

LECTURE 3

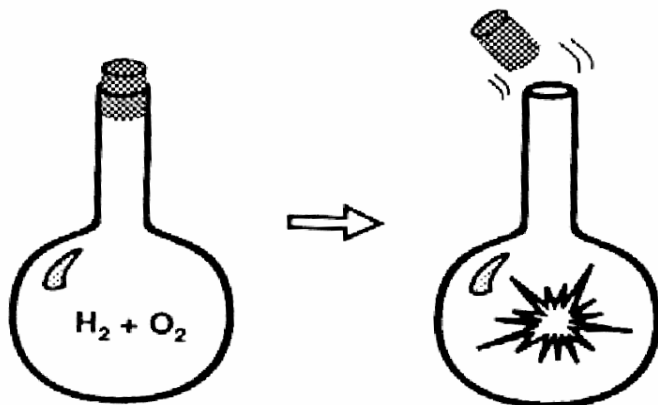
Enthalpy and Thermochemistry

Most reactions are conducted at constant pressure e.g. in open vessels in the laboratory.

Energies changes at constant pressure are called the enthalpy, given the symbol H .

Heat changes during reactions are important from mechanistic, process and safety considerations.

A reaction involves changes of both heat and work.



The simplest definition of H ; The energy change at constant pressure ΔH , is

$$\Delta H = q_p = \Delta U + p\Delta V$$

which leads to a formal definition of the enthalpy, H as

$$H = U + pV$$

In general, ΔV with liquids or solids is very small: $\Delta H \approx \Delta U$.

With gases, ΔV can be large e.g. $p\Delta V = \Delta n RT$

At 25 °C, 298.15K, $(\Delta H - \Delta U) = 2.48 \text{ kJ}$ for each mole of gas
at 500 °C, $(\Delta H - \Delta U) = 6.43 \text{ kJ mol}^{-1}$.

We use the same sign convention as for ΔU .

- Evolution of heat (*exothermic*) has negative ΔH ;
- Absorption of heat (*endothermic*) has positive ΔH .

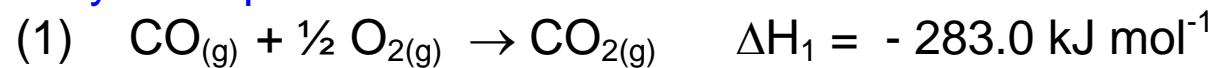
Enthalpy changes - Hess' Law

Since U, P and V are state functions, H must also be a state function. Thus, ΔH for a reaction is merely the difference between the final state (*i.e.* the products) and the initial state (*i.e.* the reactants). Any intermediate stages or reactions do not matter.

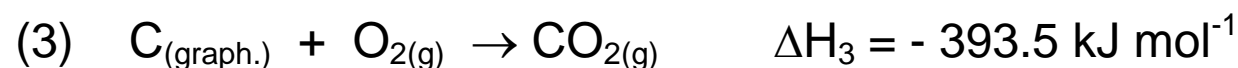
Hess' Law:

The total enthalpy change for a reaction is independent of the path by which the reaction occurs.

An easy example:

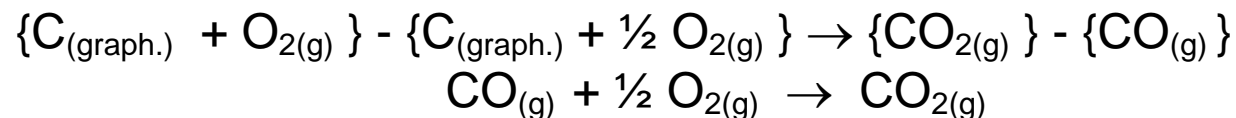


Alternatively,



Hess' Law allows us to treat the chemical equations and the enthalpy changes in the same way as algebraic equations.

Subtracting (2) from (3) gives the equivalent of (1) and leads to the same result for ΔH .



