1. Thermochemistry

Heat is a form of energy - which may take many forms:
- Kinetic energy due to motion, \( \frac{1}{2} mv^2 \)
- Potential energy due to position
- Electrical energy associated with electron flow.

Chemical Energy is a form of stored, or potential energy.

There is the possibility of liberating energy by a

In a chemical reaction such as:

\[
C + O_2 \rightarrow CO_2
\]

stored chemical energy is liberated as heat

Stored chemical energy may also be liberated as electrical energy (batteries)

\[
PbO_2(s) + Pb + 2 H_2SO_4 \rightarrow 2 PbSO_4(s) + 2 H_2O
\]

the reaction of the lead storage cell

2. Measurement of heat energy

Old, disused, system: the calorie. Defined as “Amount of heat required to raise the temperature of 1 g of water through 1 °C”.

Current S.I. unit is the Joule

Dimensions of Work : Force \( \times \) Distance
Dimensions of Force : Mass \( \times \) Acceleration
Dimensions of Acceleration : Distance \( \times \) Time\(^2\)

Energy (work) = Mass \( \times \) Distance\(^2\) \( \times \) Time\(^2\)

In S.I. units kg m\(^2\) s\(^{-2}\)

and the Joule is \( 1 \text{ kg m}^2 \text{ s}^{-2} = 1 \text{ N m} \)

e.g. the kinetic energy of a 2 kg mass moving at 1 ms\(^{-1}\)

K.E. = \( \frac{1}{2} mv^2 = \frac{1}{2} \times 2 \text{kg} \times (1 \text{ m s}^{-1})^2 = 1 \text{ kg m}^2 \text{ s}^{-2} = 1 \text{ Joule} \)

You may still see calories (especially in U.S. literature) -
1 calorie = 4.184 J
We need to define some terms, conventions in thermochemistry as they have specific meanings:

3. **System and Surroundings**
The **system** is that part of the universe on which our attention is focused.

We can define almost anything or combination of things as the system. Whatever is left over is the surroundings.

System + Surroundings = the universe

In principle, the surroundings are the rest of the universe. However, in practice the **surroundings** are the materials in close contact with the system. **The surroundings can exchange energy with the system.**

**SYSTEM**: the entire collection of “things” affected by the heat/energy changes in a thermochemical experiment or problem. This can in principle include the “surroundings”, but in a well regulated experiment it normally refers to the system under investigation.

The **system** can be **closed**: energy exchange, but no exchange of matter;
**open**: energy and matter can be exchanged
**isolated**: neither energy nor matter can be exchanged. For example a perfectly insulated, sealed container.

Energy is conserved, although the form of the energy might change in a physicochemical process. Eg. Chemical to heat energy; electrical to heat etc.
4. Direction and sign of heat “flow”

*Convention* is that the symbol for heat energy is “q” in J, or cal etc.

**q is -ve** when heat flows *from* the system *to* the surroundings; eg when energy (heat) is produced, (given off) in a reaction. This is further given the terminology “*exothermic*”

Conversely **q is +ve** when heat flows from surroundings to the system; eg when energy (heat) is absorbed in a process such as the melting of ice. These processes are “*endothermic*”

We have to take note of such variables as temperature, pressure, volume, phase (eg liquid, solid or gas) when we deal with Thermochemistry

Even at this stage of the description we can state that the “**total energy of the system and surroundings is conserved**”

*This is the First Law of Thermodynamics* and every thing in this section follows from this principle (Remember that the form of the energy can be changed, but conversion of matter to energy or the reverse requires nuclear processes, not chemistry)

We also need to introduce the concept of a **State Property**

A *state property* is a property of a system that does not depend upon the *route* taken to reach that state. Once we define the conditions of T, P, composition etc. of that piece of matter, we can define the value of that state property.

The most important characteristic of a state property is that the magnitude of the *change in the value of a state property does not depend upon the route taken to get from one state to another*. If we define the magnitude of the state property in the initial state as \( X_i \) and in the final state as \( X_f \), then the change in \( X \) (i.e., \( X \)) is given by

\[
\Delta X = X_f - X_i
\]

We shall see that thermochemical properties have this characteristic.
5. Magnitude of Heat Flow

The heat capacity is a measure of the amount of heat associated with the temperature change of a substance.

The heat capacity of a substance, often called its specific heat \( c \), is the amount of heat required to raise the temperature of 1 g of that substance by 1 °C.

\[ c = \frac{q}{\Delta T} \text{ per g of material in Joules (J)} \]

The specific heat, given the symbol “\( c \)”, which has the units energy per g per degree \( \text{eg J g}^{-1} \text{ °C}^{-1} \) is an intensive property, that is it does not depend upon the amount of the substance.

\[ q = \text{mass(g)} \times c \left( \text{J g}^{-1} \text{ °C}^{-1} \right) \times \Delta T \left( ^{\circ} \text{C} \right) \]

Note:
Sometimes the heat capacity is specified for a collection of things, for instance a calorimeter consisting of a container, thermometer, stirring device etc might be said to have a heat capacity of 150 J K\(^{-1}\). This means that 150 J are required to raise the temperature of the assembly one degree.

