

Strengths of Covalent Bonds

The strengths of bonds are measured by bond dissociation enthalpies, the enthalpies for dissociating a mole of bonds in the gas phase.



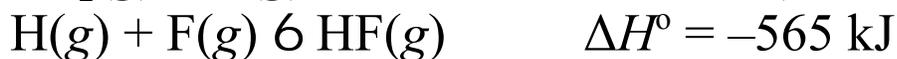
- L Note that D is always positive (endothermic).
- The atoms in a chemical bond are held together by attractive forces, so it always takes energy to break the bond.
 - Conversely, energy will always be released when a bond is made.

L Bond breaking is endothermic ($\Delta H^\circ = D > 0$).

L Bond making is exothermic ($\Delta H^\circ = -D < 0$).

Bond Dissociation Energy and ΔH_f°

- L In forming a molecule from its elements, bonds in the element must be broken to make new bonds in the compound.
- L The enthalpy of formation of the compound, ΔH_f° , is the algebraic sum of the enthalpies required to break bonds in the elements (endothermic) plus the enthalpies to make bonds in the compound (exothermic).
- The relative magnitudes of these endothermic and exothermic contributions determines whether ΔH_f° will be endothermic or exothermic.



- L Tabulated value, $\Delta H_f^\circ = -273.3 \text{ kJ}$ [Source: *NIST Chemistry WebBook*, <http://webbook.nist.gov/>]

Binary Polyatomic Molecules

- L In simple binary polyatomic molecules composed of only one kind of bond, the bond enthalpies can be calculated from the enthalpy to completely dissociate the molecule into its atoms, a process called **atomization**.

Atomization of $\text{H}_2\text{O}(g)$:



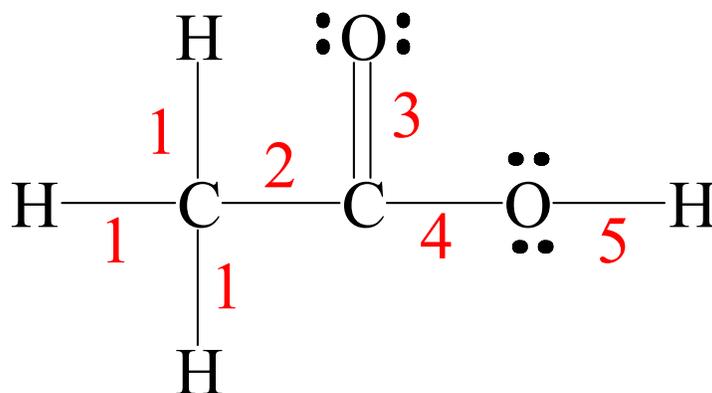
- Everything we know about the water molecule suggests that the two bonds in it are equal.
- Therefore, we assume that the bond enthalpy of each bond is

$$D(\text{O}-\text{H}) = +926 \text{ kJ}/2 = +463 \text{ kJ}$$

Polyatomic Molecules with Non-Equivalent Bonds

- L If a molecule has two or more different kinds of bonds, individual bond energies cannot be obtained from the overall atomization enthalpy.

Example: Acetic acid has 5 different kinds of bonds with 5 different bond energies.

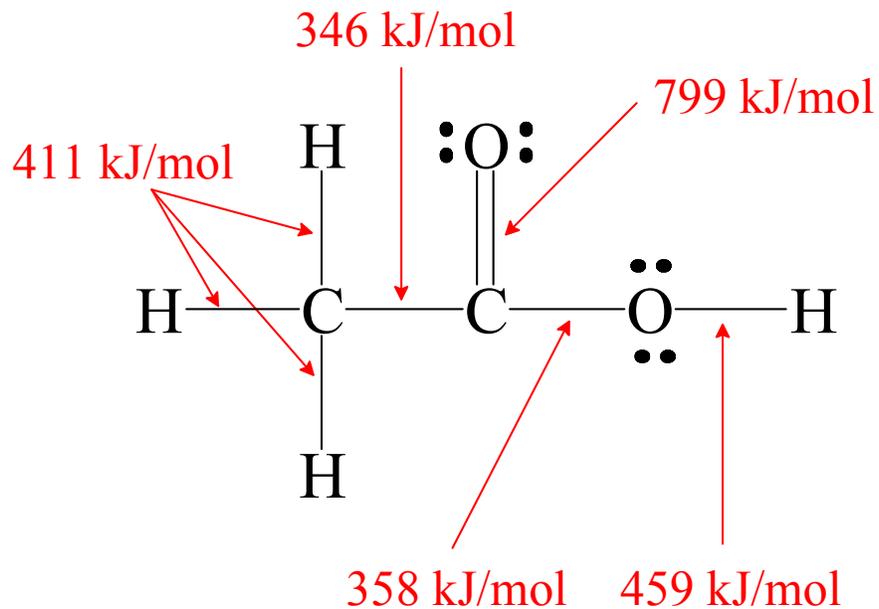


- L Typical bonds of a given type usually have approximately the same strengths in most molecules in which they are found.
- We can take bond enthalpies from molecules where they can be obtained from molecular atomization enthalpies and apply them as *approximate* bond enthalpies in other molecules.
 - Such enthalpies are tabulated as **average bond enthalpies**.

