CH-110 Advanced General Chemistry I

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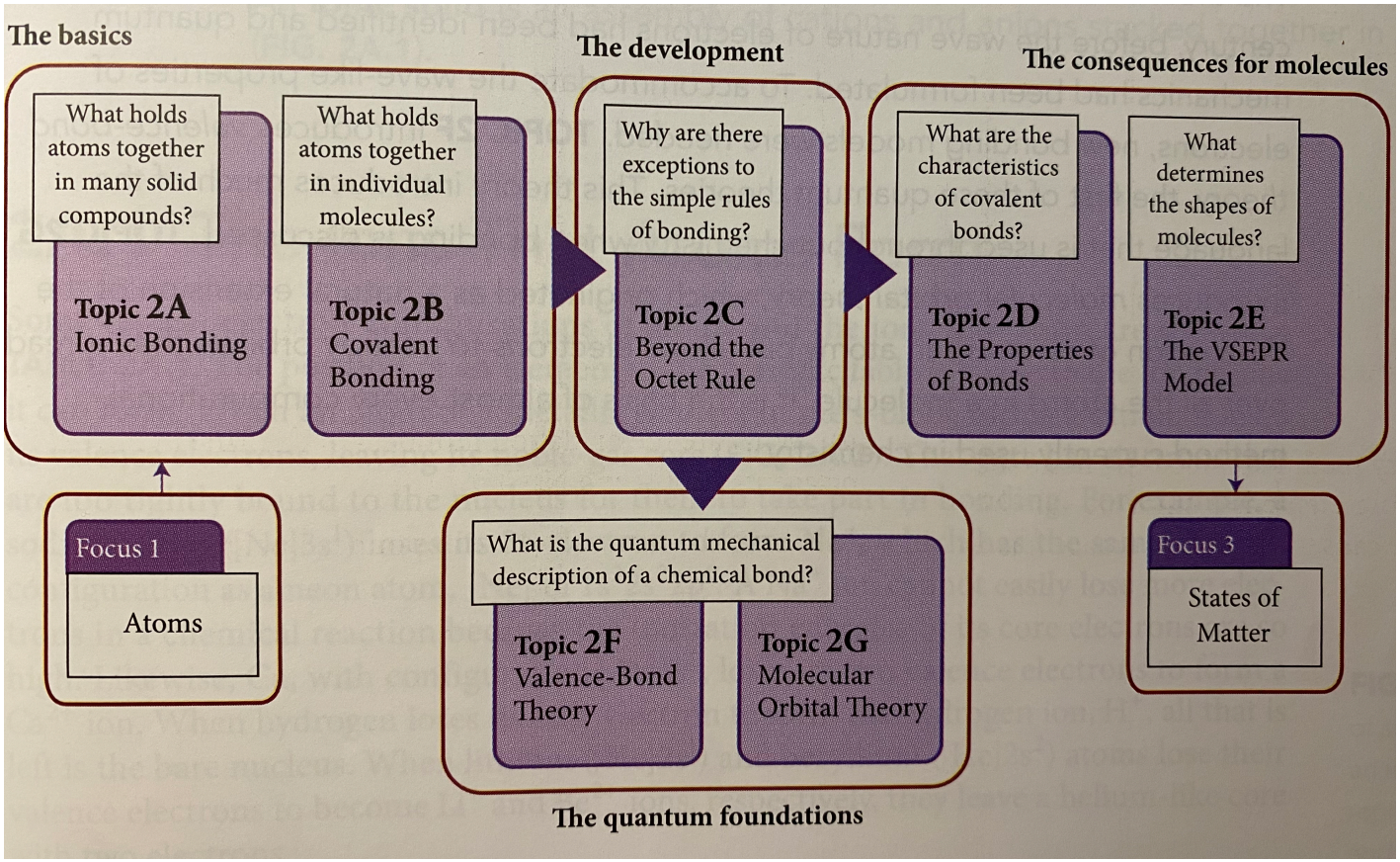
Overview Chapter 2 (Focus 2: Bonds Between Atoms)



The Properties of Bonds

Topic 2D

Topic 2D.1 Correcting the covalent model: electronegativity
Topic 2D.2 Correcting the ionic model: polarizability
Topic 2D.3 Bond strengths
Topic 2D.4 Bond lengths

WHY DO YOU NEED TO KNOW THIS MATERIAL?

- Properties of bonds vary widely. Variations in bond strength, bond length, and the distribution of electrons in a bond, are used to explain the physical and chemical properties of molecules.

WHAT DO YOU NEED TO KNOW ALREADY?

