

Thermochemistry

The study of energy changes that occur during chemical reactions:

- at constant volume $\Delta U = q_V$ no work
- at constant pressure $\Delta H = q_P$ only PV work

For practical reasons most measurements are made at constant P , so thermochemistry mostly deals with ΔH .

$$\Delta H_{\text{reaction}} = \sum_{\text{products}} H - \sum_{\text{reactants}} H$$

If $\Delta H > 0$ the reaction is **endothermic**.

If $\Delta H < 0$ the reaction is **exothermic**.

For comparison purposes we need to refer ΔH to the same T and P . To define a standard reaction enthalpy each component of the reaction must be in its **standard state** – the most stable form at **1 bar** pressure and (usually) **25°C**.

$$1 \text{ bar} = 10^5 \text{ Pa}$$

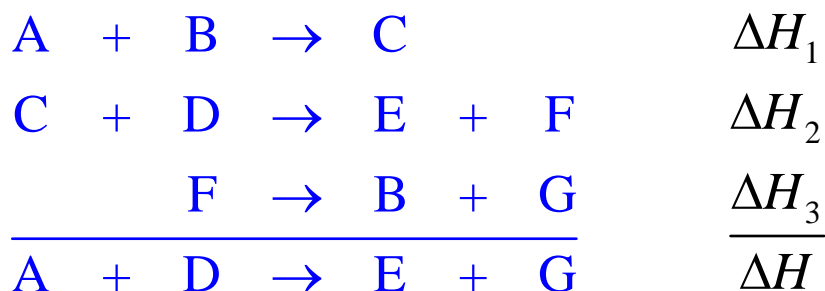
$$1 \text{ atm} = 1.01325 \text{ bar}$$

Reaction Enthalpy 1

Hess's Law

The standard enthalpy change in any reaction can be expressed as the sum of the standard enthalpy changes, at the same temperature, of a series of reactions into which the overall reaction can be formally divided.

Combine chemical equations as if mathematical equations, e.g.



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

Standard Reaction Enthalpy

ΔH° reaction enthalpy at 1 bar

ΔH_{298}° ... and at standard T

ΔH_{500}° or some other T

Reaction Enthalpy 2

Standard (molar) enthalpy of formation $\Delta H_f^\circ \equiv \Delta_f H^\circ$

Heat of formation of a substance from its elements, all substances being in their standard state.

By definition, for all elements $\Delta H_f^\circ = 0$

Enthalpy of combustion $\Delta H_c^\circ \equiv \Delta_c H^\circ$

ΔH° for total oxidation of a substance

e.g. $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$ $\Delta_c H^\circ = -2808 \text{ kJ mol}^{-1}$

Enthalpy of hydrogenation

ΔH° when an unsaturated organic compound becomes fully saturated

e.g. $C_6H_6 + 3H_2 \rightarrow C_6H_{12}$ $\Delta H^\circ = -246 \text{ kJ mol}^{-1}$

Enthalpy of atomization \equiv Bond dissociation enthalpy

ΔH° for the dissociation of a molecule into its constituent gaseous atoms

e.g. $C_2H_6(g) \rightarrow 2C(g) + 6H(g)$ $\Delta H^\circ = 2883 \text{ kJ mol}^{-1}$

Bond strength \equiv single bond enthalpy

An average value taken from a series of compounds and often combined *for a rough estimate*

