Thermochemistry

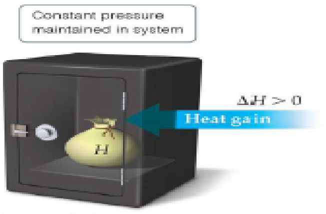
Thermochemistry is a branch of thermodynamics because a reaction vessel and its contents form a system, and chemical reactions result in the exchange of energy between the system and the surroundings. Thus we can use calorimetry to measure the energy supplied or discarded as heat by a reaction, and can identify q with a change in internal energy (if the reaction occurs at constant volume) or a change in enthalpy (if the reaction occurs at constant pressure). Conversely, if we know ΔU or ΔH for a reaction, we can predict the energy (transferred as heat) the reaction can produce.

We have already remarked that a process that releases energy by heating the surroundings is classified as exothermic and one that absorbs energy by cooling the surroundings is classified as endothermic. Because the release of energy by heating the surroundings signifies a decrease in the enthalpy of a system (at constant pressure), we can now see that an exothermic process at constant pressure is one for which $\Delta H < 0$.

Conversely, because the absorption of energy by cooling the surroundings results in an increase in enthalpy, an endothermic process at constant pressure has $\Delta H > 0$. **Endothermic** reactions absorb heat, while **exothermic** reactions release heat.

Endothermic and Exothermic

$$\Delta H = H_{\text{final}} - H_{\text{initial}} \quad \text{or} \quad \Delta H = H_{\text{products}} - H_{\text{reactants}}$$



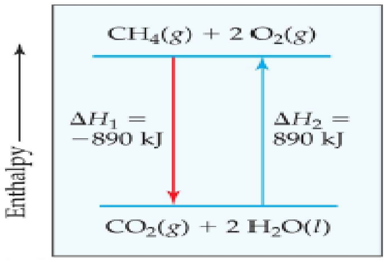
(a) An endothermic reaction

- A process is **endothermic** when ΔH is positive (>0).

(b) An exothermic reaction

ΔH is amount of heat that flows into or out of system under constant pressure.

- A process is **exothermic** when ΔH is negative (<0).



Standard enthalpy changes

The standard enthalpy change for a reaction or a physical process is the difference between the products in their standard states and the reactants in their standard states, all at the same specified temperature. In most of our discussions we shall consider the **standard enthalpy change**, $\Delta H°$, the change in enthalpy for a process in which the initial and final substances are in their standard states:

The **standard state** of a substance at a specified temperature is its pure form at 1 bar. For example, the standard state of liquid ethanol at 298 K is pure liquid ethanol at 298 K and 1 bar; the standard state of solid iron at 500 K is pure iron at 500 K and 1 bar.

As an example of a standard enthalpy change, the *standard enthalpy of vaporization*, $\Delta_{vap}H$, is the enthalpy change per mole when a pure liquid at 1 bar vaporizes to a gas at 1 bar, as in

$$H_2O\ (l) \rightarrow\ H_2O\ (g) \qquad \Delta_{vap}H^0(373K) = +40.66kJ\ mol^{\ -1}$$

As implied by the examples, standard enthalpies may be reported for any temperature.

However, the conventional temperature for reporting thermodynamic data is 298.15K (corresponding to 25°C). Unless otherwise mentioned, all thermodynamic data in this text will refer to this conventional temperature.

Enthalpies of physical change

The standard enthalpy change that accompanies a change of physical state is called the **standard enthalpy of transition** and is denoted $\Delta_{trs}H°$ .The **standard enthalpy of vaporization**, $\Delta_{vap}H°$, is one example. Another is the **standard enthalpy of fusion**, $\Delta_{fus}H°$, the standard enthalpy change accompanying the conversion of a solid to a liquid, as in

$$H_2O\ (s) \rightarrow\ H_2O\ (l) \qquad \Delta_{fus}H^0(373K) = +6.1kJ\ mol^{\ -1}$$