Note that a difference between two temperatures \( \Delta T \) is the same in °C or in K.

EXAMPLE
Consider Al metal, specific heat 0.902 J g\(^{-1}\) °C\(^{-1}\). How much heat is required to raise the temperature of 120 g Al from 25 °C to 100 °C?

\[ q = m \times c \times \Delta T = 120 \text{ g} \times 0.902 \text{ J g}^{-1} \text{ °C}^{-1} \times 75 \text{ °C} \]

\[ = 8118 \text{ J} = 8.118 \text{ kJ} \]

(Specific heat was invented by physicists and engineers, not chemists, and is therefore not tabulated on a molar basis).
EXAMPLE

The specific heat of water is 4.184 J g\(^{-1}\)°C. A lump of Al weighing 40 g is heated to 80 °C and dropped into 100 g of water at 25 °C. What is the temperature when thermal equilibrium has been reached?

Call the final temp \(T_f\) °C (for both water and Al)

\[ \text{Heat lost by Al} = \text{heat gained by water} \]

*Remembering that the Al will cool and the water will be heated:* (Since Al will cool, heat energy will be released from Al and therefore that side of the equation will be exothermic and q will be negative (-q); the other side must be +ve and equal to +q

\[ \text{Al: heat given out (-ve)} = \text{water: heat taken in (+ve)} \]

i.e. \[-(0.902 \times 40 \times (T_f - 80)) = + (100 \times 4.184 \times (T_f - 25))\]

and \(T_f = 29.4 \degree C\).

*The sign of the \(T\) is “automatically” taken care of in this approach.*

In the above example, for the Al, \(q = -1827\) J (heat energy lost); for the water, \(q = +1827\) J (heat energy gained).

The total is zero, energy is conserved.

The idea that the sign of the value of \(q\) (exo- or endo-thermic) automatically follows is illustrated by the example
**EXAMPLE:** How much heat is given off when a 50 g sample of Cu cools from 80°C to 50°C? \( c = 0.382 \, J \, g^{-1} \, \circ C^{-1} \)

\[
\Delta T = T_f - T_i = (50 - 80)\circ C = -30 \circ C
\]

\[
q = m \times c \times \Delta T = 50g \times 0.382 \, J \, g^{-1} \, \circ C^{-1} \times (-30) = -573 \, J
\]

The negative value means that the Al has lost heat.

**Calorimetry**

These processes can be measured by *calorimetry*. In a calorimeter, a reaction or other process that involves the production or absorption of heat can be directly measured. If the value of the heat capacity of the calorimeter is known and \( \Delta T \) is measured, the heat released (absorbed) in a process can be measured.

The coffee cup calorimeter: insulated vessel (so ‘no’ heat can escape), a thermometer to measure \( \Delta T \) and a known mass of water (known specific heat x mass).

If we assume that the heat capacity of the calorimeter itself is negligible and a reaction occurs which raises the temperature of the water:

Heat of reaction + heat transferred to water = 0 (since energy is conserved)

\[ q_{\text{reaction}} + m_{\text{water}} \times 4.184 \, J \, g^{-1} \, \circ C^{-1} \times (T_{\text{final}} - T_{\text{initial}}) = 0 \]

Note since \( (T_{\text{final}} - T_{\text{initial}}) \) is positive \( q \) will be negative

The *negative sign* originates from the fact that heat is *evolved, exothermic*. If the reaction *releases* heat, the calorimeter must *absorb* heat and in general we must write

\[ q_{\text{reaction}} = -q \text{ absorbed by the water} \]

Similarly, if a process *absorbs heat*, then the calorimeter must *release heat* in a measurement
EXAMPLE OF MEASUREMENT OF A HEAT OF REACTION BY CALORIMETRY

1.00 g of ammonium nitrate (NH₄NO₃) is dissolved in 50 g water in a coffee cup calorimeter and the following reaction occurs

\[
\text{NH}_4\text{NO}_3 (s) \rightarrow \text{NH}_4^+ (aq) + \text{NO}_3^- (aq)
\]

The temperature of the water, \( T \), decreases from 25.00 to 23.32 °C. Assuming that all the heat is absorbed by the water, calculate \( q \) for the reaction

\[
q_{\text{reaction}} + q \text{ for the calorimeter (in this case just the water)} = 0
\]

\[
q_{\text{reaction}} + \text{heat capacity H}_2\text{O} \times \text{mass H}_2\text{O} \times (T_{\text{final}} - T_{\text{initial}}) = 0
\]

\[
q_{\text{reaction}} + 4.184 \text{ J g}^{-1} \text{°C}^{-1} \times 50\text{ g} \times (23.32 - 25.00) = 0
\]

\[
q_{\text{reaction}} = +351 \text{ J}
\]

Note that this is a positive number and therefore the reaction in endothermic. This could have been deduced by inspection since the final temperature is less than the initial temperature and therefore heat must have been absorbed from the water in the coffee cup calorimeter.

