



CHEM 102:
Chemical bonding

Instructor: Prof.Dr. Zaki N. Kadhi m

Overview

- 1 Atomic Properties and Chemical Bonds
- 2 The Ionic Bonding Model
- 3 The Covalent Bonding Model
- 4 Bond Energy and Chemical Change
- 5 Between the Extremes:
Electronegativity and Bond Polarity
- 6 An Introduction to Metal Ic Bonding

A comparison of metals and nonmetals also.

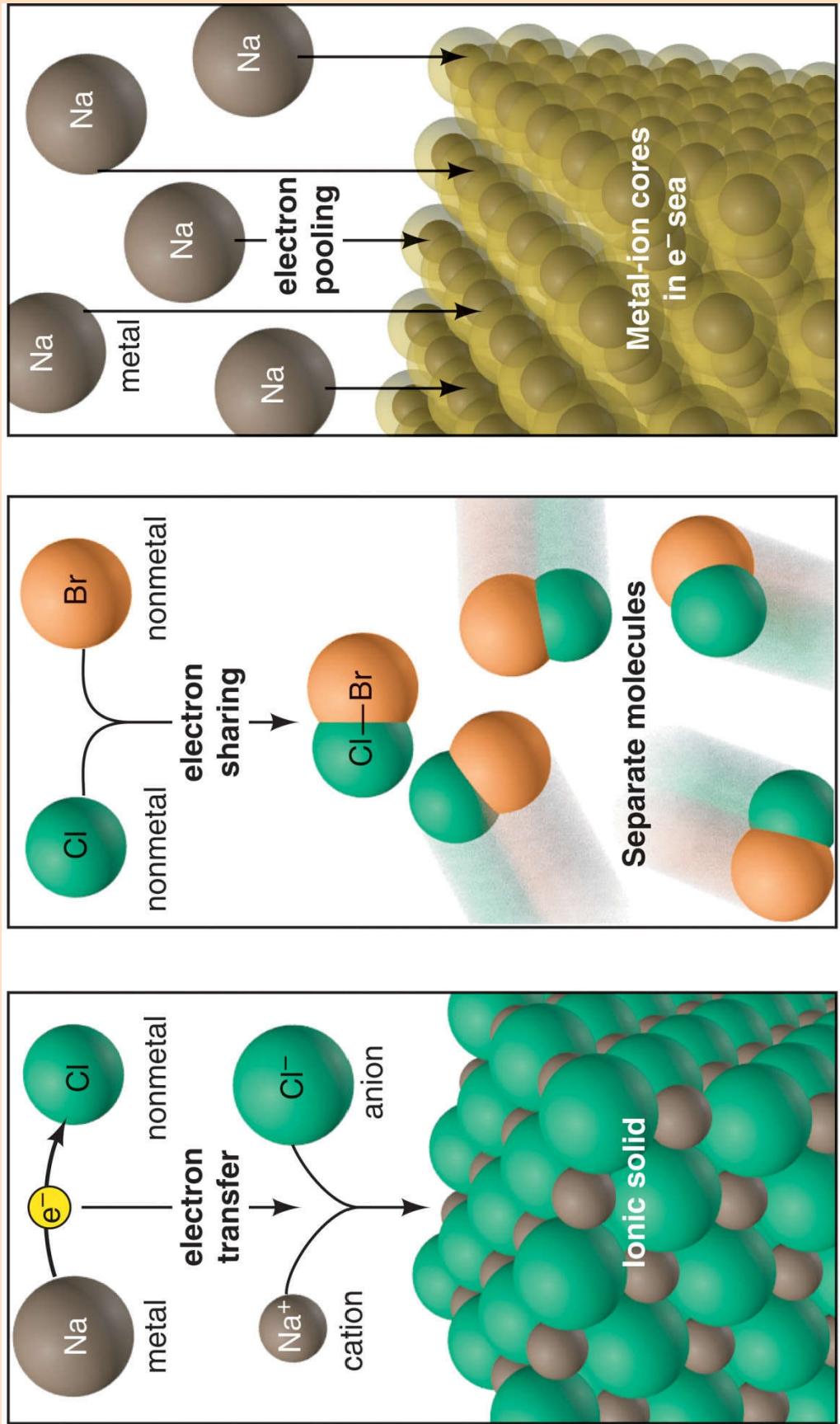
Types of Chemical Bonding

Ioni c bondi involves the transfer of electrons and is usually observed when a metal bonds to a nonmetal.

Cova ent bondi involves sharing electrons and is usually observed when a nonmetal bonds to a nonmetal.

Metal i c bondi occurs when a metal bonds to another metal.

Three models of chemical bonding.