e.g. $\Delta H^\circ(C_2H_6) = \Delta H^\circ(C-C) + 6 \Delta H^\circ(C-H)$

Temperature Dependence of ΔH°

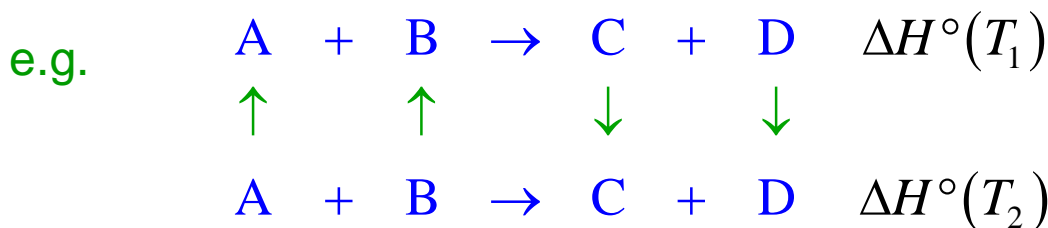
The temperature dependence of reaction enthalpies can be expressed in terms of the T dependence of the enthalpies of the reaction components:

$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p dT$$

$$\therefore \Delta H(T_2) = \Delta H(T_1) + \int_{T_1}^{T_2} \Delta C_p dT$$

$$\text{where } \Delta C_p = \sum_{\text{products}} C_p - \sum_{\text{reactants}} C_p$$

This is known as **Kirchoff's Law**.



$$\begin{aligned} \Delta H^\circ(T_2) &= (C_p(A) + C_p(B))(T_1 - T_2) \\ &\quad + \Delta H^\circ(T_1) \\ &\quad + (C_p(C) + C_p(D))(T_2 - T_1) \\ &= \Delta H^\circ(T_1) + \left(\sum_{\text{products}} C_p - \sum_{\text{reactants}} C_p \right) \Delta T \end{aligned}$$

assuming that the C_p values are T independent.

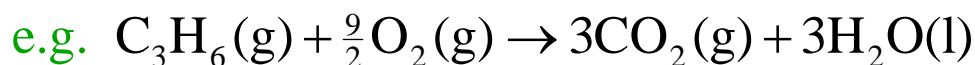
Reactions at Constant Volume

$$\Delta H_r = \Delta U_r + (PV)_{\text{products}} - (PV)_{\text{reactants}}$$

For solids and liquids $\Delta(PV) \approx 0$, so $\Delta H \approx \Delta U$

For ideal gases $\Delta(PV) = \Delta n_{\text{gas}} RT$,

so $\Delta H \approx \Delta U + \Delta n_{\text{gas}} RT$



$$\Delta H_r = \Delta U_r + \left(-\frac{5}{2}\right) RT$$

The relationship between ΔH and ΔU is particularly important when relating thermochemical enthalpies to molecular properties,

e.g. for a single bond energy $\Delta U = \Delta H - RT$

as seen in the case of $\text{O}_2(\text{g}) \rightarrow 2\text{O}(\text{g})$.

In practice, RT is usually so much smaller than ΔH that it is often ignored.

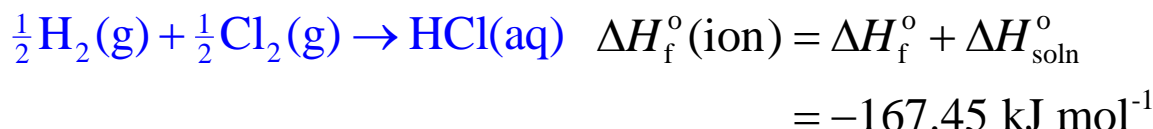
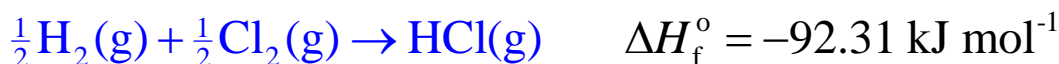
Enthalpies of Ions in Solution

Enthalpy of solution ΔH° for solution of a substance in a *stated* amount of solvent

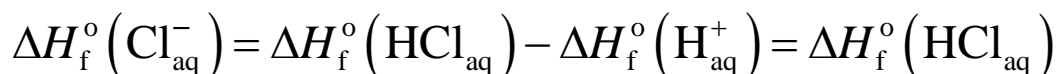
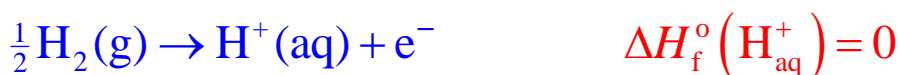
Enthalpy of dilution ΔH° for dilution of a solution to a lower concentration