- Periodic trends (Topic 1F)
- Concept of resonance (Topic 2B)
- Role of electron-pair sharing in covalent bonding (Topic 2B)

Correcting the Covalent Model: Electronegativity

Topic 2D.1

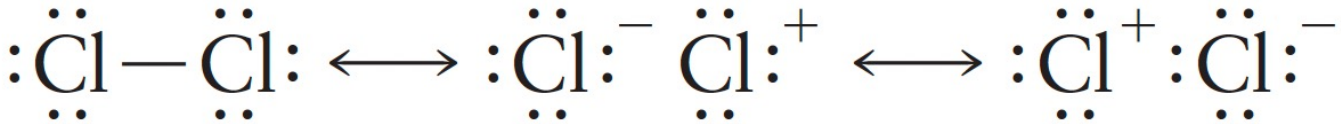
2D.1 Correcting the covalent model: electronegativity

Two extremes

Many compounds exist
somewhere in the middle

2D.1 Correcting the covalent model: electronegativity

Two extremes

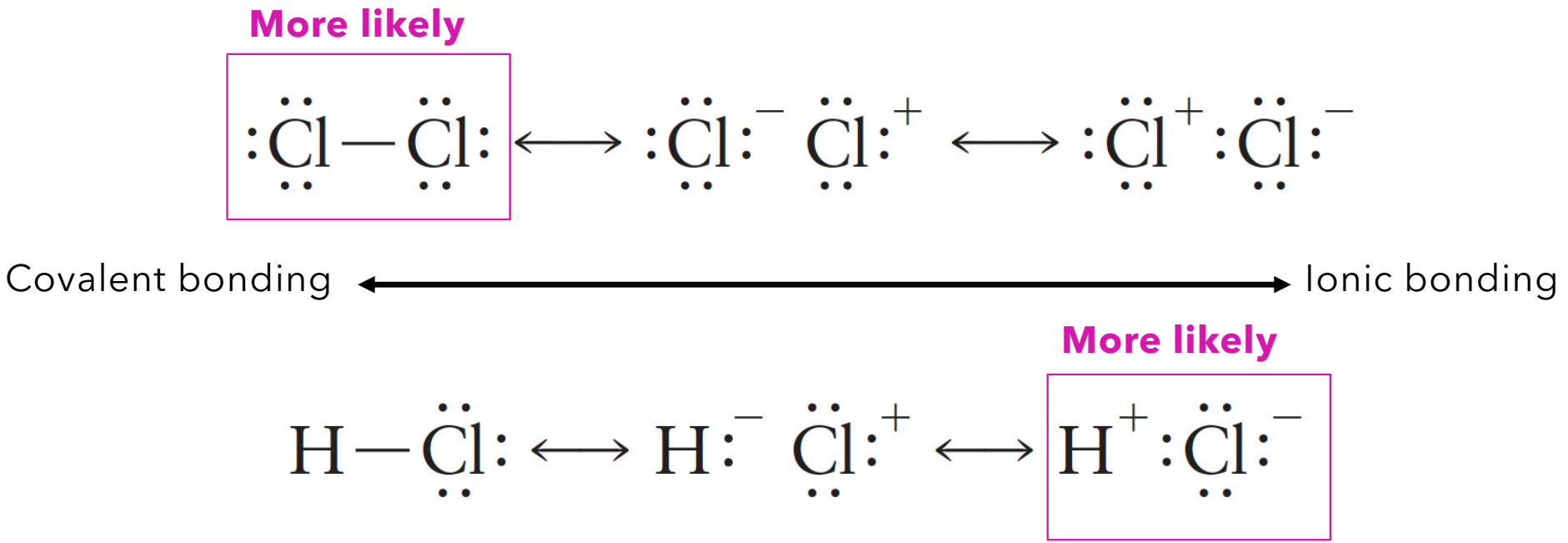


Covalent bonding ⟷ Ionic bonding

All molecules should be viewed as **resonance hybrids of purely covalent and purely ionic structures**

2D.1 Correcting the covalent model: electronegativity

Two extremes



2D.1 Correcting the covalent model: electronegativity

Partial charges

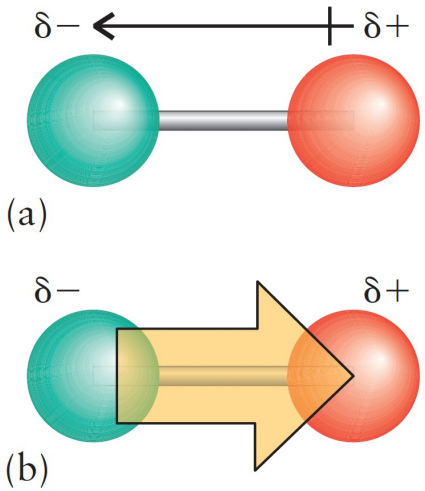
- Outcome of resonance favoring in H–Cl: small negative charge on Cl, small positive charge on H (**partial charges**)

$$^{\delta+}\mathrm{H}\text{—}\mathrm{Cl}^{\delta-}$$

- A bond with nonzero partial charge: **polar covalent bond**
- A bond with zero partial charge: **nonpolar bond**

2D.1 Correcting the covalent model: electronegativity

Electric dipole



- **Partial charges** on the two atoms in polar covalent bond form **an electric dipole.**

(a) Dipole represented by arrow that points to negative partial charge

(b) Modern convention (used here): arrows point to positive partial charge

- **The electric dipole moment** (μ) describes the magnitude of an electric dipole, units: debye (D)

