

# ❑ CHEMICAL BONDS

- ❖ What do we mean by the Chemical Bonds?
  - ❖ What determines the type of bonding in each substance?
  - ❖ How do you describe the bonding in various substances?
- We shall briefly discuss these aspects here.
- The properties of a substance are determined *in part* by the chemical bonds that hold the atoms/ions together.
- ✓ For example, sodium (a silvery metal) reacts with chlorine (a pale greenish yellow gas) to produce sodium chloride (table salt, a white solid).
  - ✓ The substances in this reaction are quite different, as are their chemical bonds. Sodium chloride, NaCl, consists of  $\text{Na}^+$  and  $\text{Cl}^-$  ions held in a regular arrangement, or crystal, by ionic bonds.

## ❖ What do we mean by Chemical Bonds?

- A chemical bond is the link.....in the form of the **net** force of attractions existing between atoms/ions in a substance.
- *When a chemical reaction occurs between atoms, some of their electrons are reorganized, resulting in a net attractive force—a chemical bond—between the atoms.*
- When **a chemical bond forms** between two atoms, the *resulting arrangement of the two nuclei and their electrons* has **a lower energy** than the total energy of the separate atoms.
- The *changes in energy responsible for the formation of bonds.*
- Therefore, bond formation depends on the electronic structures of atoms.

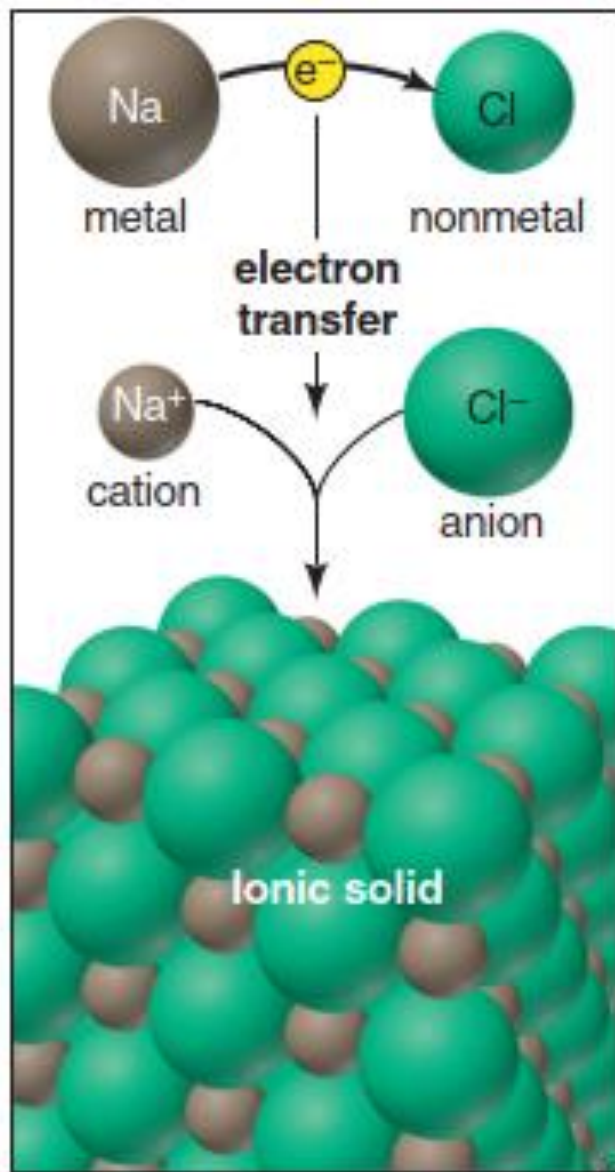
➤ If the **lowest energy can be achieved** by:

(i)....the **complete transfer of one or more electrons** from each atom of one element to those of another, then ions form and the compound is held together by the **electrostatic attraction** between them. **Ionic bonding** results from the attractive force of oppositely charged ions. ....e.g.,  $\text{Na}^+\text{Cl}^-$ .

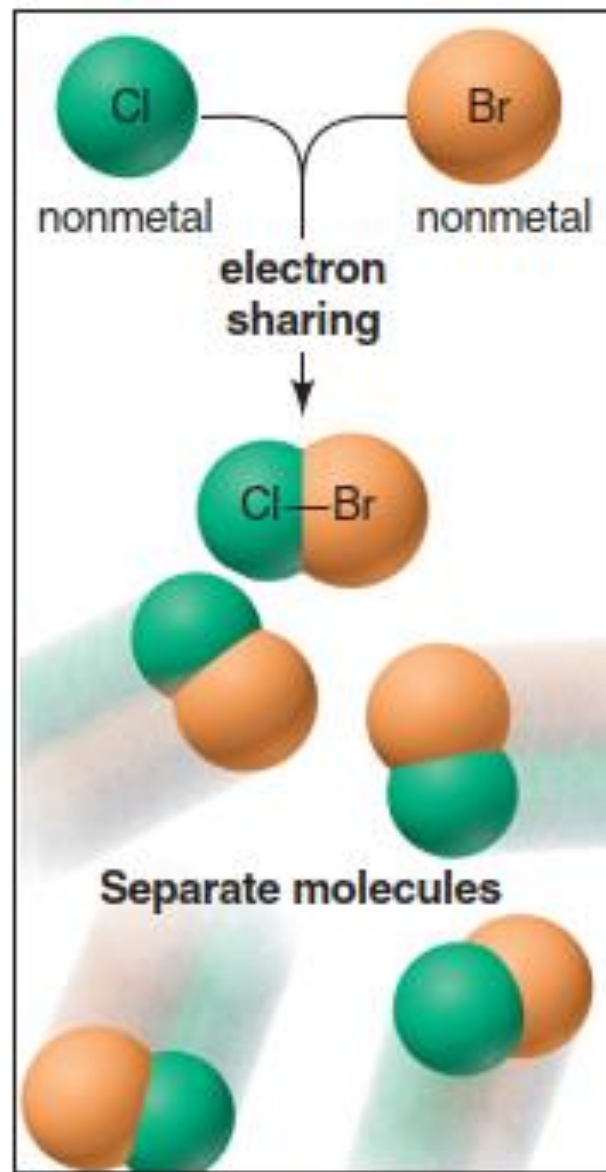
(ii).... **sharing of electrons**, which are attracted to the positively charged cores of both atoms, thus linking them. This kind of linking of the atoms is called a **covalent bond** and discrete molecules are formed. ....e.g.,  $\text{Cl}_2$ ,  $\text{CH}_4$ .

(iii).... **large numbers of cations are held together by a sea of electrons**. This **type of bond** is the **metallic bond**. For example, a piece of copper consists of a stack of copper ions held together by a sea of valence electrons, each of which comes from one of the atoms in the sample. ....e.g., Cu, Ag, .....

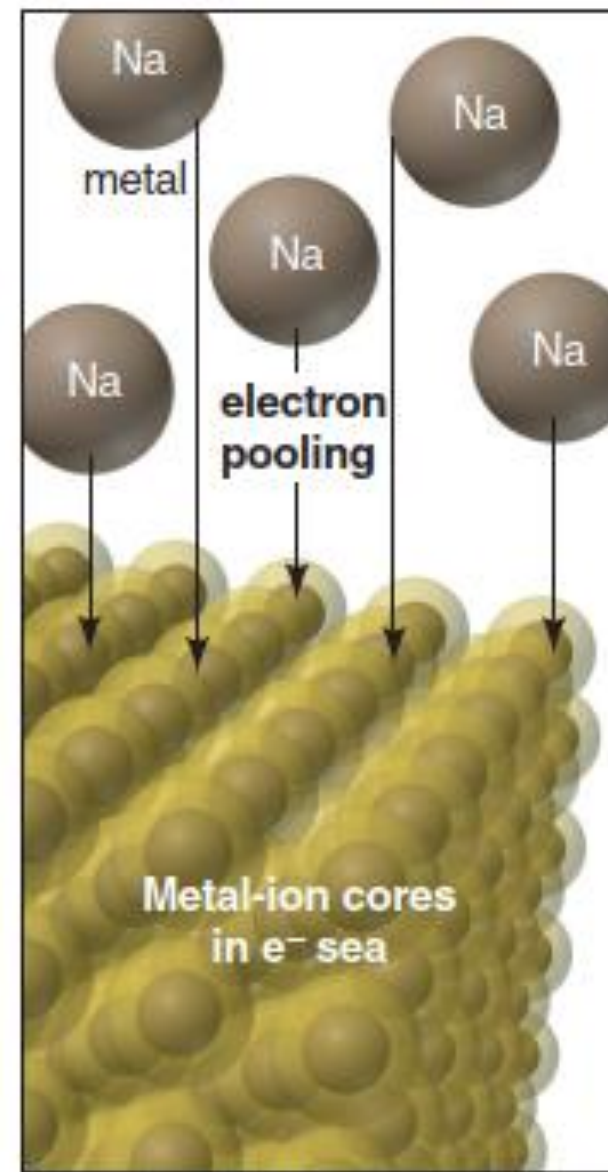
➤ We examine all these bonds in more detail in later sections.



A Ionic bonding



B Covalent bonding



C Metallic bonding

Figure 9.2 Three models of chemical bonding.

➤ Chemists generally think of **bonds** as falling into these three broad categories—*ionic, covalent, and metallic*.

❑ **What determines the type of bonding in each substance?**

❑ **How do you describe the bonding in various substances?**

➤ In this section, we will look at some simple, useful concepts of bonding that can help us answer these questions.

# ATOMIC PROPERTIES AND CHEMICAL BONDS

## ❑ What determines the type of bonding in each substance?

- In general, there is a gradation from atoms of more metallic elements to atoms of more nonmetallic elements across a period and up a group.
- Three types of bonding result from the three ways these two types of atoms can combine.

## ❑ Types of Bonding: Three Ways Metals and Nonmetals Combine

- 1. ***Metal with nonmetal***: electron transfer and ionic bonding (Figure 9.2A). We observe **ionic bonding** between atoms with large differences in their tendencies to lose or gain electrons. Such differences occur between reactive metals [Groups 1A(1) and 2A(2)] and nonmetals [Group 7A(17) and the top of Group 6A(16)].
- ✓ A metal atom (*low IE*) loses its one or two valence electrons, and a nonmetal atom (*highly negative EA*) gains the electron(s).
  - ✓ Electron transfer from metal to nonmetal occurs, and each atom forms an ion with a noble gas electron configuration.
  - ✓ The electrostatic attractions between these positive and negative ions draw them into a three-dimensional array to form an ionic solid.
  - ✓ Note that the **chemical formula** of an ionic compound is the **empirical formula** because it gives the ***cation-to-anion ratio***.



## ➤ 2. ***Nonmetal with nonmetal***: electron sharing and **covalent bonding**.

- ✓ When two atoms differ little, or not at all, in their tendencies to lose or gain electrons, we observe electron sharing and covalent bonding, which occurs most commonly between nonmetal atoms.
- ✓ Each atom holds onto its own electrons tightly (*high IE*) and attracts other electrons (highly negative EA).
- ✓ The nucleus of each atom attracts the valence electrons of the other, which draws the atoms together.
- ✓ The shared electron pair is typically localized between the two atoms, linking them in a covalent bond of a particular length and strength. In most cases, separate molecules result when atoms bond covalently. Note that the chemical formula of a covalent compound is the molecular formula because it gives the actual numbers of atoms in each molecule.



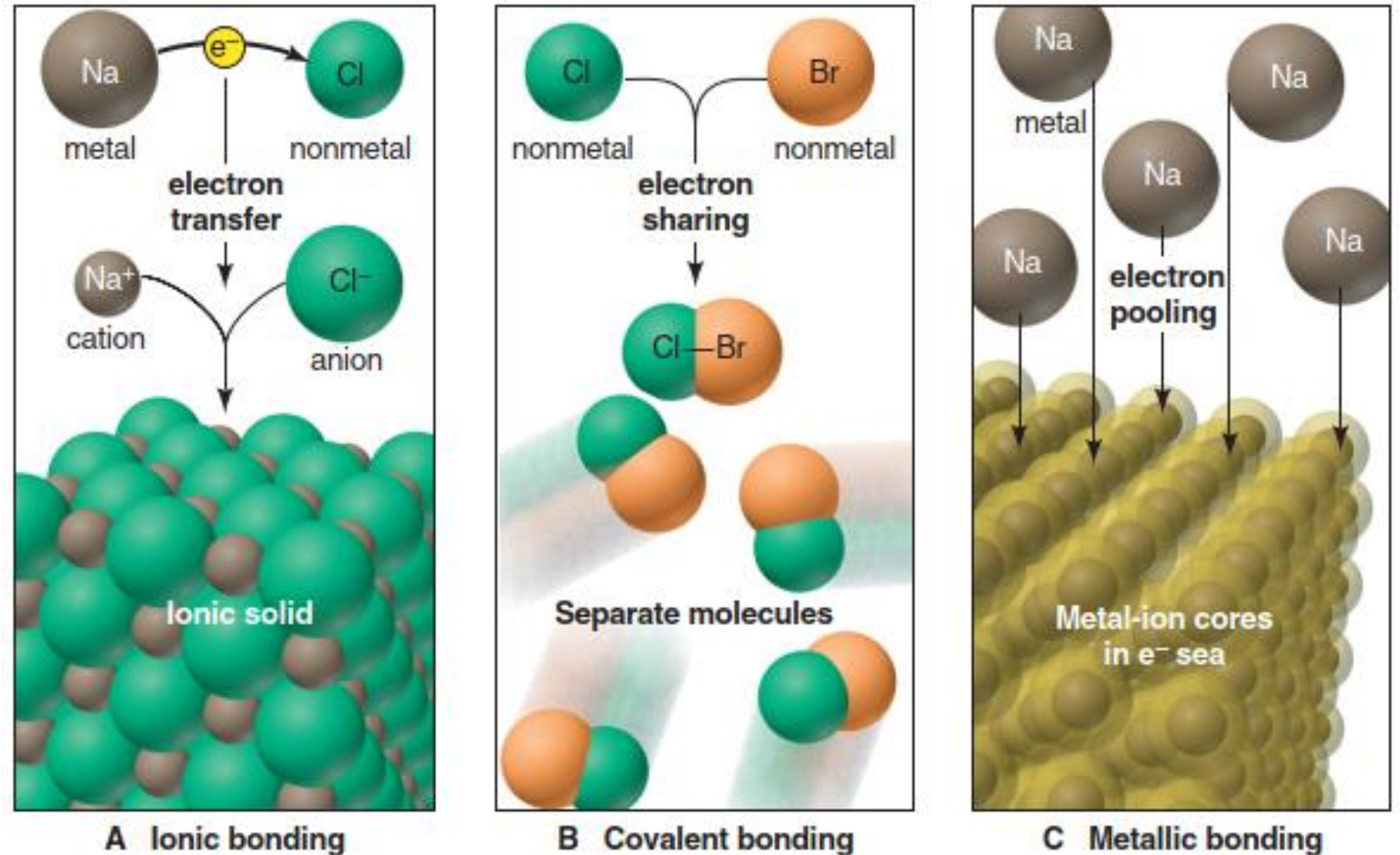
### ➤ 3. ***Metal with metal***: electron pooling and **metallic bonding**.