Selected Average Bond Enthalpies (kJ/mol)

C–C	346	C=C	602	C/C	835
C–N	305	C=N	615	C/N	887
C–O	358	C=O	799	C/O	1072
C–H	411	N–H	386	O–H	459
C–F	485	N–F	283	O–F	190
C–Cl	327	N–Cl	313	O–Cl	203
C–Br	285			O–Br	201
C–I	213			O–I	201
N–N	247	N=N	418	N/N	942
N–O	201	N=O	607		
F–F	155	F–H	565		
Cl–Cl	240	Cl–H	428		
Br–Br	190	Br–H	362		
I–I	149	I–H	295		

Average Bond Enthalpies in Acetic Acid

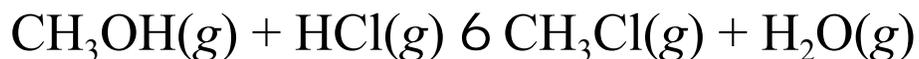


Approximate enthalpy of atomization for one mole of $\text{CH}_3\text{CO}_2\text{H}(g)$:

$$\begin{aligned}\Delta H &= (3 \times 411 \text{ kJ}) + 346 \text{ kJ} + 799 \text{ kJ} + 358 \text{ kJ} + 459 \text{ kJ} \\ &= 3195 \text{ kJ/mol}\end{aligned}$$

Estimating Reaction Enthalpy with Average Bond Enthalpies

Example: Use average bond enthalpy data to estimate ΔH° for the reaction

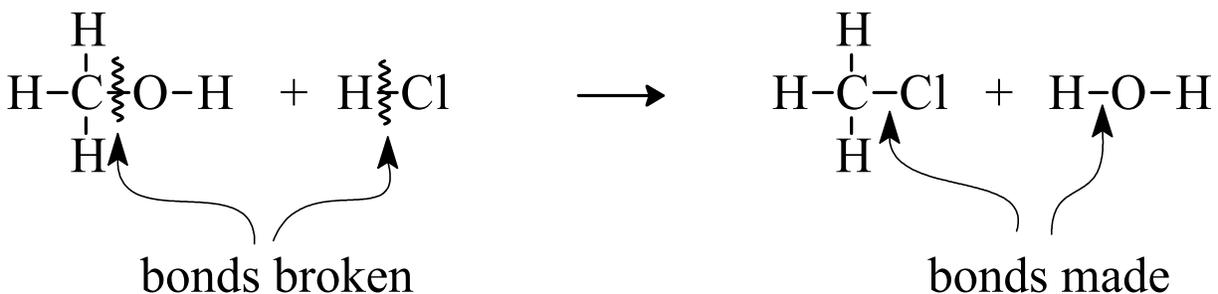


given the following average bond enthalpy data.

	C–O	H–Cl	C–Cl	O–H
D_{avg}	358 kJ	428 kJ	327 kJ	459 kJ

Estimating Reaction Enthalpy with Average Bond Enthalpies

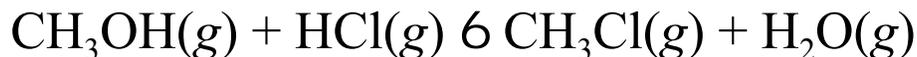
Solution: We need to identify the bonds that are broken and the bonds that are made as a result of this reaction.



Bonds broken:	1 mole C–O	+358 kJ
	1 mole H–Cl	+428 kJ
Bonds made:	1 mol C–Cl	–327 kJ
	1 mol O–H	–459 kJ
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		$\Delta H = 0 \text{ kJ}$

Comparison with Precisely Calculated Enthalpy

Calculate ΔH° for the reaction



given the following ΔH_f° data:

	CH ₃ OH(g)	HCl(g)	CH ₃ Cl(g)	H ₂ O(g)
ΔH_f°	-201.1 kJ	-92.31 kJ	-83.68 kJ	-241.83 kJ

$$\begin{aligned}\Delta H^\circ &= \{\Delta H_f^\circ(\text{CH}_3\text{Cl}) + \Delta H_f^\circ(\text{H}_2\text{O})\} \\ &\quad - \{\Delta H_f^\circ(\text{CH}_3\text{OH}) + \Delta H_f^\circ(\text{HCl})\} \\ &= \{(-83.68 \text{ kJ}) + (-241.83 \text{ kJ})\} \\ &\quad - \{(-201.1 \text{ kJ}) + (-92.31 \text{ kJ})\} \\ &= -32.1 \text{ kJ}\end{aligned}$$