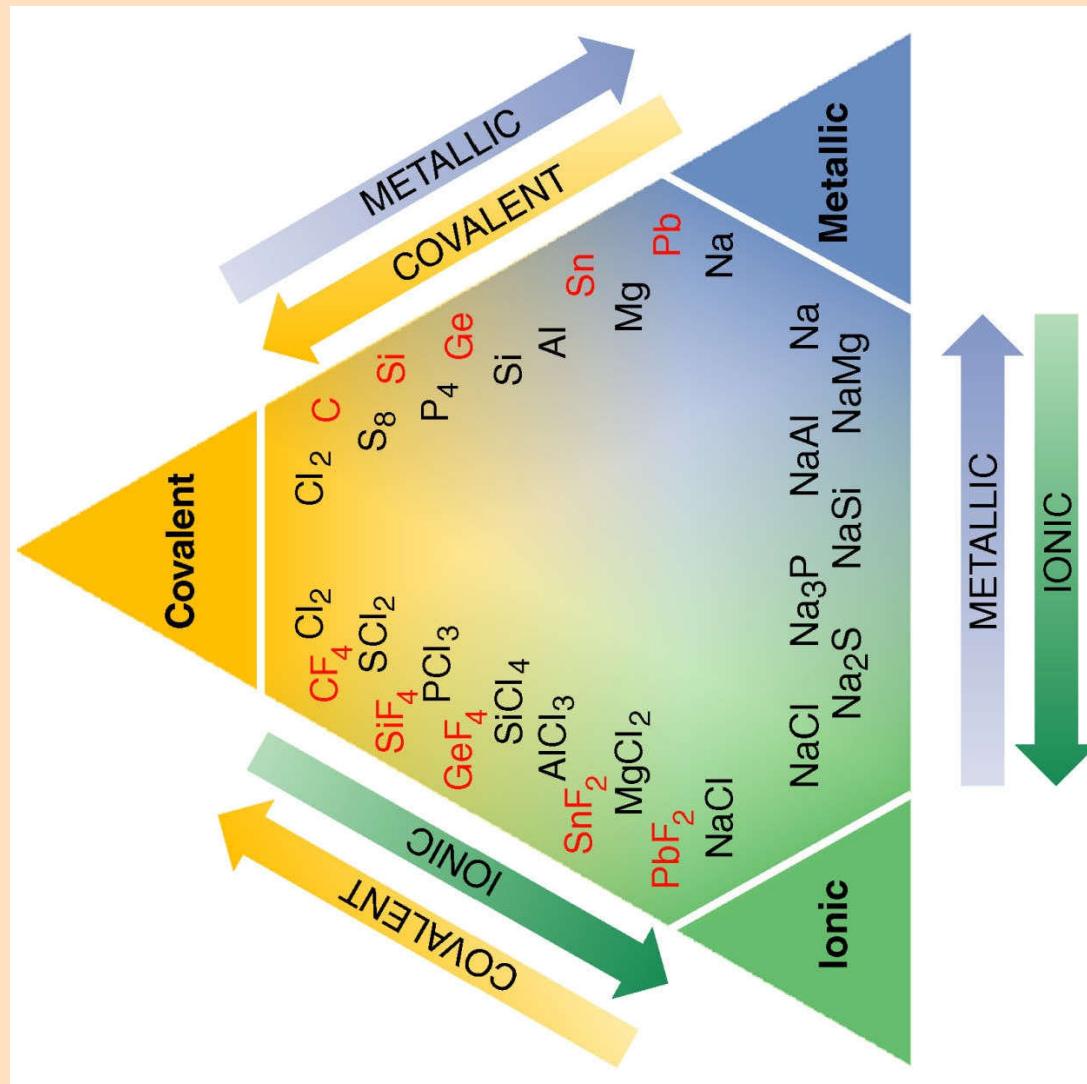


A Ionic bonding

B Covalent bonding

C Metallic bonding

Gradat ions in bond type among Periodic table elements (red type) element s.



The Ionic Bonding Model

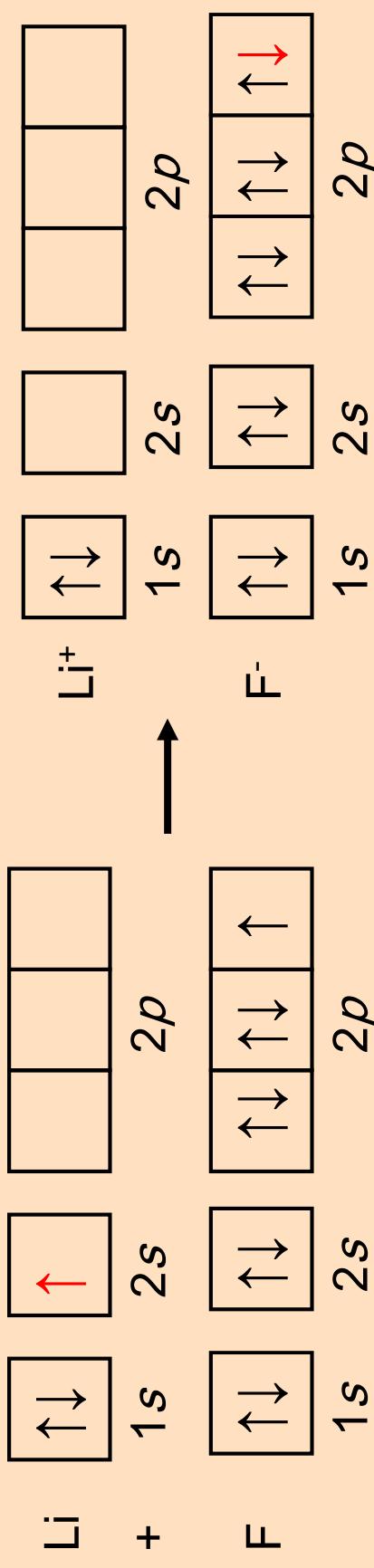
An ionic bond is formed when a metal *transfers* electrons to a nonmetal atom forming which attract each other to give a solid compound.

The total number of electrons lost by the metal atom equals the total number of electrons gained by the nonmetal atom.

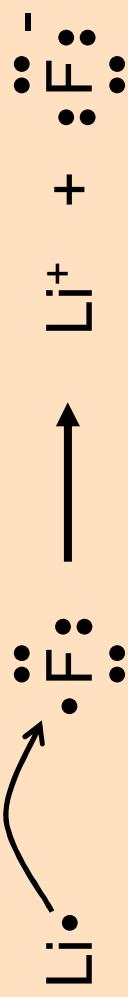
Three ways to depict electron transfer in the format ion⁺ and F⁻.



Orbi tal di agrams



Lewis et al. / ectr-dot symbol 5



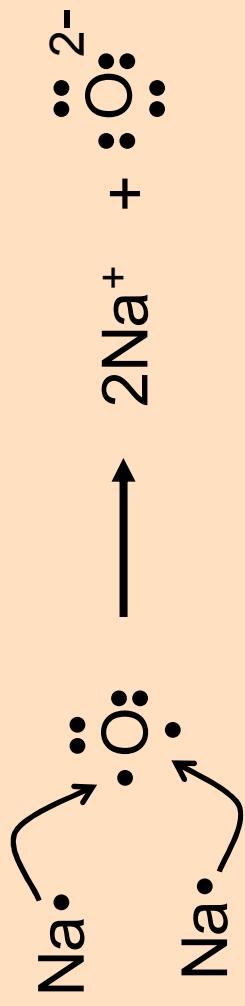
Sample Problem

Determining Ion Formation on

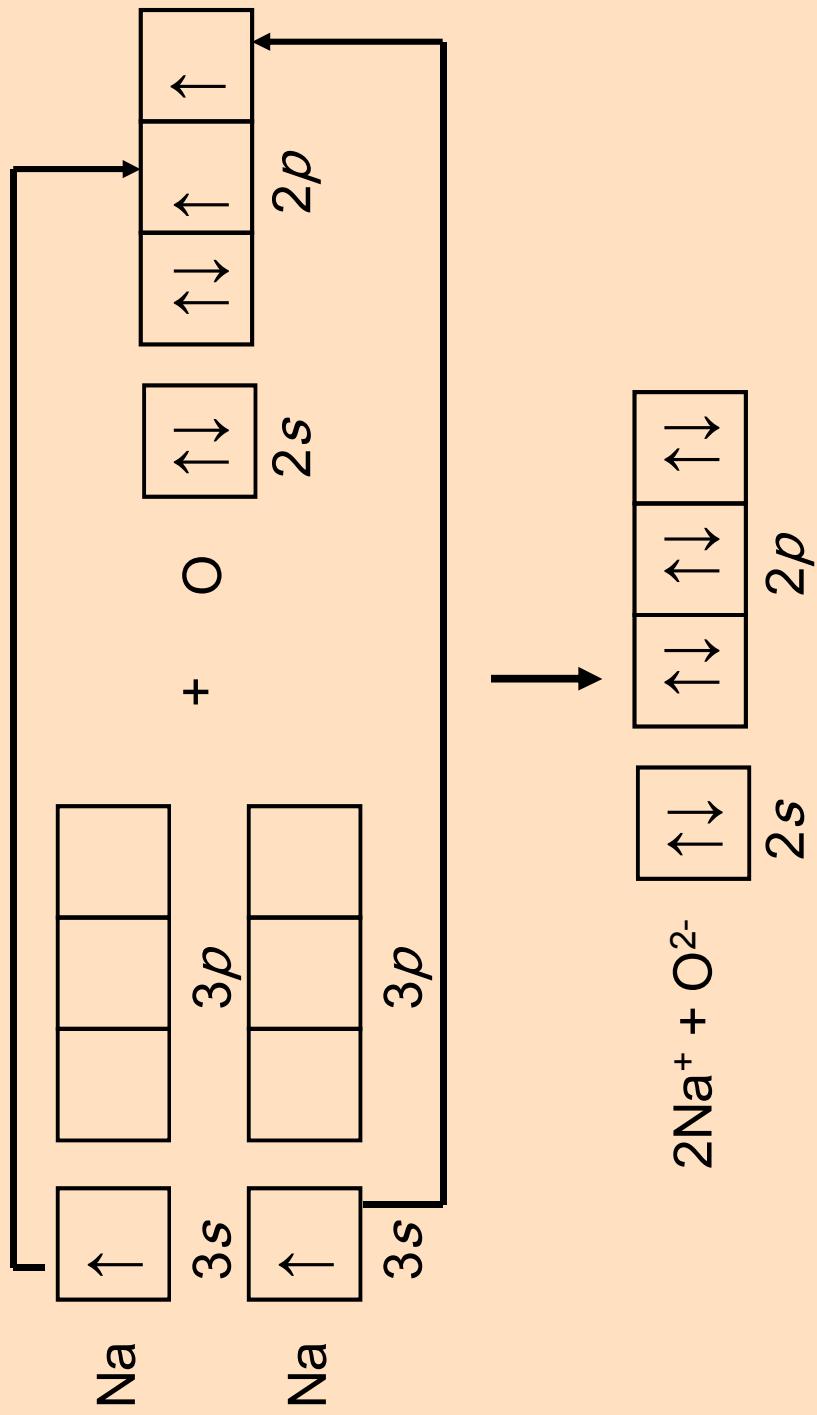
PROBLEM: Use partial orbital diagrams and Lewis symbols to depict the formation of an NaO_2^- ion from the elements in the formula of the compound formed.