- ✓ Metal atoms are relatively large, and their few outer electrons are well shielded by filled inner levels (core electrons). Thus, they lose outer electrons easily (**low IE**) and do not gain them readily (slightly negative or positive EA). **These properties lead metal atoms to share their valence electrons**, but *not by covalent bonding*.
- ✓ In the simplest model of metallic bonding, the enormous number of atoms in a sample of a metal pool their valence electrons into a “sea” of electrons that “flows” between and around each metal-ion core (nucleus plus inner electrons), thereby attracting them and holding them together.
- ✓ Unlike the localized electrons in covalent bonding, ***electrons in metallic bonding are delocalized***, moving freely throughout the entire piece of metal.

# ➤ **ATOMIC PROPERTIES AND CHEMICAL BONDS**

➤ **Types of Bonding:** In Three ways **Metals** and **Nonmetals** combine

**Figure 9.2** Three models of chemical bonding.



❑ What determines the type of bonding in each substance?

- ❑ In the world of real substances, ***there are exceptions to these idealized models***, so you can't always predict bond type from positions of the elements in the periodic table.
- ✓ As just one example, when the metal ***beryllium*** [Group 2A(2)] *combines with the nonmetal* ***chlorine*** [Group 7A(17)], the *bonding fits the* ***covalent model*** better than the ionic model.
- Thus, just as we see ***gradations in atomic behavior within a group or period***, we see ***a gradation in bonding*** from one type to another.

## ❖ IONIC BONDS

- The first explanation of chemical bonding was suggested by the properties of salts, substances now known to be ionic.
- Salts are generally crystalline solids that melt at high temperatures. Sodium chloride, for example, melts at 801°C.
- A molten salt (the liquid after melting) conducts an electric current.
- A salt dissolved in water gives a solution that also conducts an electric current.
- The electrical conductivity of the molten salt and the salt solution results from the motion of ions in the liquids.
- This suggests the possibility that ions exist in certain solids, held together by the attraction of opposite charges.

## ❑ Describing Ionic Bonds

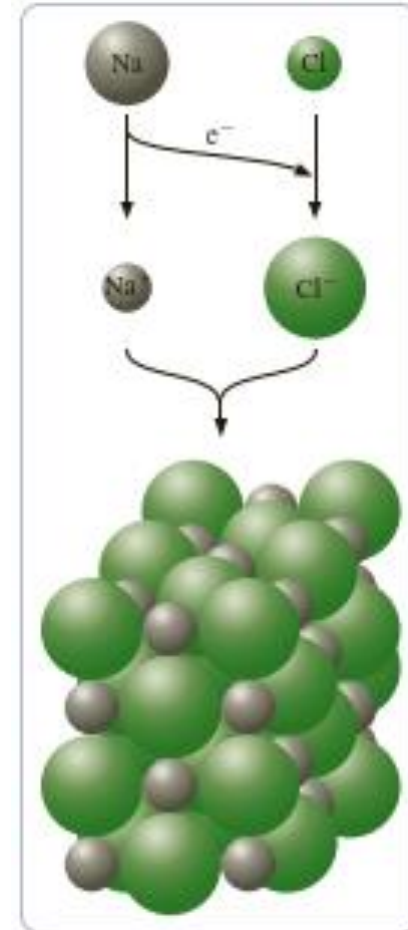
- ***An ionic bond is a chemical bond formed by the electrostatic attraction between positive and negative ions.***
- **To understand why ionic bonding occurs**, consider the transfer of a valence electron from a sodium atom (electron configuration  $[\text{Ne}]3s^1$ ) to the valence shell of a chlorine atom ( $[\text{Ne}]3s^23p^5$ ). You can represent the electron transfer by the following equation:



- According to the Lewis electron-dot symbol (in which the electrons in the valence shell of an atom or ion are represented by dots placed around the letter symbol of the element):



- **As a result of the electron transfer, ions are formed, each of which has a noble-gas configuration ( $ns^2np^6$ ).** The sodium atom has lost its 3s electron and has taken on the neon configuration,  $[\text{Ne}]$ .

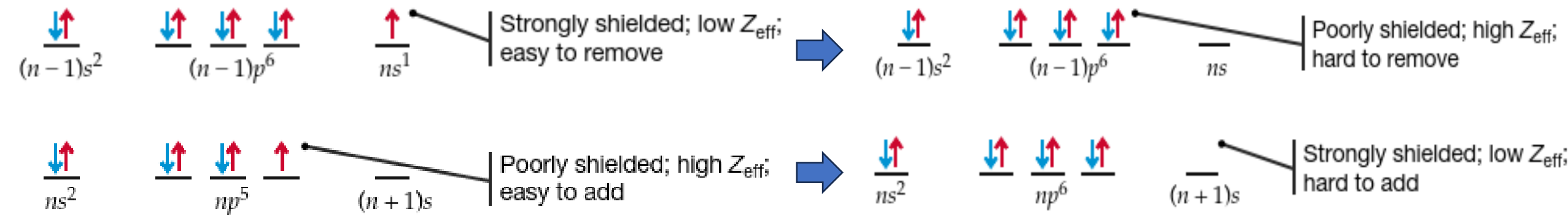


- The chlorine atom has accepted the electron into its 3p subshell and has taken on the argon configuration,  $[\text{Ne}]3s^23p^6$ .
- ***Such noble-gas configurations and the corresponding ions are particularly stable.*** This stability of the ions ***accounts in part*** for the formation of the ionic solid NaCl.
- Once a cation or anion forms, it attracts ions of opposite charge. Within the sodium chloride crystal, NaCl, every  $\text{Na}^+$  ion is surrounded by six  $\text{Cl}^-$  ions, and every  $\text{Cl}^-$  ion by six  $\text{Na}^+$  ions.

# ❑ THE OCTET RULE FOR MAIN-GROUP ATOMS

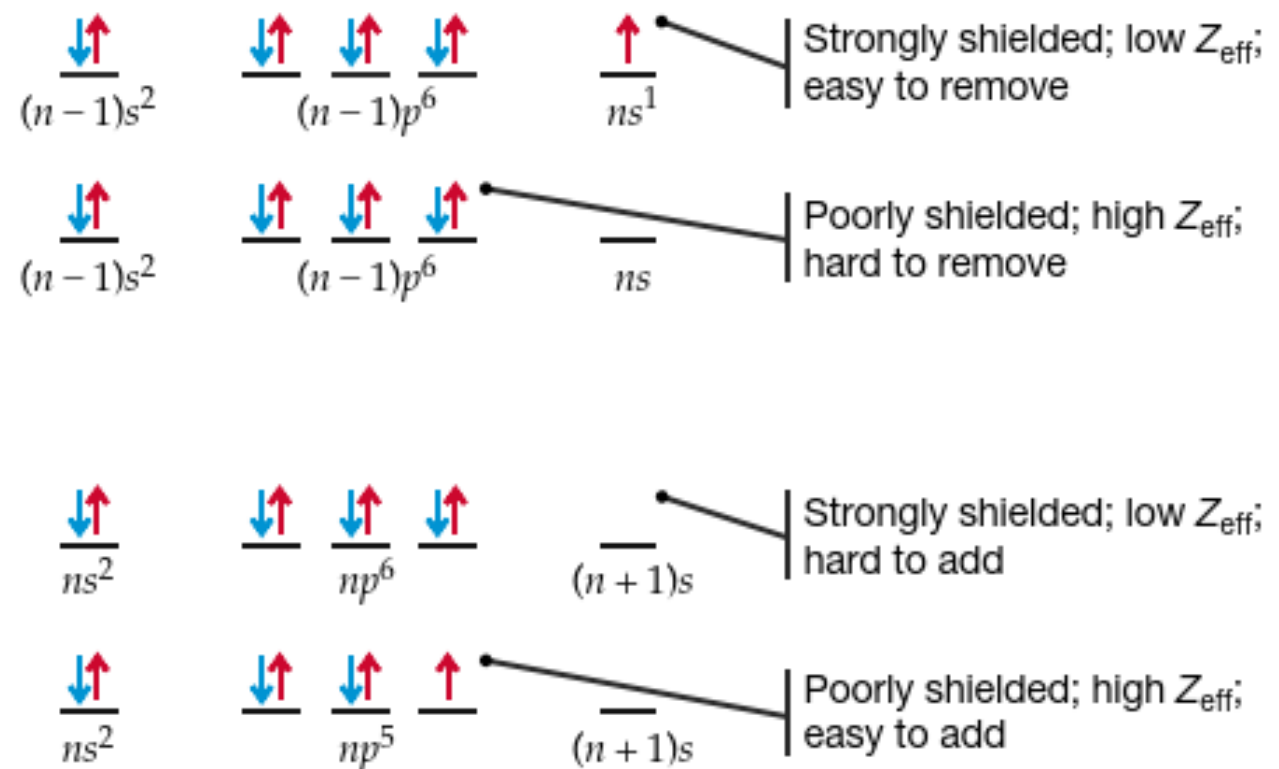
## ❖ What factors determine how many electrons an atom is likely to gain or lose?

- Electrons are most likely to be lost if they are held loosely in the first place—that is, if they feel a relatively low effective nuclear charge,  $Z_{\text{eff}}$ , and have relatively low ionization energies.
- **Valence-shell electrons in the group 1A, 2A, and 3A metals**, for instance, are shielded from the nucleus by core electrons, feel a low  $Z_{\text{eff}}$ , and are therefore lost relatively easily. Once the next lower noble-gas configuration is reached, though, loss of an additional electron suddenly becomes much more difficult because it must come from an inner shell, where it feels a much higher  $Z_{\text{eff}}$ .

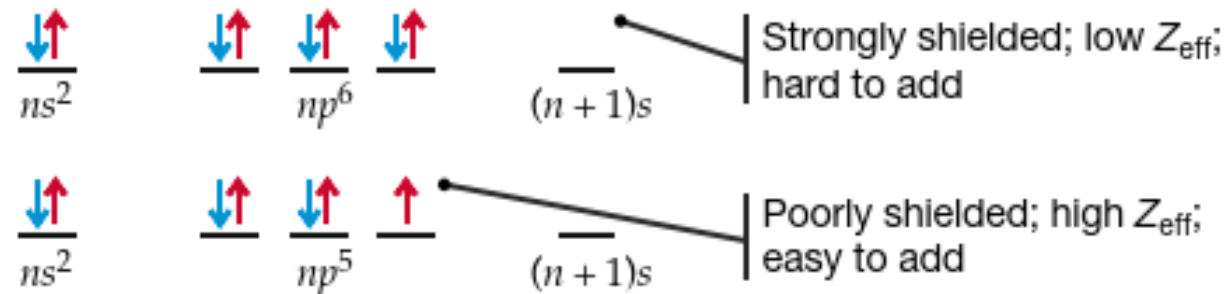
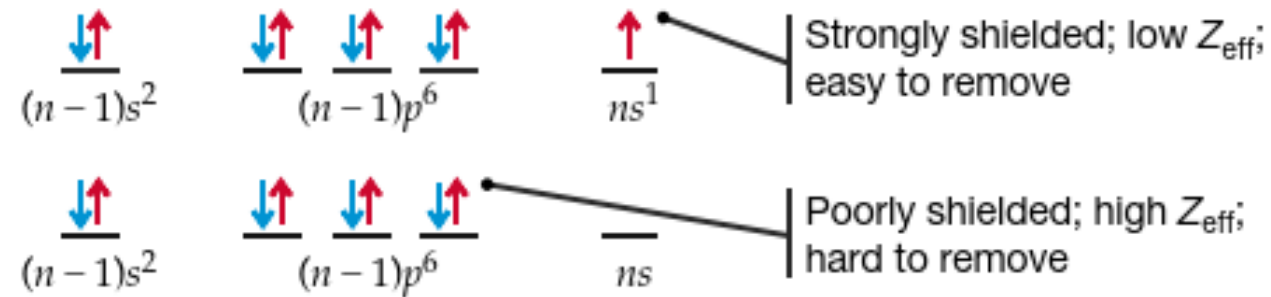




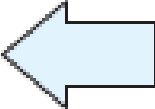
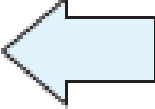
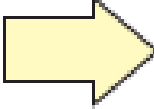
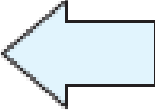
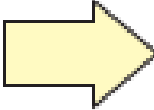
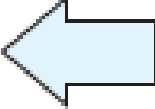
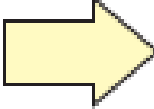
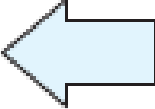
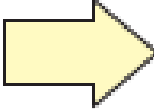
- Conversely, **electrons are most likely to be gained if they can be held tightly by a high  $Z_{\text{eff}}$** . **Valence-shell electrons in the group 6A and 7A elements**, for example, are poorly shielded, feel high values of  $Z_{\text{eff}}$ , and aren't lost easily.
- The **high  $Z_{\text{eff}}$**  thus makes possible the gain of one or more additional electrons into vacant valence-shell orbitals.
- Once the noble-gas configuration is reached, though, lower-energy orbitals are **no longer** available. Any additional electron would have to be placed in a higher-energy orbital, where it would feel only a low  $Z_{\text{eff}}$ .