Phase transitions; Changes of state

Heat energy may be consumed (produced) in changes of state at constant temperature (latent heat), where in this case, the state of the matter refers to the “phase” it is in: gas, liquid or solid. These transitions occur at fixed temperature while the phase (state) of the material changes: melting, boiling, vaporization.

For example:

Melting: latent heat of fusion or melting:

1 g ice at 0 °C \( \rightarrow \) 1 g water at 0 °C

Latent heat of melting \( q = +333 \text{ J g}^{-1} \)

i.e. endothermic: (we need to add energy to the system to cause the melting even though the temperature does not change)

Fusion is the reverse process, solidification

Vaporization: 1 g H₂O(l) at 100 °C \( \rightarrow \) 1 g H₂O(g) at 100 °C

Latent heat of evaporation \( q = +2,260 \text{ J g}^{-1} \)
Intuitively the reverse of these processes, i.e. fusion (solidification of water to form ice) and condensation (steam condensed to water at 100 °C) will be associated with the same magnitude of heat, but with the opposite sign. We shall see this is exactly the case.

The processes which involve a change of state can be carried out in a sequence of steps and these must produce the same final state, no matter the route.
Heat and Work

So far we have used $q$ to represent heat. Strictly we are interested in energy changes so that we must consider energy flows which will include both energy expressed as heat and that which appears as work.

Energy put into a system may be converted to mechanical work. Work done on a system will increase its energy content. In the above example of the change of state of CO$_2$, during the final step, (the expansion of the gas) work will be done by the gas on its surroundings.

Suppose the “system” (gas in this case) has internal energy content “$E$”, then the change in $E$ through these processes is $\Delta E$. We may increase this by adding either heat energy, $q$, or work energy, $w$ (or both). The mechanical work is...

$$w = P\Delta V, \text{ if } V = \text{constant}, \text{ no work is done.}$$

(Remember gas laws, PV has units of work or energy)

At constant pressure, the heat associated with a reaction or other process such as the one listed above, is given the symbol $q_p$

and $q_p = \Delta E + w$, where $w = P\Delta V$

at constant volume, $V = 0$ and no work is done and

$$q_v = \Delta E$$

This is the First Law of Thermodynamics

Note that $q$ and $w$ have a sign. If heat energy or work energy comes out of the system, the value of $q$ or $w$ may be negative (but the equation is unchanged).

Conclusion: When a chemical change is accompanied by work being done, the amount of heat energy evolved is correspondingly reduced in value (i.e some of the energy is ‘used up’ doing work).

By convention the value of $q$ at constant pressure,

$$q_p = \Delta H$$

$\Delta H = \Delta E + \Delta PV$

where “$H$” is a quantity called enthalpy. Since this involves the total energy content of a system, and it is not possible to determine (or calculate) absolute values, we shall see that we always deal with differences in $H$; i.e. $H$ values from standardized states.

$\Delta H$ is usually defined at $T = 25.00 \, ^oC (298.15 \, K)$ and 1 bar and for a specified amount of substance/reactants etc.
For our purposes we will consider energy changes as manifested by $\Delta H$ and ignore the $P\Delta V$ term.

As we have defined earlier, if heat is evolved, $\Delta H$ is negative, and the reaction is said to be **exothermic**.

If heat is gained by system, $\Delta H$ is positive, and the reaction is said to be **endothermic**.

e.g. for the combustion of octane:

$$C_8H_{18(l)} + \frac{25}{2}O_{2(g)} \rightarrow 8CO_{2(g)} + 9H_2O(l)$$

$\Delta H = -5476$ kJ., highly exothermic.

**Note** the state of all reactants and products must be specified in a thermochemical expression, since changes in state require energy the energy absorbed or released will depend on the state of each reactant and product.

**Note:** A $\Delta H$ value written beside an equation is based on the numbers of moles of all substances present, so we do not write “mol$^{-1}$”. If the $\Delta H$ value is associated with one reactant only it would be “per mole”, e.g. the heat of combustion of octane is $-5476$ kJ mol$^{-1}$

**Enthalpy change** in a reaction depends only on the **initial state** and the **final state** of the system.

If we could actually determine the $H$ values for the initial and final states of a system, $H_i$ and $H_f$ of a system, then the enthalpy change, $\Delta H$ is given by:

$$\Delta H = H_f - H_i$$

It does NOT depend on the route taken to go from initial to final state. As already described quantities of which this is true are said to be **state functions**.

It follows that, if a reaction or a change of state process is carried out in a series of steps, the **overall** $H$ is the sum of the $H$ values of the component steps (sometimes called **Hess’s Law**)

The value of $H$ for a reaction is the same whether it occurs in one step or in a series of steps.
A consequence of the fact that the \( H \) values are functions of state is that the \( H \) value for the reverse of a given process or reaction has the **opposite** sign.

E.g.

\[
\begin{align*}
C(s) + O_2(g) & \rightarrow CO_2(g) \quad \Delta H = -394 \text{ kJ} \quad \text{exothermic} \\
CO_2(g) & \rightarrow C(s) + O_2(g) \quad \Delta H = +394 \text{ kJ} \quad \text{endothermic}
\end{align*}
\]

6. Combining Reactions and combining \( \Delta H \) values.

*When equations are added, \( \Delta H \) values are added.*

This permits us to compute \( H \) values for reactions that would otherwise be difficult or impossible to measure.

