8 Structure and Bonding

A water molecule is bent, at about $104.5°$. If it were straight, like carbon dioxide, the pull of its two bonds would cancel, and water would very likely be a gas at room temperature; there would be no oceans. The formula tells you which atoms are in a molecule. It takes the structure, down to where the lone pairs sit, to tell you what the molecule does. The mock exam gives this chapter 10 of its 70 questions.

8.1 Ionic Bonds and Lattice Energy

A metal atom gives up electrons and a nonmetal atom takes them, so the solid is made of cations and anions. Each ion is held by every oppositely charged ion around it. This repeating three-dimensional pattern is a **lattice**, and the energy that holds it together is the **lattice energy**:

$$\mathrm{NaCl(s)} \longrightarrow \mathrm{Na^+(g) + Cl^-(g)}$$

Lattice energy
The energy needed to separate one mole of an ionic solid into gaseous ions. It is a positive number.

The reason is Coulomb's law. The energy of attraction between two ions grows with the product of their charges and falls with the distance between their centers:

$$E \propto \frac{q_+ \, q_-}{r}$$

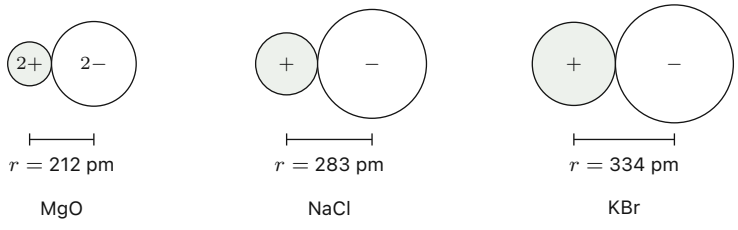
Doubling one charge doubles the energy, and halving the distance doubles it as well. Charge products on the exam differ by factors of 2 or 4, and the radii in a comparison usually differ by less than that. As a rule of thumb, compare the charges first and the sizes second.

Distance, r
The distance between the nuclei of the cation and the anion. It is about the sum of the two ionic radii.

Ranking lattice energies

Compare the product of the charges first. If two compounds have the same charges, the one with the smaller ions has the larger lattice energy. Do not rank by formula, by mass, or by the number of ions in the formula unit. A heavier ion is not a stronger ion.

RULE Larger charges first, then smaller ions. Mass and subscripts play no part.



Reading the sketch
Circles are drawn to scale. Charges set the order here, then r.

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EXAMPLE 8.1

Rank KBr, NaF, Li_2O and CaO from smallest to largest lattice energy.

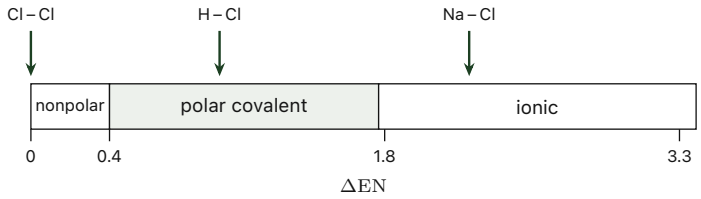
What is asked	An order of lattice energy, smallest first.
Ion charges	KBr: $1+, 1-$. NaF: $1+, 1-$. Li_2O: $1+, 2-$. CaO: $2+, 2-$.
Charge products	1, 1, 2, 4. KBr and NaF tie, so they need a second test.
Break the tie	Na^+ is smaller than K^+ and F^- is smaller than Br^-, so NaF has the smaller r and the larger lattice energy.
Check	The subscript 2 in Li_2O does not change the charge on either ion. The product is $(1)(2) = 2$, and that sits between 1 and 4.
Answer	**KBr $<$ NaF $<$ Li_2O $<$ CaO**

8.2 Electronegativity and Bond Polarity

Electronegativity
How strongly an atom pulls on the shared electrons in a bond. Fluorine is highest, 3.98.

Atoms in a bond do not always share the electrons equally. An atom with a stronger pull on the shared pair is more electronegative. For the same reason that ionization energy rises up and to the right of the periodic table, **electronegativity** does too: a small atom with a high effective nuclear charge, the net pull of the nucleus on an outer electron (Chapter 3), holds bonding electrons tightly.

What matters for a bond is the difference in electronegativity, $\Delta\mathrm{EN}$, between the two atoms. A small difference means the pair is shared nearly equally. A large difference means one atom has taken most of the pair. There is no sharp line between these cases, only a continuum, so the labels below mark regions.



Partial charge
A fraction of a full charge, written $\delta+$ or $\delta-$.