- ✓ Taking electrons from a filled octet is difficult because they are tightly held by a high  $Z_{\text{eff}}$ ;
- ✓ adding more electrons to a filled octet is difficult because, with  $s$  and  $p$  subshells full, no low-energy orbital is available.
- **Eight** is therefore the **optimum number** for **valence-shell electrons**.



**TABLE 6.2** Examples of Monatomic Ions and Their Nearest Noble Gases

Noble Gases		Metals Lose Valence Electrons				Nonmetals Gain Valence Electrons				Noble Gases
		1A (1)	2A (2)	3A (13)		5A (15)	6A (16)	7A (17)		
He		Li <sup>+</sup>								
Ne		Na <sup>+</sup>	Mg <sup>2+</sup>	Al <sup>3+</sup>		N <sup>3-</sup>	O <sup>2-</sup>	F <sup>-</sup>		Ne
Ar		K <sup>+</sup>	Ca <sup>2+</sup>			P <sup>3-</sup>	S <sup>2-</sup>	Cl <sup>-</sup>		Ar
Kr		Rb <sup>+</sup>	Sr <sup>2+</sup>					Br <sup>-</sup>		Kr
Xe		Cs <sup>+</sup>	Ba <sup>2+</sup>					I <sup>-</sup>		Xe

## ❖ Octet Rule

- ✓ Main-group elements tend to undergo reactions that leave them with eight outer-shell electrons.
- ✓ That is, main-group elements react so that they attain a noble-gas electron configuration with filled  $s$  and  $p$  subshells in their valence electron shell.
- In the formation of either an ionic bond or a covalent bond, atoms of *main-group elements* lose, gain, or share valence electrons to acquire an octet of eight valence electrons. This tendency of atoms to attain a stable electron arrangement is known as the **octet rule**.
- According to the ***octet rule of Lewis and Kossel***, ***atoms tend to interact through electronic rearrangements that produce a noble gas electronic configuration for each atom involved in the interaction.***

- ✓ We have seen why the octet rule works or how the octet rule arises.
- The rule provides a key to our qualitative understanding of the ways in which atoms bond and form compounds.
- As we'll see later, ***there are exceptions to the octet rule.***
- ✓ *A few elements achieve the **stability of helium with two valence electrons.***
- ✓ Similarly, *we do **not** use the octet rule with **transition elements**, elements in the third and lower rows of the periodic table.*
- Nevertheless, the rule is extremely useful for making predictions and for providing insights about chemical bonding.

## ❑ Energetics of Ionic Bond Formation

- Why do certain atoms bond ionically and others not?
- We have seen in a ***qualitative way*** how/why a sodium atom and a chlorine atom might be expected to form an ionic bond.
- It is instructive, however, to **look at the energy changes involved in ionic bond formation**.
- From this analysis, we can gain further understanding of the ionic bonding.
- *If atoms come to bond together, there should be a net decrease in energy, because the bonded state should be more stable and therefore at a lower energy level.*

➤ Consider again the formation of an ionic bond between a sodium atom and a chlorine atom. One can think of this as occurring in two steps:

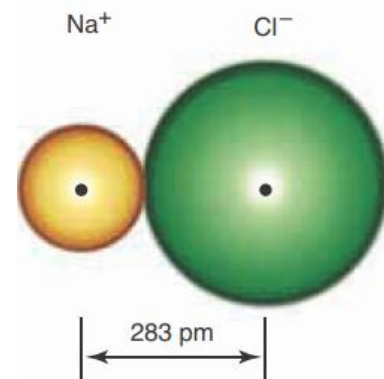
- (1) An electron is transferred between the two separate atoms to give ions.
- ✓ The *first step requires removal of the 3s electron* from the sodium atom (it **requires energy**, the first **ionization energy** of the sodium atom (g), **+496 kJ/mol**) and *the addition of this electron to the valence shell of the chlorine atom (releases energy, -349 kJ/mol, which is the **electron affinity** of the chlorine atom (g)).*
- (2) The ions then attract one another to form an ionic bond.

$E_i$ for Na	= +495.8 kJ/mol	(Unfavorable)
$E_{ea}$ for Cl	= -348.6 kJ/mol	(Favorable)
$\Delta E$	= +147.2 kJ/mol	(Unfavorable)



- So, *the process requires more energy to remove an electron from the sodium atom than is gained when the electron is added to the chlorine atom.*
- The **overall process** would be an **endothermic** process that requires  $496 - 349 = 147$  kJ/mol (Figure 2.4).
- *In other words, a gas of widely separated  $\text{Na}^+$  and  $\text{Cl}^-$  ions has a higher energy than a gas of neutral Na and Cl atoms.*
- *The formation of ions from the atoms is **NOT** in itself energetically favorable.....!!!!*
- ***How does salt NaCl form then?***
- This endothermic process corresponds to *the formation of sodium and chloride ions that are infinitely far apart*—in other words, *the positive energy change assumes that the ions do not interact with each other, which is quite different from the situation in ionic solids.*

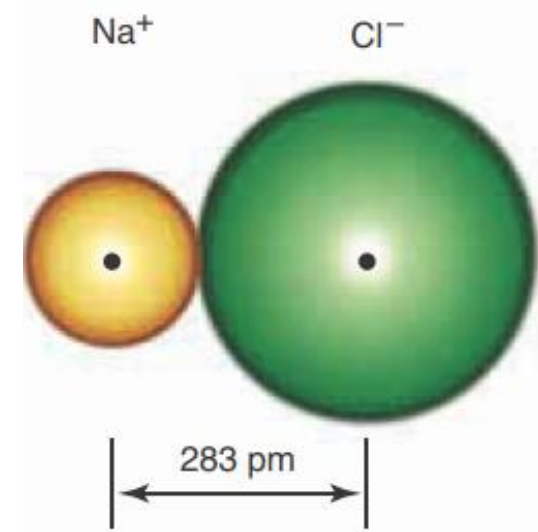
- *When positive and negative ions bond together, however, more than enough energy is released to make the overall process favorable.*
- What **principally determines** the energy released when ions bond is **the attraction of oppositely charged ions**. To see this, let's look first at **the energy obtained when a  $\text{Na}^+$  ion and a  $\text{Cl}^-$  ion come together** to form **an ion-pair molecule**. We can calculate the energy obtained when the ions come together, by using Coulomb's law.
- Let us assume that the *ions are spheres*, just touching, with the distance between the nuclei of the ions equal to this distance in the NaCl crystal.
- ✓ From experiment, this distance is known to be 283 pm, or  $2.83 \times 10^{-10}$  m.



- ✓ **Coulomb's law** states that the potential energy obtained in bringing two charges  $Q_1$  and  $Q_2$ , initially far apart, up to a distance  $r$  apart is directly proportional to the product of the charges and inversely proportional to the distance between them:

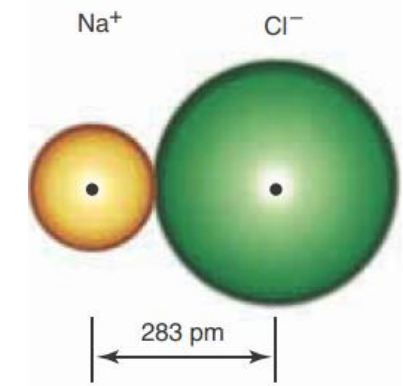
$$E = \frac{kQ_1Q_2}{r}$$

$$E = \frac{k(+z_1e)(-z_2e)}{r}$$



- ✓ Here  $k$  is a physical constant, equal to  $8.99 \times 10^9 \text{ J.m/C}^2$  (C is the symbol for coulomb).
- ✓  $Z_i$  is the charge number of the  $i$ -th ion. The charge on Na<sup>+</sup> is  $+e$  and that on Cl<sup>-</sup> is  $-e$ , where  $e$  equals  $1.602 \times 10^{-19} \text{ C}$ .

**Figure 6.9** A solid-sphere representation of the ion pair  $\text{Na}^+\text{Cl}^-(\text{g})$ . The sodium ion can be represented as a hard sphere of radius 102 pm and the chloride ion can be represented as a hard sphere of radius 181 pm. Because the two ions have opposite charges, they draw together until they touch, with a distance between their centers of  $102 \text{ pm} + 181 \text{ pm} = 283 \text{ pm}$ . They are bound together at this distance in an ionic bond. We call this value the equilibrium ion-pair separation distance.



✓ Thus, our estimate of the energy of attraction of  $\text{Na}^+$  and  $\text{Cl}^-$  ions to form *an ion pair* is

$$E = \frac{-(8.99 \times 10^9 \text{ J} \cdot \text{m}/\text{C}^2) \times (1.602 \times 10^{-19} \text{ C})^2}{2.82 \times 10^{-10} \text{ m}} = -8.18 \times 10^{-19} \text{ J}$$

✓ *The minus sign means energy is released.* This energy is for the *formation of one ion pair*.

✓ To express this for **one mole** of  $\text{Na}^+\text{Cl}^-$  **ion pairs**, we multiply by Avogadro's number,  $6.02 \times 10^{23}$ . We obtain **-493 kJ/mol for the energy** when one mole of  $\text{Na}^+$  and one mole of  $\text{Cl}^-$  come together to form  $\text{Na}^+\text{Cl}^-$  ion pairs.

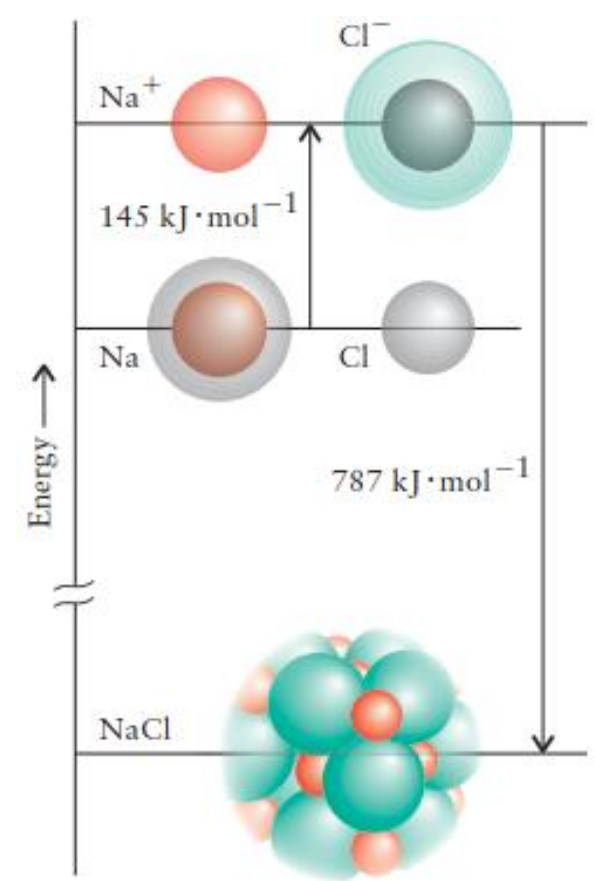
✓ *What we see...??*

- *What we see is that:*
  - ✓ *the formation of ion pairs from sodium and chlorine atoms is energetically favorable and*
  - ✓ *the energy required for the formation of ionic bonds is supplied largely by the attraction between oppositely charged ions.*
- *But it (-493 kJ/mol) does not account for the -642 kJ/mol decrease of energy!*

- Now consider what happens when gaseous  $\text{Na}^+$  and  $\text{Cl}^-$  ions come together to form a crystalline solid. The process releases a lot of energy, and **experimentally** it is found that



- Therefore, the **net change in energy** for the overall process is **(145 – 787) kJ/mol = -642 kJ/mol** (Fig. 2.4), **a huge decrease in energy**.
- We conclude that a solid composed of  $\text{Na}^+$  and  $\text{Cl}^-$  ions has a lower energy than does a collection of widely separated Na and Cl atoms.



**FIGURE 2.4...** Energy is needed to produce cations and anions from neutral atoms: the ionization energy of the metal atoms is only partly recovered from the electron affinity of the nonmetal atoms. The overall lowering of energy that drags the ionic solid into existence arises from the strong attraction between cations and anions of  $\text{NaCl}(\text{s})$ .