**Example.** What is \( \Delta H \) for \( CO + \frac{1}{2} O_2 \rightarrow CO_2 \)?

*Given:* \( C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H = -394 \text{ kJ} \quad 1 \)

*and* : \( C(s) + \frac{1}{2} O_2(g) \rightarrow CO(g) \quad \Delta H = -111 \text{ kJ} \quad 2 \)

Our task is to devise a set of equations that when added together, yield the desired reaction. This can involve rewriting a particular reaction in the reverse direction. If we do this we have to reverse the sign of the \( H \) value.

Thus:

Reverse reaction 2: \( CO \rightarrow C + \frac{1}{2} O_2 \quad \Delta H = +111 \text{ kJ} \)

Adding 1:

\[
\begin{align*}
\text{CO} + \text{C} + \text{O}_2 & \rightarrow \text{C} + \frac{1}{2}\text{O}_2 + \text{CO}_2 \\
\text{CO} +\frac{1}{2} \text{O}_2 & \rightarrow \text{CO}_2 \quad \Delta H = -283 \text{ kJ}
\end{align*}
\]

**Example:** Calculate the enthalpy of the reaction

\[
C(\text{graphite}) + 2 S(s) \rightarrow CS_2(l)
\]

given:

\[
\begin{align*}
\text{C(\text{graphite})} + O_2(g) & \rightarrow CO_2(g) \quad \Delta H_1 \quad (1) \\
\text{S(s)} + O_2(g) & \rightarrow SO_2(g) \quad \Delta H_2 \quad (2) \\
\text{CS}_2(l) + 3 O_2(g) & \rightarrow CO_2(g) + 2 SO_2(g) \quad \Delta H_3 \quad (3)
\end{align*}
\]
Since we need to derive the first equation with CS$_2$(l) on the rhs of the equation we should rewrite equation 3 in the reverse direction:

\[ \text{a) } CO_2(g) + 2 SO_2(g) \rightarrow CS_2(l) + 3 O_2(g) \quad - \Delta H_3 \]

we need 2 sulphurs so we multiply equation 2 by a factor of 2:

\[ \text{b) } 2 S(s) + 2 O_2(g) \rightarrow 2 SO_2(g) \quad 2\Delta H_2 \]

then \[ \text{c) } C(\text{graphite}) + O_2(g) \rightarrow CO_2(g) \quad \Delta H_1 \]

adding a) + b) + c)

\[ CO_2(g) + 2 SO_2(g) + 2 S(s) + 2 O_2(g) + C(\text{graphite}) + O_2(g) \rightarrow CS_2(l) + 3 O_2(g) + 2 SO_2(g) + CO_2(g) \]

OR:

\[ C(\text{graphite}) + 2 S(s) \rightarrow CS_2(l) \quad \Delta H = \Delta H_1 + 2 \Delta H_2 + (-\Delta H_3) \]

Thus stoichiometrically balanced reaction equations can be treated like algebra, and can be added and subtracted to yield a desired equation for a reaction. Similarly the $\Delta$H values can be added together taking into account the appropriate signs for each reaction. These rules are summarized in the next viewgraph, but this also applies to combined reactions and changes of state etc.

For example, suppose we wish to know the $\Delta$H for the process of converting H$_2$O(l) to H$_2$(g) and O$_2$(g) and are given the $\Delta$H values for the vaporization of liquid water and for the conversion of gaseous water to H$_2$ and O$_2$

\[ H_2O(l) \rightarrow H_2O(g) \quad \Delta H = + 44 \text{ kJ mol}^{-1} \]
\[ H_2O(g) \rightarrow H_2(g) + \frac{1}{2} O_2(g) \quad \Delta H = +242 \text{ kJ mol}^{-1} \]

Adding these 2 equations:

\[ H_2O(l) \rightarrow H_2(g) + \frac{1}{2} O_2(g) \quad \Delta H = 286 \text{ kJ mol}^{-1} \]

and schematically what we are describing is:

\[ H_2O(l) \rightarrow H_2O(g) \rightarrow H_2(g) + \frac{1}{2} O_2(g) \quad \Delta H = 286 \text{ kJ mol}^{-1} \]
Thermochemistry rules for reactions

1. The magnitude of $\Delta H$ is directly proportional to the amount of reactant or product

   Enthalpies, $H$ or changes of enthalpy, $\Delta H$ are given *per mole* of substance. Thus if the values are given per g (for example) they should be converted to the value per mole by multiplying by the molar mass in g. $\times \Delta H$ for a reaction is given for the balanced stoichiometric equation as written. This is important since stoichiometrically balanced thermochemical equations relate to the molar ratios.

