

1.5: Day 5- Ionic Compounds; Covalent Bonding

5

Day 5: Ionic Compounds; Covalent Bonding

Applying Core Ideas: Two Substances, Some Similarities, Some Big Differences



calcium fluoride



iron

Compare iron, which melts at 1811 K (1538 °C), and calcium fluoride, which melts at 1691 K (1418 °C). Are the forces between atomic-level particles similar in iron and calcium fluoride? Write in your notebook an explanation of your answer to this question.

Consider some other properties of iron and calcium fluoride.

Iron has typical metallic properties: pure solid iron has metallic luster, is malleable, and conducts electricity.

Calcium fluoride has significantly different properties: as a solid it is brittle, does not look metallic, and does not conduct electricity; when molten, calcium fluoride does conduct electricity though.

It appears that these two substances have similar attractions between atomic-level particles, but quite different properties. We need a better atomic-scale model to make sense of these differences.

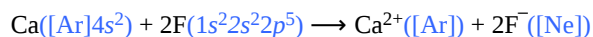
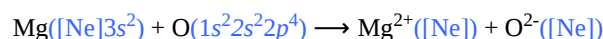
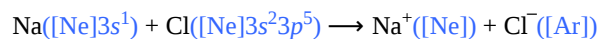
D5.1 Ionic Compounds

In metals, which have low effective nuclear charges (and low ionization energies), it is relatively easy to form positive ions within a sea of electrons so that attractions among the ions and the electrons hold the atoms together. What happens when an atom with a low ionization energy interacts with an atom with a large negative electron affinity? In such a case, transfer of one or more electrons from the atom with the low ionization energy to the one with the high electron affinity can be energetically favorable. For example, consider transfer of an electron from a Li atom to a F atom to form a cation and anion close together: an *ion pair*, Li^+F^- .

Activity 1: Analyzing Formation of an Ion Pair

From the activity above, you've worked out that the formation of the ion pair is associated with a negative ΔE : the joined ion pair is *lower in total energy (more stable)* than the two atoms from which it formed.

The gain and loss of electron(s) in forming an ion-pair typically results in a full octet for the cation and anion. For example:



When a large number of ions form, anions and cations form a structure, called an ionic crystal lattice, where there are equal numbers of anions and cations (so there is zero total electric charge); in the lattice each anion has several cations as its nearest neighbors, and each cation has several anions as its nearest neighbors (see example in Figure 1). This arrangement maximizes

anion-cation attractions (smaller r results in lower Coulomb's law energy) and minimizes anion-anion and cation-cation repulsions (greater r between anions and between cations). A compound made up of anions and cations is called an **ionic compound** and the overall attraction making an ionic crystal lattice stable is called **ionic bonding**.

Figure 1. Ionic crystal lattice. Cations (smaller spheres) and anions (larger spheres) are arranged so that there is a net attraction that makes the collection of ions stable. Move the slider to change the diameters of the ions and show lines indicating the lattice. (This is a small section of the lattice, which extends millions of times farther in all three dimensions.)

For example, when sodium cations (Na^+) and bromide anions (Br^-) come together, the crystal lattice of the compound sodium bromide, Figure 1, contains one Na^+ (green) for each Br^- (violet). The chemical formula representing the part of the lattice shown in Figure 1 is $\text{Na}_{75}\text{Br}_{75}$ because there are 75 Na^+ and 75 Br^- ions. The actual crystal is much larger so the subscripts in the formula of a real crystal would be huge. A **formula unit** is a group of chemical symbols that indicates the smallest whole number ratio of ions of each kind that make up the substance, and is typically used as the formula for ionic compounds. Thus, the formula unit (and the formula) for sodium bromide is NaBr .

All chemical substances are overall electrically neutral. Thus, in an ionic compound, the positive charge from all the cations must equal to the negative charge from all the anions. In other words, the subscripts in a formula unit of an ionic compound must result in equal quantities of positive and negative charges. If we know the charges of the ions, then we can write the formula.