## ❑ **THE FORMATION OF IONIC SOLIDS: The Lattice Energy Contribution**

- A very important point to note is that an ionic solid is ***not held*** together by the ***sum total*** of the ***attraction*** of the specific ***pairs of oppositely charged ions***.
- It is something more than that: all the cations interact to a greater or lesser extent with all the anions, all the cations repel each other, and all the anions repel each other. ***An ionic bond is a “global” characteristic of the entire crystal.***
- ***The maximum attraction of ions of opposite charge with the minimum repulsion of ions of the same charge is obtained with the formation of the crystalline solid.***
- This gives **additional stability** and additional energy is released. This is the negative of the ***lattice energy*** of NaCl.
- The ***additional energy (in going from ion pairs to the crystalline solid) equals -293 kJ/mol.***



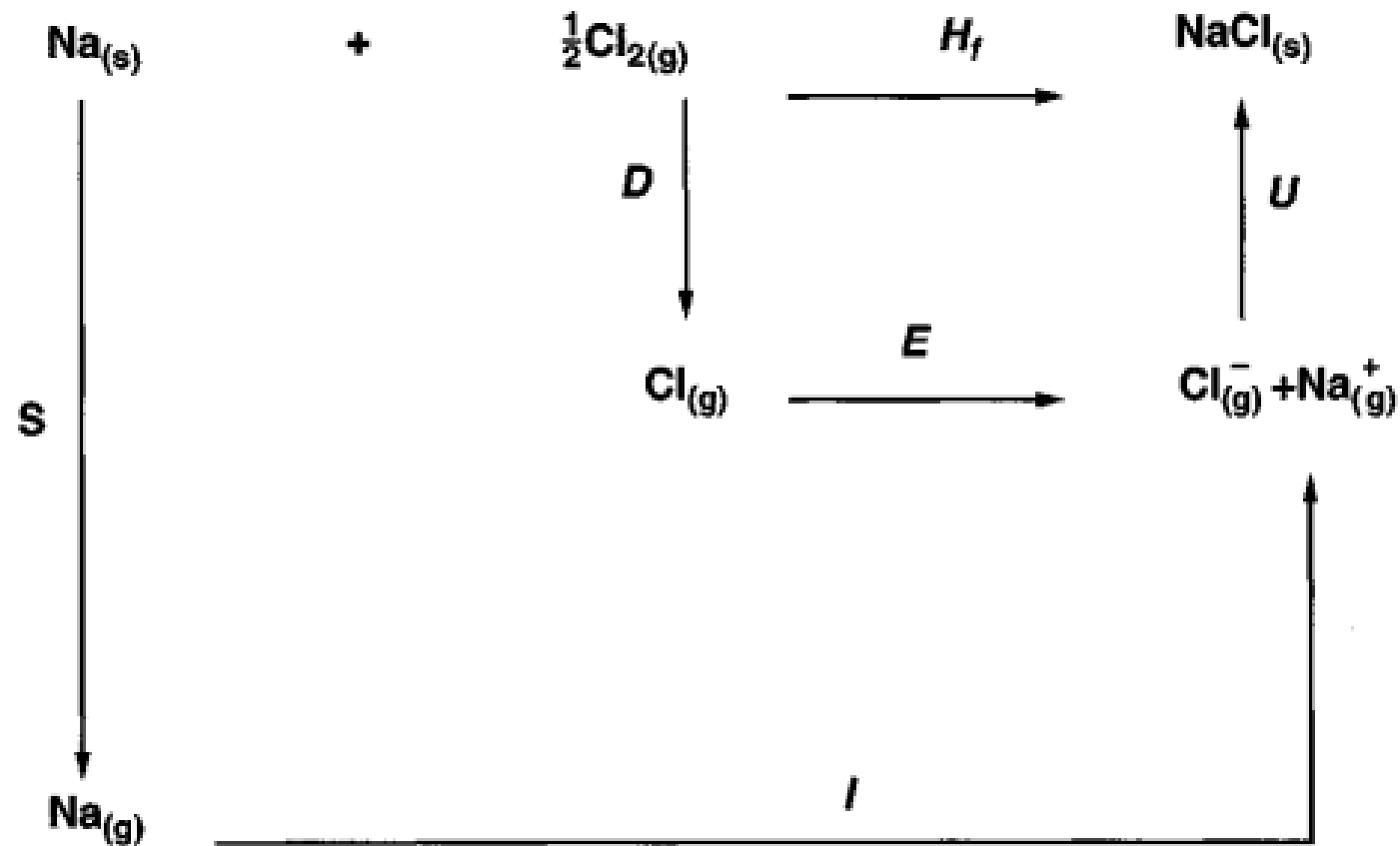
- ***The lattice energy is the change in energy that occurs when an ionic solid is separated into isolated ions in the gas phase.*** For sodium chloride, the process is



- The distances between ions in the crystal are continuously enlarged until the ions are very far apart.
- ***One can obtain an experimental value*** for this process from thermodynamic data (see the ***Born–Haber cycle*** on the next page).
- The **lattice energy** for NaCl is **786 kJ/mol** so that for ***the reverse process***, when the ***ions come together to bond, the energy is –786 kJ/mol***.
- Consequently, the net energy obtained when gaseous Na and Cl atoms form solid NaCl is  $(-786 + 147) \text{ kJ/mol} = -639 \text{ kJ/mol}$ .
- The negative sign shows that there has been a net decrease in energy, which you expect when stable bonding has occurred.

## ❑ Calculation of Lattice Energies: The Born–Haber Cycle

- *Lattice energies **cannot be determined directly** by experiment.*
- However, this quantity can be indirectly determined from experiment by means of a thermochemical “cycle” originated by Max Born and Fritz Haber in 1919 and now called the **Born–Haber cycle**.
- The calculation involves envisioning the formation of an ionic compound as occurring in a series of well-defined steps.



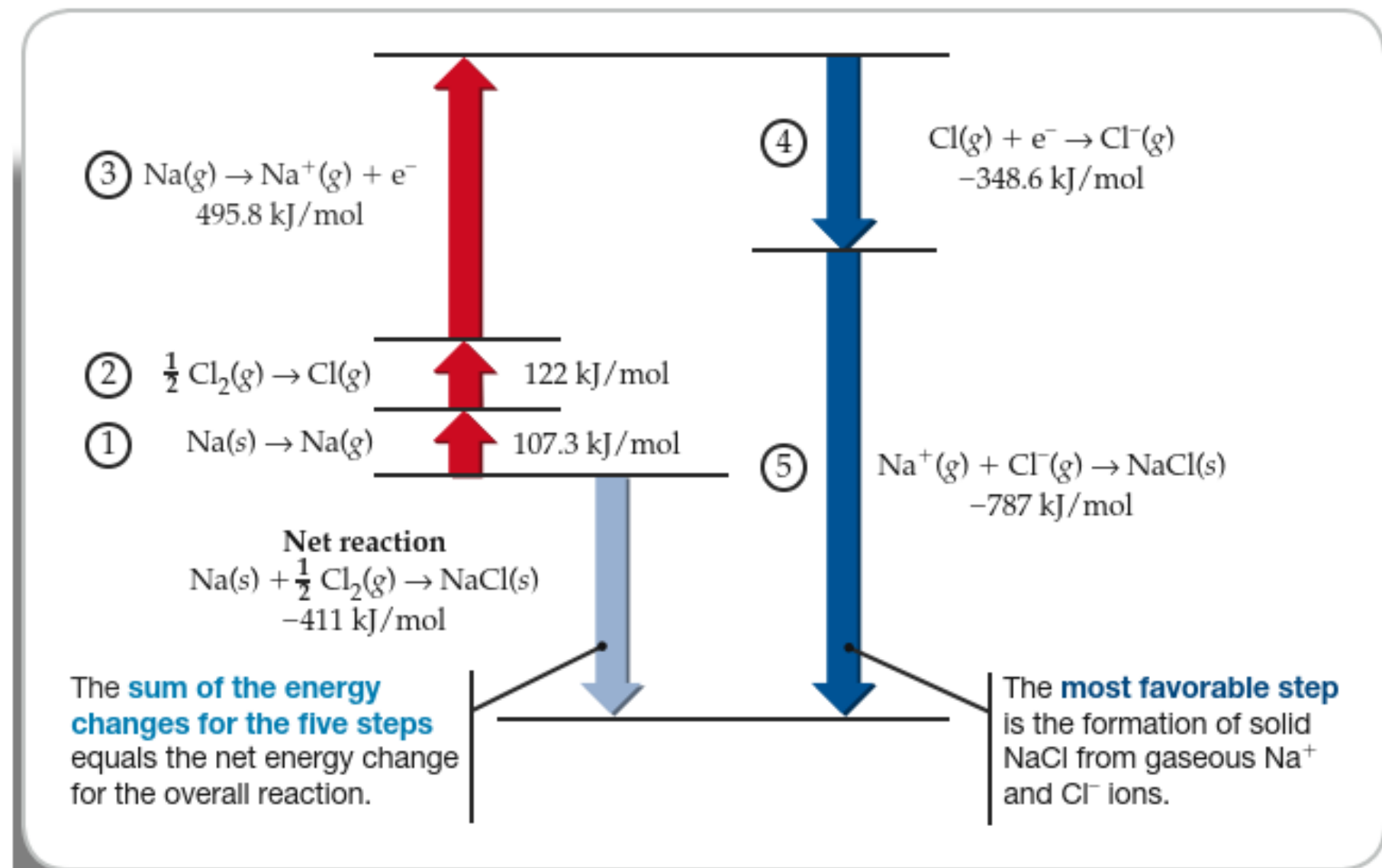
	<i>energy changes</i>	$\text{kJ mol}^{-1}$
$\text{Na}_{(\text{metal})} \rightarrow \text{Na}_{(\text{gas})}$	heat of sublimation	$S + 109.0$
$\text{Na}_{(\text{gas})} \rightarrow \text{Na}_{(\text{gas})}^+ + e^-$	ionization potential	$I + 495.9$
$\frac{1}{2}\text{Cl}_{2(\text{gas})} \rightarrow \text{Cl}_{(\text{gas})}$	$\frac{1}{2} \times$ heat of dissociation	$D + 120.9$
$e^- + \text{Cl}_{(\text{gas})} \rightarrow \text{Cl}_{(\text{gas})}^-$	electron affinity	$E - 349.2$
$\text{Na}_{(\text{gas})}^+ + \text{Cl}_{(\text{gas})}^- \rightarrow \text{Na}^+ + \text{Cl}_{(\text{solid})}^-$	lattice energy	$U - 764.4$

FIG. 5. 5 Born-Haber cycle for the formation of sodium chloride

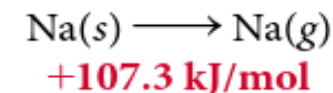
## ❑ Calculation of Lattice Energies: The Born–Haber Cycle

- The thermochemical cycle is named after the German scientists Max Born (1882–1970) and Fritz Haber (1868–1934), who introduced it to analyze the factors contributing to the stability of ionic compounds.

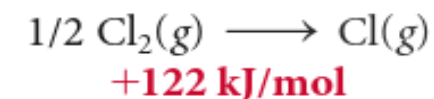
**FIGURE 3.12.** A Born–Haber cycle for the formation of  $\text{NaCl}(s)$  from  $\text{Na}(s)$  and  $\text{Cl}_2(g)$ .



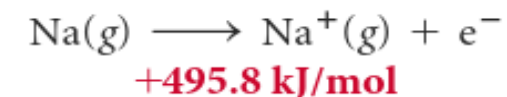
**Step 1.** Solid Na metal is converted into isolated, gaseous Na atoms, a process called sublimation. Because energy must be added to disrupt the forces holding atoms together in a solid, the heat of sublimation has a positive value: +107.3 kJ/mol for Na.



**Step 2.** Gaseous Cl<sub>2</sub> molecules are split into individual Cl atoms. Energy must be added to break molecules apart, and the energy required for bond breaking therefore has a positive value: +243 kJ/mol for Cl<sub>2</sub> (or 122 kJ/mol for 1/2 Cl<sub>2</sub>).



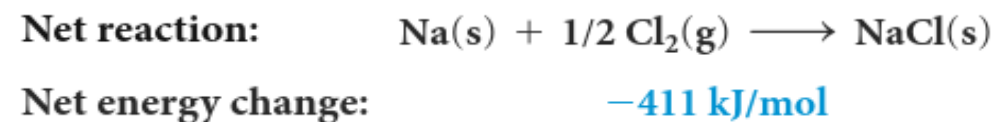
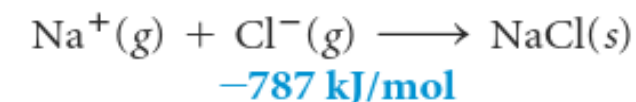
**Step 3.** Gaseous Na atoms from Step 1 are ionized into Na<sup>+</sup> plus electrons. The energy required is the first ionization energy of sodium (E<sub>i1</sub>) and has a positive value: +495.8 kJ/mol.



**Step 4.** Cl<sup>-</sup> ions are formed from Cl atoms by addition of an electron. The energy released is the electron affinity of chlorine (E<sub>ea</sub>) and has a negative value: -348.6 kJ/mol.

