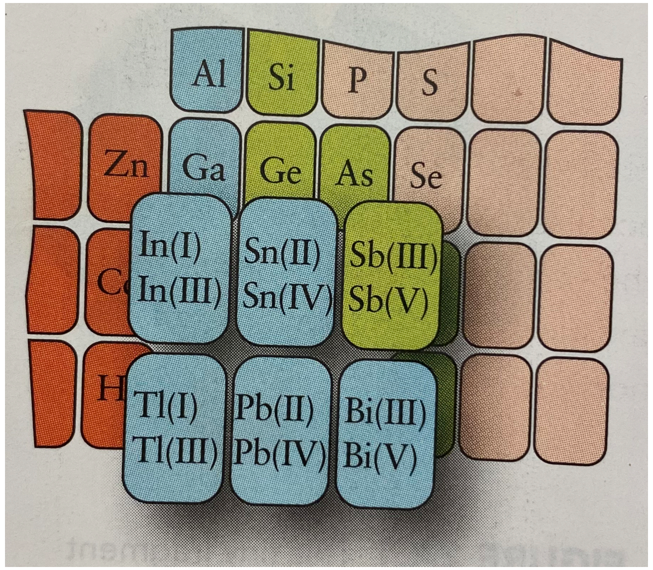


Figure 2A.3

2A.1: The ions that atoms form

Nonmetals gain electrons

- Ionization energies too high:
- Nonmetals are likely to **gain electrons** and **form anions**
- Anions with **noble gas configurations: duplet** (helium-like configuration, $1s^2$) or **octet** (eight valence-electron configuration, ns^2np^6)
- E.g. hydrogen becomes the hydride ion, H^-
- Nitrogen becomes the nitride ion, N^{3-} ($[He]2s^22p^6$)

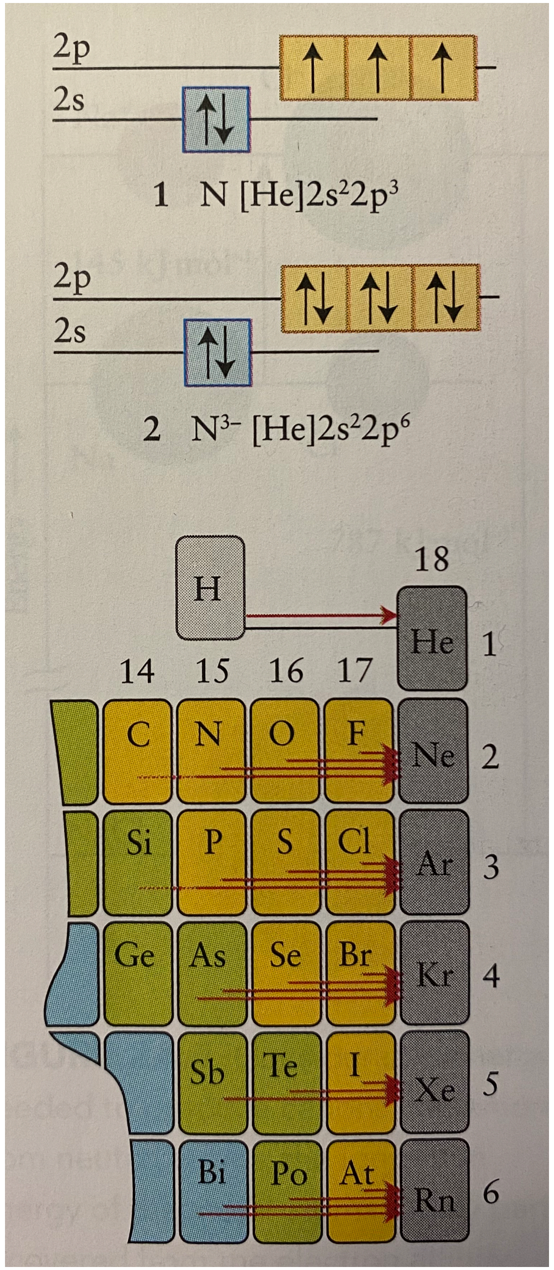


Figure 2A.4

2A.1: The ions that atoms form

Nonmetals gain electrons

- When electron affinity is positive, as for halogens, **energy is released** when an electron is added to the valence shell.
- A chloride ion ([Ne]$3s^2 3p^6$) has a lower energy than a chlorine atom ([Ne]$3s^2 3p^5$) plus a free electron.
- Adding a second electron to chloride to form Cl^{2-} requires energy.
- Add **just enough electrons to complete an octet** in a valence shell, but no more.