2. $\Delta H$ for a reaction is equal in magnitude and opposite in sign to $\Delta H$ for the reverse reaction.

   e.g. $H_2O (s) \rightarrow H_2O (l)$ \hspace{1cm} $\Delta H = +6.00 \text{ kJ mol}^{-1}$
   $H_2O (l) \rightarrow H_2O (s)$ \hspace{1cm} $\Delta H = -6.00 \text{ kJ mol}^{-1}$

3. The value of $\Delta H$ for a reaction is the same whether it occurs in one step or a series of steps:

7. Thermochemical Equations

Thermochemical equations are balanced, and give the appropriate value and sign for $\Delta H$.

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g) \hspace{1cm} \Delta H = -185 \text{ kJ}$$

… is a thermochemical equation.

- The sign of $\Delta H$ indicates whether the reaction produces heat (exothermic, $\Delta H$ negative), or absorbs heat (endothermic, $\Delta H$ positive).

- The value of $\Delta H$ refers to the number of moles as given in the equation. In the example above, 185 kJ of heat are produced when 1 mol of $H_2$ and 1 mol of $Cl_2$ react to form 2 moles of HCl.

- The physical states (phases) of all the reactants and products must be specified $s$, $l$, $g$, or $aq$. (The enthalpy of liquid water is lower than that of water vapor, clearly this is important….)
• Unless stated otherwise, we assume reactants and products to be at 25° C.

**HESS' LAW**

Thus if a thermochemical equation can be expressed as a sum of two or more equations, each with a corresponding $\Delta H$ value, $\Delta H_1, \Delta H_2, \ldots$ etc.), Then the $\Delta H$ for the overall reaction is the sum of the $\Delta H$'s for the individual reactions as defined by their appropriate balanced stoichiometric equations.

i.e. $\Delta H = \Delta H_1 + \Delta H_2 + \ldots$

**Example of independence of the value of $\Delta H$ of a reaction upon the route**

**Combustion reactions** are very important (e.g. gasoline engine). *The heat of combustion is the enthalpy change $\Delta H$ associated with the combustion of 1 mol of the substance with $O_2(g)$ producing the most thermochemically stable oxidized states of the products at 25°C and 1 atm pressure.*

For carbon: **most stable oxide is $CO_2(g)$**

For hydrogen: **most stable oxide is $H_2O(l)$ not $H_2O(g)$**

Exception to the rule: for **nitrogen the most stable state is $N_2(g)$, not an oxide!**

Eg: \[ CH_3NH_2 + 9/4 \ O_2(g) \rightarrow CO_2(g) + 5/2 \ H_2O(l) + 1/2 \ N_2(g) \]

**EXAMPLE:** *Oxidation of heptane, $C_7H_{16}(l)$*

$C_7H_{16}(l) + 11 \ O_2(g) \rightarrow 7 \ CO_2(g) + 8 \ H_2O(l) \ \ \ \Delta H = -4818 \ kJ$

This can be produced by the following reaction schemes:

**A)**

$C_7H_{16}(l) + 7.5 \ O_2(g) \rightarrow 7 \ CO(g) + 8 \ H_2O(l) \ \ \ \Delta H = -2832 \ kJ$

and

$7 \ CO(g) + 3.5 \ O_2(g) \rightarrow CO_2(g) \ \ \ \Delta H = -1986 \ kJ \ mol^{-1}$

Add these two reactions, get desired reaction with $\Delta H = -2832 + (-1986) \ kJ \ mol^{-1} = -4818 \ kJ$

**B)**

$C_7H_{16}(\ ) + 4 \ O_2(g) \rightarrow 7 \ CH_2O (g) + H_2O(l) \ \ \ \Delta H = -873 \ kJ$
and

\[ 7 \text{CH}_2\text{O}(g) + 7 \text{O}_2(g) \rightarrow 7 \text{CO}_2(g) + 7 \text{H}_2\text{O}(l) \quad \Delta H = -3945 \text{ kJ} \]

adding yields desired reaction and

\[ \Delta H = -873 \ + \ (-3945) \ = \ -4818 \text{ kJ} \]

This is fine so far as it goes. We could have all the data in tables of \( \Delta H \) values for a huge number of reactions. This is not desirable or practical and it would be much better to tabulate \( \Delta H \) values of individual compounds which could be used in any hypothetical reaction to obtain \( \Delta H_{\text{rxn}} \). This has been achieved through the use of \textit{standard enthalpies of formation}, \( \Delta H_f^o \)

The standard Molar Enthalpy of Formation is \( \Delta H \) of reaction when 1 mol of compound (in standard state) is formed from its component elements in their standard states. Symbol \( \Delta H_f^o \)

\textit{“Standard State”} is the physical state in which an element is found at 25 °C and 1 atm pressure. e.g. \( \text{H}_2, \text{O}_2, \text{N}_2, \text{Cl}_2 \) are gaseous, \( \text{Br}_2 \) a liquid, C a solid, etc.

In the case of an element known in more than one form (\textit{allotropy}) the standard state is that of lowest energy

\textit{e.g. C(graphite), not diamond.}

It follows from this definition that

\[ \Delta H_f^o \text{ of an element in its standard state is zero} \]

and that \( \Delta H_f^o \) for other forms (allotropes) of the element must be positive.