2D.1 Correcting the covalent model: electronegativity

Electronegativity (χ): Pauling vs. Mullikan

Electronegativity (χ) : **the electron-pulling power of an atom in a molecule**

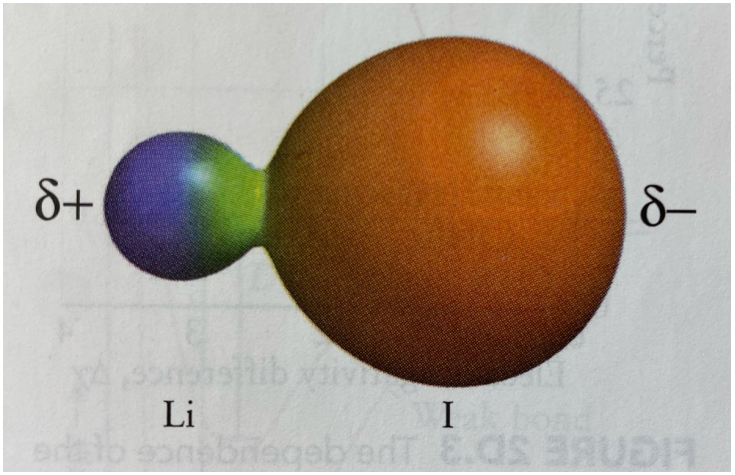


Figure 2D.1

2D.1 Correcting the covalent model: electronegativity

Electronegativity (χ): Pauling vs. Mullikan

- Pauling's electronegativities were based on dissociation energies between bonds.
- For two elements, A and B, what are the energies needed to break bonds A–A, B–B, and A–B.
- **Pauling** defined the difference in electronegativity of the two elements A and B as:

$$|\chi_A - \chi_B| = \left\{D(A-B) - \frac{1}{2}[D(A-A) + D(B-B)]\right\}$$ (no need to know by heart)

- **Mullikan** (see Topic 1F.5) used a different strategy:

$$\chi = \frac{1}{2}(I_I + E_{ea})$$

Pauling and Mullikan's electronegativities are **qualitatively similar.**

2D.1 Correcting the covalent model: electronegativity

Electronegativity (χ): Pauling values

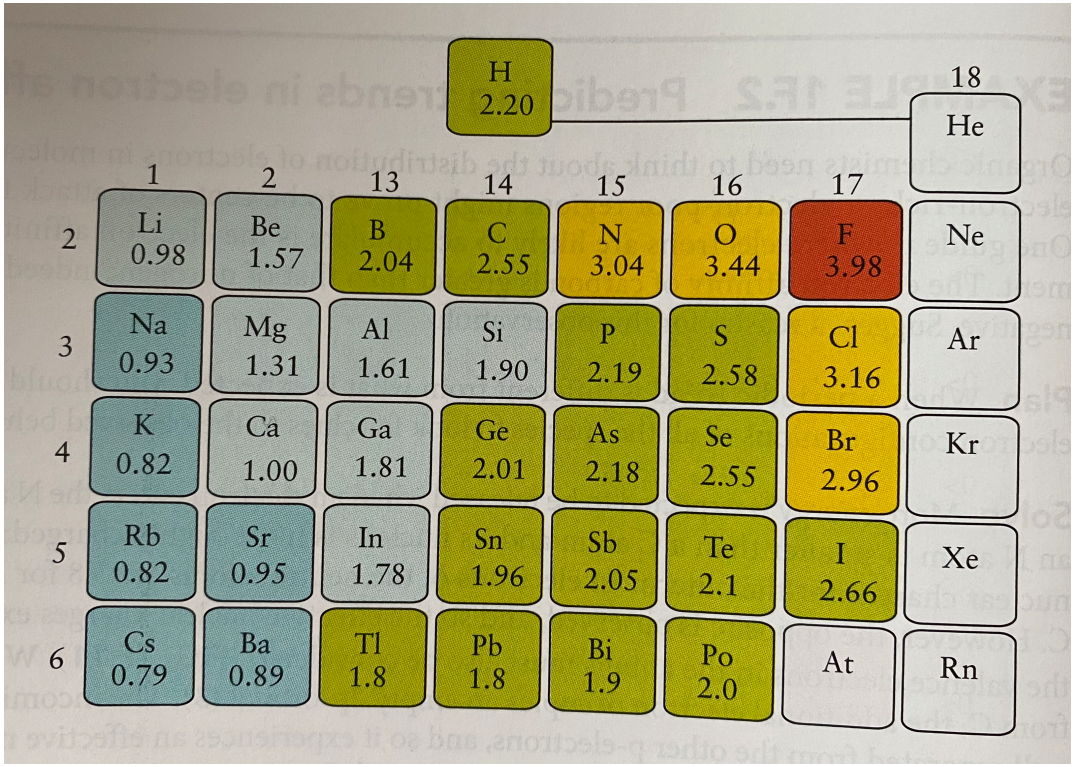


Figure 1F.12 and 2D.2

- Elements with **high ionization energies and high electron affinities**: highly electronegative
- Elements **with low ionization energies and low electron affinities**: low electronegativity.
- Careful: electropositive is used for a different concept and is NOT the opposite of electronegative.