Because enthalpy is a state function, a change in enthalpy is independent of the path between the two states. This feature is of great importance in thermochemistry, for it implies that the same value of Δ*H*° will be obtained however the change is brought about between the same initial and final states. For example, we can picture the conversion of a solid to a vapour either as occurring by sublimation (the direct conversion from solid to vapour),

$$H_2O\ (s) \rightarrow\ H_2O\ (g) \qquad\qquad \Delta_{sub}H^0$$

or as occurring in two steps, first fusion (melting) and then vaporization of the resulting liquid:

$$H_2O\ (s) \rightarrow\ H_2O\ (l) \qquad\qquad \Delta_{fus}H^0$$

$$H_2O\ (l) \rightarrow\ H_2O\ (g) \qquad\qquad \Delta_{vap}H^0$$

$$Overall\!:\ \ H_2O\ (s) \rightarrow\ H_2O\ (g) \qquad\qquad \Delta_{sub}H^0$$

Because the overall result of the indirect path is the same as that of the direct path, the overall enthalpy change is the same in each case (**1**), and we can conclude that (for processes occurring at the same temperature)

$$\Delta_{sub}H^0 =\ \Delta_{fus}H^0 +\ (g)\,\Delta_{vap}H^0$$

An immediate conclusion is that, because all enthalpies of fusion are positive, the enthalpy of sublimation of a substance is greater than its enthalpy of vaporization (at a given temperature).

Laws of Thermochemistry

Another consequence of *H* being a state function is that the standard enthalpy changes of a forward process and its reverse differ in sign and equal in magnitude:

$$\Delta H^0(A \rightarrow B) =\ -\Delta H^0(B \rightarrow H)$$

For instance, because the enthalpy of vaporization of water is +44 kJ mol^{-1} at 298 K, its enthalpy of condensation at that temperature is −44 kJ mol^{-1}.

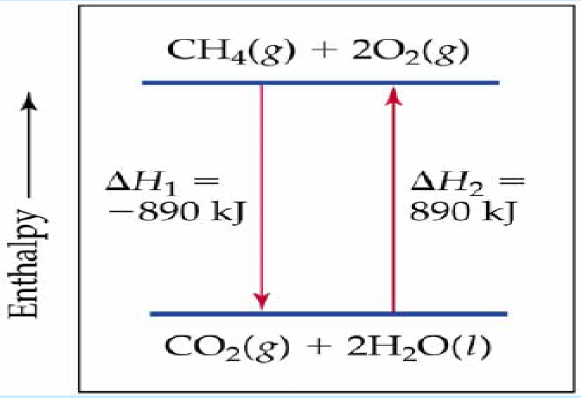
The enthalpy change for a reaction is equal in magnitude, but opposite in sign, to ΔH for the reverse reaction.

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

$\Delta H = -890$ kJ

$CO_2(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g)$

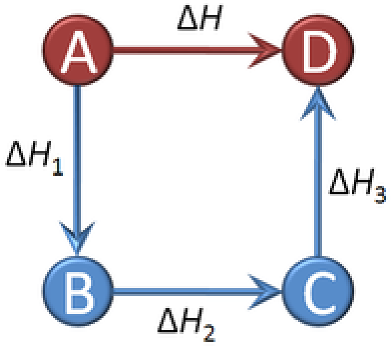
$\Delta H = 890$ kJ



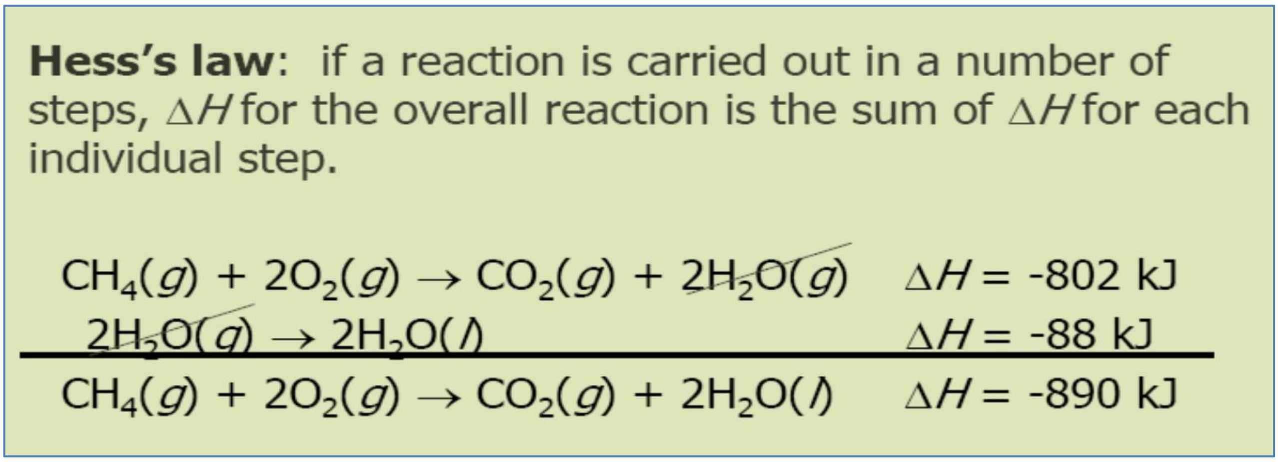
- ΔH_f ° - standard enthalpy of formation: ΔH for forming one mole of product directly from its reactants with products and reactants in standard states.
  - The standard enthalpy of formation of the most stable form of any element is zero.
- ΔH_{vap} ° – standard enthalpy of vaporization: ΔH for converting liquids to gases with products and reactants in standard states.
- ΔH_{fus} ° – standard enthalpy of fusion: ΔH for melting solids.
- ΔH_{sub} ° – standard enthalpy of sublimation: ΔH for converting solids to gases
- ΔH_{comb} ° – enthalpy of combustion: ΔH for combusting a substance with oxygen)