PLAN: Draw orbital diagrams and Lewis symbols for Na and O atoms. To attain filled outer levels, Na loses one electron and O gains two. Two Na atoms are needed for each O atom so that the number of electrons lost equals the number of electrons gained.

SOLUTION:

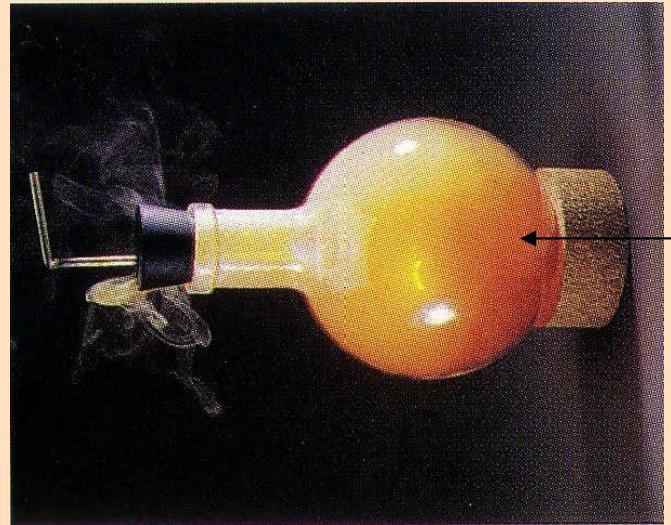


Sample Problem

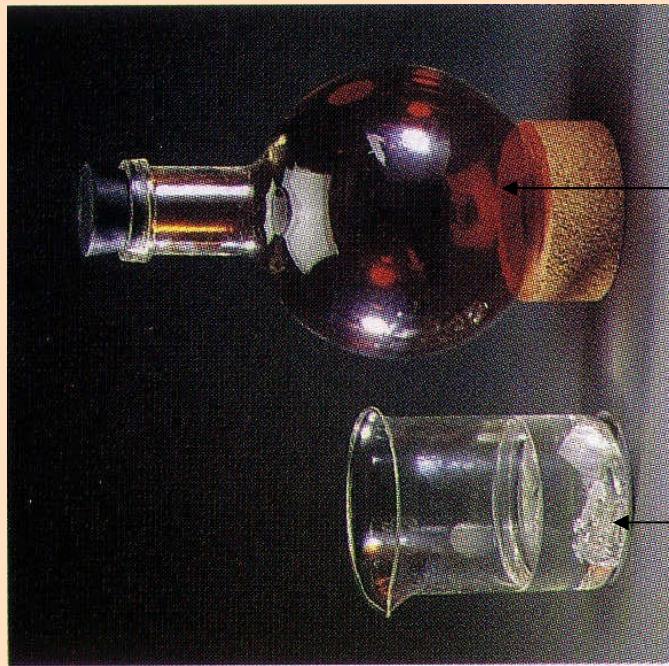


The formula is s_2Na

The exothermic formation of sodium bromide.



$\text{NaBr}(l)$



$\text{Br}_2(l)$

$\text{Na}(s)$

The Born-Haber cycle is a special case of Hess's law applied to ionic crystals only.

Definitions

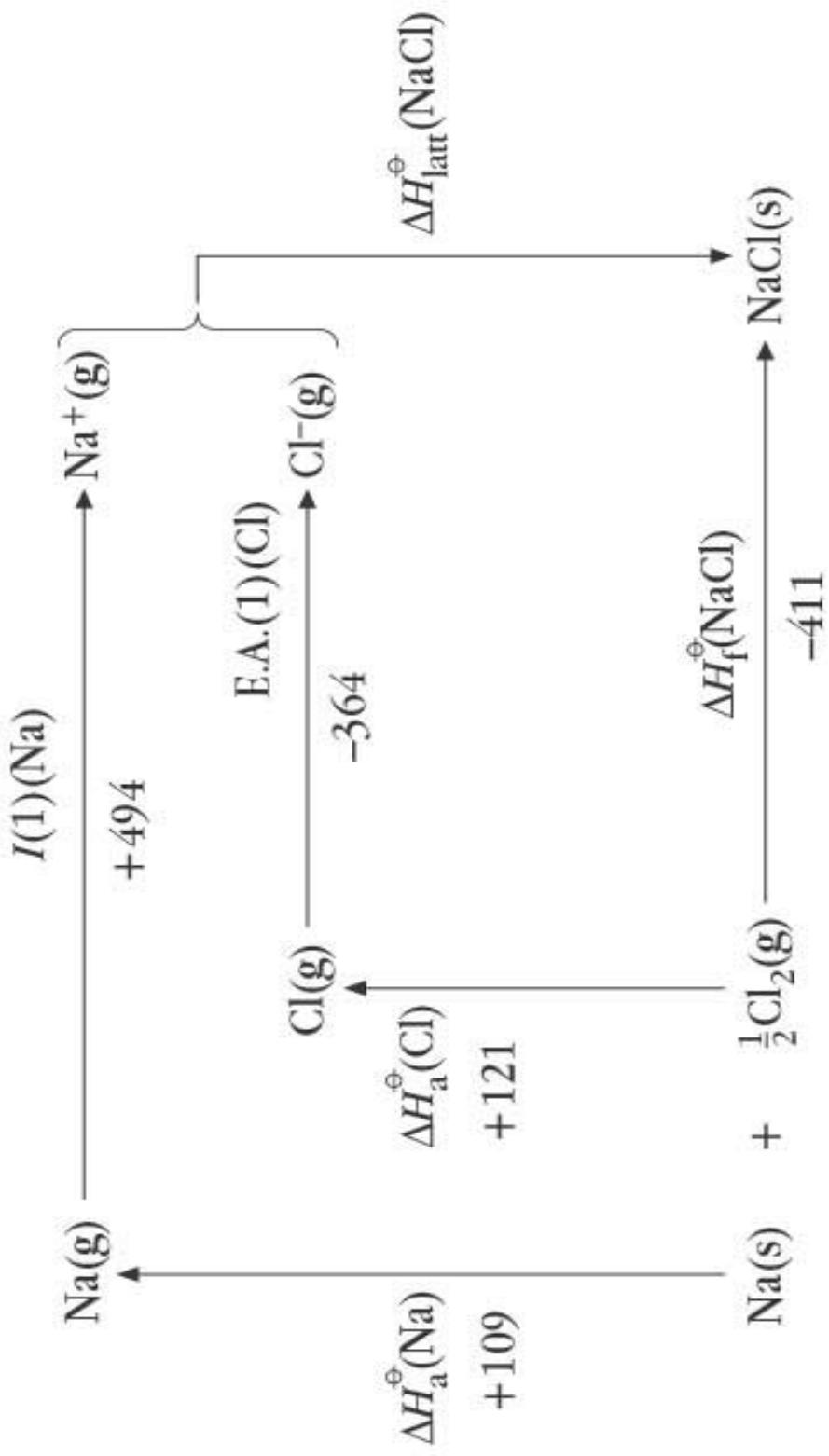
Standard enthalpy of sublimation is the heat absorbed when one mole of atoms are vaporised