Enthalpy of solution to infinite dilution $\Delta H_{\text{soln}}^\circ$ for an *infinite* amount of solvent

The enthalpy of formation for a species in solution can be found by combining $\Delta H_{\text{soln}}^\circ$ with the ΔH_f° of the gaseous species:



ΔH_f° for individual ions in solution can only be found if one is arbitrarily fixed. By **convention** this is $\text{H}^+(\text{aq})$.

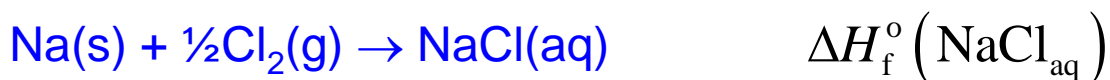


The **standard state** for a substance in solution (**not just ions**) is a concentration of 1 mole solute in 1 kg solution (1 **molal**).

Enthalpy of Formation of an Ionic Solid

Consider individual steps in the formation of NaCl.

1. $\text{Na(s)} \rightarrow \text{Na(g)}$ $\Delta H_{\text{subl}}^{\circ}(\text{Na})$
2. $\text{Na(g)} \rightarrow \text{Na}^{\text{+}}(\text{g}) + \text{e}^{-}$ $\Delta H^{\circ} = I(\text{Na}) + RT$
3. $\frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{Cl(g)}$ $\frac{1}{2}\Delta H^{\circ}(\text{Cl-Cl})$
4. $\text{Cl(g)} + \text{e}^{-} \rightarrow \text{Cl}^{-}(\text{g})$ $\Delta H^{\circ} = -E_{\text{A}}(\text{Cl}) - RT$
5. $\text{Na}^{\text{+}}(\text{g}) + \text{Cl}^{-}(\text{g}) \rightarrow \text{Na}^{\text{+}}(\text{aq}) + \text{Cl}^{-}(\text{aq})$
 $\equiv \text{NaCl(aq)}$ $\Delta H_{\text{sol}}^{\circ}(\text{Na}^{\text{+}}) + \Delta H_{\text{sol}}^{\circ}(\text{Cl}^{-})$

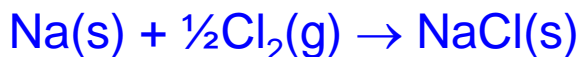


$$\Delta H_{\text{f}}^{\circ}(\text{NaCl}_{\text{aq}}) = \Delta H_{\text{subl}}^{\circ}(\text{Na}) + I(\text{Na}) + \frac{1}{2}\Delta H^{\circ}(\text{Cl-Cl}) \\ - E_{\text{A}}(\text{Cl}) + \Delta H_{\text{sol}}^{\circ}(\text{Na}^{\text{+}}) + \Delta H_{\text{sol}}^{\circ}(\text{Cl}^{-})$$