In a **nonpolar covalent** bond the pair is shared equally. In a **polar covalent** bond the pair is shared unequally, so the more electronegative atom carries a partial negative charge and the other atom a partial positive charge. In an **ionic** bond the transfer is nearly complete. The cutoffs are approximate and books place them a few tenths apart, so exam questions use differences that fall clearly inside one region.

Most misses here come from answering with the metal or nonmetal rule when numbers are given. Two nonmetals can form a bond that is polar, and the numbers decide how polar. The more polar bond always has the larger difference.

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EXAMPLE 8.2

Which bond is the most polar: C–H, N–H, O–H or Cl–H? Use EN: H 2.20, C 2.55, N 3.04, O 3.44, Cl 3.16.

What is asked	The bond with the largest difference, and which end is negative.
Differences	C – H: 0.35. N – H: 0.84. O – H: 1.24. Cl – H: 0.96.
Compare	The largest is 1.24, the O – H bond.
Direction	Oxygen has the larger EN, so oxygen is $\delta-$ and hydrogen is $\delta+$.
Check	Three differences fall between 0.4 and 1.8, so those bonds are polar covalent. C – H, at 0.35, is just below 0.4 and is close to nonpolar.
Answer	**O–H, with $\delta-$ on oxygen**

8.3 Lewis Structures

A **Lewis structure** is a bookkeeping diagram for the valence electrons. A line between two atoms is a **bonding pair**, two electrons shared. A pair of dots on one atom is a **lone pair**, two electrons that belong to that atom and are not shared. Atoms in period 2 are stable with eight electrons around them, counting each bond as two. This is the **octet rule**. Hydrogen is stable with two.

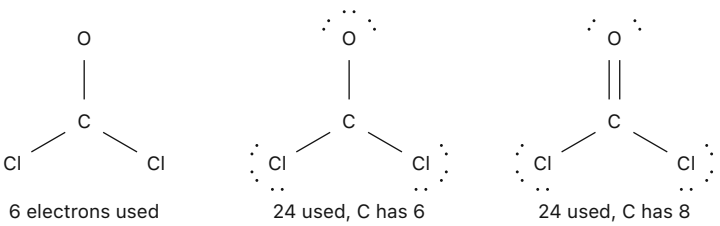
Valence electrons
The electrons in an atom's outermost shell. They are the ones that form bonds.

The **central atom** is the atom the others are attached to. It is usually written first in the formula and is usually the least electronegative. Hydrogen is never central, because it forms only one bond. Halogens are outer atoms in most molecules you will see.

Five steps

- **Count.** Add the valence electrons of all atoms. Add one for each negative charge, subtract one for each positive charge.
- **Bond.** Put the central atom in the middle and join each outer atom to it with a single bond. Each bond uses two electrons.
- **Complete the outer atoms.** Give each outer atom lone pairs until it has an octet. Hydrogen gets none.
- **Place what is left.** Any electrons still unused go on the central atom as lone pairs.
- **Check the central atom.** If it has fewer than eight, move a lone pair from an outer atom into a second bond to the central atom. Repeat until it has eight. Then recount the total.

Phosgene
$COCl_2$ has $4 + 6 + 7 + 7 = 24$ valence electrons. The sketches follow steps 2, 3 and 5.



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PRACTICE SET 8A 12 questions · 18 minutes · no calculator needed

1. Which compound has the largest lattice energy?

(A) CsI **(B)** KBr **(C)** LiF **(D)** NaCl

2. Which list ranks the compounds from lowest to highest lattice energy?

(A) CsCl < NaCl < CaS < MgS
(B) NaCl < CsCl < MgS < CaS
(C) CsCl < NaCl < MgS < CaS
(D) NaCl < CsCl < CaS < MgS

3. Electronegativities: H 2.20, Na 0.93, P 2.19, S 2.58, Cl 3.16. Which list orders the bonds from least polar to most polar?

(A) Na–Cl < P–Cl < S–Cl < S–H
(B) S–Cl < S–H < P–Cl < Na–Cl
(C) S–H < P–Cl < S–Cl < Na–Cl
(D) S–H < S–Cl < P–Cl < Na–Cl

4. How many lone pairs are on the sulfur atom in the sulfite ion, SO_3^{2-}?

(A) 0 **(B)** 1 **(C)** 2 **(D)** 3

5. How many valence electrons must appear in the Lewis structure of the phosphate ion, PO_4^{3-}?

(A) 26 **(B)** 29 **(C)** 40 **(D)** 32

6. In which molecule does the central atom have fewer than eight electrons around it?

(A) CF_4 **(B)** BF_3 **(C)** SF_4 **(D)** NF_3

7. Which is the best Lewis structure for HCN? The atoms are bonded in the order H, C, N.

(A) H—C≡N: **(B)** H—C≡N

(C) H—C≡N (N with three lone pairs) **(D)** H—N≡C:

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