2D.1 Correcting the covalent model: electronegativity

Two extremes

Small difference in electronegativity between atoms → small partial charge → resulting dipole moment is small

Covalent bond

Large difference in electronegativity between atoms → high partial charge → resulting dipole moment is large

Ionic bond

Continuum

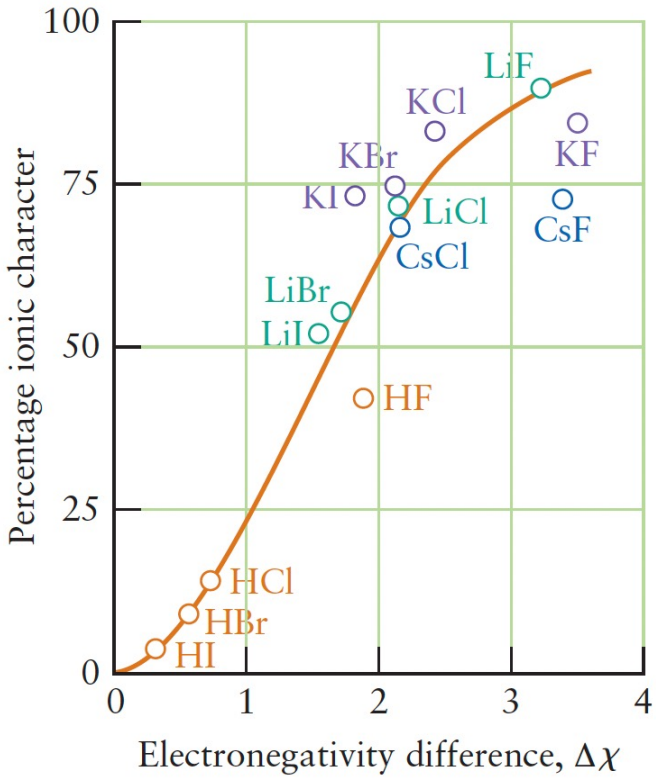
No sharp dividing lines

2D.1 Correcting the covalent model: electronegativity

Rules of thumb for A-B bonds:

$(\chi_A - \chi_B) \geq 2$:	Bond is *essentially* **ionic**
$0.5 \leq (\chi_A - \chi_B) \leq 1.5$:	Bond is **polar covalent**
$(\chi_A - \chi_B) \leq 0.5$:	Bond is *essentially* **covalent**

Figure 2D.3



2D.1 Correcting the covalent model: electronegativity

Self-test 2D.1B

- In which of the following compounds to the bonds have greater ionic character: (a) CO_2 or (b) NO_2?

2D.1 Correcting the covalent model: electronegativity

Summary

Electronegativity is a measure of the pulling power of an atom on the electrons in a bond. A **polar covalent bond** is a bond between two atoms with partial electric charges arising from their difference in electronegativity. The presence of partial charges can give rise to an electric dipole moment.

Correcting the Ionic Model: Polarizability

Topic 2D.2

2D.2 Correcting the ionic model: polarizability

From the perspective of ionic bonds

- All have some covalent character.
- Monatomic anions (Cl^-) next to cations (Na^+): cation's positive charge pulls on anion's electrons
- Electron cloud becomes polarized
- Distortion of spherical electron cloud

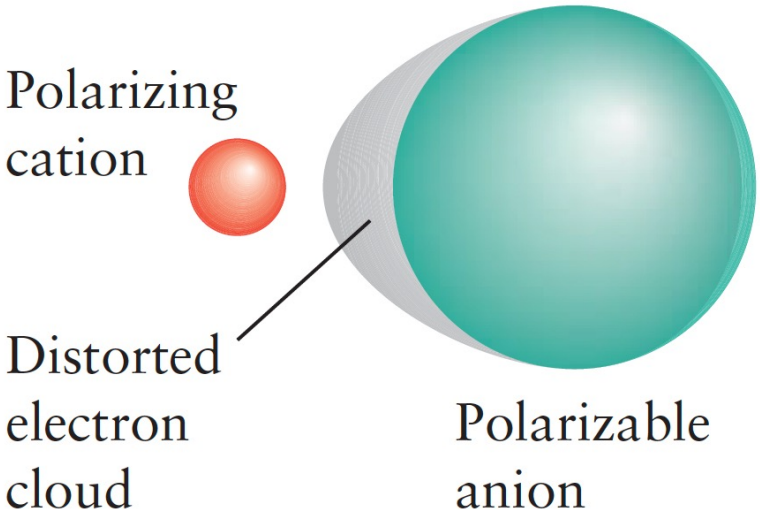


Figure 2D.4

2D.2 Correcting the ionic model: polarizability

Polarizable atoms and ions

- If atoms and ions have electron clouds that readily undergo large distortion, they are said to be **polarizable**.
- Examples: Large anions, e.g. iodide ion (I^-), Br^-, Cl^-, I, Br, Cl