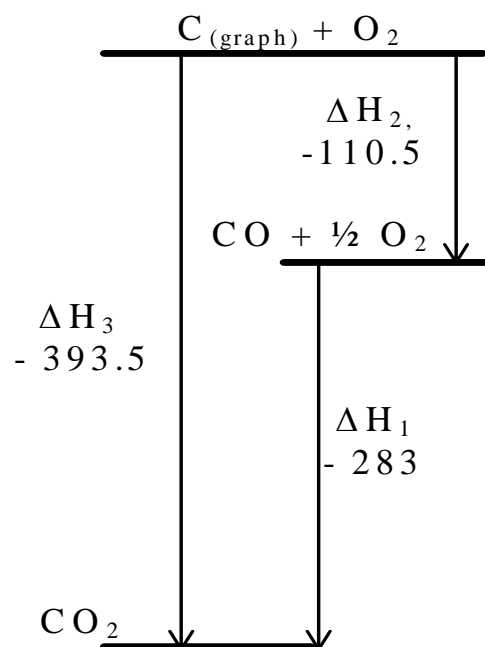
$$\Delta H = (-393.5) - (-110.5) = -283.0 \text{ kJ mol}^{-1}$$

or
$$\Delta H_3 = \Delta H_1 + \Delta H_2$$

An alternative method:

Graphical diagrams of the energy levels.

Enthalpy changes in kJ mol^{-1}



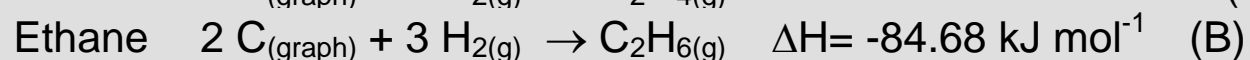
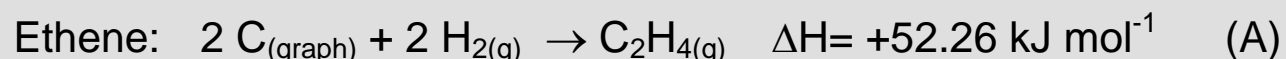
This method has a number of important applications

Most obvious consequence $\Delta H_{\text{forward}} = -\Delta H_{\text{reverse}}$.

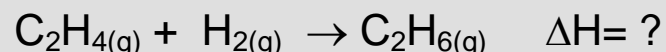
More important use: calculation of ΔH for reactions which would be difficult or impossible to carry out in practice.

Ethene and ethane are by-products from the cracking of oil. The enthalpy change at 25 °C for the reaction of graphite and hydrogen gas to form each is +52.26 kJ mol⁻¹ and -84.68 kJ mol⁻¹ respectively. Calculate the ΔH for the hydrogenation of ethene to give ethane.

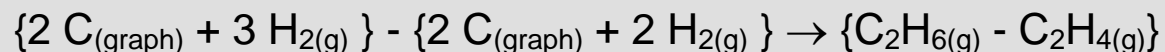
From the data given



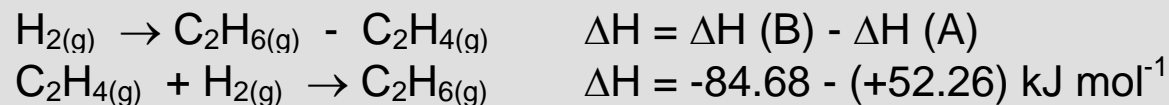
The reaction of interest is



If we subtract reaction A from reaction B,



We can now treat the chemical equations exactly like an algebraic equation



The enthalpy change for the reaction is therefore $-136.94 \text{ kJ mol}^{-1}$

Enthalpy changes in chemical reactions

ΔH is the heat absorbed or evolved when the reaction occurs at constant pressure and is the difference in enthalpy between products and the reactants.

ΔH depends on T, P as well as the components so we define a set of standard conditions

Standard temperature: 25 °C, 298.15 K.

Standard pressure: 1 bar, 100000 Pa

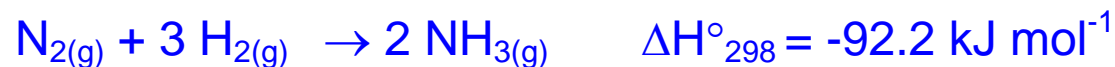
Standard state: pure component at 1 bar pressure

Note: these are for thermodynamic data NOT to be confused with 'STP' for gases, 1 atm, 0 °C.

Therefore, we define a **standard enthalpy of reaction** as the enthalpy change at 1 bar and 25 °C for a reaction with all components in their standard states - ΔH°_{298} .