Hess's law

Standard enthalpies of individual reactions can be combined to obtain the enthalpy of another reaction or the resultant heat change at constant volume or pressure in a given chemical reaction is the same whether it take place in one or several steps. This application of the First Law is called **Hess's law**:



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



Hess's law: if a reaction is carried out in a number of steps, ΔH for the overall reaction is the sum of ΔH for each individual step.

$$\begin{array}{ll} CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + \cancel{2H_2O(g)} & \Delta H = -802\ kJ \\ \underline{\cancel{2H_2O(g)} \rightarrow 2H_2O(l)} & \underline{\Delta H = -88\ kJ} \\ CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) & \Delta H = -890\ kJ \end{array}$$

Calculate the enthalpy of the reaction: $C_2H_{4(g)} + HCl_{(g)} = C_2H_5\,Cl_g$

From the following reaction:

(i) $2\,C_{(s)} + \frac{5}{2}\,H_{2(g)} + \frac{1}{2}\,Cl_{2(g)} = C_2H_5\,Cl_g \qquad \Delta H^{\circ} = -112.1\ kJ$

(ii) $\frac{1}{2}\,H_{2(g)} + \frac{1}{2}\,Cl_{2(g)} = \mathrm{HCl}_{(g)} \qquad \Delta H^{\circ} = -92.35\ kJ$

(iii) $2\,C_{(s)} + 2\,H_{2(g)} = C_2H_{4\,(g)} \qquad \Delta H^{\circ} = 52.3\ kJ$

Solution:

By adding eq (ii) to eq (iii) we get:

$\frac{5}{2}\,H_{2(g)} + 2\,C_{(s)} + \frac{1}{2}\,Cl_{2(g)} = \mathrm{HCl}_{(g)} + C_2H_{4\,(g)} \quad \Delta H^{\circ} = -92.35\ kJ + 52.3\ kJ = -40.05\ kJ$

Subtracted eq (i) from the result equation:

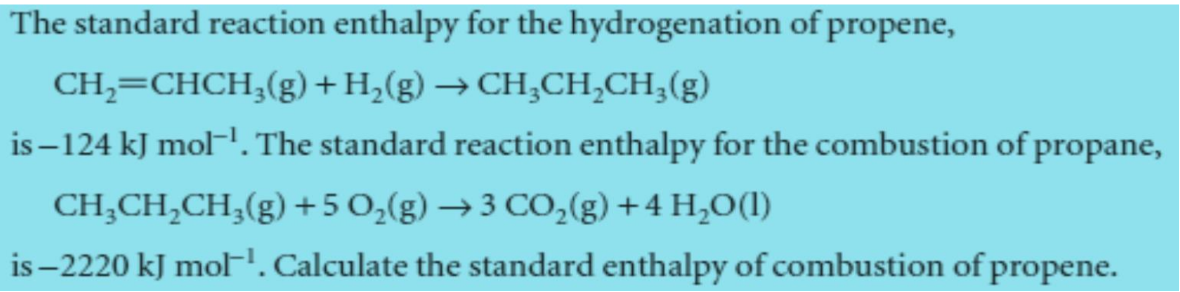
$$\frac{5}{2}\,\cancel{H}_{2(g)} + 2\,\cancel{C}_{(s)} + \frac{1}{2}\,\cancel{Cl}_{2(g)} = \mathrm{HCl}_{(g)} + C_2H_{4\,(g)}$$

$$2\,\cancel{C}_{(s)} + \frac{5}{2}\,\cancel{H}_{2(g)} + \frac{1}{2}\,\cancel{Cl}_{2(g)} = C_2H_5\,Cl_g$$

$$C_2H_5\,Cl_g = \mathrm{HCl}_{(g)} + C_2H_{4\,(g)} \quad \Delta H^{\circ} = -40.05\ kJ - (-112.1\ kJ) = +72.05\ kJ$$

$$C_2H_{4(g)} + HCl_{(g)} = C_2H_5\,Cl_g \qquad \Delta H^{\circ} = \ -72.05\ kJ$$