Standard enthalpy of bond dissociation is the energy absorbed when one mole of bonds is broken

The electron affinity is the energy absorbed when one mole of ions are formed from one mole of atoms

The standard lattice energy is the energy absorbed when one mole of ionic crystals is formed.

Standard enthalpy of atomisation is the energy absorbed when one mole of atoms are formed



$$-411 = 109 + 121 + 449 - 364 + \Delta H_i^\ominus$$

Where $\Delta H_i^\ominus = \text{standard lattice energy of NaCl}$
 $= -726 \text{ kJ/mol}$

For MgCl₂ we will need 2 × EA for 2 atoms of Cl

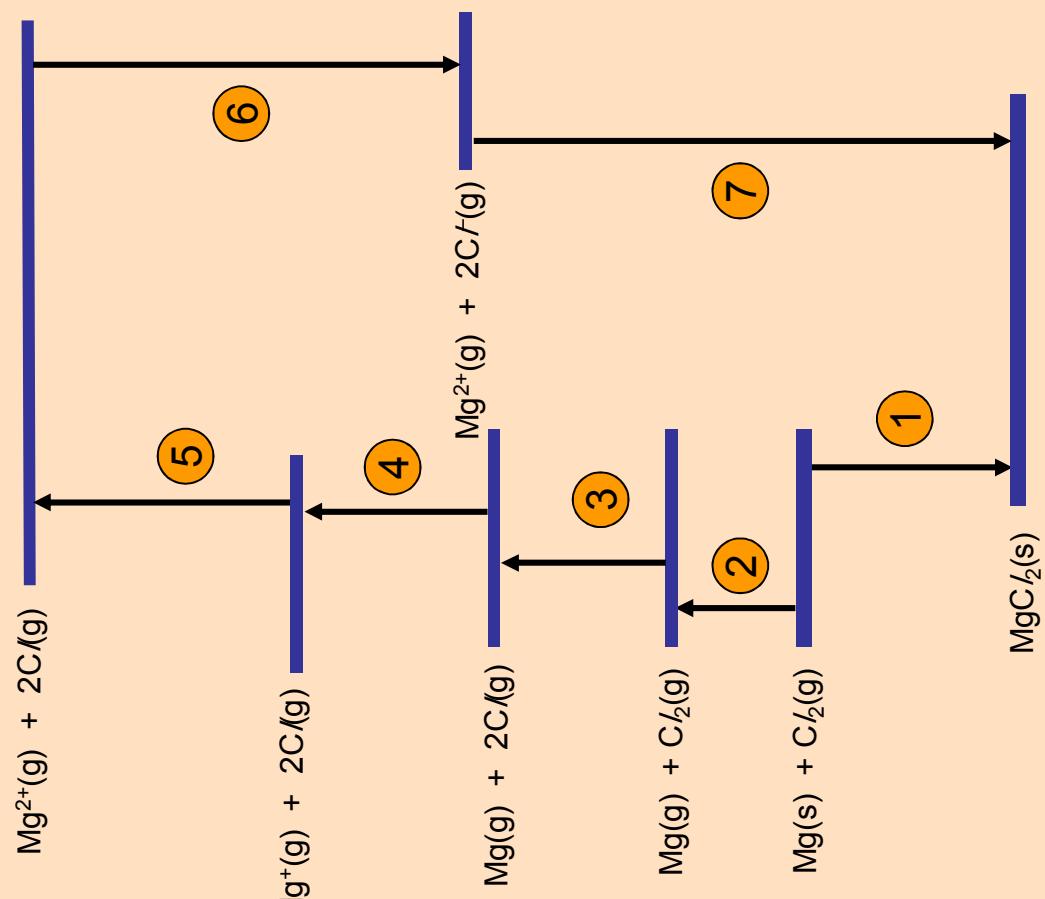
Be careful to note if bond dissociation energy (BDE) is given or atomisation energy for chlorine or other diatomic gas

