

CHEMICAL THERMODYNAMICS

energy = anything that has the capacity to do work

work = force acting over a distance

Energy (E) = Work = Force x Distance

First Law of Thermodynamics: energy cannot be created or destroyed.

Different forms of energy include **electrical**, **heat** (thermal), **light** (radiant), **nuclear**, **chemical**. Energy can be converted between these forms e.g. chemical energy during a chemical reaction is released and light and heat energy (e.g. thermite process).

KE (kinetic energy) = $\frac{1}{2} m v^2$ (unit = $\text{kg}\cdot\text{m}^2\cdot\text{s}^{-2}$)

Joule (J) = the amount of energy needed to move a 1 kg mass a distance of 1 meter.

1 J = 1 N·m = $1 \text{ kg}\cdot\text{m}^2\cdot\text{s}^{-2}$ ($\text{kg}\cdot\text{m}^2/\text{s}^2$)

Energy conversion factors

1 calories (cal)	4.184 joules (J)
1 Calorie (Cal) or kilocalorie (kcal)	1000 cal = 4184 J
1 kilowatt-hour (kWh)	3.60×10^6 J

calorie (cal) = the amount of energy needed to raise one gram of water by 1°C

kcal = energy needed to raise 1000 g of water 1°C

food Calories = kcals

system = the material or process we are studying the energy changes within

surroundings = everything else in the universe

$\Delta\text{Energy}_{\text{universe}} = 0 = \Delta\text{Energy}_{\text{system}} + \Delta\text{Energy}_{\text{surroundings}}$

- when energy flows out of a system, ΔE_{system} is –
- when energy flows into the surroundings, $\Delta E_{\text{surroundings}}$ is +
 - ✓ $\Delta E = E_{\text{final}} - E_{\text{initial}}$
 - ✓ $\Delta E_{\text{reaction}} = E_{\text{products}} - E_{\text{reactants}}$
 - ✓ $\Delta E = q + w$; q = heat energy; w = work energy

$\Delta E > 0$ (positive) system gains energy

$\Delta E < 0$ (negative) system releases energy

Internal energy = sum (Σ) of the **kinetic** and **potential energies** of all the particles that compose the system.

thermal equilibrium = heat flows from matter with *high temperature* to matter with *low temperature* until both objects reach the same temperature

specific heat capacity = the amount of heat energy required to raise the temperature of one gram of a substance by 1°C. Units $\text{Jg}^{-1}\text{C}^{-1}$ ($\text{J/g}\cdot\text{C}$) or $\text{Jg}^{-1}\text{K}^{-1}$.

$$q = m \times C_s \times \Delta T$$

q = heat (J); m = mass (g); C_s = specific heat capacity; ΔT = temperature change (°C)

molar heat capacity = the amount of heat energy required to raise the temperature of one mole of a substance 1°C.

When gases expand, ΔV is +, but the system is doing work on the surroundings so w is – (negative).

$$-\text{Work} = \text{External Pressure} \times \text{Change in Volume}; w = -P\Delta V;$$

to convert the units to joules use $101.3 \text{ J} = 1 \text{ atm}\cdot\text{L}$

Measuring ΔE for chemical reactions: Calorimetry at Constant Volume (experiment)

at constant volume ($w=0$), $\Delta E_{\text{system}} = q_{\text{system}}$

$$q_{\text{surroundings}} = q_{\text{calorimeter}} = -q_{\text{system}}$$

$$-\Delta E_{\text{reaction (rxn)}} = -q_{\text{rxn}} = q_{\text{cal}} = C_{\text{cal}} \times \Delta T$$

ΔT = temperature change (using a thermometer); q_{cal} = heat absorbed by bomb calorimeter; C_{cal} = heat capacity of bomb calorimeter apparatus.

enthalpy, H , of a system = sum of the internal energy of the system and the product of pressure and volume ($H = E + PV$).