Activity 2: Predicting Chemical Formulas

Some ions consist of a group of atoms with an overall charge. Examples are sulfate dianion, SO_4^{2-} , dihydrogen phosphate anion, H_2PO_4^- , and ammonium cation, NH_4^+ . It is quite useful to be able to recognize such **polyatomic ions** and their charges. If you need to refresh your knowledge of polyatomic ions, use the reference table as you do the next two exercises.

D5.2 Lattice Energy

Refer back to Activity 1. The third step involved bringing one Li^+ ion close to one F^- ion, which lowered the energy. When a large number of oppositely charged ions are brought close together to form a crystal lattice (Figure 1), the energy is lowered even more, because more ions are close together in a structure where attractive forces predominate over repulsive forces.

The **lattice energy** of an ionic compound is defined as the decrease in energy when the ionic crystal lattice forms from the separated ions. Lattice energy can be calculated using a modified form of Coulomb's law; some calculated lattice energies are in Table 1. (Note that because lattice energy is defined as a decrease in energy, a large positive lattice energy corresponds to a large negative ΔE , that is, a very stable (low energy) ionic solid.)

Substance	Lattice Energy (kJ/mol)
NaI	682
CaI_2	1971
MgI_2	2293
NaOH	887
Na_2O	2481
NaNO_3	755
$\text{Ca}_3(\text{PO}_4)_2$	10,602
CaCO_3	2804

Table 1. Representative calculated lattice energies. Data from *CRC Handbook of Chemistry and Physics* (2004).

Lattice energies have a wide range of values depending on which ions make up a compound. Consider, for example, why the lattice energy increases as you go from NaI , to CaI_2 , to MgI_2 (first three rows in Table 1).

According to Coulomb's law,

$$E_p = k_e \frac{Q_1 Q_2}{r}$$

the lattice energy is directly proportional to the sizes of the charges on the ions and inversely proportional to the distance between them (the sum of their ionic radii). Thus, we can compare NaI, CaI₂, and MgI₂ with respect to magnitudes of charges and sizes of ions.

Magnitudes of Charges: NaI consists of 1+ ions and 1− ions; CaI₂ and MgI₂ consist of 2+ ions and 1− ions.

Because the magnitude of $Q_1 Q_2$ is larger, the lattice energies of CaI₂ and MgI₂ should be larger than for NaI.

Sizes of ions: All three compounds contain I[−] anions, so we only need to compare cation radii.

The radii of Ca²⁺ and Na⁺ are similar. This can be estimated from the periodic table: Na⁺ and Ca²⁺ are both smaller than K⁺, Na⁺ because it is above K⁺ in the periodic table, and Ca²⁺ because it is isoelectronic with K⁺ but has more protons in the nucleus. It is reasonable to assume that the radii are not very different, and the [ionic-radius](#) table confirms this: Na⁺ 116 pm; Ca²⁺ 114 pm. Thus, r is not a major factor affecting lattice energy for NaI and CaI₂.

The radius of Mg²⁺ is significantly smaller than for Ca²⁺ (and Na⁺) because Mg is directly above Ca in the periodic table and the ions have the same charge. Thus, MgI₂ should have a larger lattice energy than CaI₂, which is consistent with the values in the table.

Activity 3: Comparing Lattice Energies

When looking at Table 1, you may have noticed that lattice energies for compounds containing 2+ and 2− ions are nearly quadruple those for similar compounds containing 1+ and 1− ions of similar size (compare NaNO₃ and CaCO₃). This observation is consistent with the general rule that lattice energies are highest for substances with small, highly charged ions.

D5.3 Properties of Ionic Compounds

The physical and chemical properties of an ionic compound are determined by the *ions* that constitute the compound. The compound's properties are quite different from the properties of the elements that reacted to form the compound. For example, both sodium and chlorine react with water, but sodium chloride (NaCl) dissolves in water without reacting. In other words, sodium *ions* and chloride *ions* do not react with water, but sodium *atoms* and Cl₂ *molecules* do.

https://mediaspace.wisc.edu/id/0_zns...&st=137&ed=154

Figure 2. Sodium reacts vigorously with water, producing a gas and making the water basic (as indicated by the pink color of phenolphthalein in the water). Adding sodium ions to water, in the form of table salt, NaCl, is much less exciting!