e.g. BDE for chlorine is 242 KJ/mol

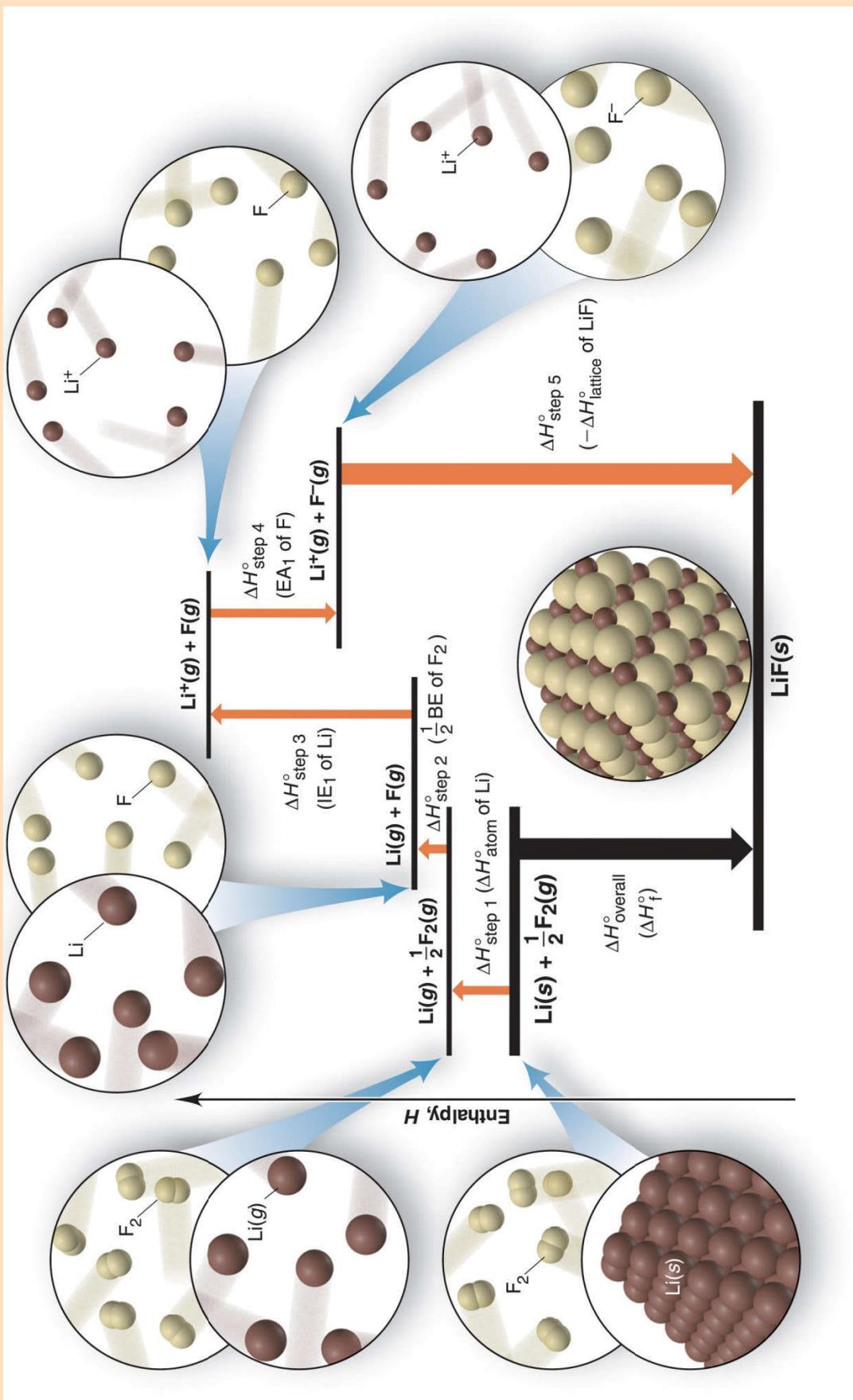
ΔH_a^Θ for chlorine is half this value 121 KJ/mol

Born-Haber Cycle - MgC₂

- ① Ent halpy of forma^t ion of MgC
 $Mg(s) + C_2(g) \longrightarrow MgC_2(s)$
- ② Ent halpy of sublimation of magnesium
 $Mg(s) \longrightarrow Mg(g)$
- ③ Ent halpy of atomisation of chlorine
 $\frac{1}{2}C_2(g) \longrightarrow C(g) \quad \text{x2}$
- ④ 1st ionisation Energy of magnesium
 $Mg(g) \longrightarrow Mg^+(g) + e^-$
- ⑤ 2nd ionisation Energy of magnesium
 $Mg^+(g) \longrightarrow Mg^{2+}(g) + e^-$
- ⑥ Electron affinity of chlorine
 $C(g) + e^- \longrightarrow C\bar{T}(g) \quad \text{x2}$
- ⑦ Latice Enthalpy of MgC₂
 $Mg^{2+}(g) + 2C\bar{T}(g) \longrightarrow MgC_2(s)$



The Born-Haber cycle for lithium fluoride



Periodic Trends in Lattice Energy

Lattice energy is the energy required to separate a solid of an ionic solid into gaseous ions.

Lattice energy is a measure of the strength of the ionic bond.

Coulomb's Law

$$\text{Electrostatic energy} = \frac{\text{charge A} \times \text{charge B}}{\text{distance}}$$

$$\text{Electrostatic energy}_{\text{cat}} = \frac{\text{cation charge} \times \text{anion charge}}{\text{cation radius} + \text{anion radius}} \propto \Delta H_{\text{lattice}}^{\circ}$$

Periodic Trends in Lat t ice Energy

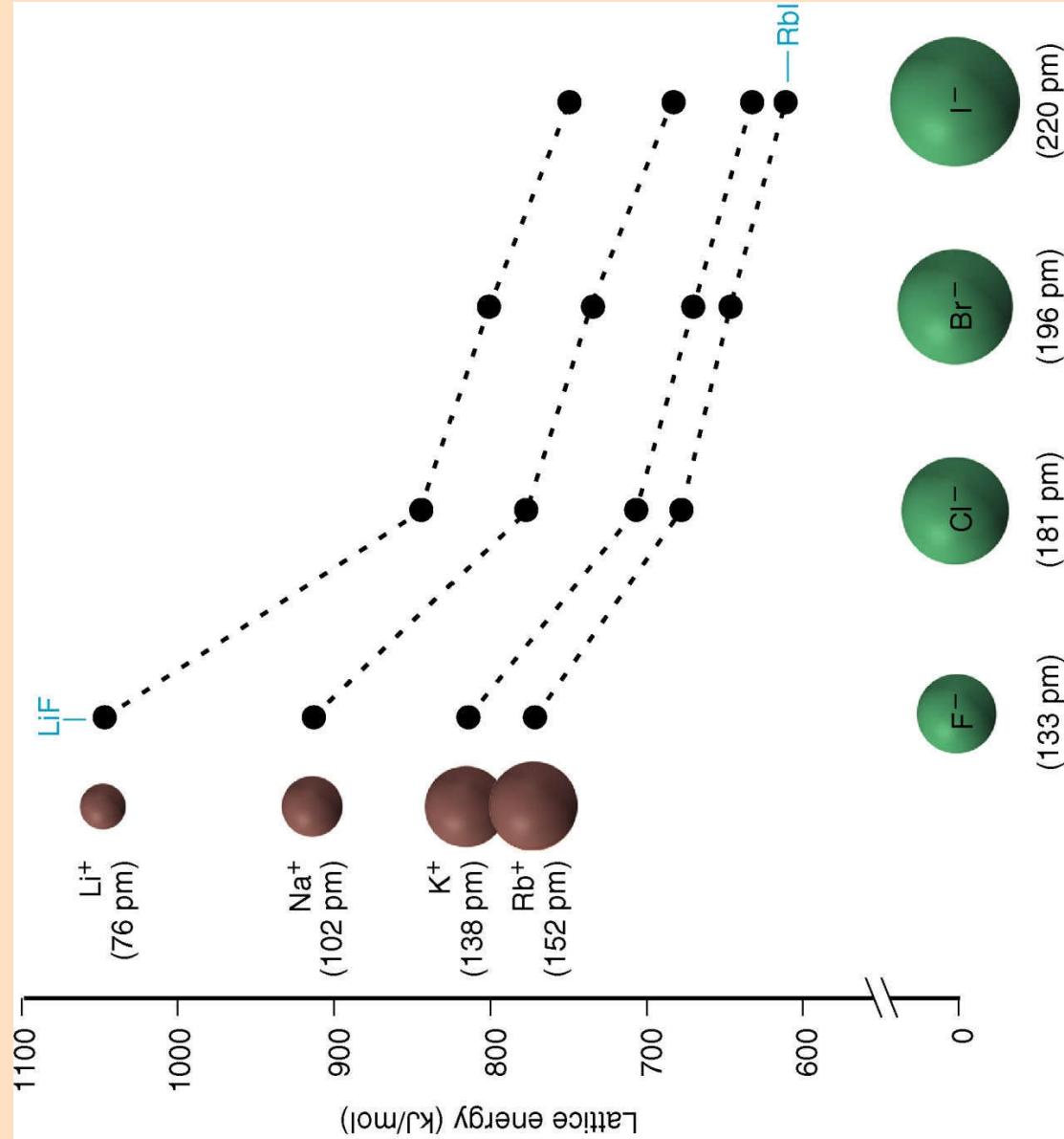
Lat t ice energy is af f ecti ~~s~~höyc sānzi/ oni c charge

As ionic size i ncreases lat t ice energies.