Example:



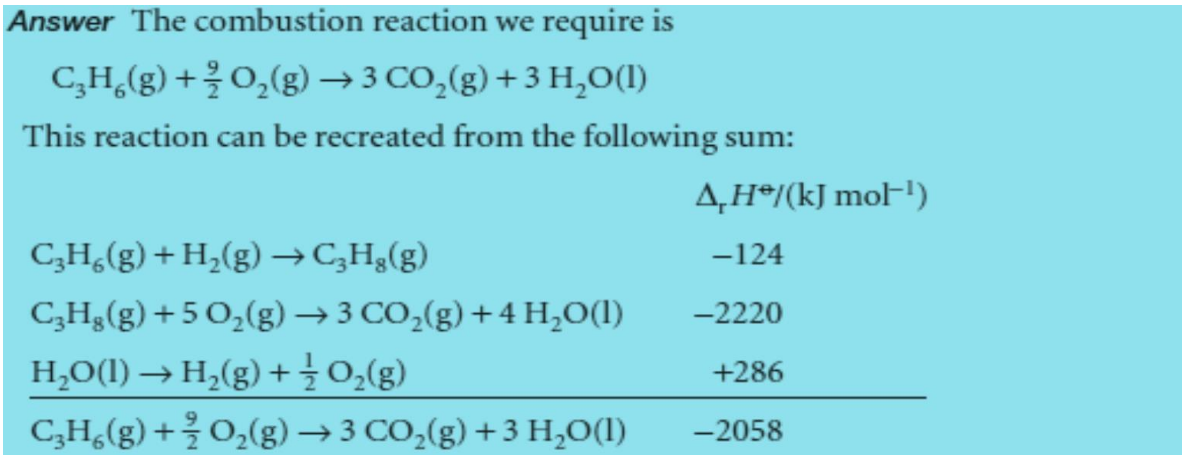
The standard reaction enthalpy for the hydrogenation of propene,

$$CH_2{=}CHCH_3(g) + H_2(g) \rightarrow CH_3CH_2CH_3(g)$$

is -124 kJ mol^{-1}. The standard reaction enthalpy for the combustion of propane,

$$CH_3CH_2CH_3(g) + 5\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(l)$$

is -2220 kJ mol^{-1}. Calculate the standard enthalpy of combustion of propene.

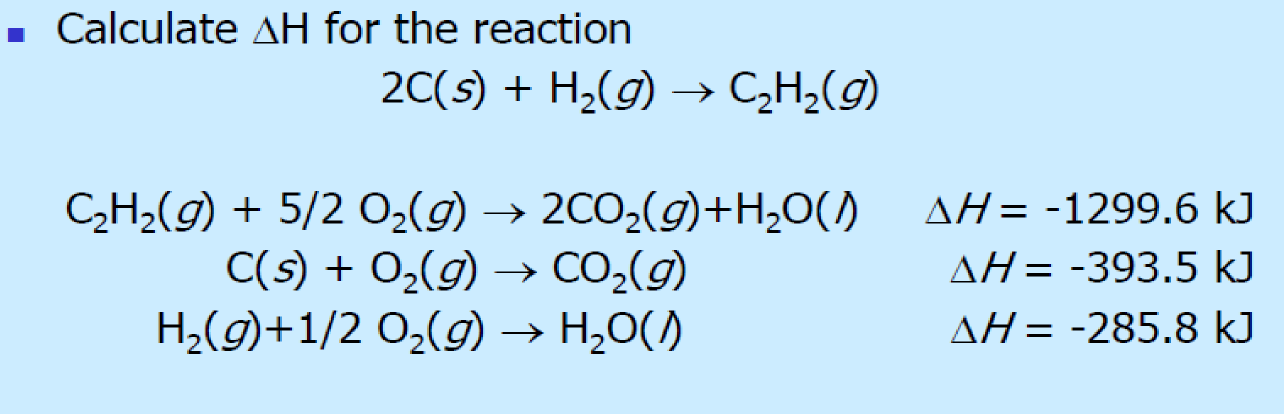


Answer The combustion reaction we require is

$$C_3H_6(g) + \tfrac{9}{2}\,O_2(g) \rightarrow 3\,CO_2(g) + 3\,H_2O(l)$$

This reaction can be recreated from the following sum:

	$\Delta_r H^{\ominus}/(\text{kJ mol}^{-1})$
$C_3H_6(g) + H_2(g) \rightarrow C_3H_8(g)$	-124
$C_3H_8(g) + 5\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(l)$	-2220
$H_2O(l) \rightarrow H_2(g) + \tfrac{1}{2}\,O_2(g)$	$+286$
$C_3H_6(g) + \tfrac{9}{2}\,O_2(g) \rightarrow 3\,CO_2(g) + 3\,H_2O(l)$	-2058



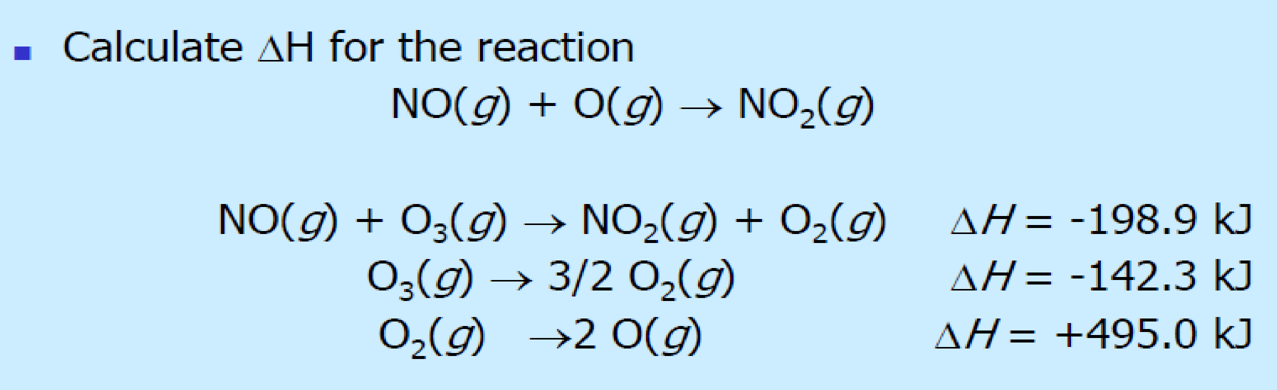
- Calculate ΔH for the reaction

$$2C(s) + H_2(g) \rightarrow C_2H_2(g)$$

$C_2H_2(g) + 5/2\ O_2(g) \rightarrow 2CO_2(g)+H_2O(l)$ $\Delta H = -1299.6$ kJ

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H = -393.5$ kJ

$H_2(g)+1/2\ O_2(g) \rightarrow H_2O(l)$ $\Delta H = -285.8$ kJ



- Calculate ΔH for the reaction

$$NO(g) + O(g) \rightarrow NO_2(g)$$

$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$ $\Delta H = -198.9$ kJ

$O_3(g) \rightarrow 3/2\ O_2(g)$ $\Delta H = -142.3$ kJ

$O_2(g) \rightarrow 2\ O(g)$ $\Delta H = +495.0$ kJ

The following conventions apply when we use ΔH

In a thermochemical equation, the enthalpy change of a reaction is shown as a ΔH value following the equation for the reaction. This ΔH value indicates the amount of heat associated with the reaction involving the number of moles of reactants and products *as shown in the chemical equation*. For example, consider this equation:

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H = -286\text{ kJ}$$

This equation indicates that when 1 mole of hydrogen gas and 1/2 mole of oxygen gas at some temperature and pressure change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released to the surroundings. If the coefficients of the chemical equation are multiplied by some factor, the enthalpy change must be multiplied by that same factor (ΔH is an extensive property):

(two-fold increase in amounts)

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) \qquad \Delta H = 2 \times (-286\text{ kJ}) = -572\text{ kJ}$$

(two-fold decrease in amounts)

$$\frac{1}{2}H_2(g) + \frac{1}{4}O_2(g) \longrightarrow \frac{1}{2}H_2O(l) \qquad \Delta H = \frac{1}{2} \times (-286\text{ kJ}) = -143\text{ kJ}$$

The enthalpy change of a reaction depends on the physical state of the reactants and products of the reaction (whether we have gases, liquids, solids, or aqueous solutions), so these must be shown. For example, when 1 mole of hydrogen gas and 1/2 mole of oxygen gas change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released. If gaseous water forms, only 242 kJ of heat are released.