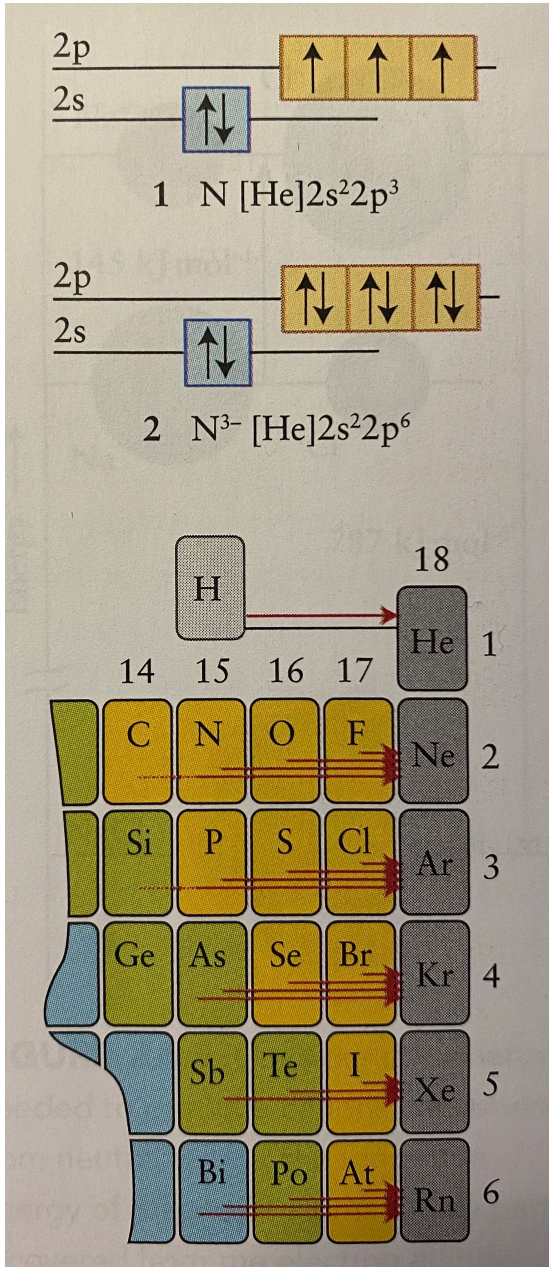


Figure 2A.4

2A.1: The ions that atoms form

Summary

To predict the electron configuration of a monatomic **cation**, remove the outermost electrons **in the order *n*p, *n*s and (*n*-1)d.**

d-block elements and elements lower in the p-block often display variable valence.

For a monatomic **anion**, **add electrons** until the next **noble-gas configuration** has been reached.

The transfer of electrons results in the formation of an octet (or duplet) of electrons in the valence shell on each of the ions.

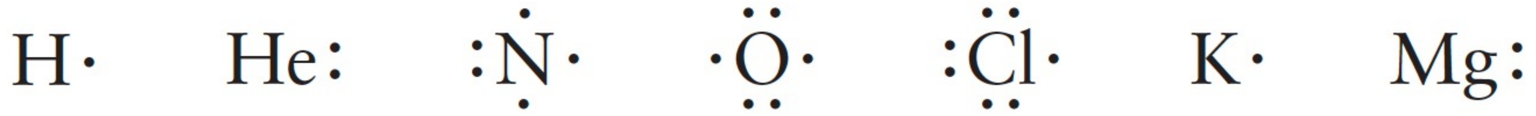
Lewis Symbols

Topic 2A.2

2A.2: Lewis symbols

G. N. Lewis

- G. N. Lewis was among the first to recognize that the recently discovered electron was key to chemical bonding.
- He devised a simple way to keep track of valence electrons when atoms form ions.
- Each valence electron is **represented as a dot**
- Arranged **around the element**
- Modern interpretation: a single dot is an electron in an orbital, **a pair of dots represents two paired electrons sharing an orbital**.



