

Enthalpy (H)

A substance energy can be measured by Enthalpy.

Enthalpy (H) is the **heat transferred** between the system and the surroundings during a chemical reaction carried out under **constant pressure**. Again, we can only measure the change in enthalpy ΔH .

Enthalpy H is the total energy content of a sample at a constant pressure. The heat gained or lost by a substance is:

$$\Delta H = q_p = n C \Delta T = n C (T_{\text{final}} - T_{\text{initial}})$$

C is molar heat capacity : C ; J/mole.K,

n : mole ,

T : Kelvin

The units of ΔH kJ/mole

There are four ways to calculate enthalpy (A, B, C, D)

A) Calorimetry

B) From tables of standards values

C) Hess's Law

D) Bond energies

and also stoichiometry.

A) Molar enthalpy change (First Way)

Molar enthalpy change is the enthalpy change for one mole $n = 1$.

$$\Delta H = C \Delta T = C (T_{\text{final}} - T_{\text{initial}})$$

Heating: Endothermic: Absorb heat: $\Delta H > 0$.

$$T_{\text{final}} > T_{\text{initial}} \text{ so, } T_{\text{final}} - T_{\text{initial}} > 0$$

$$\Delta H = C \Delta T = C (T_{\text{final}} - T_{\text{initial}}) > 0.$$

Cooling: Exothermic: Release heat: $\Delta H < 0$.

$$T_{\text{final}} < T_{\text{initial}} \text{ so, } T_{\text{final}} - T_{\text{initial}} < 0$$

$$\Delta H = C \Delta T = C (T_{\text{final}} - T_{\text{initial}}) < 0.$$

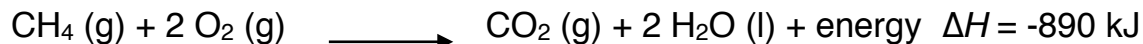
When two substance of different temperature are in contact.

$$\text{Heat gained} = \text{Heat lost.}$$

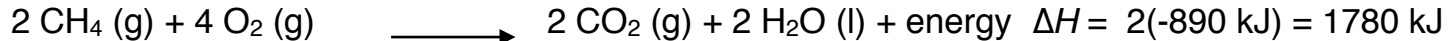
Enthalpy is an extensive property

1) The *magnitude* of enthalpy is directly proportional to the amount of reactant consumed.

Example: If one mole of CH₄ is burned in oxygen to produce CO₂ and water, 890 kJ of heat is released to the surroundings. If two moles of CH₄ are burned then 2x 890 = 1780 kJ of heat is released.

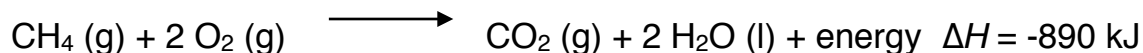


So:

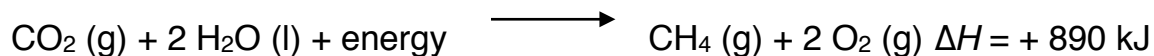


2) The sign of ΔH depends on the direction of the reaction. The enthalpy change for a reaction is equal in magnitude but opposite in sign to ΔH for the reverse reaction.

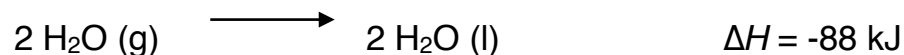
Example:



So:



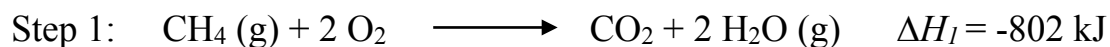
3) Enthalpy change depends on state:



B) Hess's Law (Second Way)

Hess's Law: if a reaction is carried out in a series of steps, ΔH for the reaction is the sum of ΔH for each of the steps.

The ΔH is independent of the number of steps and the nature of the path.



ΔH is sensitive to the states of the reactants and products.

Hess's law allows us to calculate enthalpy data for reactions which are difficult to carry out directly.

C) Using standard enthalpy of formation (Third Way)

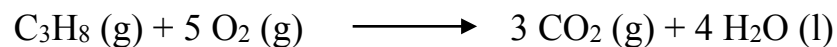
Using Enthalpy of Formation to Calculate Enthalpies of Reaction

$$\Delta H^{\circ}_{\text{rxn}} = \sum n \Delta H^{\circ}_{\text{f}}(\text{products}) - \sum m \Delta H^{\circ}_{\text{f}}(\text{reactants})$$

Where n and m are the stoichiometric coefficients.