2D.2 Correcting the ionic model: polarizability

Polarizing power

- Atoms and ions that cause large distortions are said to be **polarizing**.
- Increases as size decreases and increases as charge of cation increases
- Examples: Small and highly charged cations, Li^{+}, Be^{2+}, Mg^{2+}, and Al^{3+}

2D.2 Correcting the ionic model: polarizability

Trends

→ Cations get smaller and more highly charged from left to right → more polarizing

For example: Be^{2+} is more polarizing than Li^{+}

→ Cations get larger down a group → less polarizing

For example, Na^{+} is less strongly polarizing than Li^{+}, Mg^{2+} is less polarizing than Be^{2+}

Diagonal relationships: Polarizing power increases from Li^{+} to Be^{2+}, decreases from Be^{2+} to Mg^{2+}. Li^{+} and Mg^{2+} should be similar.

2D.1 Correcting the covalent model: electronegativity

Self-test 2D.2B

- In which of the compounds CaS and CaO do the bonds have greater covalent character?

2D.2 Correcting the ionic model: polarizability

Summary

Compounds composed of highly polarizing cations and highly polarizable anions have significant covalent character in their bonding.

Bond Strengths

Topic 2D.3

2D.3 Bond strengths

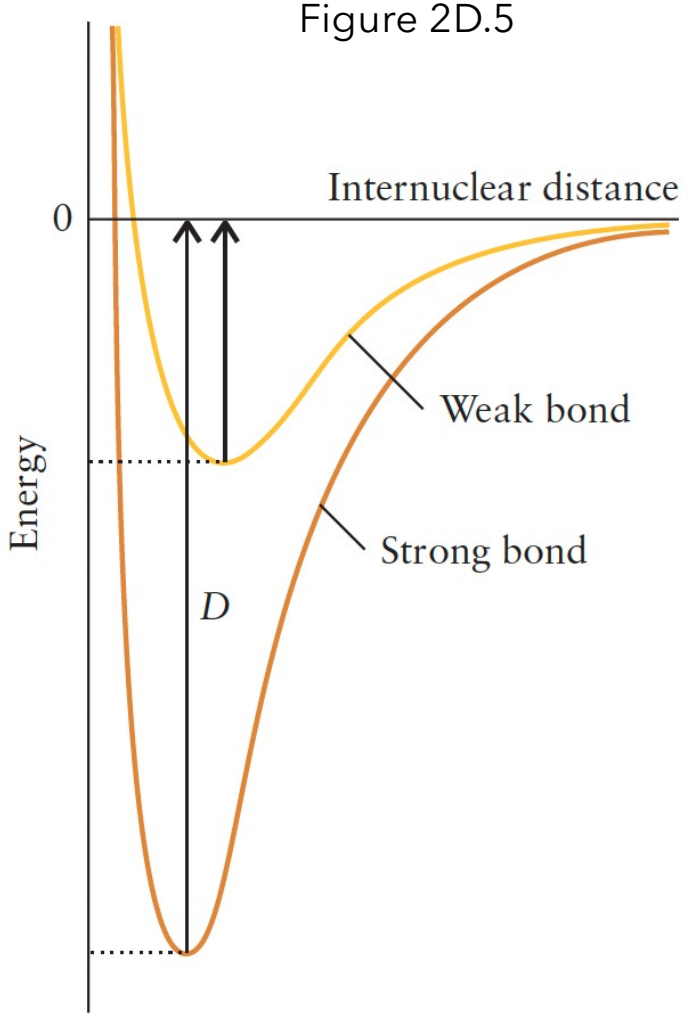
Dissociation energy

- The strength of a bond is measured by its dissociation energy, *D*, the energy required to separate the bonded atoms completely.
- Depth of the well
- Each atom retains one electron:

$$\mathrm{H{-}Cl(g)} \rightarrow \cdot\,\mathrm{H(g)} + \cdot\,\mathrm{Cl(g)}$$

- Strongest known bond between nonmetals: Carbon monoxide triple bond: C≡O (1062 kJ/mol)
- Weakest bond: iodine in I_2 (139 kJ/mol)

Figure 2D.5



2D.3 Bond strengths

Dissociation energies of diatomic molecules

TABLE 2.3 Bond Dissociation Energies of Diatomic Molecules ($kJ \cdot mol^{-1}$)

Molecule	Bond dissociation energy
H_2	424
N_2	932
O_2	484
CO	1062
F_2	146
Cl_2	230
Br_2	181
I_2	139
HF	543
HCl	419
HBr	354
HI	287

- Actual dissociation energies of **diatomic molecules**

TRENDS (look at Lewis structures)

- $N_2 > O_2 > F_2$: triple > double > single bond:

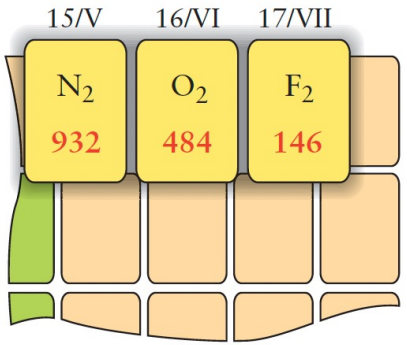


Figure 2D.6

2D.3 Bond strengths

C—C vs. C=C vs. C≡C

- A double bond is not twice as strong as a single bond: One C=C bond (623 kJ/mol) vs. two single C–C bonds (696 kJ/mol)
- One C≡C bond (837 kJ/mol) vs. three single C–C bonds (1044 kJ/mol)
- **Why is there a loss in energy for multiple bonds?** Repulsions between electron pairs in a multiple bond, not quite as effective at bonding as one pair in a single bond

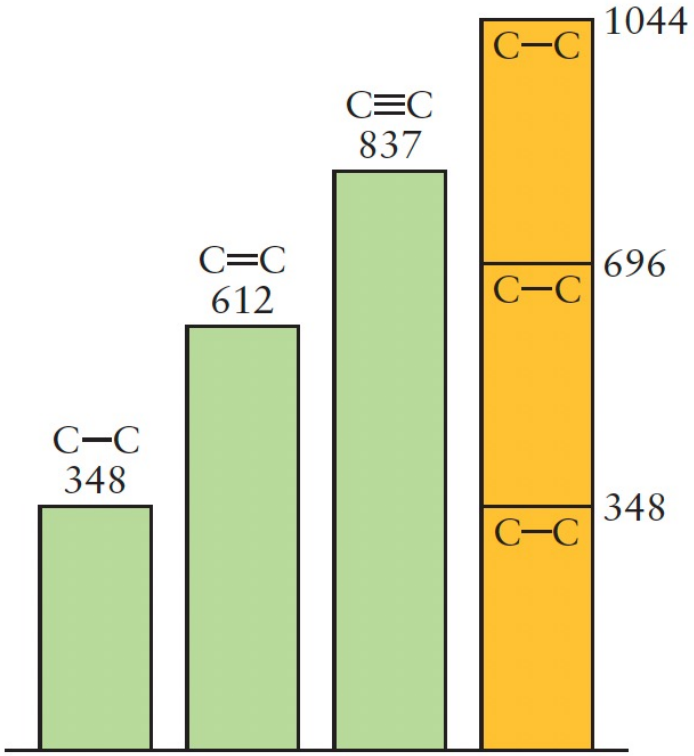


Figure 2D.7

2D.3 Bond strengths

Average bond dissociation energies

- Average for one type of bond, precise bond dissociation energy depends on context
- For example, C–H bond could be in methane (CH_4), ethane (C_2H_6) and ethene (C_2H_4)

TABLE 2.4 Average Bond Dissociation Energies ($kJ \cdot mol^{-1}$)

Bond	Average bond dissociation energy	Bond	Average bond dissociation energy
C—H	412	C—I	238
C—C	348	N—H	388
C═C	612	N—N	163
C···C*	518	N═N	409
C≡C	837	N—O	210
C—O	360	N═O	630
C═O	743	N—F	195
C—N	305	N—Cl	381
C—F	484	O—H	463
C—Cl	338	O—O	157
C—Br	276		

*In benzene.

2D.3 Bond strengths

Summary: **Factors that influence bond strength**

- Bond order: C≡C > C=C > C–C
- Resonance: C=C > C–C(benzene) > C–C
- Lone pairs on neighbouring atoms: F–F < H–H
- Atomic radii: HF > HCl > HBr > HI

The smaller the radius, the stronger the bond.