Lat t ice energy t heref ore decreases down a group on t he periodic t able.

As ionic charge i ncreases lat t ice energies

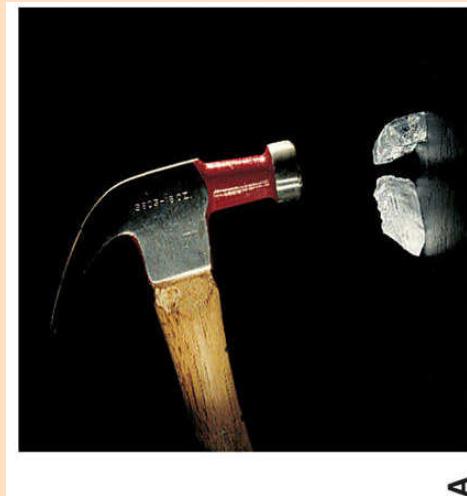
Trends in lattice energy.



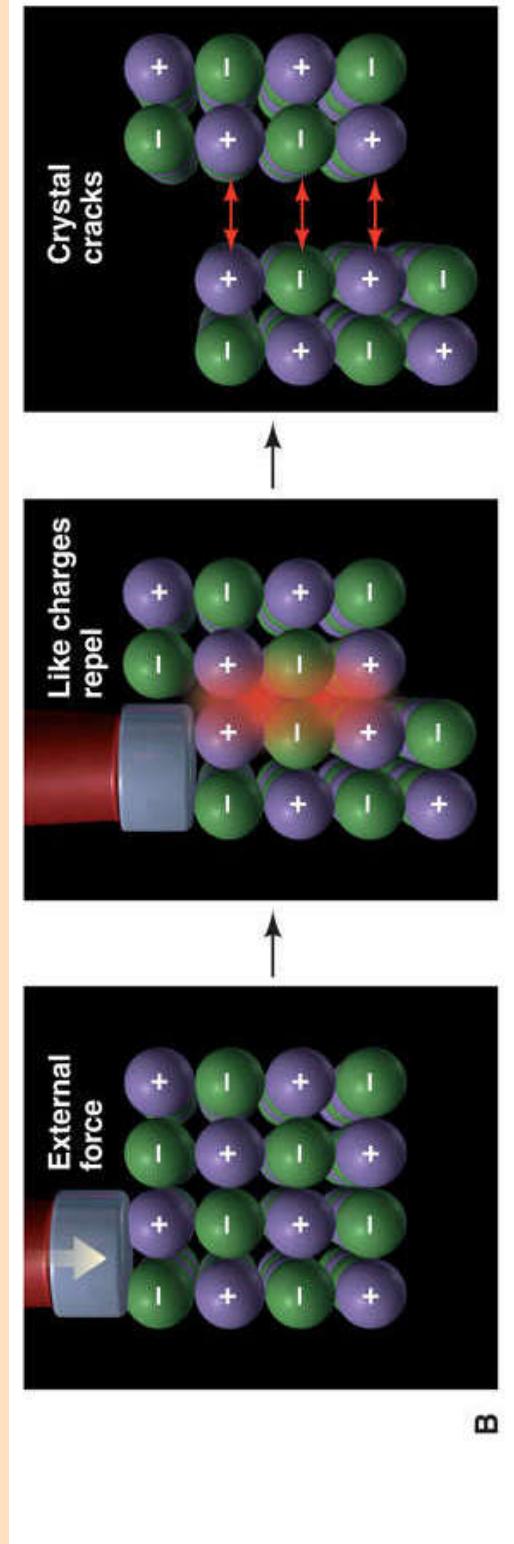
Properties of Ionic Compounds

- Ionic compounds tend to be hard, rigid, and brittle, with high melting points.
- Ionic compounds do not conduct electricity in the solid state at all.
 - In the solid state, the ions are fixed in place in the lattice and do not move.
- Ionic compounds conduct electricity when melted or dissolved.
 - In the liquid state or in solution, the ions are free to move and carry a current.

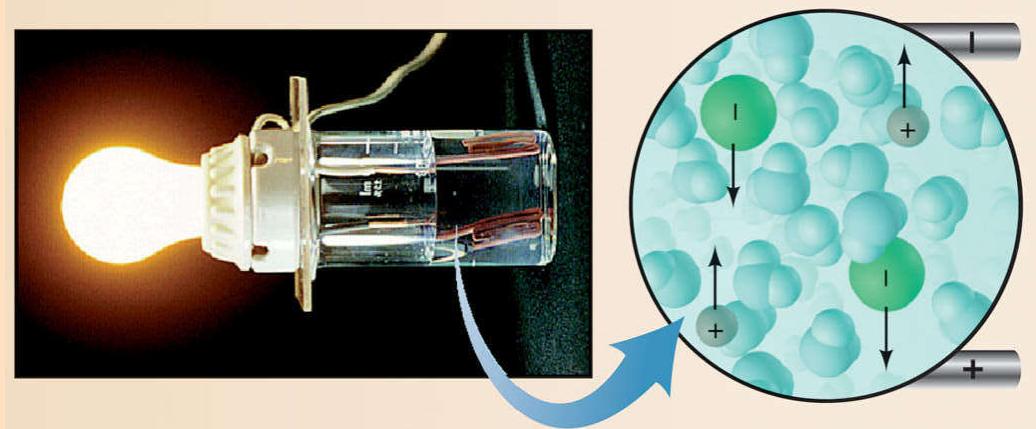
Why ionic compounds crack.