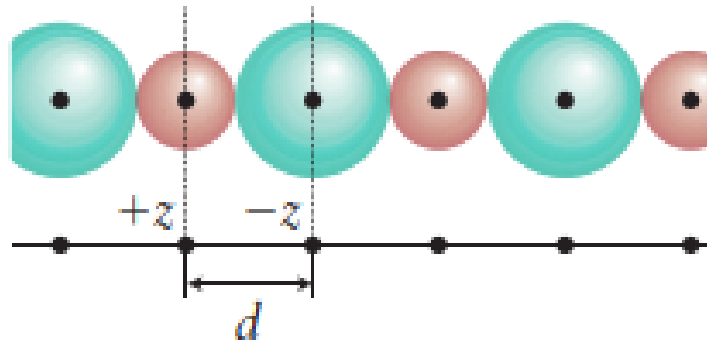


**Step 5.** Lastly, solid NaCl is formed from Na<sup>+</sup> and Cl<sup>-</sup> ions. The energy change is a measure of the overall electrostatic interactions between ions in the solid. It is the amount of energy released when isolated ions condense to form a solid, and it has a negative value: -787 kJ/mol for NaCl.



## ❑ *Calculation of lattice energy*

- *Using Coulomb's law for all these interactions, it is possible to calculate the energy of the entire crystal*, and such calculations have been done by chemists for many different types of crystals.
- *The resultant energy is called the lattice energy of the crystal.*
- In calculating *lattice energies*, we picture a crystal as made up of small **hard** (impenetrable) **spherical particles** situated at lattice positions, as depicted in Figure .....



- *In actuality*, the particles are not completely impenetrable and wiggle, or vibrate, a little bit about their equilibrium positions, but our hard-sphere model is perfectly adequate for such calculations.

- Our starting point for understanding the interaction between ions in a solid is the expression for the Coulomb potential energy of the interaction of two individual ions:

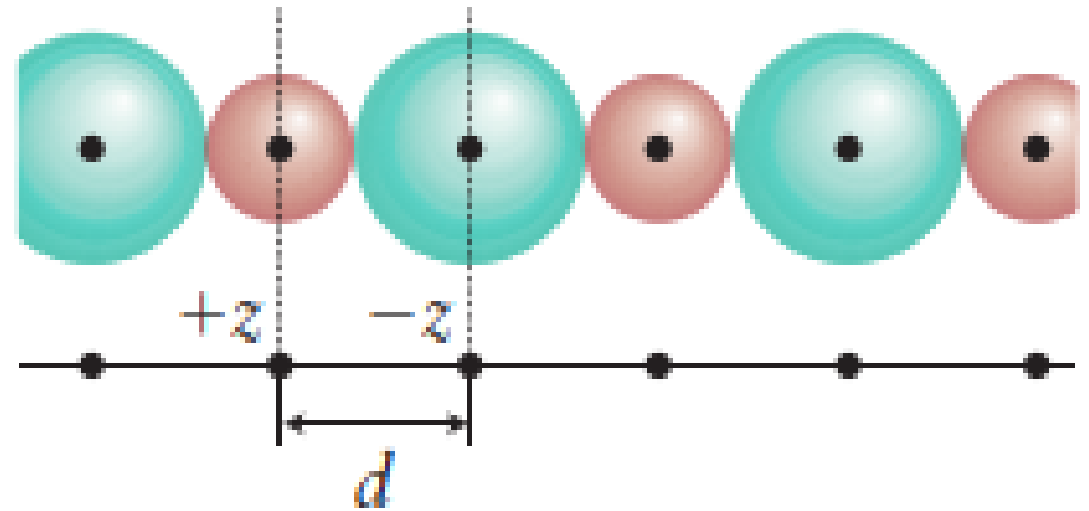
$$E_{p,12} = \frac{(z_1 e) \times (z_2 e)}{4\pi\epsilon_0 r_{12}} = \frac{z_1 z_2 e^2}{4\pi\epsilon_0 r_{12}} \quad (1)^*$$

- ✓ In this expression,  $e$  is the fundamental charge (the absolute value of the charge of an electron),  $z_1$  and  $z_2$  are the charge numbers of the two ions,  $r_{12}$  is the distance between the centers of the ions, and  $\epsilon_0$  (“epsilon zero”) is the vacuum permittivity.



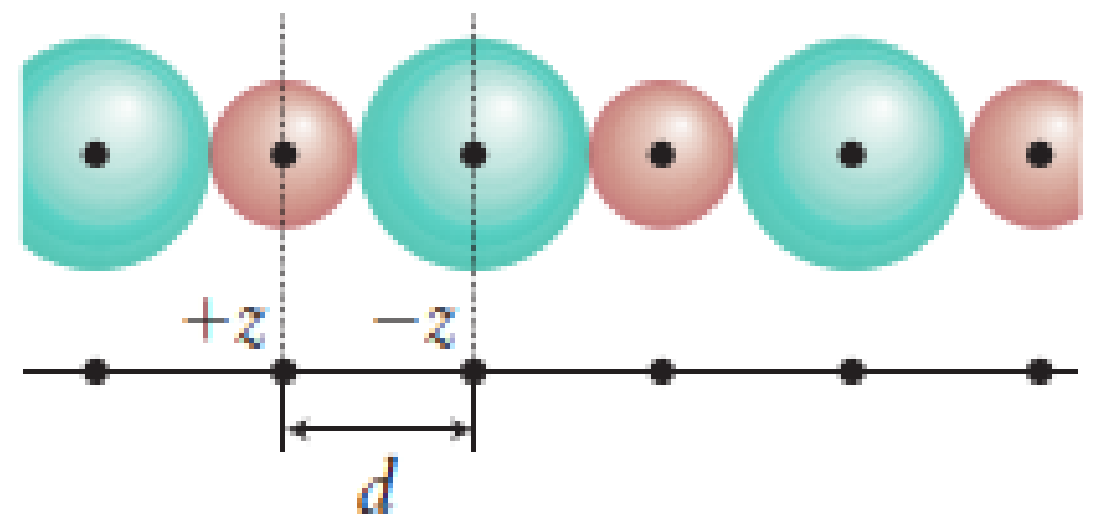
- Each ion in a solid experiences attractions from all the other oppositely charged ions and repulsions from all the other like-charged ions.
- The total potential energy is the sum of all these contributions.
- Each cation is surrounded by anions, and there is a large negative (energy-lowering) contribution from the attraction of the opposite charges.
- Beyond those nearest neighbors, there are cations that contribute a positive (repulsive, energy-raising) term to the total potential energy of the central cation.

**FIGURE 2.6** The arrangement used to calculate the potential energy of an ion in a line of alternating cations (red spheres) and anions (green spheres). We concentrate on one ion, the “central” ion denoted by the vertical dotted line.



- There is also a negative contribution from the anions beyond those cations, a positive contribution from the cations beyond them, and so on, to the edge of the solid.
- These repulsions and attractions become progressively weaker as the distance from the central ion increases, but because the nearest neighbors of an ion give rise to a strong attraction, the net outcome of all these contributions is a lowering of energy.
- Our task is to assess how far the energy is lowered by using the Coulomb potential energy expression in Eq. 1.
- To calculate the electrostatic potential energy of an ionic solid we start with a simple model: a single line of uniformly spaced alternating cations and anions, with  $d$  the distance between their centers, the sum of the ionic radii (Fig. 2.6).

**FIGURE 2.6** The arrangement used to calculate the potential energy of an ion in a line of alternating cations (red spheres) and anions (green spheres). We concentrate on one ion, the “central” ion denoted by the vertical dotted line.



- If the charge numbers of the ions have the same absolute value (+1 and -1, or +2 and -2, for instance), then  $z_1 = +z$ ,  $z_2 = -z$ , and  $z_1 z_2 = -z^2$ .
- The potential energy of the central ion is calculated by summing all the Coulomb potential energy terms, *with negative terms representing attractions to oppositely charged ions and positive terms representing repulsions from like-charged ions*.
- with  $d = r_{\text{cation}} + r_{\text{anion}}$  the distance between the centers of neighboring ions.

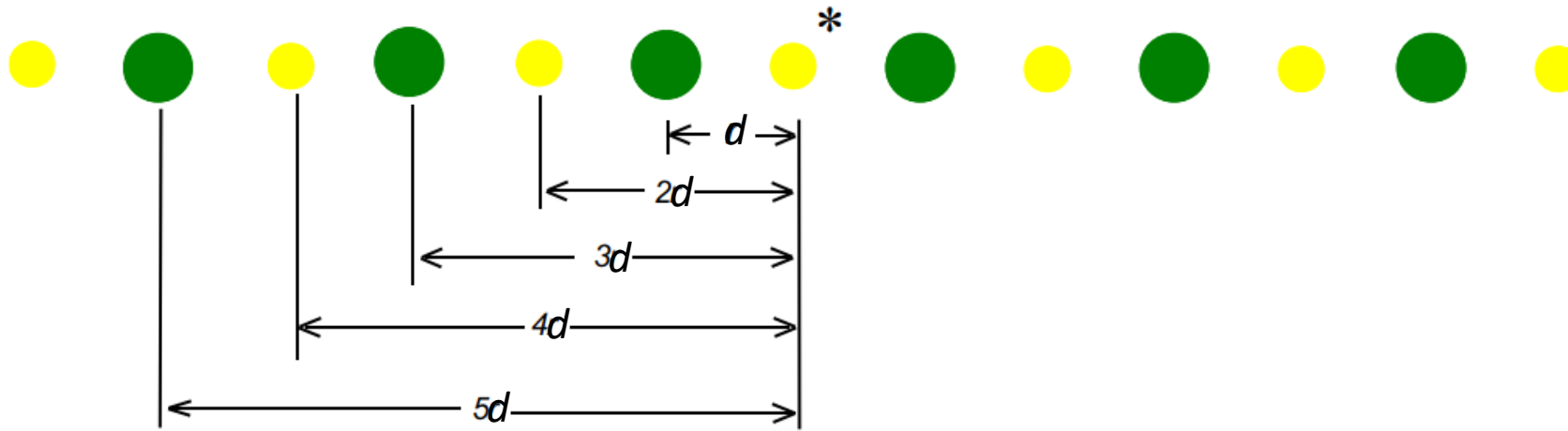


FIGURE 7.2 A “lattice” composed of a chain of alternating positive and negative ions.

- For the ***interaction arising from ions extending in a line to the right of the central ion***, the total potential energy of the central ion is

$$\begin{aligned} E_p &= \frac{1}{4\pi\epsilon_0} \times \left( -\frac{z^2 e^2}{d} + \frac{z^2 e^2}{2d} - \frac{z^2 e^2}{3d} + \frac{z^2 e^2}{4d} - \dots \right) \\ &= \frac{z^2 e^2}{4\pi\epsilon_0 d} \times \overbrace{\left( -1 + \frac{1}{2} - \frac{1}{3} + \frac{1}{4} - \dots \right)}^{-\ln 2} \\ &= -\frac{z^2 e^2}{4\pi\epsilon_0 d} \times \ln 2 \end{aligned}$$

- Next, we **multiply  $E_p$  by 2** to obtain the total energy arising from interactions with ions **on each side** of the ion.
- We then multiply by Avogadro's constant,  $N_A$ , to obtain the potential energy per mole of ions.

- We have found that the **molar potential energy of a one-dimensional crystal** in which cations and anions alternate along a line has the form

$$E_p = -2 \ln 2 \times \frac{z^2 N_A e^2}{4\pi\epsilon_0 d}$$

- The calculation can be **extended to three-dimensional arrays** of ions with different charge numbers  $z_A$  and  $z_B$ :

$$E_p = -A \times \frac{|z_A z_B| N_A e^2}{4\pi\epsilon_0 d}$$

- The **factor  $A$**  is a **positive numerical constant** called the **Madelung constant** (named after the German physicist Erwin Madelung); **its value depends on how the ions are arranged (geometric arrangements) in the crystal**. For a **rock salt structure**,  **$A = 1.748$** .
- Table 15C.3 lists Madelung constants for other common structures.

Table 15C.3 Madelung constants

Structural type	<i>A</i>
Caesium chloride	1.763
Fluorite	2.519
Rock salt	1.748
Rutile	2.408
Sphalerite (zinc blende)	1.638
Wurtzite	1.641

## ❑ What does this equation tell us?

$$E_p = -A \times \frac{|z_A z_B| N_A e^2}{4\pi\epsilon_0 d}$$

- Because the ***potential energy is negative***, there is ***a net lowering of energy***, which means that *the attraction between opposite charges overcomes the repulsion between like charges*.
- The potential energy is ***strongly negative*** when
  - ✓ *the ions are highly charged (large values of **z**) and*
  - ✓ *the separation between them is small (small values of **d**), which is the case when the ions themselves are small.*
- In all cases, the ***energy lowering*** that occurs when an ionic solid forms ***is greatest*** for ***small, highly charged ions***.