Example:

Calculate the $\Delta H^{\circ}_{\text{rxn}}$ for:



$$\Delta H^{\circ}_{\text{rxn}} = 3(-393.5 \text{ kJ}) + 4(-285.8 \text{ kJ}) - 1(-103.85 \text{ kJ}) - 5(0) = -2220 \text{ kJ.}$$

TABLE 6.2 Standard Enthalpies of Formation for Several Compounds at 25°C

Compound	$\Delta H^{\circ}_{\text{f}}$ (kJ/mol)
$\text{NH}_3(\text{g})$	-46
$\text{NO}_2(\text{g})$	34
$\text{H}_2\text{O}(\text{l})$	-286
$\text{Al}_2\text{O}_3(\text{s})$	-1676
$\text{Fe}_2\text{O}_3(\text{s})$	-826
$\text{CO}_2(\text{g})$	-394
$\text{CH}_3\text{OH}(\text{l})$	-239
$\text{C}_8\text{H}_{18}(\text{l})$	-269

Example 2:

The combustion reaction for methanol is



Using the standard enthalpies of formation from Table 6.2 and Equation (6.1), we have

$$\begin{aligned} \Delta H^\circ_{\text{reaction}} &= 2 \times \Delta H^\circ_f \text{ for } \text{CO}_2(g) + 4 \times \Delta H^\circ_f \text{ for } \text{H}_2\text{O}(l) - \\ &\quad 2 \times \Delta H^\circ_f \text{ for } \text{CH}_3\text{OH}(l) \\ &= 2 \times (-394 \text{ kJ}) + 4 \times (-286 \text{ kJ}) - 2 \times (-239 \text{ kJ}) \\ &= -1454 \text{ kJ} \end{aligned}$$

TABLE 6.2 Standard Enthalpies of Formation for Several Compounds at 25°C

Compound	ΔH°_f (kJ/mol)
$\text{NH}_3(g)$	-46
$\text{NO}_2(g)$	34
$\text{H}_2\text{O}(l)$	-286
$\text{Al}_2\text{O}_3(s)$	-1676
$\text{Fe}_2\text{O}_3(s)$	-826
$\text{CO}_2(g)$	-394
$\text{CH}_3\text{OH}(l)$	-239
$\text{C}_8\text{H}_{18}(l)$	-269

D) Bond Enthalpies and the Enthalpies of Reactions (Fourth Way)

We can use bond enthalpies to calculate the enthalpy for a chemical reaction. In a chemical reaction bonds need to be broken and then new bonds form. The enthalpy of the reaction is given by:

ΔH_{rxn} = energy required to break bonds - energy released when bonds form

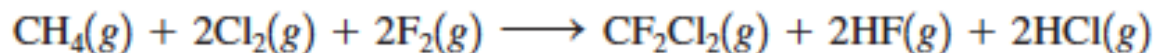
$$\Delta H_{\text{rxn}} = \sum n D(\text{bonds broken}) - \sum m D(\text{bonds formed})$$

TABLE 8.4 Average Bond Energies (kJ/mol)							
Single Bonds				Multiple Bonds			
H—H	432	N—H	391	I—I	149	C=C	614
H—F	565	N—N	160	I—Cl	208	C≡C	839
H—Cl	427	N—F	272	I—Br	175	O=O	495
H—Br	363	N—Cl	200	S—H	347	C=O*	745
H—I	295	N—Br	243	S—F	327	C≡O	1072
		N—O	201	S—Cl	253	N=O	607
C—H	413	O—H	467	S—Br	218	N=N	418
C—C	347	O—O	146	S—S	266	N≡N	941
C—N	305	O—F	190			C≡N	891
C—O	358	O—Cl	203	Si—Si	340	C=N	615
C—F	485	O—I	234	Si—H	393		
C—Cl	339	F—F	154	Si—C	360		
C—Br	276	F—Cl	253	Si—O	452		
C—I	240	F—Br	237				
C—S	259	Cl—Cl	239				
		Cl—Br	218				
		Br—Br	193				

*C=O(CO₂) = 799

Example 1:

Using the bond energies listed in Table 8.4, calculate ΔH for the reaction of methane with chlorine and fluorine to give Freon-12 (CF_2Cl_2).

**Solution:****Reactant Bonds Broken:**

$$\text{CH}_4: \quad 4 \text{ mol C—H} \qquad 4 \text{ mol} \times \frac{413 \text{ kJ}}{\text{mol}} = 1652 \text{ kJ}$$

$$2\text{Cl}_2: \quad 2 \text{ mol Cl—Cl} \qquad 2 \text{ mol} \times \frac{239 \text{ kJ}}{\text{mol}} = 478 \text{ kJ}$$

$$2\text{F}_2: \quad 2 \text{ mol F—F} \qquad 2 \text{ mol} \times \frac{154 \text{ kJ}}{\text{mol}} = 308 \text{ kJ}$$

$$\text{Total energy required} = \underline{2438 \text{ kJ}}$$

Product Bonds Formed:

$$\text{CF}_2\text{Cl}_2: \quad 2 \text{ mol C—F} \quad 2 \text{ mol} \times \frac{485 \text{ kJ}}{\text{mol}} = 970 \text{ kJ}$$

and

$$2 \text{ mol C—Cl} \quad 2 \text{ mol} \times \frac{339 \text{ kJ}}{\text{mol}} = 3678 \text{ kJ}$$

$$\text{HF:} \quad 2 \text{ mol H—F} \quad 2 \text{ mol} \times \frac{565 \text{ kJ}}{\text{mol}} = 1130 \text{ kJ}$$