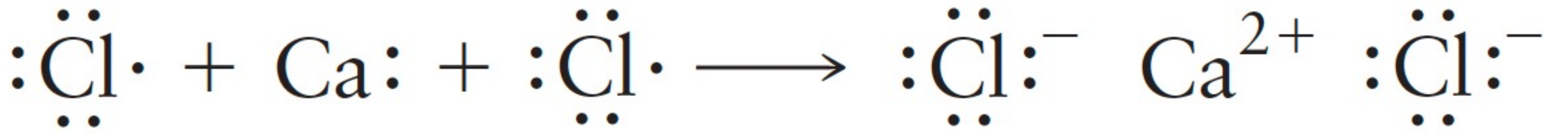
Lewis symbol rules for ionic solids

- Represent the **cation** by **removing the appropriate number of dots** from the symbol from the atom of the metallic element.
- Represent the **anion** by transferring those dots to the Lewis symbol for the atom of the nonmetallic element to **complete its valence shell**.
- If necessary, **adjust the numbers of atoms** of each kind so that all the dots removed from the atoms of the metallic element are accommodated by the atoms of the nonmetallic element.
- Write the **charge** of each ion as a superscript.

2A.2: Lewis symbols

Lewis symbol rules with calcium chloride as an example

- Calcium atom loses two valence electrons: Ca^{2+}
- Chloride gains one electron: Cl^{-}
- The ratio of two chloride ions for each calcium ion results in the formula $CaCl_2$.
- **Note**: this formula denotes a **formula unit**, not a molecule. There are no individual $CaCl_2$ molecules, a crystal of calcium chloride consissts of a huge number of these ions in 3D arrays, with two Cl^{-} ions for each Ca^{2+} ion.



Summary

Formulas of compounds consisting of the monatomic ions of main-group elements can be predicted by assuming that **cations have lost all their valence electrons** and **anions have gained electrons in their valence shells until each ion has an octet** of electrons, or a duplet in the case of H, Li, and Be.

The Energetics of Ionic Bond Formation

Topic 2A.3

A crystal of NaCl

- A crystal of NaCl has a lower energy compared to separated Na plus Cl atoms
- The formation of the solid is imagined as taking place **in three hypothetical steps**, starting with gaseous sodium and chlorine atoms:

1. Electrons are removed from gaseous sodium atoms.
2. These removed electrons attach to gaseous chlorine atoms.
3. The resulting gaseous cations and anions clump together as a solid crystal.

$Na(g) \rightarrow Na^{+}(g) + e^{-}(g)$	Energy required = 494 kJ/mol
$Cl(g) + e^{-} \rightarrow Cl(g)$	Energy released = 349 kJ/mol
	Net change in energy: +145 kJ/mol

A gas of widely separated Na^{+} and Cl^{-} ions has a higher energy than a gas of neutral Na and Cl ions.

The lattice energy

- What happens when Na^+ and Cl^- come together to form a crystalline solid:
- Lattice energy usually very large.
- "Lattice": orderly arrangement of ions in a crystal

$Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$ Energy released = 787 kJ/mol

- The net change in energy for the overall process is 145 – 787 kJ/mol = **–642 kJ/mol**

$Na(g) + Cl(g) \rightarrow NaCl(s)$ Energy released = 642 kJ/mol

- **Conclusion**: A solid composed of Na^+ and Cl^- ions has a much lower energy than a widely separated Na and Cl atoms.