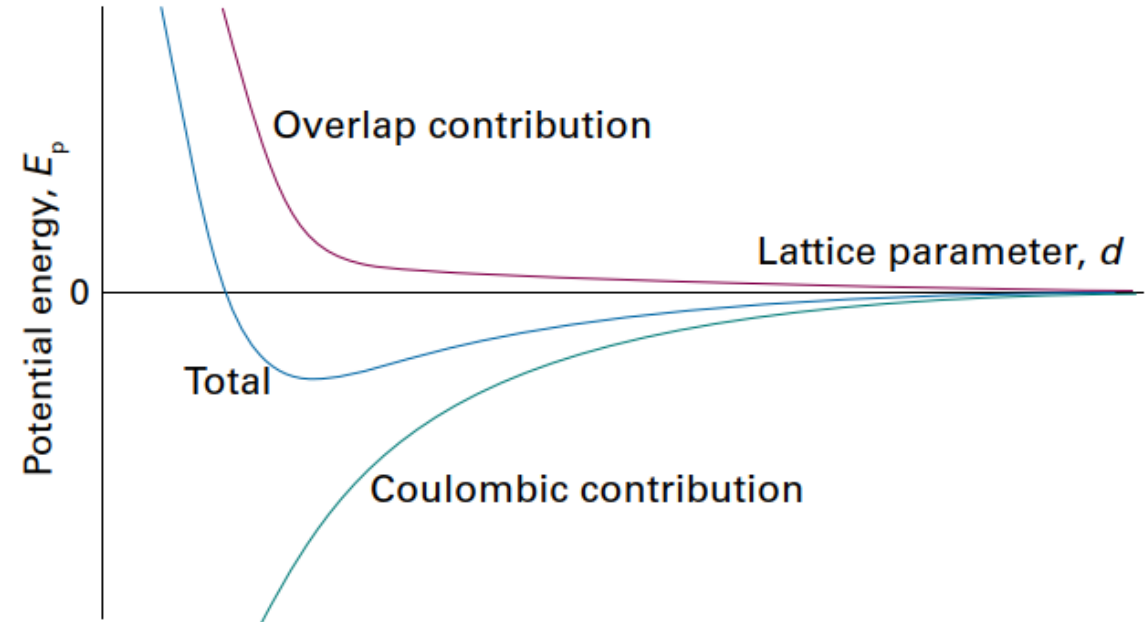
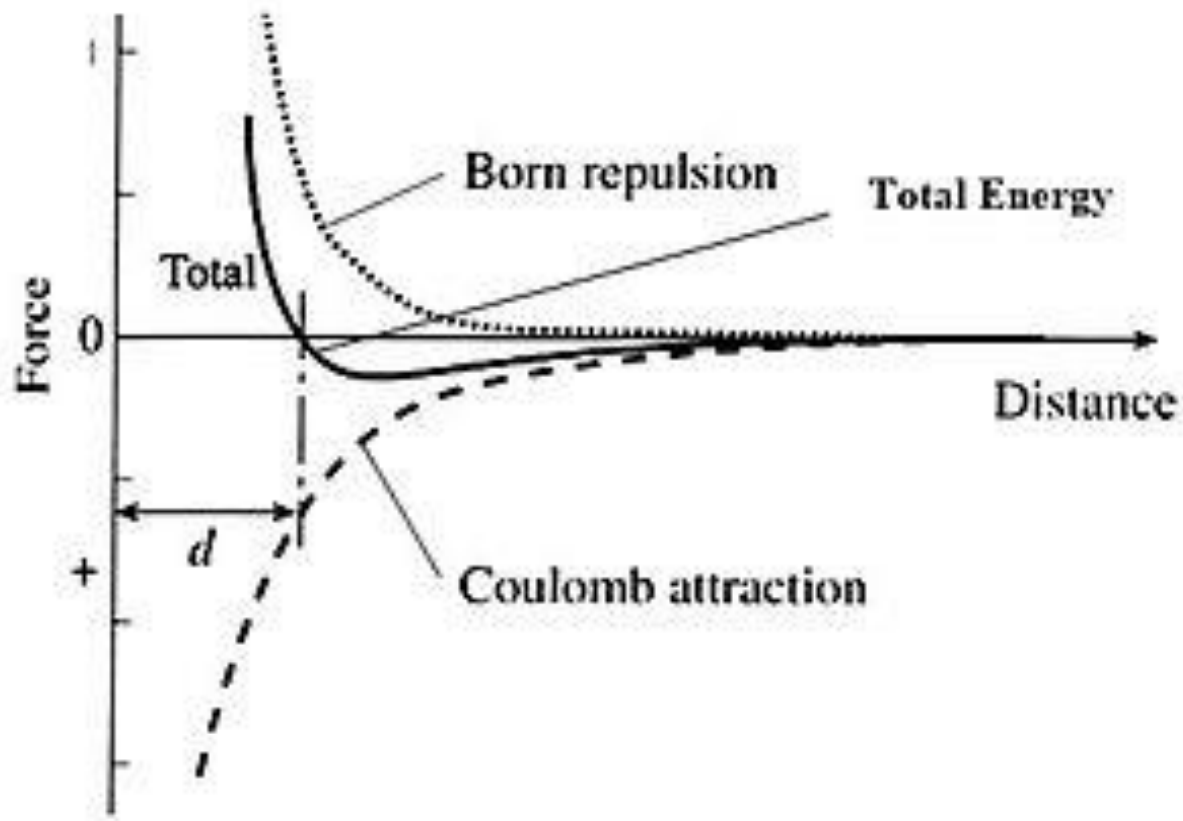
- For example, there is a strong interaction between the  $\text{Mg}^{2+}$  and the  $\text{O}^{2-}$  ions in magnesium oxide, ***MgO***, because the ions have high charges and small radii.
- ✓ This strong interaction is one reason why magnesium oxide survives at such high temperatures that it can be used for ***furnace linings***.
- ✓ It is an example of a “***refractory***” material, a substance that can withstand high temperatures.
- ✓ One of the reasons ***why all ionic compounds are solids at room temperature*** is because of the ***large amount of energy that must be supplied to break up these extended crystal lattices***.
- The *potential energy becomes more and more negative as the separation  $d$  decreases*. However, a collection of ions *does not collapse to a point* because repulsive effects between neighbors become important as soon as they come into contact, and the energy quickly rises again.

- The ***Coulomb interaction is not the only contribution*** to the lattice energy.
- When atomic orbitals overlap to form bonding and antibonding molecular orbitals and both kinds of orbitals are full, there is an increase in energy because the antibonding orbital is raised in energy more than the bonding orbital is lowered.
- This ***positive contribution to the potential energy depends on the overlap of the atomic orbitals***, and, because orbitals decay exponentially with distance, at large distances from the nucleus it is often modelled by writing

- ✓ To take the repulsion effects between close neighbors in an ionic solid into account it is commonly supposed that the repulsive contribution to the potential energy rises exponentially with decreasing separation.

$$E_{repulsion} = B \exp\left(\frac{-d}{d^*}\right)$$

- ✓ For example, in the Born approximation,  $B$  is a constant and  $d^*$  is a number with units of length, which is usually empirically determined from compressibility data.
- ✓ A typical value of  $d^*$  is 0.345 Å.
- ✓ The total energy of the ionic bond between two atoms is then calculated as the ***combination of net electrostatic and the closed-shell repulsion energies***, as shown in the figure at the right.



$$E_{repulsion} = B \exp\left(\frac{-d}{d^*}\right)$$

- This **repulsion force is short range** and is typically modeled as falling off exponentially or with a high power of the distance  $r$  between atoms.

## □ Total lattice energy of a crystal....

- Having in hand a formula for the *electrostatic repulsion energy*, we can now add it to the Coulomb contribution to obtain an equation that gives us the total lattice energy.
- At the equilibrium bond distance, the forces on all the ions are zero, and we can use this fact to eliminate the constant  $B$ :

$$\left[ \frac{dE}{dr} \right]_{r=r_0} = 0.$$

- The *energy at the minimum* is given by the **Born–Mayer** equation:

$$E_{p,\min} = -\frac{N_A |z_A z_B| e^2}{4\pi\epsilon_0 d} \left( 1 - \frac{d^*}{d} \right) A \quad \text{Born–Mayer equation}$$

- Provided zero-point contributions to the energy are ignored, the negative of this potential energy can be identified with the lattice energy.

### ❖ *What does this equation tell us?*

- As before, the ***negative sign of this potential energy tells us that the ions have a lower potential energy*** when they are present as a solid rather than widely separated as a gas.
- The ***greatest stabilization*** is expected when the ions are highly charged (so  $|z_1 z_2|$  is large) and small (so  $d$  is small, but not smaller than  $d^*$ ).
- The ***energy released by the attraction between ions of unlike charge more than makes up for the endothermic nature of ionization energies, making the formation of ionic compounds an exothermic process.***
- ***The strong attractions also cause most ionic materials to be hard and brittle with high melting points***—for example, NaCl melts at 801 °C.

- Table 6.6 lists the *calculated values of the lattice energy per formula unit for a number of ionic solids.*
- ***You can see that the agreement between the calculated and experimental values is quite good,*** which lends credence to the hard-sphere model of ionic crystals that we have used for our calculations.

**TABLE 6.6** Calculated and experimental lattice energies of some selected ionic compounds

Compound	Calculated lattice energies/ aJ·formula unit <sup>-1</sup>	Measured lattice energies/ aJ·formula unit <sup>-1</sup>
NaF	-1.51	-1.54
NaCl	-1.28	-1.31
NaBr	-1.22	-1.25
KF	-1.34	-1.38
KCl	-1.16	-1.20
KBr	-1.11	-1.15
CaF <sub>2</sub>	-4.38	-4.40
CaCl <sub>2</sub>	-3.77	-3.77
Na <sub>2</sub> O	-4.12	-4.11
K <sub>2</sub> O	-3.72	-3.71
CaO	-5.67	-5.65

- Notice from Table 6.6 that the value of the lattice energy for NaCl(s),  $-1.28$  aJ per formula unit, is about one and a half times the magnitude of the coulombic energy per NaCl(g) ion pair of  $-0.816$  aJ that we calculated from simple electrostatic ion-pair attractions.
- Similarly, from Table 6.6 we see that the value of the lattice energy for CaO(s) is  $-5.67$  aJ per formula unit, also about one and a half times the magnitude of the coulombic energy per CaO(g) ion pair of  $-3.85$  aJ.
- *These higher energies result from considering the interactions of **all** the neighboring ions, next neighboring ions, and so forth, when calculating the lattice energy of an ionic crystal.*



➤ This relationship helps us explain the effects of ionic size and charge on trends in lattice energy:

1. **Effect of ionic size.** As we move ***down a group***, ionic radii increase, so the electrostatic energy between cations and anions decreases; thus, lattice energies should decrease as well. Figure 9.7 shows that, for the alkali-metal halides, ***lattice energy decreases down*** the group whether we hold the cation constant (LiF to LiI) or the anion constant (LiF to RbF).

2. **Effect of ionic charge.** *Across a period, ionic charge changes.* For example, ***lithium fluoride and magnesium oxide*** have ***cations and anions of about equal radii*** ( $\text{Li}^+ = 76 \text{ pm}$  and  $\text{Mg}^{2+} = 72 \text{ pm}$ ;  $\text{F}^- = 133 \text{ pm}$  and  $\text{O}^{2-} = 140 \text{ pm}$ ). The ***major difference*** is between ***singly charged***  $\text{Li}^+$  and  $\text{F}^-$  ions and ***doubly charged***  $\text{Mg}^{2+}$  and  $\text{O}^{2-}$  ions. The difference in the lattice energies of the two compounds is striking:

$$\Delta H_{\text{lattice}}^\circ \text{ of LiF} = 1050 \text{ kJ/mol} \quad \text{and} \quad \Delta H_{\text{lattice}}^\circ \text{ of MgO} = 3923 \text{ kJ/mol}$$

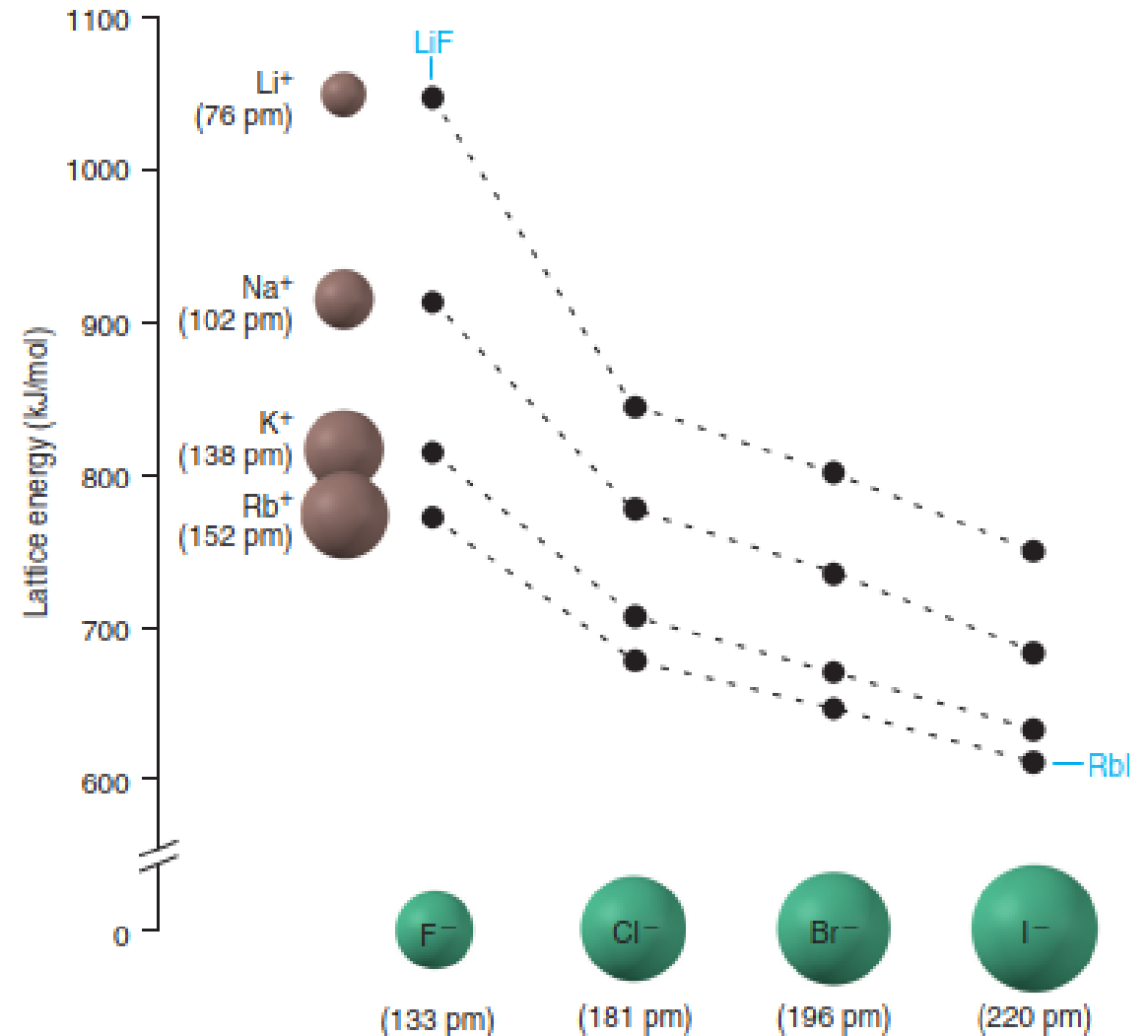
- This ***nearly four-fold increase*** in  $\Delta H_{\text{lattice}}$  reflects the four-fold increase in the product of the charges ( $1 \times 1$  vs.  $2 \times 2$ ) in the numerator in Equation.
- ✓ The ***very large lattice energy of MgO more than compensates for the energy required to form the  $\text{Mg}^{2+}$  and  $\text{O}^{2-}$  ions.***
- ✓ In fact, the lattice energy is the reason that compounds with 2+ cations and 2- anions even exist.
- The **magnitude of the lattice energy** of an ionic solid depends on ***the charges*** of the ions, their ***sizes***, and their ***arrangement in the solid***.
- The attractive interaction between two oppositely charged ions increases as the magnitudes of their charges increase and as the distance between their centers decreases.