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g) \qquad \Delta H = -242\text{ kJ}$$

A negative value of an enthalpy change, ΔH, indicates an exothermic reaction; a positive value of ΔH indicates an endothermic reaction. If the direction of a chemical equation is reversed, the arithmetic sign of its ΔH is changed (a process that is endothermic in one direction is exothermic in the opposite direction).

Enthalpies of chemical change

Standard enthalpies of formation ($\Delta_f H^\circ$)

The **standard enthalpy of formation**, $\Delta_f H^\circ$, of a substance is the standard reaction enthalpy for the formation of the compound from its elements in their reference states. The **reference state** of an element is its most stable state at the specified temperature and 1 bar. For example, at 298 K the reference state of nitrogen is a gas of N_2 molecules, that of mercury is liquid mercury, that of carbon is graphite, and that of tin is the white (metallic) form. Standard enthalpies of formation are expressed as enthalpies per mole of molecules or (for ionic substances) formula units of the compound. The standard enthalpy of formation of liquid benzene at 298 K, for example, refers to the reaction $6\ C(s,\ graphite) + 3\ H_2(g) \rightarrow C_6H_6(l)$ and is +49.0 kJ mol^{-1}. The standard enthalpies of formation of elements in their reference states are zero at all temperatures because they are the enthalpies of such 'null' reactions as $N_2(g) \rightarrow N_2(g)$

Enthalpy of Combustion ($\Delta_f H^\circ$)

Standard enthalpy of combustion ($\Delta_c H^\circ$) is the enthalpy change when 1 mole of a substance burns (combines vigorously with oxygen) under standard state conditions; it is sometimes called "heat of combustion." For example, the enthalpy of combustion of ethanol, −1366.8 kJ/mol, is the amount of heat produced when one mole of ethanol undergoes complete combustion at 25 °C and 1 atmosphere pressure, yielding products also at 25 °C and 1 atm.

$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2 + 3H_2O(l) \qquad \Delta H^\circ_{298} = -1366.8\ kJ$$

$$\Delta_c H^\circ = [3\Delta_f H^\circ\ H_2O + 2\Delta_c H^\circ CO_2] - [\Delta_f H^\circ (C_2H_5OH\ +\ \Delta_f H^\circ (O_2)]$$

$$\Delta_f H^\circ (O_2) = 0\ \ for\ elements$$

Enthalpy of neutralization (ΔH_n)

The **enthalpy of neutralization** (ΔH_n) is the change in enthalpy that occurs when one equivalent of an acid and a base undergo a neutralization reaction to form water and a salt.

Dilute solution should be used to avoid enthalpy changes due to mixing of acid and base. If one mole of a strong monoprotic acid (HCl, HNO_3 etc…) is mixed with 1 mole of strong base (NaOH, KOH etc…) neutralization take place as:

$$H_3O^+(aq) + OH^-(aq) = 2H_2O\ (l) \qquad \Delta H^\circ = -57.32kJ$$

Since these acid and base are completely ionized in dilute solution, the enthalpy change is always -57.32kJ.

For a weak acid or base the enthalpy of neutralization is not the same, but less than -57.32kJ. In this case neutralization involves ionization of the acid or the base in addition to neutralization. The heat required to ionize the weak acid or the weak base is known as the **enthalpy of ionization**. The enthalpy of ionization of a weak acid can be calculated from the enthalpies of neutralization of strong acid and weak acid by strong base. For example, in the neutralization of acetic acid by sodium hydroxide, the enthalpy of neutralization is -55.43kJ mol^{-1}. The enthalpy of ionization will therefore be equal to+1.89 $kJmol^{-1}$.