Ionic compounds have many physical properties in common:

- they usually have melting points and boiling points well above room temperature.
- they are crystalline solids with distinct crystal shapes
- they are brittle, will shatter if struck by a hammer, and can easily be cleaved (cleave means to break along smooth planes, as shown in this [video](#)).
- they are electrical insulators when solid but conduct electricity when molten (liquid). (See this [video](#).)
- when an ionic compound dissolves in water, the solution conducts electricity much more effectively than pure water.

Because all ionic compounds have similar properties, it is useful to be able to identify an ionic compound from its chemical formula. In general, ionic compounds contain cations of metals from the left side of the periodic table and anions of nonmetals from the right side of the periodic table. If a compound's chemical formula contains a polyatomic ion, then the compound is an ionic compound.

The properties of ionic compounds can be interpreted in terms of ions. In the solid phase, ions are essentially fixed in their positions in a crystal lattice. Lattice shapes depend on the number and type of ions in the formula, but each lattice has a distinctive shape that results in the lowest energy (maximum lattice energy). Because distances between ions are small, lattice energies are large. It requires a lot of energy to overcome attractions among the ions, making the crystal hard. The lattice shape is related to the shape of the macroscopic crystal. When a crystal cleaves, the cleavage planes are parallel to planes in the crystal lattice. (To see why, watch this [video](#).)

When an ionic solid melts, the anions and cations are free to move randomly among each other. Although the average minimum distance between ions is still small (just a little larger than in the crystalline solid), some anions may be next to other anions and some cations near other cations. Hence, the electrostatic attractions are not as strong and the electrostatic repulsions are greater than in the solid phase; that is, part of the lattice energy needs to be overcome before an ionic compound melts.

When an ionic compound boils to form a gas, the ions continue to move randomly but also are so far apart that their electrostatic attractions are negligible. All of the lattice energy must be overcome for an ionic compound to boil.

Electric current is the movement of electric charge from one place to another. Electric charge is carried by any moving charged particle. In a liquid ionic compound, where ions can move independently, electric charge is conducted by ions. When a solid ionic compound dissolves in water, the ions separate and can move independently throughout the solution. Movement of ions conducts electricity through the solution, just as it does in the molten liquid.

Activity 4: Explaining Properties of Ionic Compounds

Activity 5: Reflection

In your course notebook, write down as many properties of metals and of ionic compounds as you can remember. Then check to make certain your list is complete. Then write your explanation for each property in terms of ions, crystal lattices, attractive forces, and energy. Make sure your list provides a good summary you can use to review later for an exam.

Applying Core Ideas: Comparing Hydrogen Atoms and Helium Atoms

The boiling point of helium is 4.22 K (−268.93 °C), a consequence of very weak London dispersion forces (LDFs) between He atoms. Even when two He atoms are only a short distance apart, there is very little attraction.

When two H atoms get close there is a much stronger attraction: the two atoms become a H₂ molecule by forming a covalent chemical bond. For the H₂ molecules to have enough energy to break that bond, separating the two H atoms, the temperature needs to be similar to the temperature of the Sun (5778 K)!

Why do He atoms behave so differently from H atoms? We need to refine our models of structure and energy still further. This is done in the next sections.

D5.4 Covalent Bonding: Molecular Orbitals

Activity 6: Covalent Chemical Bonds

In your notebook, write a few sentences describing your understanding of covalent chemical bonds. What constitutes a covalent bond? How does it form? What holds the atoms together in a molecule? As you work through this section, make additional notes to review later.

If you wrote that a covalent bond involves sharing electrons between atoms, that's a good start. But how does sharing electrons hold atoms together?

Just as a balance of Coulomb's-law attractions and repulsions affects the electron(s) and nucleus in an atom, coulombic interactions affect electrons and nuclei in a molecule. The major difference is that in a molecule, each electron interacts with two or more nuclei; this additional interaction provides the stabilization that allows the molecule to exist. If a collection of separate atoms were more stable than a molecule, the molecule would simply fall apart into individual atoms.