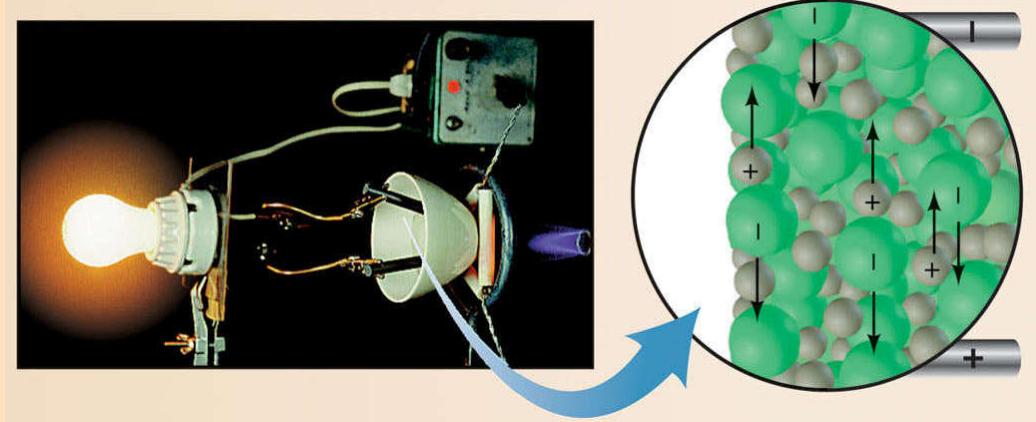
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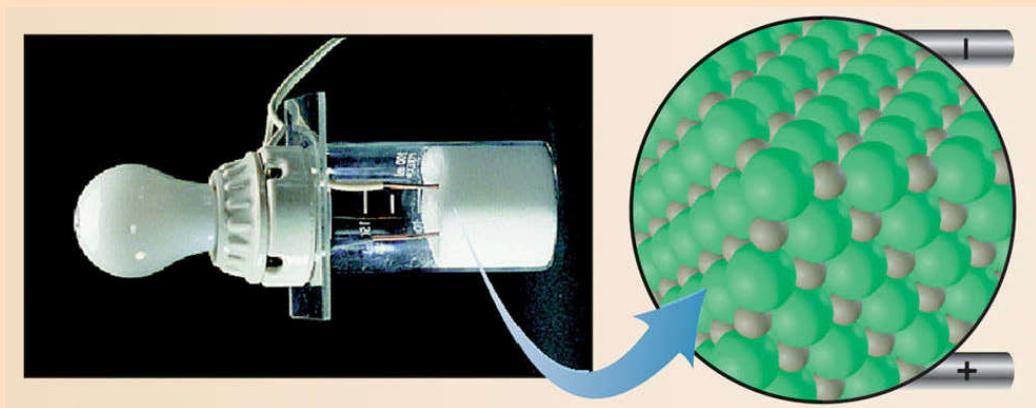
Electrical conductivity and ion mobility.



Ionic compound dissolved in water



Molten ionic compound

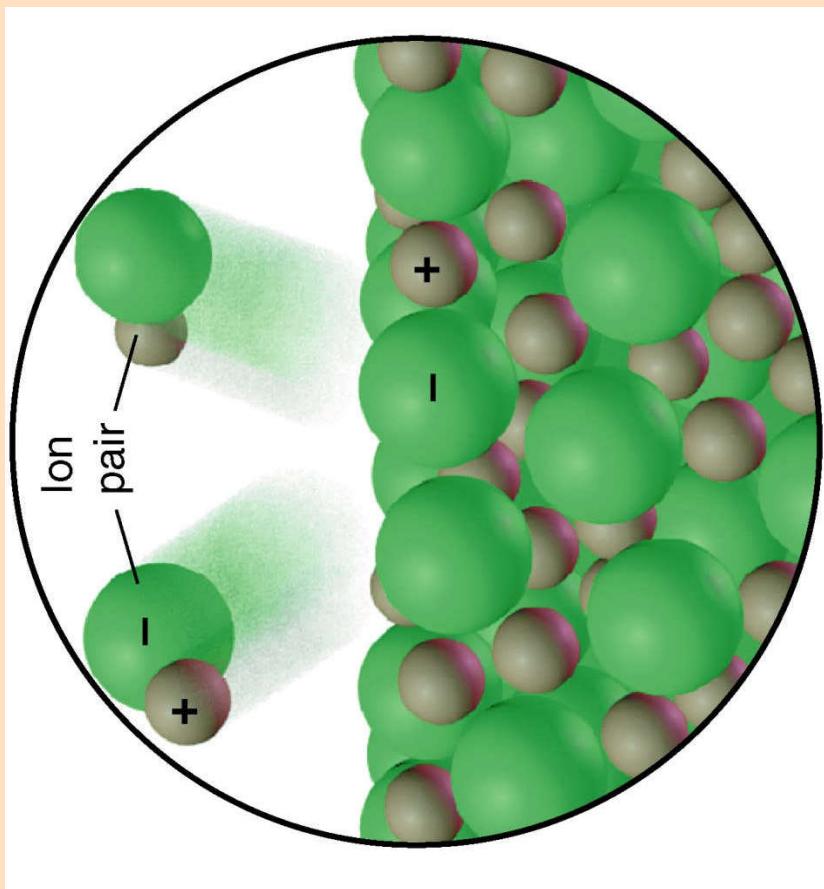


Solid ionic compound

Table 9.1 Melting and Boiling Points of Some Ionic Compounds

Compound	mp (°C)	bp (°C)
CsBr	636	1300
Nal	661	1304
MgCl ₂	714	1412
KBr	734	1435
CaCl ₂	782	>1600
NaCl	801	1413
LiF	845	1676
KF	858	1505
MgO	2852	3600

Ion pairs formed when an ionic compound vaporizes.

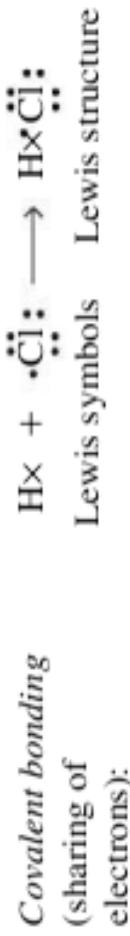
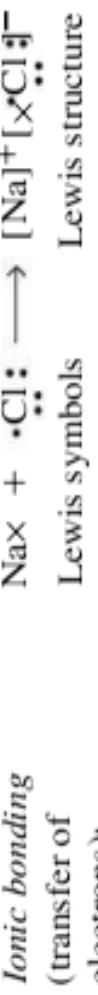


Interionic attraction ions are so strong that when an ionic compound is vaporized, ion pairs are formed.

Lewis Theory: An Overview

ideas associated with Lewis's theory follow:

1. Electrons, especially those of the outermost (valence) electronic shell, play a fundamental role in chemical bonding.
2. In some cases, electrons are *transferred* from one atom to another. Positive and negative ions are formed and attract each other through electrostatic forces called **ionic bonds**.
3. In other cases, one or more pairs of electrons are *shared* between atoms. A bond formed by the sharing of electrons between atoms is called a **covalent bond**.
4. Electrons are transferred or shared in such a way that each atom acquires an especially stable electron configuration. Usually this is a noble gas configuration, one with eight outer-shell electrons, or an **octet**.

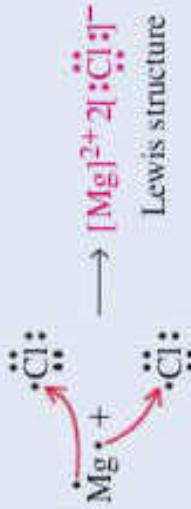


Write Lewis structures for the following compounds: (a) BaO; (b) MgCl₂; (c) aluminum oxide.