- Lattice energies are large when the distance between ions is small and when the charges  $z_1$  and  $z_2$  are large. A small distance means that the ions are close together, which implies that they have small ionic radii.
- Thus, ***for a given arrangement of ions, the lattice energy increases as the charges on the ions increase and as their radii decrease.***
- The variation in the magnitude of lattice energies depends more on ionic charge than on ionic radius because ionic radii vary over only a limited range compared to charges.
- Thus, if  $z_1$  and  $z_2$  are held constant, the largest lattice energies belong to compounds formed from the smallest ions, as listed in the following Table.

## □ Periodic Trends in Lattice Energy

➤ The lattice energy results from electrostatic interactions among ions, so its magnitude depends on ionic size, ionic charge, and ionic arrangement in the solid. Therefore, we expect to see periodic trends in lattice energy.

**Figure 9.7** Trends in lattice energy. The lattice energies are shown for compounds formed from a given Group 1A(1) cation (left side) and one of the Group 7A(17) anions (bottom). LiF (smallest ions) has the highest lattice energy, and RbI (largest ions) has the lowest.



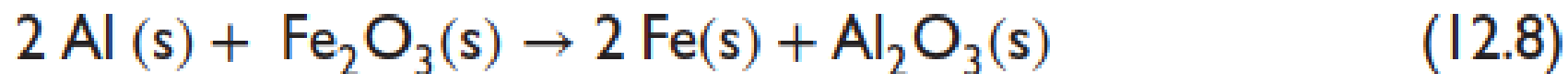
➤ Note that the lattice energy for  $\text{AlCl}_3$  (Table 12.4) is considerably larger than for  $\text{MgCl}_2$  or  $\text{NaCl}$ , even though each cation has the same electron configuration. All three of the given factors support this observation (the ionic radii of six-coordinate  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Al}^{3+}$  are 102, 72, and 54pm). When comparisons are made between the sodium halides, the decreasing lattice energy as one descends the halogens is a direct result of the periodic trend for the ionic radius of the halide, which increases down the group.

➤ Likewise, a comparison of the lattice energies of the alkali metal chlorides increases as the ionic radius of the cation decreases. The main differences between the lattice energies of the isoelectronic  $\text{LiF}$  and  $\text{BeO}$  are the increased charge and smaller ionic radius of the ions in the latter compound.

**TABLE 12.4** Lattice energies for selected ionic solids.

Ionic Solid	$U_0$ , kJ/mol	Ionic Solid	$U_0$ , kJ/mol
NaF	−914	LiCl	−840
NaCl	−787	NaCl	−787
NaBr	−728	KCl	−701
NaI	−681	RbCl	−682
LiF	−1,036	CsCl	−630
BeO	−4,443	$\text{Al}_2\text{O}_3$	−15,916
$\text{MgCl}_2$	−2,526	$\text{Fe}_2\text{O}_3$	−14,774
$\text{AlCl}_3$	−5,492		

- The *more negative lattice energy* for  $\text{Al}_2\text{O}_3$  compared to  $\text{Fe}_2\text{O}_3$  results from **the smaller ionic radius of the  $\text{Al}^{3+}$  cation**. The  $\text{Al}^{3+}$  ion has an ionic radius of 54 pm, as compared with the 65 pm ionic radius of  $\text{Fe}^{3+}$ .
- ✓ This example serves to illustrate ***the importance of the interionic separation term ( $d$ )***. A difference of less than 10 pm in the ionic radius causes  $\text{Al}_2\text{O}_3$  to have a lattice energy that is >1100 kJ/mol more negative than that for  $\text{Fe}_2\text{O}_3$ .
- In turn, the more negative lattice energy of  $\text{Al}_2\text{O}_3$  is the ***main thermodynamic driving force*** for the ***thermite reaction***, given by Equation (12.8).
- The **thermite reaction**, which is a common chemical demonstration, is so exothermic (−851.5 kJ/mol) that it generates temperatures up to 3000°C (*hot enough to produce molten iron*). This reaction was used during the Civil War to repair torn-up railroad tracks.



□ ***Ionic solids typically have high melting points and are brittle. The coulombic interaction between ions in a solid is large when the ions are small and highly charged.***

➤ We can now see why nature has adopted an ionic solid, ***calcium phosphate, for our skeletons***: the doubly charged small  $\text{Ca}^{2+}$  ions and the triply charged  $\text{PO}_4^{3-}$  ions attract one another very strongly and clump together tightly to form a ***rigid, insoluble solid*** (Fig. 2.8).

**FIGURE 2.8** A micrograph of bone, which owes its rigidity to calcium phosphate. The overlay shows part of the crystal structure of calcium phosphate. Phosphate ions are polyatomic ions; however, as shown in the inset, they are nearly spherical and fit into crystal structures in much the same way as monatomic ions of charge  $-3$ .

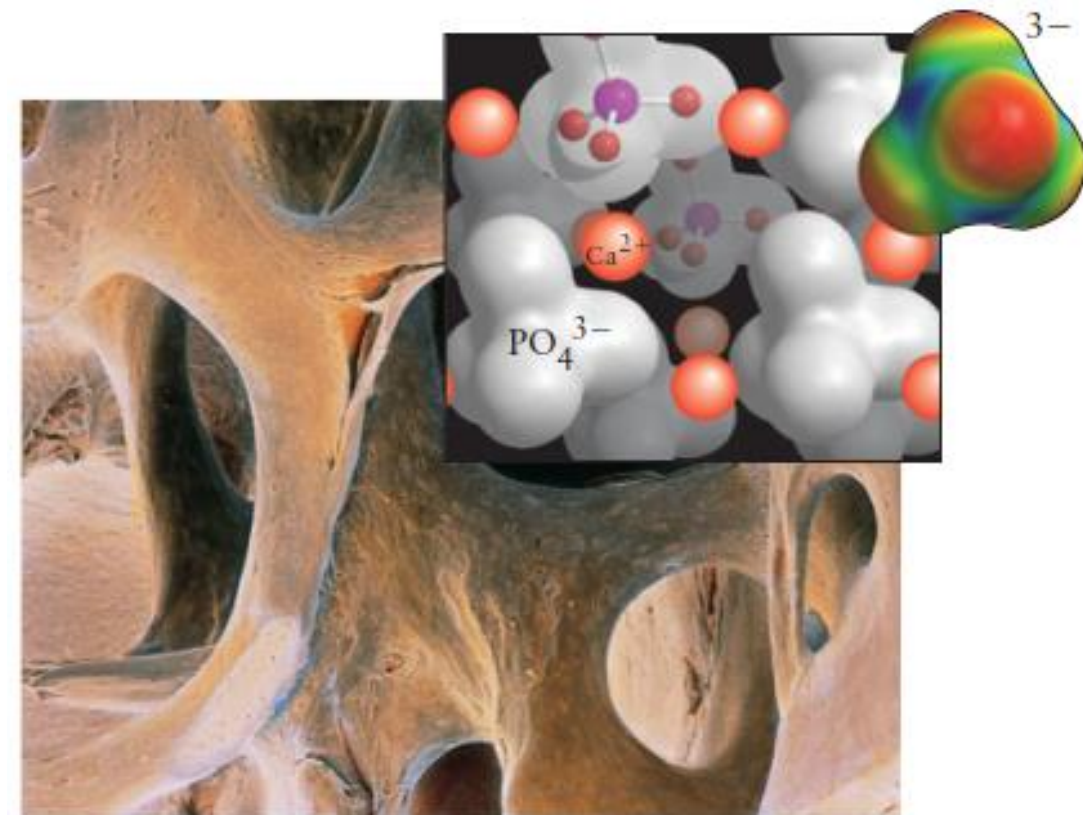


Table 8.1 lists the lattice energies for a number of ionic compounds. The large positive values indicate that the ions are strongly attracted to one another in ionic solids.

**TABLE 8.1    Lattice Energies for Some Ionic Compounds**

Compound	Lattice Energy (kJ/mol)	Compound	Lattice Energy (kJ/mol)
LiF	1030	MgCl <sub>2</sub>	2526
LiCl	834	SrCl <sub>2</sub>	2127
LiI	730		
NaF	910	MgO	3795
NaCl	788	CaO	3414
NaBr	732	SrO	3217
NaI	682		
KF	808	ScN	7547
KCl	701		
KBr	671		
CsCl	657		
CsI	600		



- Table 9.1 lists the ***lattice energies and the melting points*** of several common ionic compounds.
- There is a ***rough correlation*** between lattice energy and melting point.
- The larger the lattice energy, the more stable the solid and the more tightly held the ions. It takes more energy to melt such a solid, and so the solid has a higher melting point than one with a smaller lattice energy.
- Note that  $\text{MgCl}_2$ ,  $\text{MgO}$ , and  $\text{CaO}$  have unusually high lattice energies. The first of these ionic compounds has a doubly charged cation ( $\text{Mg}^{2+}$ ) and in the second and third compounds there is an interaction between two doubly charged species ( $\text{Mg}^{2+}$  or  $\text{Ca}^{2+}$  and  $\text{O}^{2-}$ ). The coulombic attractions between two doubly charged species, or between a doubly charged ion and a singly charged ion, are much stronger than those between singly charged anions and cations.

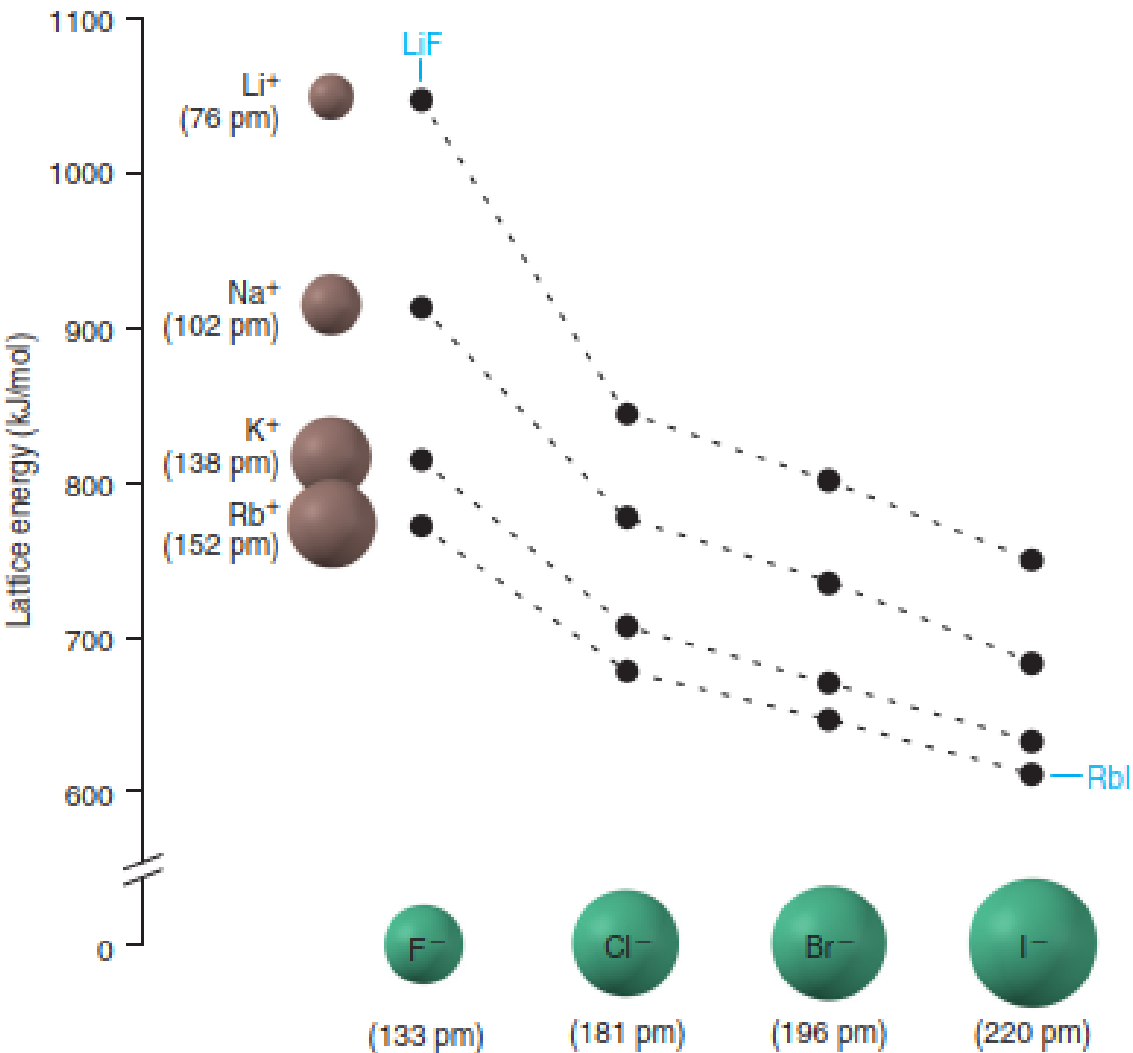
**Table 9.1****Lattice Energies and Melting Points of Some Ionic Compounds**

