



## Models of Chemical Bonding

- Bonds are forces holding atoms or ions together
- Bonds form as a result of lowering of the total energy (energy of separated species is higher than that of bonded species)

### 9.1 Types of Bonding

- Bond formation is accompanied by rearrangement of valence electrons
- Complete transfer of electrons between metals (low  $I$ ) and nonmetals (high  $A$ )
  - Formation of ions → **ionic bonding**
  - Electrostatic attraction between oppositely charged ions

#### • Sharing of electrons between nonmetals (high $I$ , high $A$ )

- Formation of molecules → **covalent bonding**
- Attraction between the nuclei and the shared electrons
- The shared electrons are localized between the bonded atoms

#### • Sharing of electrons between metals (low $I$ , low $A$ )

- Formation of metallic solids → **metallic bonding**
- Attraction between metal cations and a “sea” of shared electrons
- The shared electrons are delocalized in the entire volume of the metal

### Lewis Symbols for Atoms and Ions

- Lewis symbol → chemical symbol + a dot for each valence electron

|   | 1A(1)  | 2A(2)  | 3A(13)     | 4A(14)     | 5A(15)     | 6A(16)     | 7A(17)     | 8A(18)     |
|---|--------|--------|------------|------------|------------|------------|------------|------------|
|   | $ns^1$ | $ns^2$ | $ns^2np^1$ | $ns^2np^2$ | $ns^2np^3$ | $ns^2np^4$ | $ns^2np^5$ | $ns^2np^6$ |
| 2 | • Li   | • Be • | • B •      | • C •      | •• N ••    | •• O ••    | •• F ••    | •• Ne ••   |
| 3 | • Na   | • Mg • | • Al •     | • Si •     | •• P ••    | •• S ••    | •• Cl ••   | •• Ar ••   |

- For metals, the # of dots equals the max. # of e<sup>s</sup> lost in cation formation

- For nonmetals, the # of unpaired dots equals the # of e<sup>s</sup> gained in anion formation or the # of covalent bonds the element forms

## 9.2 The Ionic Bonding Model

- **The octet rule** – when atoms bond, they gain, lose, or share electrons in order to attain an **octet** (eight) or a **duplet** (two) configuration of a noble gas

- Most  $s$ - and  $p$ -block metals form cations by losing all valence electrons (losing all dots)
  - $s$ -block metals achieve the electron configuration of the previous noble gas;  $p$ -block metals achieve a pseudo-noble gas electron configuration
- Nonmetals form anions by gaining electrons until they reach the configuration of the next noble gas

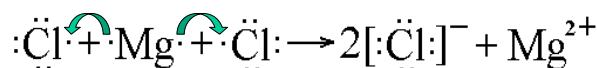
- Electrons lost by the metal are gained by the nonmetal
- Both positive and negative ions reach **octet** (or **duplet**) electron configurations

### Example:

Predict the formula of magnesium chloride using Lewis structures.

**Mg** – group 2 → 2 valence e<sup>-</sup> → loss of 2 e<sup>-</sup>

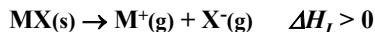
**Cl** – group 17 → 7 valence e<sup>-</sup> → gain of 1 e<sup>-</sup>



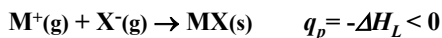
**Formula:** MgCl<sub>2</sub>

## Lattice Energy (Lattice Enthalpy)

- Lattice enthalpy** ( $\Delta H_L$ ) – the enthalpy change for the separation of **1 mol** of an ionic compound into isolated gaseous ions



- At constant pressure the lattice enthalpy is numerically equal to the heat of formation of one mol of the ionic compound from gaseous ions



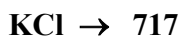
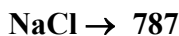
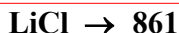
- The heat released in the formation comes from the potential energy drop due to the attraction between the oppositely charged ions

$$E_p \propto \frac{q_1 q_2}{r_{12}}$$

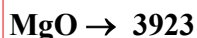
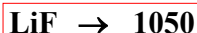
- Potential energy of interaction between two ions with charges  $q_1$  and  $q_2$  separated by a distance  $r_{12}$
- ⇒ The lattice enthalpy increases with increasing the charge of the ions and decreasing the distance between them (decreasing the size of the ions)
- The charge factor is more dominant
- The size factor becomes important only when comparing ionic compounds with equivalent ionic charges