2A.3: The energetics of ionic bond formation

The lattice energy

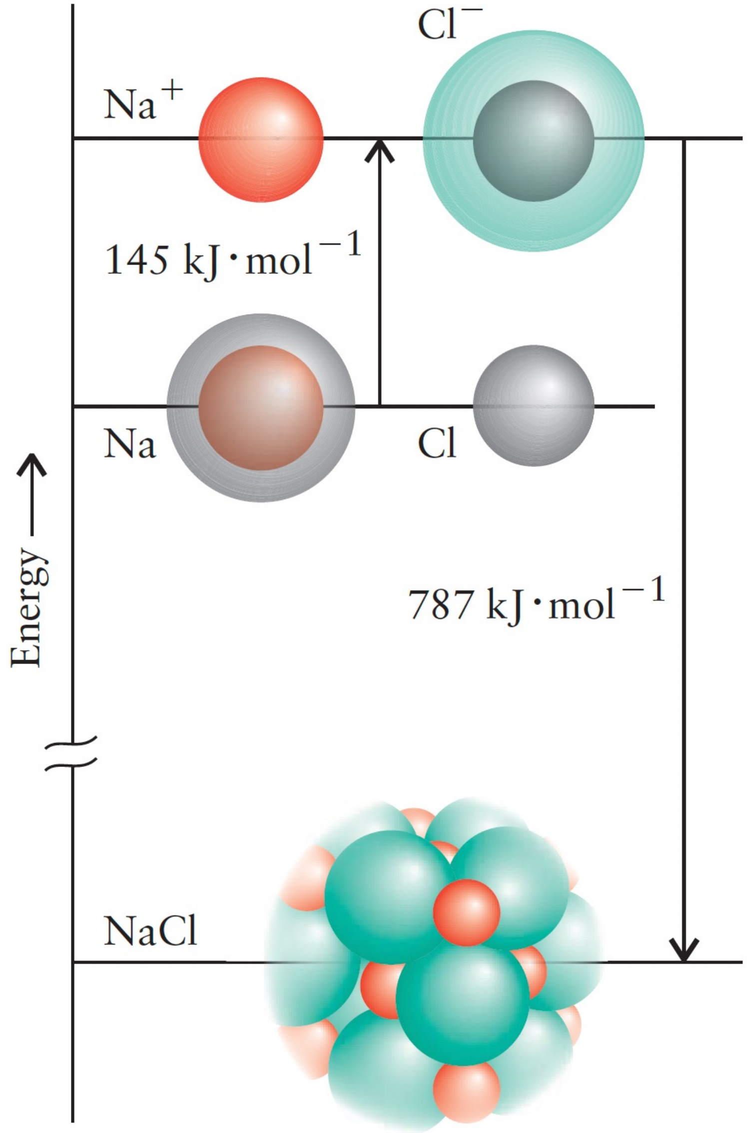


Figure 2A.6

2A.3: The energetics of ionic bond formation

Summary

The decrease in energy that accompanies the formation of an ionic solid is due largely to the attraction between oppositely charged ions.