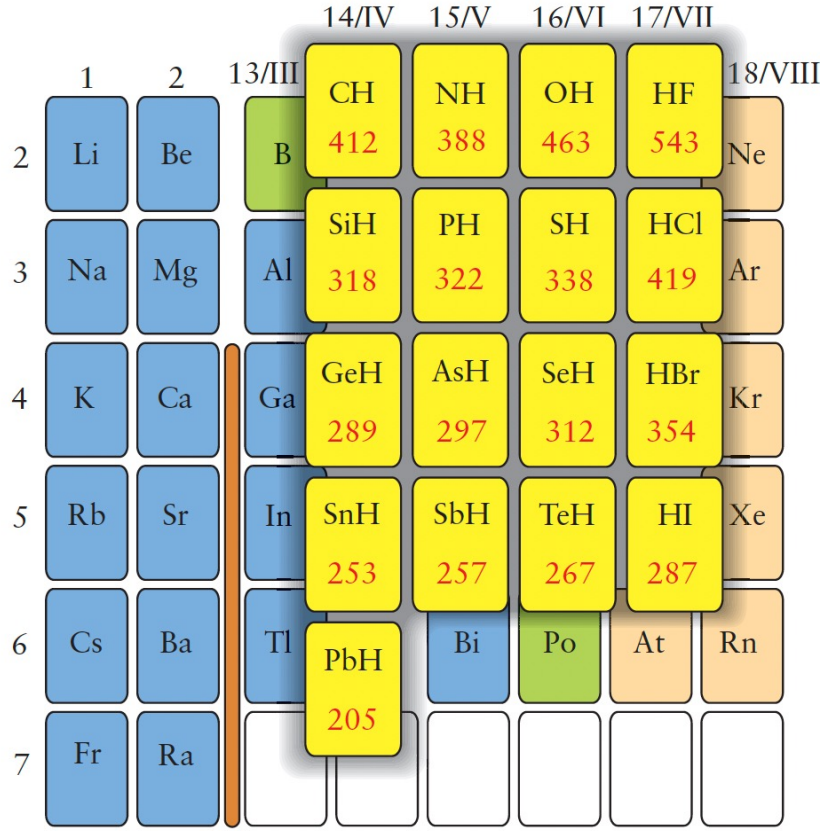


Figure 2D.8

2D.3 Bond strengths

Summary

The strength of a bond between two atoms is measured by its dissociation energy: the greater the dissociation energy, the stronger the bond. Bond strength between the same two atoms increases as the multiplicity of a bond increases, decreases as the number of lone pairs on neighbouring atoms increases, and decreases as the atomic radii increase.

Bond Lengths

Topic 2D.4

2D.4 Bond lengths

Bond length

- Internuclear distance between the centers of two atoms = bond length
- Bond lengths affect size and shape of molecule
- For example, DNA replication, enzyme binding into active sites
- Determined by spectroscopy or x-ray diffraction

2D.4 Bond lengths

Figure 2D.5

Bond length

TABLE 2.5 Average and Actual Bond Lengths

Bond	Average bond length (pm)	Molecule	Bond length (pm)
C—H	109	H_2	74
C—C	154	N_2	110
C=C	134	O_2	121
C···C*	139	F_2	142
C≡C	120	Cl_2	199
C—O	143	Br_2	228
C=O	112	I_2	268
O—H	96		
N—H	101		
N—O	140		
N=O	120		

*In benzene.

2D.4 Bond lengths

Summary: **Factors that influence bond length**

- Bond order: C≡C < C=C < C–C
- Resonance: C=C < C–C(benzene) < C–C
- Lone pairs on neighbouring atoms: F–F > H–H
- Atomic radii: HF < HCl < HBr < HI

The smaller the radius, the shorter the bond (see Figure 2D.9).

These trends are **opposite** of the ones for bond strength.

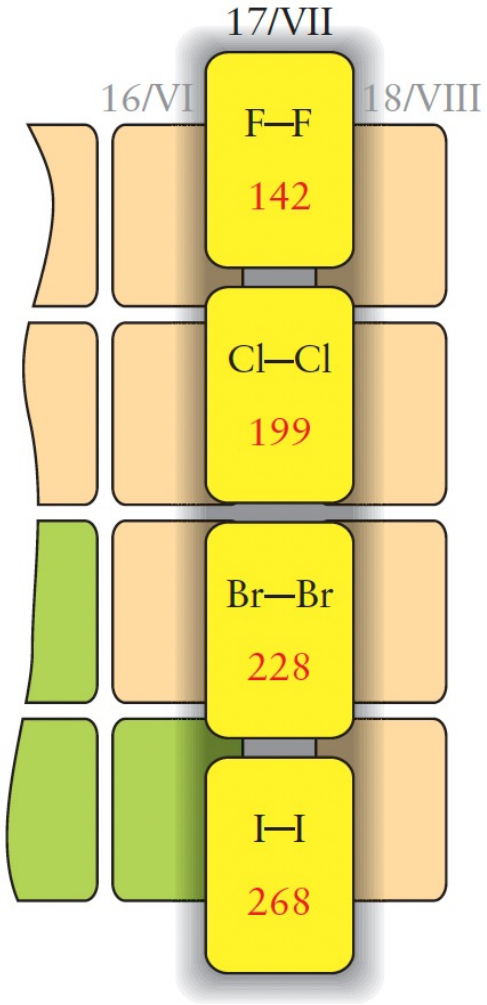


Figure 2D.9

2D.4 Bond lengths

Covalent radius

- Contribution an atom makes to the length of a covalent bond = covalent radius
- Measured as half of the distance between the centers (nuclei) of neighboring atoms joined by a covalent bond
- Covalent radii may be added to estimate bond lengths in molecules
- Tabulated values are averages of radii in polyatomic molecules