Step 5 could be creation of solid NaCl instead of solution



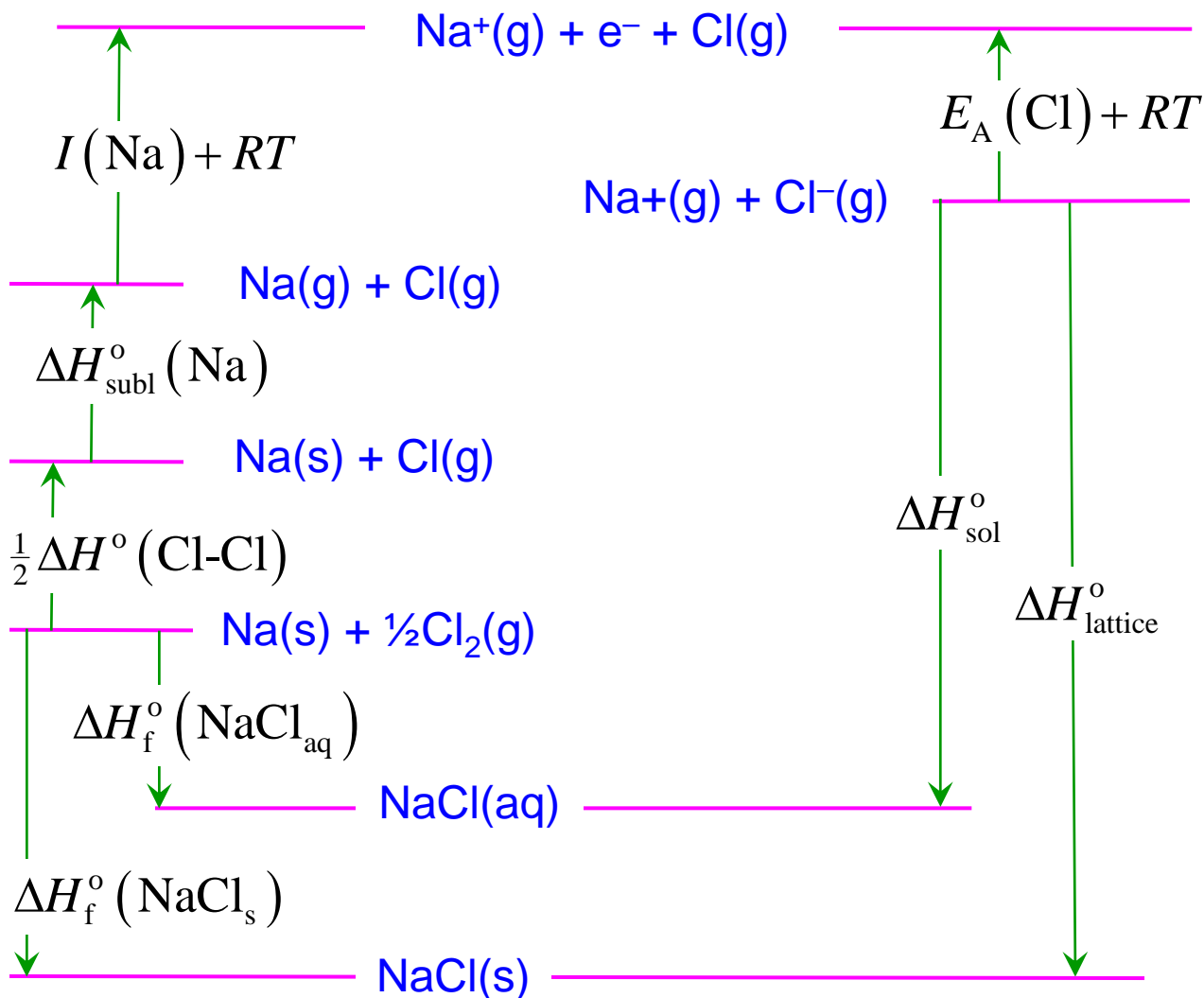
leading us to the enthalpy of formation of solid NaCl:



$$\Delta H_{\text{f}}^{\circ}(\text{NaCl}_{\text{s}}) = \Delta H_{\text{subl}}^{\circ}(\text{Na}) + I(\text{Na}) + \frac{1}{2}\Delta H^{\circ}(\text{Cl-Cl}) \\ - E_{\text{A}}(\text{Cl}) + \Delta H_{\text{lattice}}^{\circ}(\text{NaCl})$$

The Born-Haber Cycle

Enthalpy changes can also be expressed in a diagram, e.g.



Since H is a state variable, the sum of enthalpy changes around the cycle must be zero. Consequently, if all but one of the enthalpy changes is known, it can be readily calculated.

This is equivalent to using Hess's Law to sum reaction steps.