By Hess’ Law:

\[ \Delta H \text{ of Reaction} = \]
\[ (\text{Total } \Delta H_f^o \text{ of all Products}) + (- \text{ Total } \Delta H_f^o \text{ of all Reactants}) \]

On this basis we can write:

\( \Delta H \) for any chemical reaction can be written as the algebraic sum of the reactions in which each compound, reactant and product is produced from its constituent elements in their standard states.

Since \( \Delta H_f^o = \) heat of formation for any substance is defined as the \( \Delta H \) for the reaction in which 1 mol of substance is produced from its constituent elements in their standard states:

\( \Delta H \text{ (for any reaction)} = \text{sum of } \Delta H_f^o \text{’s of products minus the sum of the } \Delta H_f^o \text{’s of the reactants} \]

\[ = \Sigma \Delta H_f^o \text{’s (products)} - \Sigma \Delta H_f^o \text{’s (reactants)} \]
This works for all reactions including **enthalpy of atomization of the elements**:

\[ \text{H}_2(\text{g}) \rightarrow 2 \text{H}(\text{g}) \text{ atomic hydrogen} \quad \Delta H = +432 \text{ kJ}, \]

So: \[ \Delta H_f^o (\text{H, atomic}) = \frac{432}{2} = 216 \text{ kJ mol}^{-1} \]

**Note that the value of 432 kJ mol\(^{-1}\) is called the bond dissociation energy of H\(_2\)(g).** Note also that it is **by definition** \(2 \times \Delta H_f^o (\text{H-atom})\)

\[ \text{C(graphite)} \rightarrow \text{C(diamond)} \quad \Delta H_f^o = +1.895 \text{ kJ mol}^{-1} \]

\[ \text{C(graphite)} \rightarrow \text{C(atomic, gas)} \quad \Delta H_f^o = +717 \text{ kJ mol}^{-1} \]

*This is also applicable to the atomization of compounds as we shall see in the section on bond energies.*

**For compounds,**

e.g. \[ \text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \]

\[ \Delta H = -394 \text{ kJ.} \quad \Delta H_f^o \text{ CO}_2(\text{g}) = -394 \text{ kJ mol}^{-1} \]

**Reactions**

**Example.** Using \(\Delta H_f^o\) values calculate the enthalpy of combustion of methane, \(\text{CH}_4(\text{g})\)

\[ \text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) \]

\[ \Delta H_f^o \quad -75 \quad 0 \quad -394 \quad 2 \times (-286) \]

\[ \Delta H_{\text{reaction}} = [ -394 + 2 \times (-286) ] - [ (-75) ] \]

\[ = -891 \text{ kJ per mol of CH}_4 \]

**Example.** Benzene, \(\text{C}_6\text{H}_6(\text{l})\) has enthalpy of combustion of \(-3271 \text{ kJ mol}^{-1}\). What is its \(\Delta H_f^o\)?

First write down the balanced combustion reaction:

\[ \text{C}_6\text{H}_6(\text{l}) + 15/2 \text{O}_2(\text{g}) \rightarrow 6 \text{ CO}_2(\text{g}) + 3 \text{H}_2\text{O}(\text{l}) \]

\[ \Delta H_f^o \quad 0 \quad 6 \times (-394) \quad 3 \times (-286) \]

Note: in a problem like this a table of the appropriate \(\Delta H_f^o\) would be provided (not however for the elements in their standard states)>

\[ 3 \times (-286) + 6 \times (-394) - \Delta H_f^o(\text{benzene}) - 0 = -3271 \text{ kJ mol}^{-1} \]

\[ \Delta H_f^o(\text{benzene}) = +49 \text{ kJ mol}^{-1} \]
Note the difference in the $\Delta H^\circ$ values:

**Methane** \[ C + 2 \text{H}_2 \rightarrow \text{CH}_4 \]

$\Delta H^\circ = -75 \text{ kJ mol}^{-1}$ Exothermic

**Benzene** \[ 6 \text{C} + 3 \text{H}_2 \rightarrow \text{C}_6\text{H}_6 \]

$\Delta H^\circ = +49 \text{ kJ mol}^{-1}$ Endothermic

Benzene is less stable than its component elements. It is an endothermic compound. Most compounds have a negative $\Delta H^\circ$ value and are more stable than their elements.

8. **Experimental Determination of $H$ by calorimetry**

Reaction occurs inside a strong container or “bomb” surrounded by water to absorb the heat energy.

Heat evolved in reaction = Heat absorbed by water + heat absorbed by “bomb”

**Example.** 1.00 g of sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ is burnt, and the temperature rises from 25.00 °C to 27.32 °C. The mass of water is $1.50 \times 10^3$ g, and the heat capacity of the bomb 837 J K$^{-1}$. The specific heat of water is 4.184 J g$^{-1}$ K$^{-1}$. Calculate the heat evolved per mole of sucrose.