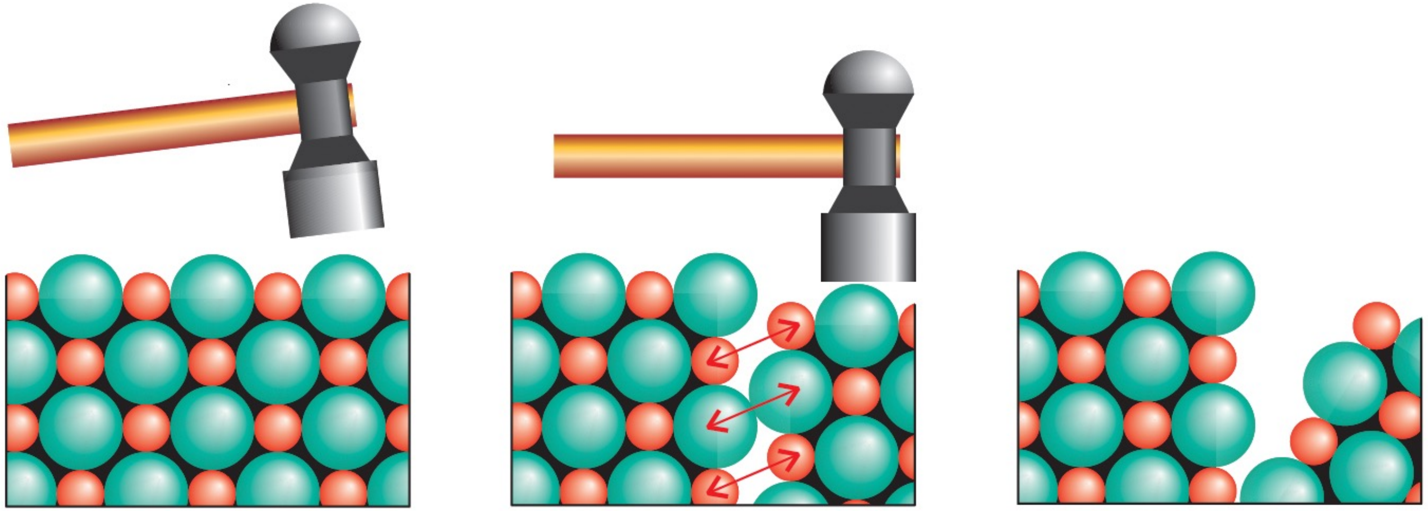
Interactions Between Ions

Topic 2A.4

Properties of an ionic solid

- In an ionic solid, there are **no specific bonds.**
- All the cations are attracted to all the anions to some extent.
- All the cations repel one another, all the anions repel one another, to some extent.
- An ionic bond is a **"global" interaction characteristic** of the entire crystal, a net lowering of energy of the entire crystal relative to widely separated neutral atoms
- Ionic solids have a **high melting point**: a high temperature is needed before the ions have enough energy to move past one another and the solid melts to form a liquid.
- **Brittleness**: when an ionic solid is struck by a mechanical force, ions with the same charges come into contact and repel one another, the solid shatters into fragments

Why ionic solids are brittle



(a) (b) (c)

Figure 2A.7

(d) (e)

(a) The original solid consists of an orderly arrangement of cations and anions.

(b) A hammer blow can push ions with same charges into adjacent positions; this proximity of like charges results in strong repulsive forces (arrows).

(c) As a result of the repulsive forces, the solid breaks apart.

(d) The smooth faces of this calcite crystal result from the regular arrangement of calcium and carbonate ions.

(e) The blow of a hammer has shattered the crystal, leaving flat, regular surfaces consisting of planes of ions.