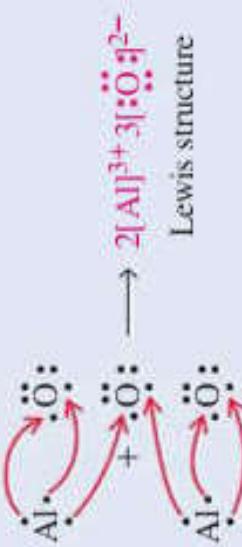
- (a) Ba loses two electrons, and O gains two.



- (b) A Cl atom can accept only one electron because it already has seven valence electrons. One more will give it a complete octet. Conversely, a Mg atom must lose two electrons to have the electron configuration of the noble gas neon. So two Cl atoms are required for each Mg atom.



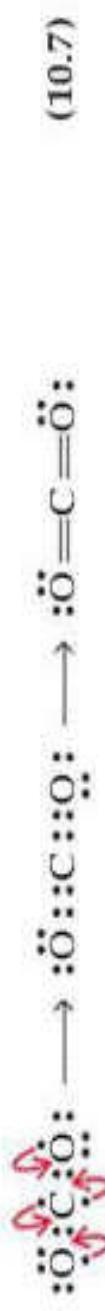
- (c) The formula of aluminum oxide follows directly from the Lewis structure. The combination of one Al atom, which loses three electrons, and one O atom, which gains two, leaves an excess of one lost electron. To match the numbers of electrons lost and gained, the formula unit must be based on *two* Al atoms and *three* O atoms.



First, let's apply the ideas about Lewis structures to CO_2 . From the Lewis symbols, we see that the C atom can share a valence electron with each O atom, thus forming two carbon-to-oxygen single bonds.

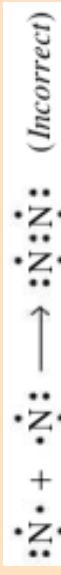


But this leaves the C atom and both O atoms still shy of an octet. The problem is solved by shifting the unpaired electrons into the region of the bond, as indicated by the red arrows.

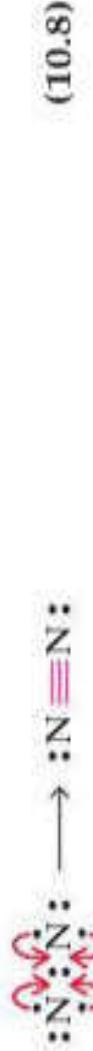


In Lewis structure (10.7), the bonded atoms are seen to share *two* pairs of electrons (a total of four electrons) between them—a **double covalent bond** ($=$).

Now let's try our hand at writing a Lewis structure for the N_2 molecule. Our first attempt might again involve a single covalent bond and the incorrect structure shown below.



Each N atom appears to have only six outer-shell electrons, not the expected eight. The situation can be corrected by bringing the four unpaired electrons into the region between the N atoms and using them for additional bond pairs. In all, we now show the sharing of *three* pairs of electrons between the N atoms. The bond between the N atoms in N_2 is a **triple covalent bond** (\equiv). Double and triple covalent bonds are known as **multiple covalent bonds**.



A Strategy for Writing Lewis Structures

At this point, let us incorporate a number of the ideas that we have considered so far into a specific approach to writing Lewis structures. This strategy is designed to give you a place to begin, as well as consecutive steps to follow to achieve a plausible Lewis structure.

1. Determine the total number of valence electrons that must appear in the structure.

Examples: In the *molecule* CH₃CH₂OH, there are 4 valence electrons for each C atom, or 8 for the two C atoms; 1 for each H atom, or 6 for the six H atoms; and 6 for the lone O atom. The total number of valence electrons in the Lewis structure of CH₃CH₂OH is

$$8 + 6 + 6 = 20$$

In the *polyatomic ion* PO₄³⁻, there are 5 valence electrons for the P atom and 6 for each O atom, or 24 for all four O atoms. To produce the charge of 3⁻, an additional 3 valence electrons must be brought into the structure. The total number of valence electrons in the Lewis structure of PO₄³⁻ is

$$5 + 24 + 3 = 32$$

In the *polyatomic ion* NH₄⁺, there are 5 valence electrons for the N atom and 1 for each H atom, or 4 for all four H atoms. To account for the charge of 1⁺, one of the electrons must be *lost*. The total number of valence electrons in NH₄⁺ is

$$5 + 4 - 1 = 8$$

2. Identify the central atom(s) and terminal atoms.
3. Write a plausible skeletal structure. Join the atoms in the skeletal structure by *single* covalent bonds (single dashes, representing two electrons each).
4. For each bond in the skeletal structure, subtract *two* from the total number of valence electrons.
5. With the valence electrons remaining, *first* complete the octets of the terminal atoms. *Then*, to the extent possible, complete the octets of the central

atom(s). If there are just enough valence electrons to complete octets for all the atoms, the structure at this point is a satisfactory Lewis structure.

- 6.** If one or more central atoms are left with an incomplete octet after step 5, move lone-pair electrons from one or more terminal atoms to form *multiple* covalent bonds to central atoms. Do this to the extent necessary to give all atoms complete octets, thereby producing a satisfactory Lewis structure.

Write a plausible Lewis structure for cyanogen, C_2N_2 , a poisonous gas used as a fumigant and rocket propellant.

Step 1. Determine the total number of valence electrons. Each of the two C atoms (group 14) has *four* valence electrons, and each of the two N atoms (group 15) has *five*. The total number of valence electrons is $4 + 4 + 5 + 5 = 18$.

Step 2. Identify the central atom(s) and terminal atoms. Because the C atoms have a lower electronegativity (2.5) than do the N atoms (3.0), C atoms are central atoms, and N atoms are terminal atoms.

Step 3. Write a plausible skeletal structure by joining atoms through *single* covalent bonds.



Step 4. Subtract *two* electrons for each bond in the skeletal structure. The three bonds in this structure account for 6 of the 18 valence electrons. This leaves 12 valence electrons to be assigned.

Step 5. Complete octets for the terminal N atoms, and to the extent possible, the central C atoms. The remaining 12 valence electrons are sufficient only to complete the octets of the N atoms.



Step 6. Move lone pairs of electrons from the terminal N atoms to form multiple bonds to the central C atoms. Each C atom has only four electrons in its valence shell and needs four more to complete an octet. Thus, each C atom requires two additional pairs of electrons, which it acquires if we move two lone pairs from each N atom into its bond with a C atom, as shown below.



Formal Charge

Instead of writing Lewis structure (10.14) for the nitronium ion in Example 10-6, we might have written the following structure.



Despite the fact that this structure satisfies the usual requirements—the correct number of valence electrons and an octet for each atom—we have marked it improbable because it fails in one additional requirement. Have you noticed that in our strategy for writing Lewis structures, once the total number of valence electrons has been determined, there is no need to keep track of which electrons came from which atoms? Nevertheless, after we have a plausible Lewis structure, we can go back and assess where each electron apparently came from, and in this way we can evaluate formal charges. **Formal charges (FC)** are apparent charges on certain atoms in a Lewis structure that arise when atoms have not contributed equal numbers of electrons to the covalent bonds joining them. In cases where more than one Lewis structure seems possible, formal charges are used to ascertain which sequence of atoms and arrangement of bonds is most satisfactory.