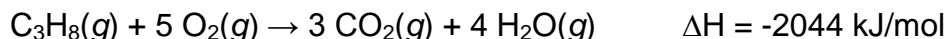
enthalpy change, ΔH , of a reaction = the heat evolved in a reaction at constant pressure; $\Delta H_{\text{rxn}} = q_{\text{rxn}}$ at constant pressure.

exothermic = chemical reactions that release heat ($\Delta H = \text{negative, -, } < 0$): temperature increases.

endothermic = chemical reactions that absorb heat ($\Delta H = \text{positive, +, } > 0$): temperature decreases.

For covalent molecules during a chemical reaction,
bond breaking = endothermic and bond forming = exothermic.

- we calculate the enthalpy change (ΔH) for the number of moles of reactants in the reaction as written, e.g.



When one mole of propane reacts with five moles of oxygen, 2044 KJ of energy is released. When a hydrocarbon (propane, C_3H_8) takes part in the **combustion reaction** much heat and light energy is given off (released to the surroundings) so $\Delta H < 0$.

Measuring ΔH : Calorimetry at Constant Pressure (experiment)

Reactions often done in aqueous solutions at constant pressure. Can use a polystyrene/polymer (coffee) cup and lid + thermometer.

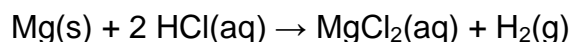
$$q_{\text{reaction}} = -q_{\text{solution}} = -(\text{mass}_{\text{solution}} \times C_{s, \text{solution}} \times \Delta T)$$

$$\Delta H_{\text{reaction}} = q_{\text{constant pressure}} = q_{\text{reaction}}$$

- $\Delta H = -m.C.\Delta T$
- to get $\Delta H_{\text{reaction (rxn)}}$ per mol, divide by the number of moles (i.e. Jmol^{-1}).

PRACTICE EXAMPLE ONE

What is $\Delta H_{\text{rxn/mol Mg}}$ for the reaction :



if 0.158 g Mg reacts in 100.0 mL of solution changes the temperature from 25.6°C to 32.8°C? Specific heat (of water) = $4.18 \text{ Jg}^{-1}\text{K}^{-1}$.

PRACTICE EXAMPLE TWO

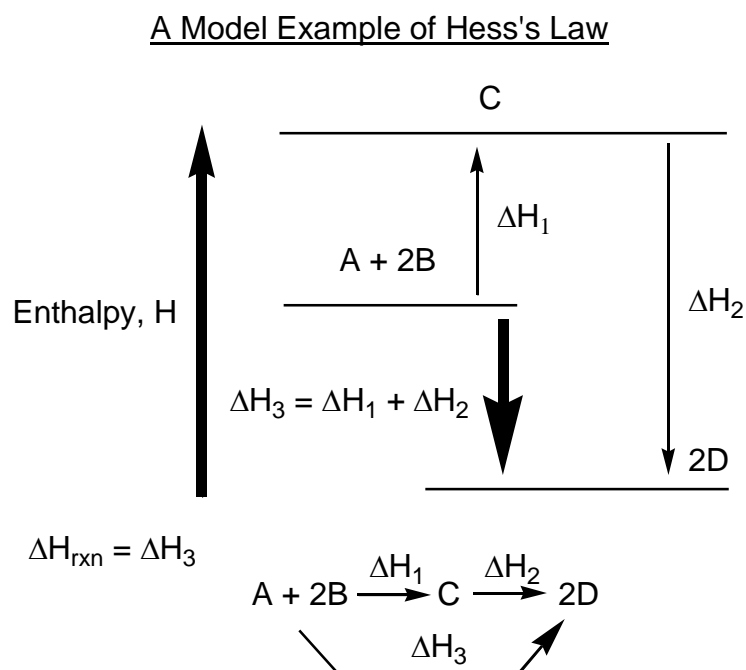
What is the heat evolved (ΔH_{rxn}) if 25 cm³ of 1 M sodium hydroxide solution react with 25 cm³ of 1 M hydrochloric acid? The start temperature was 25 °C and the final temperature 31.7 °C. The density of the solutions are assumed to be 1 gcm⁻³ and the specific heat (of water) = $4.18 \text{ Jg}^{-1}\text{K}^{-1}$.

ΔH is an extensive mathematical number and can be multiplied, subtracted etc. and the sign reversed (see Hess's Law calculations).