$$\text{HCl:} \quad 2 \text{ mol H—Cl} \quad 2 \text{ mol} \times \frac{427 \text{ kJ}}{\text{mol}} = 3854 \text{ kJ}$$

$$\text{Total energy released} = \underline{\underline{3632 \text{ kJ}}}$$

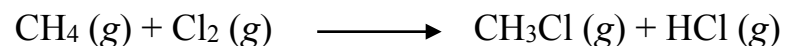
We now can calculate ΔH :

$$\begin{aligned} \Delta H &= \text{energy required to break bonds} - \text{energy released when bonds form} \\ &= 2438 \text{ kJ} - 3632 \text{ kJ} \\ &= -1194 \text{ kJ} \end{aligned}$$

Since the sign of the value for the enthalpy change is negative, this means that 1194 kJ of energy is released per mole of CF_2Cl_2 formed.

Example 2:

We illustrate the concept with the reaction between methane, CH₄ and chlorine:



In this reaction one C-H bond and one Cl-Cl bond are broken while one C-Cl bond and one H-Cl bond are formed. (values in table 8.4 next page)

So

$$\Delta H_{\text{rxn}} = [D(\text{C-H}) + D(\text{Cl-Cl})] - [D(\text{C-Cl}) + D(\text{H-Cl})] = -104 \text{ kJ.}$$

or

$$\Delta H_{\text{rxn}} = [4D(\text{C-H}) + D(\text{Cl-Cl})] - [3D(\text{C-H}) + D(\text{C-Cl}) + D(\text{H-Cl})] = -104 \text{ kJ.}$$

The overall reaction is exothermic which means that the bonds formed are stronger than the bonds broken.

Notes:

The molar heat capacity (C) depends on the number of atoms.

$$\Delta H = q_p = n C \Delta T = n C (T_{\text{final}} - T_{\text{initial}})$$

For all metals, the molar heat capacity is around 25 J/K.mole, because it is for 1 atom only.

Water has three atoms (HO, 1 O and 2 H). The molar heat capacity for liquid water is: $3 \times 25 = 75$ J/K.mole.

This also applies to the molar heat capacity of ionic compounds. The molar heat capacity for AlCl_3 is 92 J/K.mole, which is almost 4×25 because AlCl_3 has 4 atoms (1 Al and 3 Cl)

Table 1 Molar Heat Capacities of Elements and Compounds

Element	C (J/K•mol)	Compound	C (J/K•mol)
Aluminum, Al(s)	24.2	Aluminum chloride, AlCl_3 (s)	92.0
Argon, Ar(g)	20.8	Barium chloride, BaCl_2 (s)	75.1
Helium, He(g)	20.8	Cesium iodide, CsI(s)	51.8
Iron, Fe(s)	25.1	Octane, C_8H_{18} (l)	254.0
Mercury, Hg(l)	27.8	Sodium chloride, NaCl(s)	50.5
Nitrogen, N_2 (g)	29.1	Water, H_2O (g)	36.8
Silver, Ag(s)	25.3	Water, H_2O (l)	75.3
Tungsten W(s)	24.2	Water, H_2O (s)	37.4

Molar heat capacity (C) is related to specific heat (c_p)

$$\Delta H = q_p = n C \Delta T = m c_p \Delta T$$

$$M \text{ (g/mol)} \times c_p \text{ (J/K}\cdot\text{g)} = C \text{ (J/K}\cdot\text{mol)}$$

$$\text{(molar mass)(specific heat) = (molar heat capacity)}$$

Example: water: molar mass 18 g/mole

molar mass of water x specific heat of water = molar heat capacity of water

$$18 \times 4.18 = 75.24$$

Table 1 Some Specific Heats at Room Temperature

Element	Specific heat (J/g•K)	Element	Specific heat (J/g•K)
Aluminum	0.897	Lead	0.129
Cadmium	0.232	Neon	1.030
Calcium	0.647	Nickel	0.444
Carbon (graphite)	0.709	Platinum	0.133
Chromium	0.449	Silicon	0.705
Copper	0.385	Silver	0.235
Gold	0.129	Water	4.18
Iron	0.449	Zinc	0.388

Table 1 Molar Heat Capacities of Elements and Compounds

Element	C (J/K•mol)	Compound	C (J/K•mol)
Aluminum, Al(s)	24.2	Aluminum chloride, AlCl ₃ (s)	92.0
Argon, Ar(g)	20.8	Barium chloride, BaCl ₂ (s)	75.1
Helium, He(g)	20.8	Cesium iodide, CsI(s)	51.8
Iron, Fe(s)	25.1	Octane, C ₈ H ₁₈ (l)	254.0
Mercury, Hg(l)	27.8	Sodium chloride, NaCl(s)	50.5
Nitrogen, N ₂ (g)	29.1	Water, H ₂ O(g)	36.8
Silver, Ag(s)	25.3	Water, H ₂ O(l)	75.3
Tungsten W(s)	24.2	Water, H ₂ O(s)	37.4