## Examples:

Lattice enthalpies in kJ/mol:



↑  
Size factor –  $\Delta H_L$  decreases moderately with increasing the size of the ion (Li<sup>+</sup> < Na<sup>+</sup> < K<sup>+</sup>)



↑  
Charge factor –  $\Delta H_L$  increases greatly with increasing the charges of the ions (Li<sup>+</sup>, F<sup>-</sup> Mg<sup>2+</sup>, O<sup>2-</sup>)

~x4

- Lattice enthalpies are measured indirectly through Hess's law using the **Born-Haber cycle**

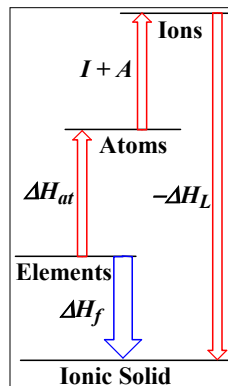
Atomization of elements →  $\Delta H_{at}$   
(formation of gas phase atoms)

Ionization (cations) →  $I$

Ionization (anions) →  $A$

Formation of solid (from gaseous ions) →  $-\Delta H_L$

Formation of solid (from elements) →  $\Delta H_f$



$$\Delta H_f = \Delta H_{at} + (I + A) + (-\Delta H_L)$$

**Example:** Calculate the lattice enthalpy of KBr

$$\Delta H_f = \Delta H_{at} + (I + A) + (-\Delta H_L)$$

$$\Delta H_L = \Delta H_{at} + I + A - \Delta H_f$$

$$\Delta H_L = \Delta H_f(\text{K, g}) + \Delta H_f(\text{Br, g}) + I(\text{K}) + A(\text{Br}) - \Delta H_f(\text{KBr, s})$$

Data from Appendix B and Figures 8.12 & 8.14:

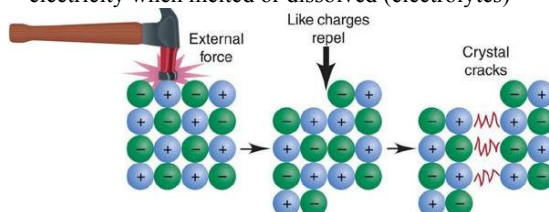
$$\Delta H_L = (89) + (112) + (419) + (-325) - (-394) \text{ kJ/mol}$$

$$\Delta H_L = 689 \text{ kJ/mol}$$

- The Born-Haber cycle shows that the energy required for atoms to lose or gain electrons is supplied by the lattice energy of ionic solids

## The Properties of Ionic Compounds

- Ionic solids are crystalline solids (regular three-dimensional arrays of stacked ions)
  - High melting and boiling points – very strong attractions between the ions (hard to separate)
  - Hard, rigid and brittle
  - Do not conduct electricity in the solid state, but conduct electricity when melted or dissolved (electrolytes)



## 9.3 The Covalent Bonding Model

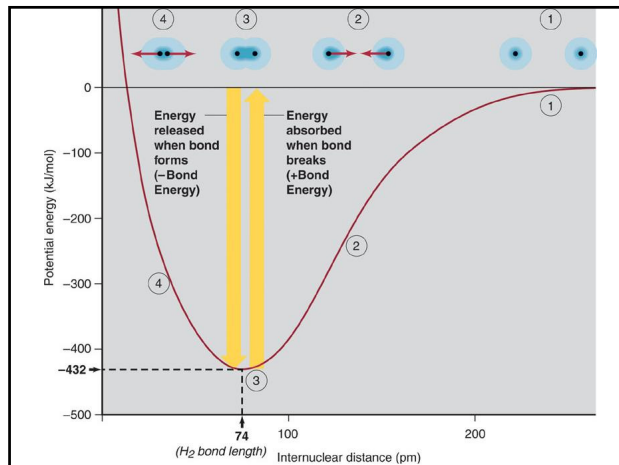
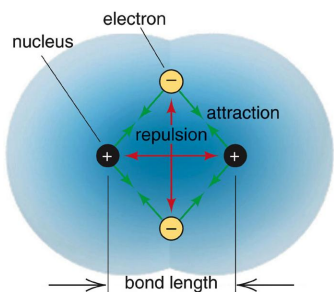
### Formation of covalent bonds