Hess's Law: The change in enthalpy (ΔH) for a stepwise reaction is the sum (Σ) of the enthalpy changes of the steps.

$$\Delta H_{\text{reaction}} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \dots = \Sigma \Delta H (1,2,3,4,\dots)$$

For example, using an **energy level diagram** to show all the steps (these could also be *intermediate* steps in a chemical reaction):



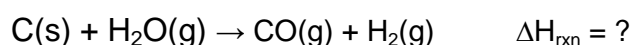
Let A, B, be the reactants in a chemical reaction. C is an intermediate and D is the product. Step **one** ($A + 2B$) is *endothermic* ($\Delta H_1 > 0$ or positive) and step **two** is *exothermic* ($\Delta H < 0$ or negative); overall **change in enthalpy is negative** (exothermic); $\Delta H_3 < 0$.

Also, any equation could be arranged to find an unknown ΔH (e.g. $\Delta H_2 = ?$) if we know ΔH_1 and ΔH_3 beforehand. These values usually come from data tables provided in an exam.

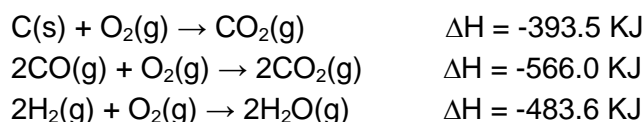
$$\Delta H_2 = \Delta H_3 - \Delta H_1$$

So Hess's law can be used to find any unknown value of ΔH if we know all the others!

Find the ΔH_{rxn} for the following reaction:



using these enthalpies - they are combustion reactions:



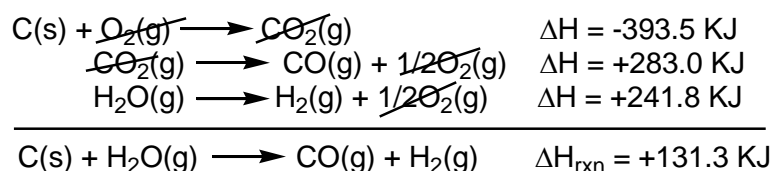
*Solution: We just have to determine how to **sum** these reactions to get the overall reaction of interest. We do this by manipulating the reactions with known ΔH 's in such a way as to get the reactants of interest on the left, the products of interest on the right and other species to cancel.*

1. $\text{C(s)} + \text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)} \quad \Delta H = -393.5 \text{ KJ}$
2. $1/2 \times [2\text{CO}_2\text{(g)} \longrightarrow 2\text{CO(g)} + \text{O}_2\text{(g)}] \quad \Delta H = 1/2 \times (+566.0 \text{ KJ})$
3. $1/2 \times [2\text{H}_2\text{O(g)} \longrightarrow 2\text{H}_2\text{(g)} + \text{O}_2\text{(g)}] \quad \Delta H = 1/2 \times (+483.6 \text{ KJ})$

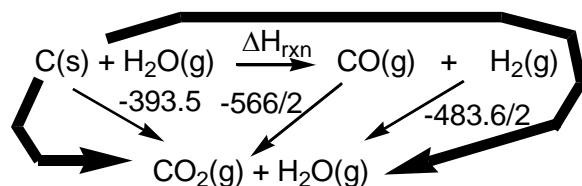
The **step 1.** remains unchanged as C(s) is a reactant.

The **step 2.** reverses the equation and changes the sign of ΔH ; match the coefficients (x 1/2).

The **step 3.** reverses the equation and changes the sign of ΔH ; match the coefficients (x 1/2).