Heat of reaction + heat gained (or lost) by water + heat gained (or lost) by the calorimeter = 0

Heat of reaction + ((heat capacity $\text{H}_2\text{O}$) x Mass $\text{H}_2\text{O}$ x $\Delta T$ $\text{H}_2\text{O}$) + heat capacity calorimeter x $\Delta T$ calorimeter = 0

Heat of reaction + 4.184 J g$^{-1}$K$^{-1}$ x 1.50 x $10^3$ g x ($T_f$ $\text{H}_2\text{O}$ - $T_i$ $\text{H}_2\text{O}$) + 837 J K$^{-1}$ x ($T_f$ calorimeter - $T_f$ calorimeter) = 0

Heat of reaction + 4.184 J g$^{-1}$K$^{-1}$ x 1.50 x $10^3$ g x (27.32 - 25.00) + 837 J K$^{-1}$ x (27.32 - 25.00) = 0

Heat of reaction = $-16502$ j = $-16.5$ kJ g$^{-1}$

Total heat produced by combustion of 1 g sucrose

$= -16.5$ kJ g$^{-1}$ (Exothermic)

heat evolved per mole of sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ is

$(-16.5$ kJ g$^{-1}) \times (342.3$ g mol$^{-1}) = -5650$ kJ mol$^{-1}$
9. BOND ENERGIES

The concept we will explore here is that of relating enthalpy changes to energies stored in individual bonds in a molecule. We will see that we can use enthalpies to deduce average bond energies, $BE$, and the reverse process of using bond energies to deduce enthalpies.

The bond energies are related to the enthalpy required to break a molecule into its constituent atoms, which of course has the consequence of breaking all the bonds.

E.g.

$$\text{CH}_4(\text{g}) \rightarrow \text{C}(\text{atomic, g}) + 4\text{H}(\text{atomic, g}) \quad \Delta H = 1662 \text{ kJ mol}^{-1}$$

**Important: all reactants and products must be gases**

This enthalpy is required to break 4 C-H bonds to make gaseous atoms. These processes are always endothermic.

We define: TOTAL BONDING ENERGY (TBE)

*TBE of a molecule is the energy (enthalpy) required to dissociate 1 mol of a gaseous compound into free constituent atoms.* It is sometimes called the *heat of atomization*. Note that we can write for this reaction, $TBE = \Delta H = \Delta H_f^o (\text{C, atomic, g}) + 4\Delta H_f^o (\text{H, atomic, g}) - \Delta H_f^o (\text{CH}_4, \text{g})$

In the case of the example above, we broke 4 C-H bonds and therefore, on average, each bond requires:

$$4 \times \text{BE}(\text{C-H}) = 1662 \quad \text{and} \quad \text{BE}(\text{C-H}) = 1662/4 = 415.5 \text{ kJ mol}^{-1} \text{ of C-H bonds}$$

This is then the "bond energy" of a C-H bond in CH₄.

The bond energy is the averaged contribution of the bond between a pair of atoms A-B to the total binding energy (BE) of a molecule. Bond energies lie in the range 120-1200 kJ mol⁻¹.
**Atomization of diatomic molecules**

The only case where the BE is *not* the average BE is in the atomization of a diatomic molecule.

Thus: \[ O_2(g) \rightarrow 2 \text{O(atomic, g)} \quad \Delta H^o = 498.4 \text{ kJ mol}^{-1} \]

and this is TBE of \( O_2 \) molecule and since there is only one O-O bond it equals the O-O bond energy. **(Note: this does not imply that there is only a “single” bond between the 2 O-atoms)**

Note that we make 2 O-atoms in this reaction. We can also write \( \Delta H \) for this reaction in terms of \( H_f^o \)

\[ \Delta H^o = 2 \Delta H_f^o (\text{O, atomic, g}) - \Delta H_f^o (O_2, g) \]

\[ = 2 \times 249.2 - 0 \text{ kJ mol}^{-1} \quad \text{O}_2(g) = 498.4 \text{ kJ mol}^{-1} \]

**Note that the \( \Delta H_f^o \) of an O-atom is half the bond energy, since 2 O-atoms are produced per \( O_2(g) \) molecule.**

**Bond energies in organic molecules containing C-H, C-C, C-O, C-N etc.**

The bond energies are almost constant in such molecules; i.e. the C-C bond energy in one molecule is the same as the C-C BE in another molecule, *provided that the “bond order” is the same in the two molecules.*

For example, alkane hydrocarbons: \( C_nH_{2n+2} \), which contain only single bonds; i.e. C-C and C-H are all single bonds (bond order = 1)

\( n = 1: \) CH\(_4\), methane

\( n = 2: \) C\(_2\)H\(_6\), ethane

\( n = 3: \) C\(_3\)H\(_8\), propane

We can compute C-C and C-H BE’s from enthalpy of atomization data.
Propane $C_3H_8$, 2 C-C bonds, 8 C-H bonds

$\Delta H_f^0 (C_3H_8,g) = -103.9 \text{ kJ mol}^{-1}$

$C_3H_8(g) \rightarrow 3 \text{C(atomic, g)} + 8 \text{H(atomic, g)}$

$\Delta H^o$ for this reaction is the TBE by definition, and

$\Delta H^o = 3 \Delta H_f^0 (\text{C, atomic, g}) + 8 \Delta H_f^0 (\text{H, atomic, g}) - \Delta H_f^0 (C_3H_8,g)$