- **Covalent bond** – a result of atoms sharing a pair of electrons



- ❖ The electron density between the nuclei increases

- ❖ The two positive nuclei are attracted to the negative charge of the shared pair of  $e^-$



- **Octet rule** – in covalent bonding atoms share pairs of electrons until they reach **octet** (or **duplet**) configurations of noble gases

- The number of shared  $e^-$  pairs equals the number of electrons an atom needs in order to complete its octet (or duplet) structure

- **Lewis structures** – diagrams showing the distribution of electrons in a molecule

- **Shared (bonding)**  $e^-$  pairs – between the atoms (can be expressed as lines representing bonds)

- **Lone**  $e^-$  pairs – not involved in bonding (not shared)

### Example:

Write the Lewis structures of HCl and  $\text{Cl}_2$  and determine the number of shared and lone  $e^-$  pairs.



**3 lone pairs at Cl and 1 bonding (shared) pair**



**6 lone pairs at Cl and 1 bonding (shared) pair**

### Types of bonds

- **Single bond** – a single bonding (shared) pair
- **Multiple bonds** – double or triple bonds (2 or 3 bonding pairs)

- **Bond order** – number of bonds linking two atoms



### Bond Energy (Enthalpy) and Bond Length

- **Bond enthalpy ( $\Delta H_B$ )** – the enthalpy change for the dissociation of one mole bonds from molecules in the gas phase



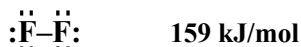
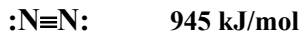
- $\Delta H_B$  is a measure of the **strength** and **stability** of chemical bonds

Large  $\Delta H_B \Leftrightarrow$  stronger bonds

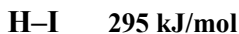
- The strength of the bond between a given pair of atoms varies slightly in different molecules

- **Average bond enthalpies ( $\Delta H_B$ )** – averaged over many compounds

- Bond strength ( $\Delta H_B$ ) increases with increasing the bond order

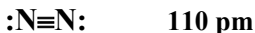


- In general, bond strength ( $\Delta H_B$ ) increases with decreasing the size of the bonded atoms



- Bond length** – the distance between the nuclei of two bonded atoms

– Bond lengths increase with decreasing the bond order



– Bond lengths increase with increasing the size of the bonded atoms



– Average bond lengths – averaged over many comp.

- In general, a shorter bond is a stronger bond

**Table 9.4** The Relation of Bond Order, Bond Length, and Bond Energy

| Bond | Bond Order | Average Bond Length (pm) | Average Bond Energy (kJ/mol) |
|------|------------|--------------------------|------------------------------|
| C–O  | 1          | 143                      | 358                          |
| C=O  | 2          | 123                      | 745                          |
| C≡O  | 3          | 113                      | 1070                         |
| C–C  | 1          | 154                      | 347                          |
| C=C  | 2          | 134                      | 614                          |
| C≡C  | 3          | 121                      | 839                          |
| N–N  | 1          | 146                      | 160                          |
| N=N  | 2          | 122                      | 418                          |
| N≡N  | 3          | 110                      | 945                          |

- Covalent radii** of atoms – contributions of individual atoms to the lengths of covalent bonds (average values are tabulated and depend on the bond order)