Just as electron(s) occupy stable atomic orbitals around a single nucleus in an atom, electrons occupy stable orbitals around multiple nuclei in a molecule. *An orbital that extends over two or more atomic nuclei* is called a **molecular orbital (MO)**; in the MO model, a molecular orbital forms when atomic orbitals (AOs) overlap (or interpenetrate).

To understand this better, think about the formation of a H₂ molecule from two ground-state hydrogen atoms (labeled as H_A and H_B in Figure 3). When H_A is sufficiently far away from H_B—for example, more than 400 pm apart (top of Figure 3)—its electron (e_A) occupies the lowest-energy atomic orbital, the 1s orbital. The same is true for H_B.

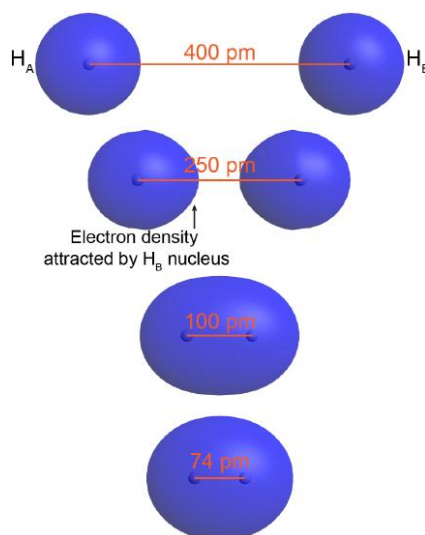


Figure 3. Evolution of electron density as two H atoms (H_A and H_B) approach each other. The electron densities are shown as boundary-surface plots.

When H_A and H_B are closer, e_A begins to experience significant Coulomb's-law attraction towards H_B 's nucleus. For example, at 250 pm apart (Figure 3, second from top) the orbital occupied by e_A is no longer spherical around H_A 's nucleus but rather is distorted—there is more electron density on the side toward H_B . Although H_A 's nucleus attracts e_A more strongly than H_B 's nucleus does (because H_B 's nucleus is screened by e_B), there is a net increase in the positive charge interacting with e_A . This lowers e_A 's potential energy. The same argument applies to e_B .

When the two atoms are even closer—for example, 100 pm apart— e_A and e_B become *delocalized* over both nuclei: both electrons occupy a *molecular orbital*, which surrounds both nuclei. Notice that in this H_2 molecular orbital, there is significant electron density *in between* the two nuclei, attracting both nuclei. This *lowers* the overall energy relative to the energy of the two separate hydrogen atoms.

As the two atoms get closer still, there is a minimum in the overall energy for the molecule. For H_2 the minimum is at 74 pm (bottom of Figure 3). At internuclear distances smaller than 0.74 Å, the energy rises again due to increasing nucleus-nucleus repulsion. In a ground-state H_2 molecule *the distance between nuclei of two bonded atoms*, the **bond length**, is 74 pm.

Figure 4 allows you to explore how the electron density changes as two H atoms interact to form H_2 (or how an H_2 molecule dissociates into two separate H atoms). The blue dot on the potential energy curve shows the corresponding internuclear distance (bond length) and potential energy of the molecule. The ground-state H_2 molecule is more stable than the two separated ground-state H atoms. (The energy of the separated atoms is set to be 0 kJ/mol in Figure 4.) The magnitude of the energy reduction, 436 kJ/mol, is called the **bond energy**, *the energy required to break the bond, completely separating the atoms*.

Figure 4. A graph of energy versus distance between two hydrogen atoms shows minimum energy at a separation of 74 pm (the bond length). At the minimum, the energy is 436 kJ/mol less than the energy of the separated atoms; this is the bond energy.

What we have just described is one of two ways that the two H 1s atomic orbitals can overlap/combine to form an H_2 molecular orbital. It occurs when the two 1s atomic orbitals are *in-phase*. **In-phase** means that *wave functions describing electrons A and B both have maxima in the same direction at the same time*.

The second possibility is that the two overlapping 1s atomic orbitals are **out-of-phase**, which means that *one atomic wave function is positive and the other atomic wave function is negative*. This is shown in Figure 5, where the two phases (positive and negative) are shown in green and yellow.