Showing this using a Hess's Law enthalpy diagram (it is not necessary to include the O_2 here):

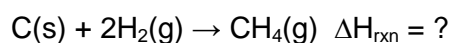


$$\Delta H_{\text{rxn}} + 1/2 \times (-566 + -483.6) = -393.5 \text{ KJ}$$

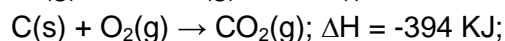
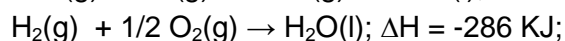
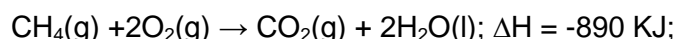
$$\Delta H_{\text{rxn}} = -393.5 - [1/2 \times (-566 + -483.6)] = +131.3 \text{ KJ}$$

PRACTICE EXAMPLE THREE

Calculate the standard **enthalpy of formation** (here $\Delta H_{\text{rxn}} = \Delta H_f^\circ$) of methane:



from the following enthalpy changes (they are the *enthalpies of combustion*):



[ans = -76 KJ/mol]

standard state is the state of a material at a defined set of conditions:

- pure gas at exactly 1 atm pressure
- pure solid or liquid in its most stable form at exactly 1 atm pressure and temperature of interest
- usually 25°C
- substance in a solution with concentration 1 M

the **standard enthalpy change**, ΔH° , is the enthalpy change when all reactants and products are in their standard states.

the **standard enthalpy of formation**, ΔH°_f , = the enthalpy change for the reaction forming 1 mole of a pure compound from its constituent elements; the elements must be in their standard states; the ΔH°_f for a pure element in its standard state = 0 kJ/mol.

elements \rightarrow compounds ΔH°_f or
 compounds \rightarrow elements $-\Delta H^\circ_f$

We can use these two concepts - decomposing of a compound into its elements and the forming of a compound from its elements to calculate the **enthalpy change of any reaction**:

reactants \rightarrow elements $\Delta H_1 = -\sum \Delta H^\circ_f(\text{reactants})$
 elements \rightarrow products $\Delta H_2 = +\sum \Delta H^\circ_f(\text{products})$ so:

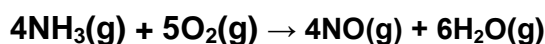
reactants \rightarrow products $\Delta H^\circ_{\text{reaction}} = \Delta H_1 + \Delta H_2$

We can look at it another way:

The ΔH° for the reaction is then the sum of the ΔH°_f for the component reactions:

$$\Delta H^\circ_{\text{reaction}} = \sum n \Delta H^\circ_f(\text{products}) - \sum n \Delta H^\circ_f(\text{reactants})$$

E.g. Use standard enthalpies to find $\Delta H^\circ_{\text{reaction}}$ for the reaction:



$\Delta H^\circ_f \text{NH}_3(\text{g}) = -45.9 \text{ kJ mol}^{-1}$, $\text{O}_2(\text{g}) = 0.0$; $\text{NO}(\text{g}) = +91.3$; $\text{H}_2\text{O}(\text{g}) = -241.8$

These values can be found in the book (Appendix II B A-7 to A-12).

Remember to multiply the ΔH°_f by the number of moles (stoichiometric amount).

Answer: $\Delta H^\circ_{\text{reaction}} = [4(+91.3 \text{ kJ}) + 6(-241.8 \text{ kJ})] - [4(-45.9 \text{ kJ}) + 5(0.0 \text{ kJ})]$
 $= -1085.6 \text{ kJ} - (-183.6 \text{ kJ})$
 $= \mathbf{-902.0 \text{ kJ; it's an exothermic reaction!}}$

PRACTICE EXAMPLE FOUR

Calculate the enthalpy change for the following reaction.



$$\Delta H_{\text{f}}^{\circ} \text{C}_2\text{H}_4(\text{g}) = +52.4 \text{ kJmol}^{-1}; \text{CO}_2(\text{g}) = -393.5; \text{H}_2\text{O}(\text{l}) = -285.8$$

In the U.S.A., each person uses > 105 kWh of energy per year.

Most comes from the combustion of **fossil fuels** (e.g. coal, methane, petroleum); **global air temperature** has **risen** 0.6 °C in the past 100 years. These cannot be replenished and release other pollutants into the atmosphere during complete or partial combustion.

The CO₂ produced is a **greenhouse gas** (causes a rise in air and sea temperatures).

Renewable energy sources are increasingly in demand (e.g. solar, wind, hydroelectric). Our greatest unlimited supply is the sun. Burning hydrogen in oxygen/air as a fuel is much safer for the environment!