The Strengths and Lengths of Bonds

– bond strengths and lengths depend largely on the bond order (single, double or triple) and have similar values in different molecules

9.6 Bond Strengths

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

  A-B(g) → A(g) + B(g) $DH^o = DH_B > 0$

- DH_B is a measure of the strength and stability of chemical bonds

  Large DH_B ⇔ stronger bonds

Table 9.2 Bond enthalpies of diatomic molecules, kJ/mol

Molecule	ΔH_B
H_2	436
N_2	944
O_2	496
CO	1074
F_2	158
Cl_2	242
Br_2	193
I_2	151
HF	565
HCl	431
HBr	366
HI	299

- Bond strength (DH_B) increases with increasing the bond order

:N≡N: **:Ö=Ö:**

:F–F:

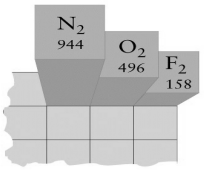


Fig. 9.17

- Bond strength (DH_B) increases as the atomic radius of the bonded atoms decreases
- Lone pairs on neighboring atoms decrease bond strength (DH_B)

H–H **436 kJ/mol**

:F–F: **158 kJ/mol**

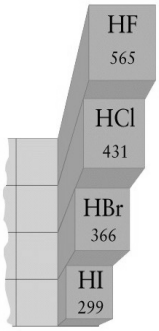


Fig. 9.18

9.7 Bond Strengths in Polyatomic Molecules

- The strength of the bond between a given pair of atoms varies slightly in different molecules
- **Average bond enthalpies** (DH_B) – averaged over many compounds
- Average bond enthalpies can be used to estimate the enthalpy changes of reactions in the gas phase (only approximate values)

  DH^o**(reaction) =** DH_B**(broken) -** DH_B**(formed)**

  – energy is absorbed (+) to break the bonds of the reactants and emitted (-) during forming the bonds of the products

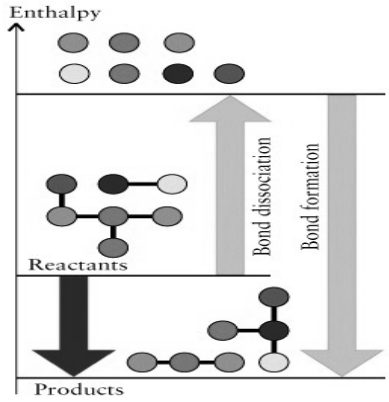


Fig. 9.22

Table 9.3 Average bond enthalpies, kJ/mol

Bond	Average bond enthalpy	Bond	Average bond enthalpy
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.

Example: Estimate the standard enthalpy of the reaction $CH_4(g) + 2F_2(g) \rightarrow CH_2F_2(g) + 2HF(g)$

1. Lewis structures are needed to get the bond order

2. bonds broken (reactants):

4 C–H (412 kJ/mol), 2 F–F (158 kJ/mol)

3. bonds formed (products):

2 C–H (412 kJ/mol), 2 C–F (484 kJ/mol), 2 H–F (565 kJ/mol)

$DH^o = DH_B$**(broken) -** DH_B**(formed) = [4×412 + 2×158] - [2×412 + 2×484 + 2×565] = -958 kJ**

(this value is only an estimate, the exact value can be calculated using DH_f^o data)

9.8 Bond Lengths

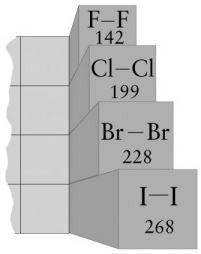
- **Bond length** – the distance between the centers of two bonded atoms

Table 9.4 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		

*In benzene.

- Bond lengths decrease with increasing the bond order
- Bond lengths increase with increasing the size of the bonded atoms



N≡N **O=O**

F–F

110 pm **121 pm**

142 pm

- In general shorter bonds are stronger

Fig. 9.23

- **Covalent radii** of atoms – contributions of individual atoms to the lengths of covalent bonds
  - average values are tabulated
  - values depend on the bond order
- Bond lengths equal the sum of the covalent radii of the bonded atoms

Example: Estimate the bond lengths in **HCN**

1. Lewis structure: **H–C≡N:**

2. Covalent radii: –H (37 pm), –C (77 pm), ≡C (60 pm), ≡N (55 pm)

3. r(H–C) = 37+77=114pm; r(C≡N) = 60+55=115pm