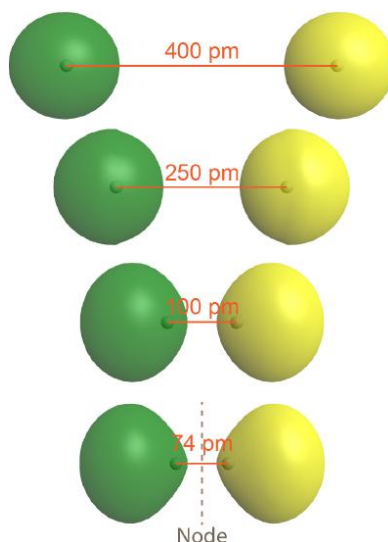


Figure 5. The out-of-phase combination of two H 1s atomic orbitals to form an H₂ molecular orbital. The electron densities are shown as boundary-surface plots.

The result is a molecular orbital with a *node* halfway between the two H atoms. (The node, where electron density is zero, is a plane perpendicular to a line connecting the two nuclei, the internuclear axis). Note that the bottom depiction in Figure 5 is a *single molecular orbital* with one node, just as the bottom depiction in Figure 3 is a *single molecular orbital* but without a node.

As is true of atomic orbitals, a molecular orbital with more nodes has higher energy, which makes sense because the presence of the node reduces electron density between the nuclei (compared to the electron densities of the individual atoms). This reduction in electron density results in less electron-nucleus attraction than if the atomic orbitals had not interacted at all.

D5.5 Molecular Orbital (MO) Diagram

When two H atoms come together to form H₂, both in-phase overlap and out-of-phase overlap of 1s atomic orbitals are possible and both occur. Hence, two 1s atomic orbitals (AOs) overlap to form two molecular orbitals (MOs). This is true in general: the number of MOs formed equals the total number of AOs from which they are derived.

A **MO diagram** shows the relative energies of MOs and AOs and indicates which MOs form from overlap of which AOs. For example, Figure 6 shows the MO diagram of the H₂ molecule. A MO lower in energy than the AOs from which it is derived is called a **bonding MO**. An electron occupying this bonding MO increases the stability of the bond (strengthens the bond). The H₂ bonding MO is labeled " σ_{1s} "; the subscript "1s" designates that it is derived from the 1s AOs.

A MO higher in energy than the AOs from which it is derived is called an **antibonding MO**—an electron occupying this MO decreases the stability of the bond (weakens the bond). The H₂ antibonding MO is labeled as " σ_{1s}^* "; the "*" denotes that it is an antibonding MO.

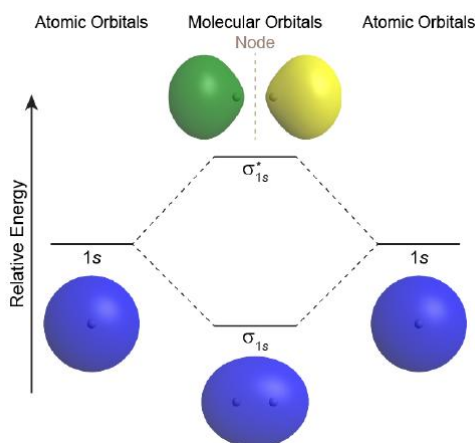
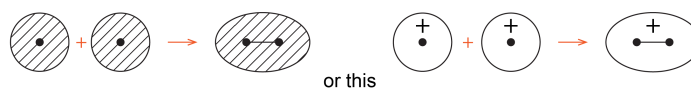


Figure 6. Molecular-orbital energy-level diagram for a H_2 molecule. Electron densities of the atomic and molecular orbitals are shown as boundary-surface plots. The vertical axis is relative energy. Horizontally, atomic orbitals of the two separated H atoms are on either side and the molecular orbitals of the H_2 molecule is in the middle. This is typical for molecular-orbital diagrams.

The Greek letter in the MO labels denotes the symmetry of the MO with respect to the internuclear axis (the line connecting the two nuclei). Greek letters σ , π , δ are analogous to the Roman letters s , p , d that designate shapes of atomic orbitals. A MO that is cylindrically symmetric is called a **sigma MO** and designated σ . (Cylindrically symmetric means that if you stood the molecule on end and spun it around the internuclear axis it would look the same all the time—just as a cylinder would look if you stood it on end and spun it).