### Example:

Rank the following bonds by their strengths and lengths: C–C, C=N, C≡N, C–S

**Bond strength:**  $\text{C}\equiv\text{N} > \text{C}=\text{N} > \text{C}-\text{C} > \text{C}-\text{S}$



**Bond length:**  $\text{C}-\text{S} > \text{C}-\text{C} > \text{C}=\text{N} > \text{C}\equiv\text{N}$

## The Properties of Covalent Compounds

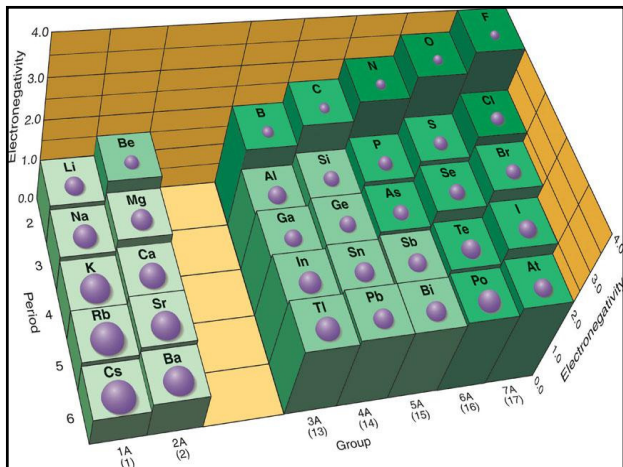
- Molecular compounds** – most covalent compounds consist of molecules (water, sugar, ...)
  - Low melting and boiling points – the forces holding the molecules together are much weaker than the covalent bonds inside the molecules
  - Soft solids (often gases or liquids)
  - Poor electrical conductors in the solid state as well as when melted or dissolved (non-electrolytes)
- Covalent network solids** – three-dimensional arrays of covalently bonded atoms (diamond, quartz, ...)
  - Very high melting and boiling points – very strong covalent bonds hold the atoms together
  - Extremely hard
  - Poor electrical conductors

## 9.5 Electronegativity and Bond Polarity

– There is no clear cut between ionic and covalent bonds – pure ionic and pure covalent bonds are only limiting models

### Electronegativity

- Electronegativity (EN)** – the ability of an atom to attract the shared electrons in a bond (electron-pulling power)
  - In general, EN increases with increasing the ionization energy and electron affinity of atoms
  - EN increases **up** and to the **right** in the periodic table (opposite to the atomic size trend)



• EN can be used to determine the **oxidation numbers** of elements in compounds

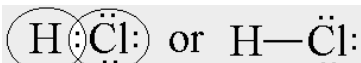
- The more electronegative atom in a bond is assigned all shared (bonding) electrons
- Each atom in a bond is assigned all unshared (lone pair) electrons

$$\Rightarrow \text{Ox\#} = (\#\text{valence } e^-) - (\#\text{shared } e^- + \#\text{unshared } e^-)$$

**Example: HCl** (Cl is more EN than H)

$$\text{Cl} \rightarrow \text{Ox\#} = 7 - (2 + 6) = -1$$

$$\text{H} \rightarrow \text{Ox\#} = 1 - (0 + 0) = +1$$



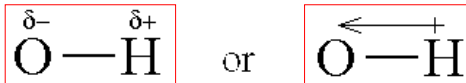
## Polar Covalent Bonds

• The EN difference ( $\Delta\text{EN}$ ) between the bonded atoms determines the character of a covalent bond

- **Nonpolar covalent bond** -  $\Delta\text{EN} = 0$  → equal sharing of the bonding electrons (**H-H**, **F-F**, ...)

- **Polar covalent bond** -  $\Delta\text{EN} > 0$  → unequal sharing of the bonding electrons (**H-O**, **C-F**, ...)

- The more electronegative atoms acquire **partial negative charges** (have greater share of the bonding electrons)
- The less electronegative atoms acquire **partial positive charges**



Formation of a **bond dipole** expressed by a **polar arrow**

- Polar arrow points from ( $\delta+$ ) to ( $\delta-$ )
- Bond polarity increases with increasing  $\Delta\text{EN}$

**Example:**

Which of the following bonds is more polar?