Bond enthalpies

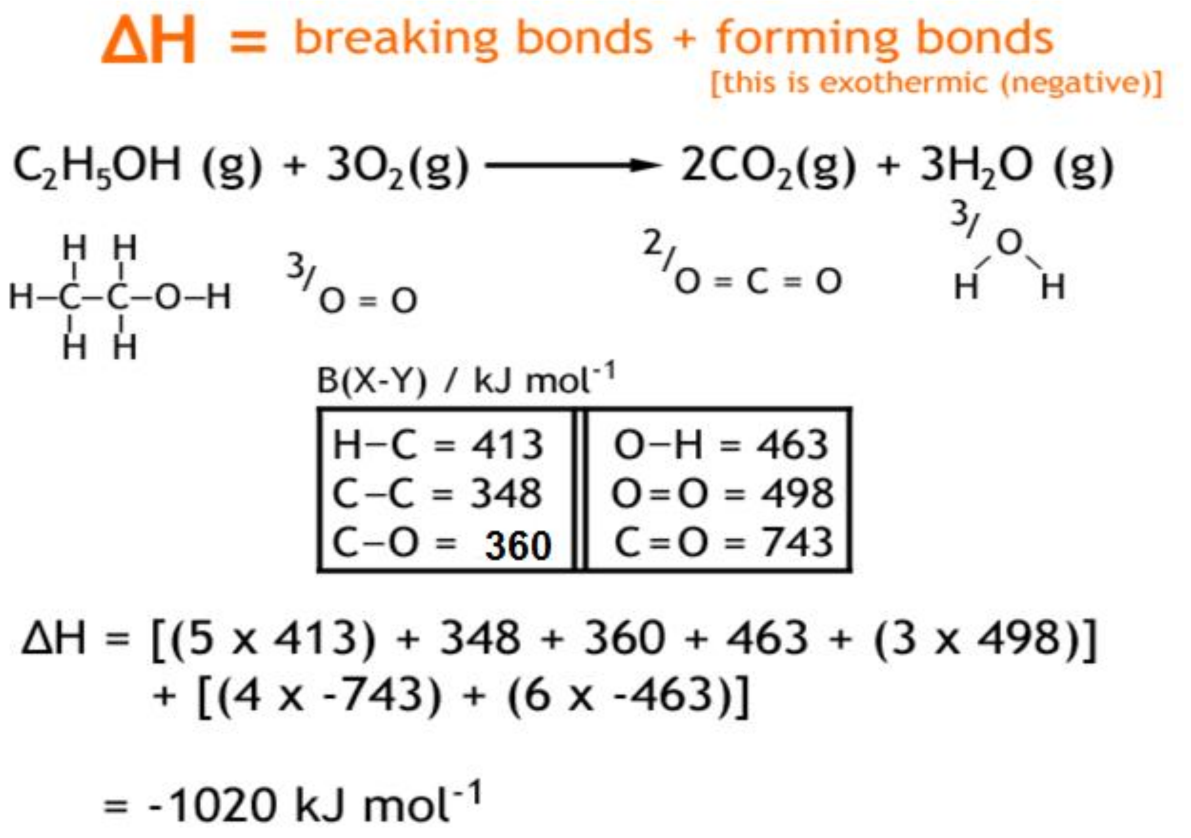
The amount of enthalpy required to break 1mole of a particular bond in a given compound and separate the resulting gaseous atoms or radicals from one another. It depends on the nature of the atoms linked by the bond and the nature of the molecule as a whole. The bond dissociation enthalpy of a hydrogen molecule is 435.9kJ mol^{-1}.

$$H_{2(g)} = 2H_{(g)} \qquad \Delta H^\circ = 435.9kJ\ mol^{-1}$$

In the case of water, the bond dissociation of an OH linkage is 497.8kJ and the enthalpy required to break the O-H bond in the residual group is 428.5 kJ.

$$H_2O_{(g)} = H_{(g)} + OH_{(g)} \qquad \Delta H^\circ = 497.8\ kJ\ mol^{-1}$$

$$OH_{(g)} = H_{(g)} + O_{(g)} \qquad \Delta H^\circ = 428.5\ kJ\ mol^{-1}$$



ΔH = breaking bonds + forming bonds

[this is exothermic (negative)]

$C_2H_5OH\ (g) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O\ (g)$

B(X-Y) / kJ mol^{-1}

H–C = 413
C–C = 348
C–O = 360
O–H = 463
O=O = 498
C=O = 743

ΔH = [(5 x 413) + 348 + 360 + 463 + (3 x 498)] + [(4 x -743) + (6 x -463)]

= -1020 kJ mol^{-1}

Example: calculate the bond enthalpy for a C-O bond in methanol from the following date:

(i) $C_{(s)} + 2\,H_{2(g)} + \frac{1}{2}O_{2(g)} \quad = \quad CH_3OH \quad = -200\ kJ/mol$

(ii) $C_{(s)} = C_{(g)} \qquad\qquad \Delta H^{\circ} = \ 716.8\ kJ\ /mol$

(iii) $2\ H_{2(g)} + \ = 4H_{(g)} \qquad\qquad \Delta H^{\circ} = \ 872\ kJ/mol$

(iv) $\frac{1}{2}O_{2(g)} \ = \ O_{(g)} \qquad\qquad \Delta H^{\circ} = \ 249\ kJ/mol$

The bond enthalpy of C-H is 413 kJ/mol and for O-H is 463.6 kJ/mol.