The superscript ° indicates that the components are in their standard states at standard pressure and the subscript indicates the temperature.

Thermochemical equations:

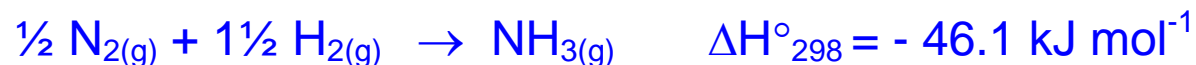


Translated into English says:

“when 1 mol of nitrogen reacts with three moles hydrogen to form 2 moles of ammonia at 25 °C and 1 bar pressure, -92.2 kJ is evolved”

NB: “the enthalpy of reaction is -92.2 kJ mol⁻¹” is ambiguous.

Or



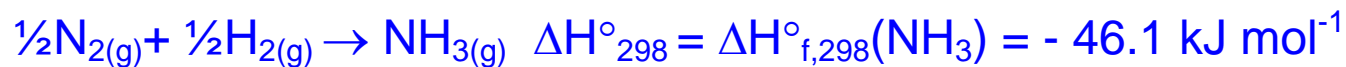
Standard enthalpy of formation

ΔH_f° is the enthalpy change when 1 mole of a compound is formed under standard conditions from its constituent elements in their standard states.

Values are quoted at the standard temperature of 25 °C or 298.15 K. Tables of $\Delta H_{f,298}^\circ$ are available – Atkins Appendix 1.

It is not possible to define an absolute measure of enthalpy so we need a reference value.

For elements in their standard states, $\Delta H_{f,298}^\circ = 0$

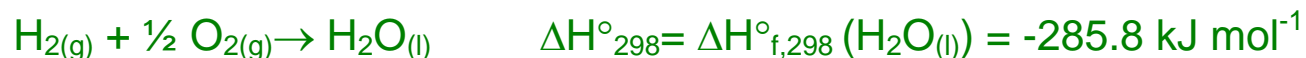


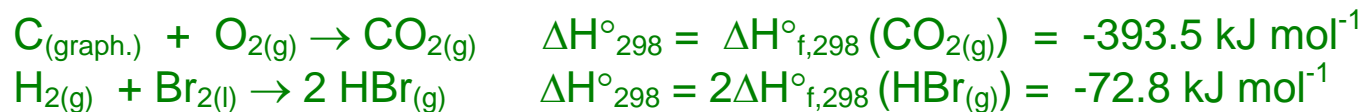
The *standard state* is the one with lowest energy

e.g. carbon: solid graphite is taken, not diamond or fullerene

Br and I often react in the vapour but the standard states are the liquid and solid respectively.

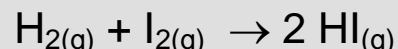
Examples





In each of the three reactions, the enthalpy of the reactants is zero so that the enthalpy change for the reaction represents the enthalpy of formation of the products.

Calculate the enthalpy change for the gas phase reaction between hydrogen and iodine vapour at 25 °C.



$\Delta H^{\circ}_{\text{f},298}$ for $\text{H}_{2(\text{g})}$ is 0 since it is an element in its standard state.

However, the standard state for iodine is the solid so that $\Delta H^{\circ}_{\text{f},298}$ for $\text{I}_{2(\text{g})} \neq 0$. $\Delta H^{\circ}_{\text{f},298}$ for $\text{HI}_{(\text{g})}$ is 26.48 kJ mol⁻¹.

$$\Delta H^{\circ}_{\text{f},298} (\text{I}_{2(\text{g})}) = \Delta H^{\circ}_{\text{f},298} (\text{I}_{2(\text{s})}) + \Delta H^{\circ} (\text{I}_{2(\text{s})} \rightarrow \text{I}_{2(\text{g})}) = 0 + 62.44 \text{ kJ mol}^{-1}$$