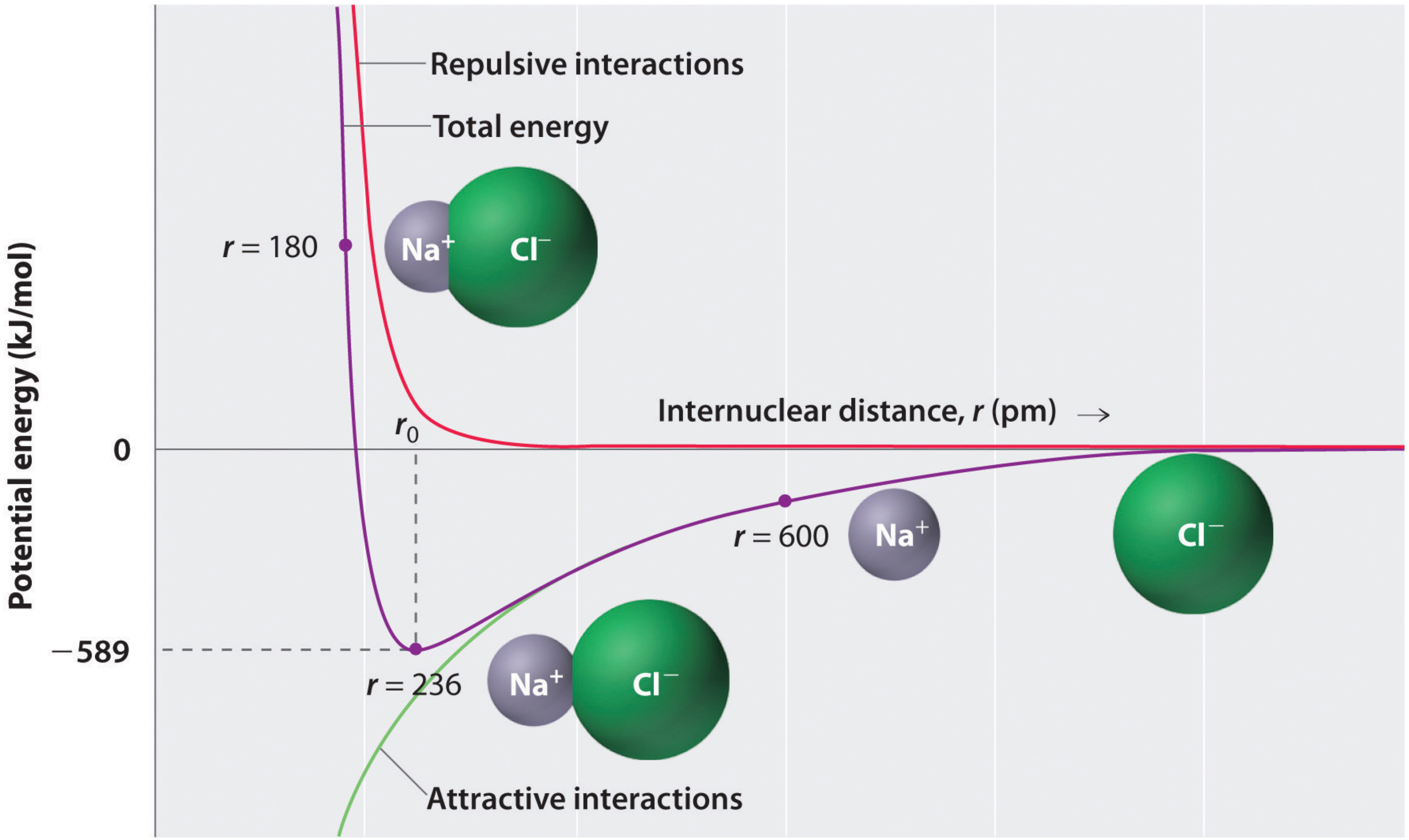
Coulomb potential energy of two individual ions

$$E_{p,12} = \frac{(z_1 e)\times(z_2 e)}{4\pi\varepsilon_0 r_{12}} = \frac{\mathrm{z_1 z_2 e^2}}{4\pi\varepsilon_0 r_{12}}$$

- $z_1 e$: charge of ion 1 with e, the fundamental charge
- $z_2 e$: charge of ion 2
- r_{12}: distance between the centers of the two ions
- ε_0: the electric constant
- **Note**: The charge number, z, is positive for cations and negative for anions, and the charge of an ion is ze, where e is the fundamental charge. Chemists, however, almost always refer to z itself as the charge and speak of a cahrge of +1, –1, and so on → Chemists typically refer to charge as **multiples of the fundamental charge**.

Figure 2A.10

Potential energy of interaction



Potential energy in a 3D array of ions with different charges

- Every ion in an ionic solid is attracted to all the oppositely charged ions and repelled from all the other ions with like charges.