Chemists often use simple 2D drawings to show both the shape and phase of AOs and MOs. So the sphere of a $1s$ AO is drawn as a circle and its phase is indicated by two different colors or shading/no shading or plus/minus sign. For example, formation of the σ_{1s} MO from two $1s$ AOs can be drawn as:



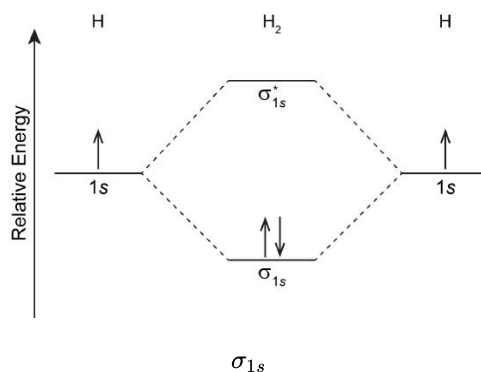
where the black dots represent H nuclei, the circles with hatching (or $+$ sign) represent boundary-surface plots of H $1s$ AOs, each with positive phase, and the oval with hatching (or $+$ sign) represents the H_2 σ_{1s} MO, also with positive phase.

D5.6 Electron Configurations and Bond Order

Just as an atom has an electron configuration, so does a molecule. The molecular ground-state electron configuration can be obtained by filling MOs, facilitated by MO diagrams such as the one shown in Figure 6, following rules similar to those for atomic electron configurations:

- Sum all the electrons from all the atoms that make up the molecule.
- Each MO can hold *at most* two electrons. (Two electrons occupying the same orbital must have opposite spin.)
- In the MO diagram the MOs are arranged in order of increasing energy.
- Add electrons to the lowest-energy MO first and then to successively higher-energy MOs (Aufbau principle)
- If two or more MOs have the same energy (are degenerate), apply Hund's rule: assign one electron to each degenerate MO before pairing any electrons

For the H_2 molecule: there is one electron from each H atom, so there are two electrons in H_2 . There is only one lowest-energy MO, σ_{1s} , therefore the two electrons, with opposite spin, will fill it. The ground state electron configuration of H_2 is $(\sigma_{1s})^2$.



(1.5.1)

Activity 7: Molecular Orbitals and Electromagnetic Radiation

The two electrons in the σ_{1s} MO, which are shared between the two H atoms, form a covalent bond. The configuration $(\sigma_{1s})^2$ indicates a *single, sigma* covalent bond. In general, a **covalent bond** involves *overlap of two or more AOs that leads to increased electron densities close to atomic nuclei so that the electrons' energies are lowered*. Electrons are shared between pairs of atomic nuclei, or more widely among several nuclei within a molecule.

In some cases more than two electrons can be shared between two nuclei. This gives rise to the idea of **bond order**, which is *the number of shared electron pairs between two atoms*. Using a MO diagram, bond order can be defined as:

$$\text{Bond Order} = \frac{1}{2} (n_{\text{bonding } e^-} - n_{\text{antibonding } e^-}) = \frac{1}{2} (n_b - n_a)$$

where $n_{\text{bonding } e^-}$ is the number of electrons in bonding MOs and $n_{\text{antibonding } e^-}$ is the number of electrons in antibonding MOs. There is a factor 1/2 because two shared electrons make one bond. In general a greater number of shared electrons means a stronger bond, so the larger the bond order is, the stronger the bond is.

Activity 8: Molecular Orbitals for He

Day 5 Pre-Class Podia Problem: Melting Points of Salts

This Podia problem is based on today's pre-class material; working through that material will help you solve the problem.

The formulas and melting points of four salts are listed below. All four compounds have the same crystal lattice as NaCl. Write a clear, concise explanation of the differences in melting points using scientifically appropriate language and including any relevant data.

NaF 996 °C NaCl 801 °C KCl 770 °C CaO 2572 °C

Two days before the next whole-class session, this Podia question will become live on [Podia](#), where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use [this link](#) to report them. A similar link will be included in each day's material. We appreciate your comments.

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