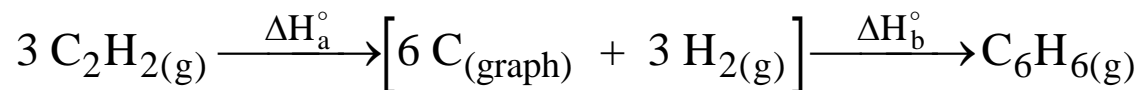
$$\begin{aligned} \Delta H^{\circ} &= \{2 \Delta H^{\circ}_{\text{f},298} (\text{HI}_{(\text{g})})\} - \{\Delta H^{\circ}_{\text{f},298} (\text{H}_{2(\text{g})}) + \Delta H^{\circ}_{\text{f},298} (\text{I}_{2(\text{g})})\} \\ &= \{2 (26.48)\} - \{0 + 62.44\} \\ &= -9.48 \text{ kJ (mol H}_2\text{)}^{-1} \end{aligned}$$

Note: Because of the stoichiometry, $\Delta H^{\circ} = -4.74 \text{ kJ (mol HI)}^{-1}$

Applications of enthalpies of formation



We can use Hess' Law to write this reaction as if it has an intermediate stage:



so $\Delta H_{298}^\circ (\text{reaction}) = \Delta H_a^\circ + \Delta H_b^\circ$.

$$\Delta H_a^\circ = 3 (- \Delta H_{f, 298}^\circ (\text{C}_2\text{H}_2(\text{g}))) \quad \text{and} \quad \Delta H_b^\circ = \Delta H_{f, 298}^\circ (\text{C}_6\text{H}_6(\text{g})).$$

$$\Delta H_{298}^\circ (\text{reaction}) = [3 (- \Delta H_{f, 298}^\circ (\text{C}_2\text{H}_2(\text{g})))] + [\Delta H_{f, 298}^\circ (\text{C}_6\text{H}_6(\text{g}))]$$

or $\Delta H_{298}^\circ (\text{reaction}) = \Delta H_{f, 298}^\circ (\text{C}_6\text{H}_6(\text{g})) - 3 (\Delta H_{f, 298}^\circ (\text{C}_2\text{H}_2(\text{g})))$

$$\Delta H_{298}^\circ (\text{reaction}) = + 82.9 - (3 \times + 226.7) = - 597.2 \text{ kJ mol}^{-1}$$

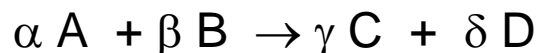
A more general way of writing the result of this calculation is

$$\Delta H_{298}^\circ (\text{reaction}) = \Delta H_{f, 298}^\circ (\text{Products}) - \Delta H_{f, 298}^\circ (\text{Reactants})$$

or $\Delta H_{298}^{\circ}(\text{reaction}) = \sum v_i \Delta H_{f,298}^{\circ}(\text{products}) - \sum v_i \Delta H_{f,298}^{\circ}(\text{reactants})$

v_i represents the stoichiometric coefficient.

Hence, for a general reaction of the form



then

$$\Delta H_{298}^{\circ} = [\gamma \Delta H_{f,298}^{\circ}(\mathbf{C}) + \delta \Delta H_{f,298}^{\circ}(\mathbf{D})] - [\alpha \Delta H_{f,298}^{\circ}(\mathbf{A}) + \beta \Delta H_{f,298}^{\circ}(\mathbf{B})]$$

This method can be used to calculate ΔH for any reaction where we have $\Delta H_{f,298}^{\circ}$ data for the components.

Calculate the enthalpy of reaction at 25 °C for the following reaction.



$$\Delta H_{298}^{\circ}(\text{reaction}) = \sum v_i \Delta H_{f,298}^{\circ}(\text{products}) - \sum v_i \Delta H_{f,298}^{\circ}(\text{reactants})$$

$$= [6 \Delta H_{f,298}^{\circ}(\text{FeO}(\text{s})) + 3 \Delta H_{f,298}^{\circ}(\text{H}_2\text{O}(\text{l})) + \Delta H_{f,298}^{\circ}(\text{N}_2(\text{g}))] \\ - [3 \Delta H_{f,298}^{\circ}(\text{Fe}_2\text{O}_3(\text{s})) + 2 \Delta H_{f,298}^{\circ}(\text{NH}_3(\text{g}))]$$

$$= [6(-266.3) + 3(-285.8) + 0] - [3(-824.2) + 2(-46.1)]$$

$$= [-2455.2] - [-2564.8]$$

$$= 109.6 \text{ kJ mol}^{-1}$$

Note: For clarity, the units have been omitted from the intermediate stages of the calculation. All enthalpy values are in kJ mol^{-1} .