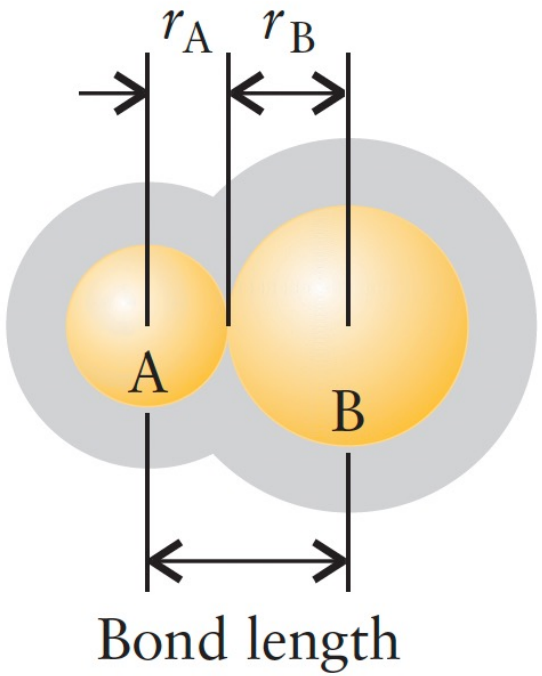
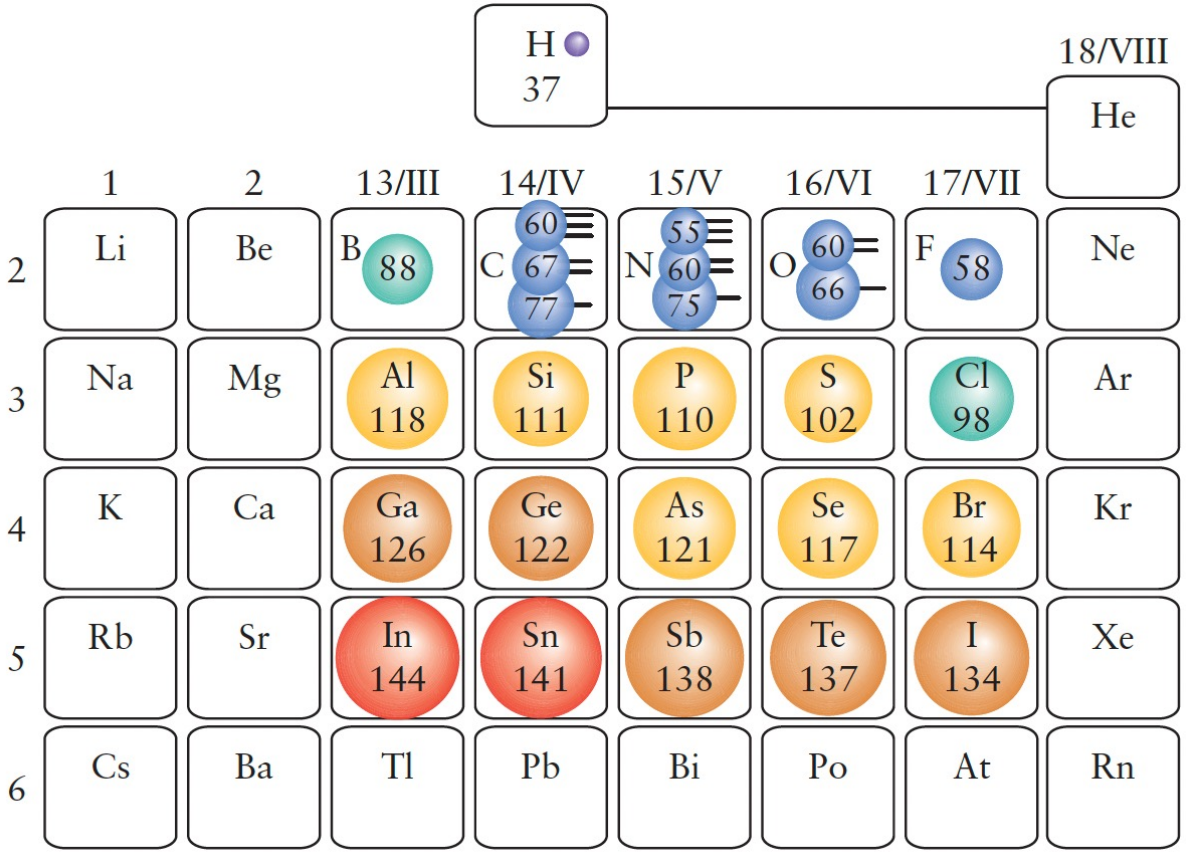


Figure 2D.8

Figure 2D.5

Covalent radii of hydrogen and p-block elements (in pm)



2D.4 Bond lengths

Summary

The covalent radius of an atom is the contribution it makes to the length of a covalent bond; covalent radii are added together to estimate the lengths of bonds in molecules.

The skills you have mastered are the ability to

- Explain the concept of electronegativity and use it to assess whether a bond is polar.
- Explain how resonance is used to improve the description of a covalent bond by introducing ionic character into it.
- Estimate relative ionic or covalent character.
- Explain how the concept of polarizability is used to improve the description of an ionic bond.
- Predict and explain periodic trends in the polarizability of anions and the polarizing power of cations.
- Predict and explain relative bond strengths and bond lengths

Summary: You have learned that the electronegativity of an element enables you to identify which atom in a bond has the greater share of the electron pair. Chemical bonds show a range of character, from completely covalent to completely ionic. You have seen that bond strengths are approximately transferrable between molecules and that atoms make characteristic contributions to the length of bonds.