Solution: the enthalpy change for the dissociation of $CH_3OH_{(g)}$ is :

$$CH_3OH \ = C_{(g)} + \ 4H_{(g)} + \ O_{(g)} \qquad \Delta H^{\circ} = ?$$

Adding (ii), (iii) and (iv) gives

$$C_{(s)} + 2\,H_{2(g)} + \ \frac{1}{2}O_{2(g)} = \ C_{(g)} \ + \ 4H_{(g)} + \ O_{(g)} \ \ \Delta H^{\circ} = 1837.9kJ$$

Now subtracting eq (i) from the above equation gives:

$$CH_3OH \ = C_{(g)} + \ 4H_{(g)} + \ O_{(g)} \qquad \Delta H^{\circ} = 2037.8kJ$$

Since in methanol, there are three C-H, one C-O and one O-H bonds

$$2037.8kJ = 3(\Delta H^{\circ}_{(C-H)} + 1(\Delta H^{\circ}_{(o-H)}) + (\Delta H^{\circ}_{(C-O)})$$

$$2037.8kJ = 3 \times (415) + (463.6) + (\Delta H^{\circ}_{(C-O)})$$

$$(\Delta H^{\circ}_{(C-O)} = 329\ kJ/mol$$

Unsolved example:

- Calculate the enthalpy of the reaction:

$$C_2H_{4\,(g)} + Br_{2\,(g)} = C_2H_4Br_{2\,(g)}$$

The bond enthalpies (kJmol^{-1}) are $\Delta H^{\circ}_{(C-H)} = 415,$ $\Delta H^{\circ}_{(C=C)} = 610,$ $\Delta H^{\circ}_{(C-C)} = 348$, $\Delta H^{\circ}_{(C-Br)} = 276,$ $\Delta H^{\circ}_{(Br-Br)} = 193$.

The Temperature-Dependence of Reaction Enthalpies

The standard enthalpies of many important reactions have been measured at different temperatures. However, in the absence of this information, standard reaction enthalpies at different temperatures may be calculated from heat capacities and the reaction enthalpy at some other temperature. In many cases heat capacity data are more accurate that reaction enthalpies so, providing the information is available, the procedure we are about to describe is more accurate that a direct measurement of a reaction enthalpy at an elevated temperature.

when a substance is heated from T_1 to T_2, its enthalpy changes from $H(T_1)$

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

Because this equation applies to each substance in the reaction, the standard reaction enthalpy changes from

$$\Delta_r H^{\circ}(T_2) = \Delta_r H^{\circ}(T_1) + \int_{T_1}^{T_2} \Delta_r C_P^{\circ} dT$$

$$\Delta_r C_P^{\circ} = \sum\nolimits_{Products} C_P^{\circ} - \sum\nolimits_{reactants} C_P^{\circ}$$

This equation is known as **Kirchhoff's law** which expressing the temperature dependence of the thermal quantities associated with a chemical reaction through the difference in heat capacities between the products and reactants. It is normally a good approximation to assume that $\Delta_r C_p$ is independent of the temperature.

Example:

The standard enthalpy of formation of gaseous H_2O at 298 K is -241.82 kJ mol^{-1}. Estimate the value at 100 ^{0}C given the following values of molar heat capacities at constant pressure: $H_2O(g)$: 33.58 kJ mol^{-1}; H_2 (g) : 28.84 kJ mol^{-1}; O_2 (g) : 29.37 kJ mol^{-1}. Assume heat capacities are independent of T.

$$\Delta_r H^0(T_2) = \Delta_r H^0(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^0 dT = \Delta_r H^0(T_1) + (T_2 - T_1)\Delta_r C_p^0$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$$

$$\Delta_r C_p^0 = \Delta_r C_{p,m}^0(H_2O,g) - \{C_{p,m}^0(H_2,g) + \frac{1}{2}C_{p,m}^0(O_2,g)\}$$

It follows that

$$\Delta_r H^0(373K) = -241.82 kJ\,mol^{-1} + (75K)(-9.94 kJ\,mol^{-1})$$

$$= -242.6 kJ\,mol^{-1}$$

Unsolved example:

The enthalpy of fusion of water at 273K is 6.0kJ/mol-1 at constant pressure of 1 atm. Calculate its value at 263K.

$$C_{p(H2O)l} = 74.46\ Jmol^{-1}K^{-1}$$

$$C_{p(H2O)s} = 37.2\ Jmol^{-1}K^{-1}$$