	<b>Lattice Energy (kJ/mol)</b>	<b>Melting Point (°C)</b>
LiF	1017	845
LiCl	828	610
NaCl	788	801
NaBr	736	750
$\text{MgCl}_2$	2527	714
MgO	3890	2800
CaO	3414	2580

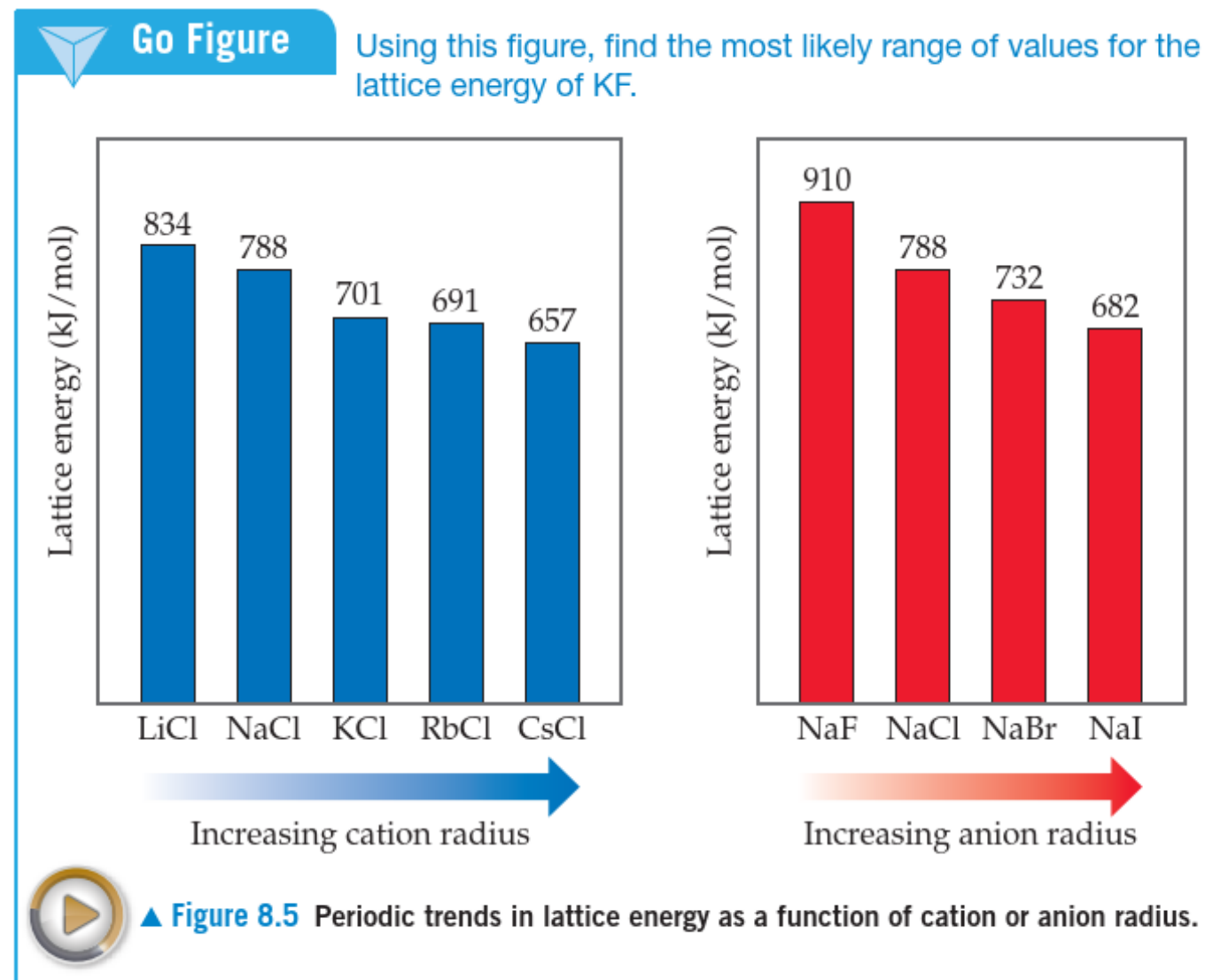
# Periodic Trends in Lattice Energy

The lattice energy results from electrostatic interactions among ions, so its magnitude depends on ionic size, ionic charge, and ionic arrangement in the solid. Therefore, we expect to see periodic trends in lattice energy.

**Figure 9.7** Trends in lattice energy. The lattice energies are shown for compounds formed from a given Group 1A(1) cation (left side) and one of the Group 7A(17) anions (bottom). LiF (smallest ions) has the highest lattice energy, and RbI (largest ions) has the lowest.



➤ Because lattice energy decreases as distance between ions increases, lattice energies follow trends that parallel those in ionic radius. In particular, because ionic radius increases as we go down a group of the periodic table, we find that, for a given type of ionic compound, lattice energy decreases as we go down a group. Figure 8.5 illustrates this trend for the alkali chlorides  $MCl$  ( $M = \text{Li, Na, K, Rb, Cs}$ ) and the sodium halides  $\text{NaX}$  ( $X = \text{F, Cl, Br, I}$ ).



## ❑ *How the Model Explains the Properties of Ionic Compounds?*

➤ *The central role of any model is to explain the facts. With atomic-level views, we can see how the ionic bonding model accounts for the properties of ionic solids:*

**1. Electrical conductivity.** Ionic compounds typically do not conduct electricity in the solid state but do conduct when melted or dissolved. According to the model, the solid consists of fixed ions, but when it melts or dissolves, the ions can move and carry a current.

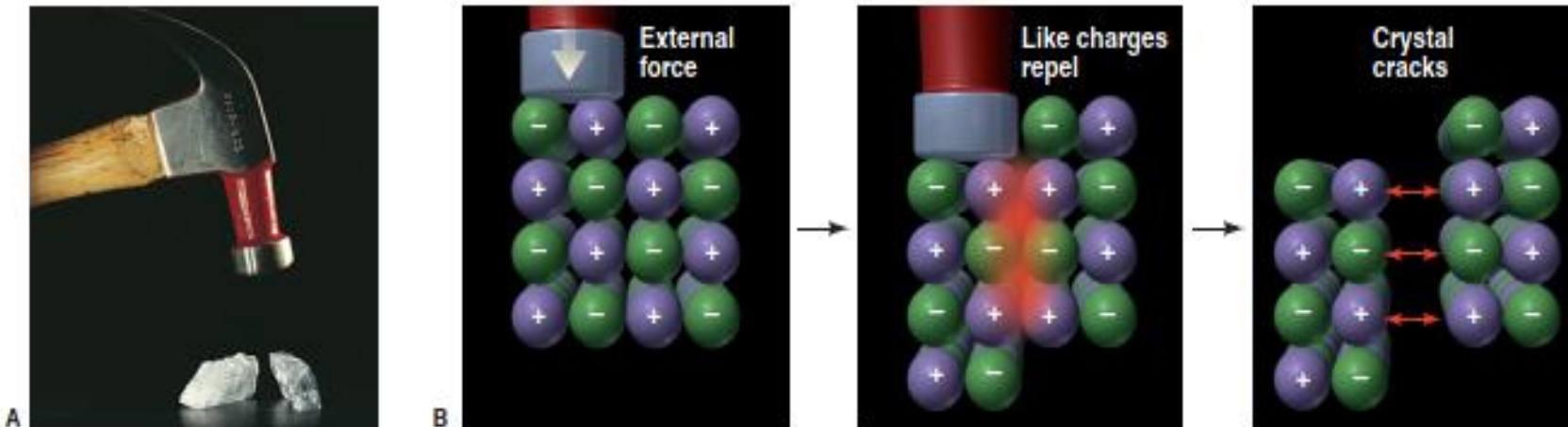
**2. Thermal conductivity.** Large amounts of energy are needed to free the ions from their fixed positions and separate them. Thus, we expect ionic compounds to have high melting points and much higher boiling points.

✓ In fact, the *interionic attraction is so strong that the vapor consists of ion pairs, gaseous ionic molecules*, rather than individual ions.

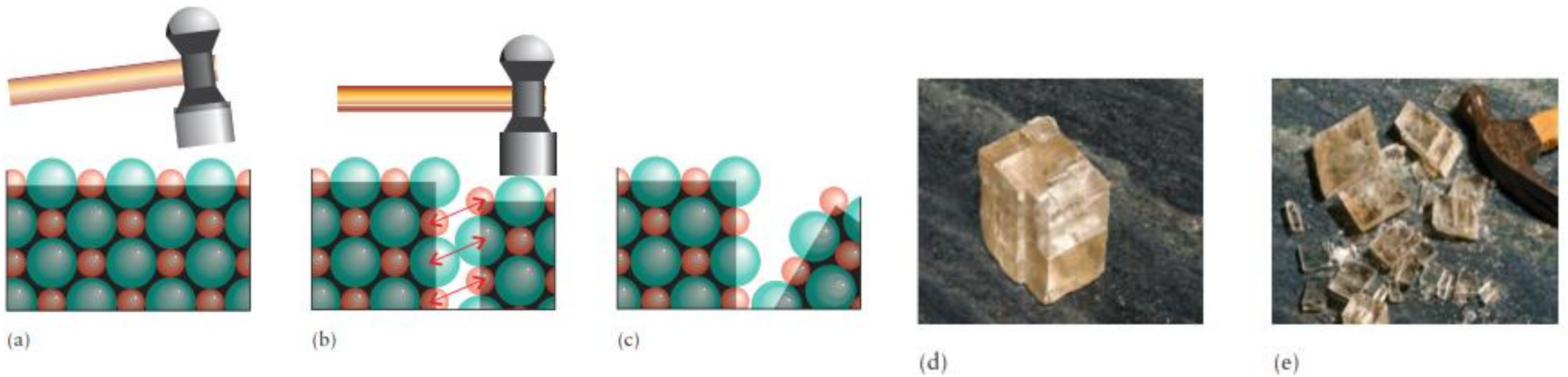
✓ In their normal state, as you know, ionic compounds are solid arrays of ions, and no separate molecules exist.

**3. Physical behavior.** As a typical ionic compound, a piece of rock salt (NaCl) is **hard (does not dent)**, **rigid (does not bend)**, and **brittle (cracks without deforming)**.

- ✓ These *properties arise from the strong attractive forces* that hold the ions in specific positions. *Moving them out of position requires overcoming these forces*, so **rock salt does not dent or bend**.
- ✓ **If enough force is applied, ions of like charge are brought next to each other**, and **repulsions between them crack the sample suddenly** (Figure 9.8).



**Figure 9.8** Why ionic compounds crack. A, Ionic compounds crack when struck with enough force. B, When a force moves like charges near each other, repulsions cause a crack.



**FIGURE 2.5** This sequence of images illustrates why ionic solids are brittle. (a) The original solid consists of an orderly array of cations and anions. (b) A hammer blow can push ions with like charges into adjacent positions; this proximity of like charges raises strong repulsive forces (as depicted by the double-headed arrows). (c) As the result of these repulsive forces, the solid breaks apart into fragments. (d) The smooth faces of this calcite crystal result from the regular arrangement of the calcium and carbonate ions. (e) The blow of a hammer has shattered the crystal, leaving flat, regular surfaces consisting of planes of ions. Compare this image with the result of striking a metallic crystal. The cationic cores in the electron sea are mobile.

- By assessing this interaction quantitatively, ***we can see what determines the lattice energy of the solid***, the difference in energy between the ions packed together in a solid and the ions widely separated as a gas. High lattice energy indicates that the ions interact strongly with one another to give a tightly bonded solid.
- The strong electrostatic interactions between charged ions account for the typical properties of ionic solids, such as their high melting points and their brittleness. A high temperature is required before the ions are able to move past one another to form a liquid.
- Ionic solids are brittle because of the same strong attractions and repulsions. We cannot just push a block of ions in one region of the crystal past the ions in a neighboring region: when we strike an ionic solid, ions with like charges come into contact and repel one another. The resulting repulsions cause it to shatter into fragments (Fig. 2.5).