**O-H** (in **H<sub>2</sub>O**) or **N-H** (in **NH<sub>3</sub>**)

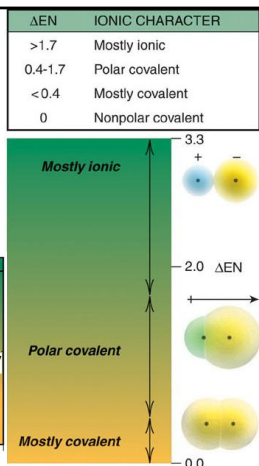
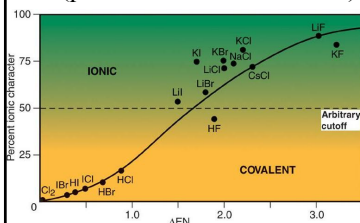
**EN order** → **H < N < O**

⇒  $\Delta\text{EN}(\text{O-H}) > \Delta\text{EN}(\text{N-H})$

⇒ **the O-H bond is more polar**

## Partial ionic character of polar covalent bonds

- Due to the partial charges
- Ionic character increases with increasing of  $\Delta\text{EN}$
- No bonds are 100% ionic (partial covalent character)



|  |   |  |  |  |  |   |
|--|---|--|--|--|--|---|
| Sodium chloride<br>NaCl                            | Magnesium chloride<br>MgCl <sub>2</sub>                 | Aluminum chloride<br>AlCl <sub>3</sub>   | Silicon tetrachloride<br>SiCl <sub>4</sub>   | Phosphorus trichloride<br>PCl <sub>3</sub>   | Disulfur dichloride<br>S <sub>2</sub> Cl <sub>2</sub>  | Chlorine<br>Cl <sub>2</sub>   |
| $\text{Na}^+ + \text{:}\ddot{\text{Cl}}\text{:}^-$ | $\text{Mg}^{2+} + 2 \text{:}\ddot{\text{Cl}}\text{:}^-$ | $\begin{array}{c} \text{:}\ddot{\text{Cl}}\text{:} \quad \text{:}\ddot{\text{Cl}}\text{:} \quad \text{:}\ddot{\text{Cl}}\text{:} \\   \quad   \quad   \\ \text{Al} \\   \quad   \quad   \\ \text{:}\ddot{\text{Cl}}\text{:} \quad \text{:}\ddot{\text{Cl}}\text{:} \quad \text{:}\ddot{\text{Cl}}\text{:} \end{array}$ | $\begin{array}{c} \text{:}\ddot{\text{Cl}}\text{:} \quad \text{:}\ddot{\text{Cl}}\text{:} \quad \text{:}\ddot{\text{Cl}}\text{:} \\   \quad   \quad   \\ \text{Si} \\   \quad   \quad   \\ \text{:}\ddot{\text{Cl}}\text{:} \quad \text{:}\ddot{\text{Cl}}\text{:} \quad \text{:}\ddot{\text{Cl}}\text{:} \end{array}$ | $\begin{array}{c} \text{:}\ddot{\text{Cl}}\text{:} \quad \text{:}\ddot{\text{P}}\text{:} \quad \text{:}\ddot{\text{Cl}}\text{:} \\   \\ \text{Cl} \end{array}$ | $\begin{array}{c} \text{:}\ddot{\text{Cl}}\text{:} \quad \text{:}\ddot{\text{S}}\text{:} \quad \text{:}\ddot{\text{S}}\text{:} \quad \text{:}\ddot{\text{Cl}}\text{:} \\   \quad   \\ \text{Cl} \quad \text{Cl} \end{array}$ | $\text{:}\ddot{\text{Cl}}\text{:} \quad \text{:}\ddot{\text{Cl}}\text{:}$ |
| $\Delta\text{EN} = 2.1$                            | $\Delta\text{EN} = 1.8$                                 | $\Delta\text{EN} = 1.5$  | $\Delta\text{EN} = 1.2$  | $\Delta\text{EN} = 0.9$  | $\Delta\text{EN} = 0.5$  | $\Delta\text{EN} = 0$   |

## 9.6 Metallic Bonding (see page 382 in textbook)

### The Electron-sea Model

- A metallic solid can be viewed as an array of metal cations (nuclei + core electrons) attracted by a sea of their valence electrons
  - The valence electrons are delocalized (shared between all atoms)
- **Properties of metals**
  - **Good electrical and heat conductors** – due to the mobility of the electron-sea
  - **Moderately high melting points** – the attractions between the cations and the electron-sea are not greatly disturbed by melting

- **High boiling points** – the metal ions and electrons have to be separated
- **Malleable and ductile** – metal cations can slide past each other without disturbing the interaction with the electron-sea too much