$$E_p = A \times \frac{N_A z_1 z_2 e^2}{4\pi\varepsilon_0 d}$$

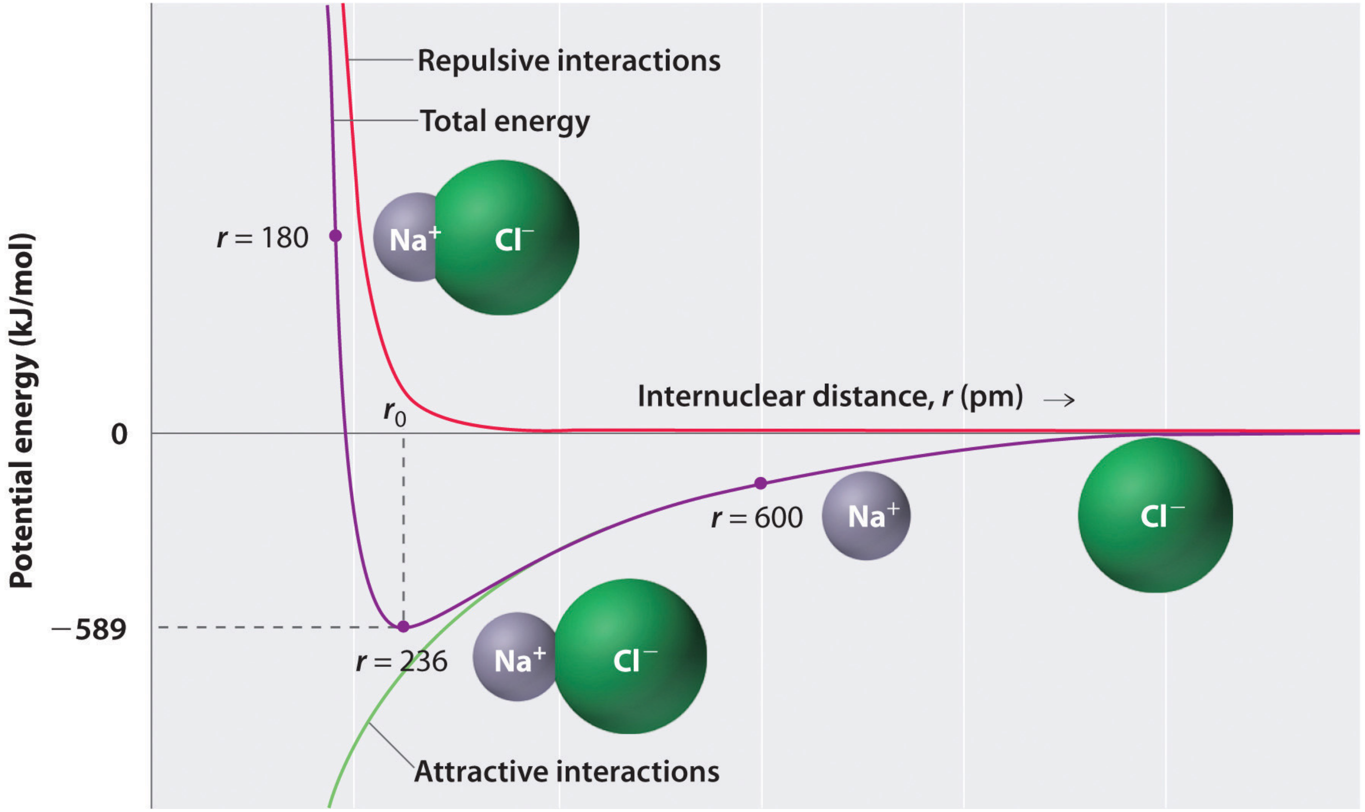
- Note that $z_1 z_2$ is **negative**, as the ions have opposite charges.
- The factor A is a numerical coefficient called the **Madelung constant**, its value depends on how the ions are arranged about one another (see **Topic 3G**)
- The potential energy **is strongly negative** when the ions are highly charged (large values of z) and when the separation between them is small (small values of d)

Summary

Ionic solids typically have:

- high melting points and are brittle.
- large lattice energy when the ions are small and highly charged.

Their interaction can be described by the coulomb potential



The skills you have mastered are the ability to

- Write the electron configuration for an ion.
- Account for the formation of ions in terms of ionization energy, electron affinity, and the electrostatic interactions between them.
- Predict the chemical formula of an ionic compound and draw its formula unit by using Lewis symbols
- Account for the origin and magnitude of the lattice energy.

Summary: You have learned that in ionic bonding, electrons are transferred from one atom to another and that the patterns of ionic bond formation can be represented by formula units based on Lewis symbols. You have seen that the greater the charge and the smaller the ion, the greater the energy lowering when an ionic solid forms from widely separated atoms.