$= 3 \times 715 + 8 \times 218 - (-103.9) = 3992.9 \text{ kJ mol}^{-1}$

Therefore $8 \times \text{BE(C-H)} + 2 \times \text{BE(C-C)} = 3992.9 \text{ kJ mol}^{-1}$  \text{1}$

However while we have TBE for $C_3H_8(g)$, the molecule has two sorts of bonds (C-C and C-H) and we cannot deduce the individual energies. \textit{Need further information}

Butane $C_4H_{10}$; 3 C-C bonds, 10 C-H bonds

$\Delta H_f^0 (C_4H_{10},g) = -127 \text{ kJ mol}^{-1}$

$C_4H_{10}(g) \rightarrow 4 \text{C(atomic, g)} + 10 \text{H(atomic, g)}$

$\Delta H^o = 4 \Delta H_f^0 (\text{C, atomic, g}) + 10 \Delta H_f^0 (\text{H, atomic, g}) - \Delta H_f^0 (C_4H_{10},g)$

$= 4 \times 715 + 10 \times 218 - (-127) = 5167 \text{ kJ mol}^{-1} = \text{TBE}$

Therefore: $10 \times \text{BE(C-H)} + 3 \times \text{BE(C-C)} = 5167 \text{ kJ mol}^{-1}$  \text{2}$

Need to solve equations 1 and 2 for BE(C-C) and BE(C-H)

Simultaneous equations:

\text{i x 3:} \quad 24 \times \text{BE(C-H)} + 6 \times \text{BE(C-C)} = 11978.7 \text{ kJ mol}^{-1}$

\text{2 x 2:} \quad 20 \times \text{BE(C-H)} + 6 \times \text{BE(C-C)} = 10334 \text{ kJ mol}^{-1}$

Subtracting: $4 \times \text{BE(C-H)} = 1644.7 \text{ kJ mol}^{-1}$

$\text{BE(C-H)} = 1644.7 / 4 = 411.2 \text{ kJ mol}^{-1}$ of C-H bonds

and $\text{BE(C-C)} = 351.7 \text{ kJ mol}^{-1}$ of C-C bonds
Note that the value for BE(C-H) is slightly different from the value obtained from atomizing CH\(_4\)(g). Note also that different tables often provide slightly different values of BE’s. Don’t worry about this, you will be provided with data as necessary! (M&H table has problems)

**Multiple bonds**

If we have bonds in a molecule with a different bond order, ie single, double, triple, we treat them in exactly the same way. *Note that the BE of a C=C bond is not 2 x BE(C-C) etc.* Thus:

\[
\text{H}_2\text{C} = \text{CH}_2 \rightarrow \text{H}_2\text{C} + \text{CH}_2, \Delta H = +611 \text{ kJ}
\]

\[
\text{H} = \text{C} = \text{CH} \rightarrow \text{HC} + \text{CH}, \Delta H = +837 \text{ kJ}
\]

Bond strength is increasing 1 < 2 < 3.

Similarly with diatomic molecules:

<table>
<thead>
<tr>
<th></th>
<th>F-F</th>
<th>O=O</th>
<th>N≡N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>153</td>
<td>498</td>
<td>941</td>
</tr>
</tbody>
</table>

A selection of Bond Dissociation Energies, kJ mol\(^{-1}\)

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>S</th>
<th>F</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>436</td>
<td>414(411)</td>
<td>389</td>
<td>464</td>
<td>339</td>
<td>565</td>
<td>431</td>
</tr>
<tr>
<td>C</td>
<td>347(352)</td>
<td>293</td>
<td>351</td>
<td>259</td>
<td>485</td>
<td>331</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>159</td>
<td>222</td>
<td></td>
<td></td>
<td>272</td>
<td></td>
<td>201</td>
</tr>
<tr>
<td>O</td>
<td></td>
<td></td>
<td>138</td>
<td>184</td>
<td>205</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td></td>
<td></td>
<td></td>
<td>226</td>
<td>285</td>
<td>255</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>153</td>
<td>255</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>243</td>
<td></td>
</tr>
</tbody>
</table>

The values of C-C and C-H in () are “better” values

<table>
<thead>
<tr>
<th></th>
<th>ČC</th>
<th>ČN</th>
<th>ČN</th>
<th>ČN</th>
<th>ČN</th>
</tr>
</thead>
<tbody>
<tr>
<td>C≡C</td>
<td>820</td>
<td>890</td>
<td>941</td>
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<tr>
<td>C≡C</td>
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<td></td>
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<td>715</td>
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<tr>
<td>C≡S</td>
<td>477</td>
<td></td>
<td>418</td>
<td></td>
<td>498</td>
</tr>
<tr>
<td>S≡O</td>
<td>498</td>
<td></td>
<td>607</td>
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<td></td>
</tr>
</tbody>
</table>

(MH Table 8.4, p211)
Important relationship
The enthalpy change of a given gas phase reaction equals the TBE(reactants) minus the TBE(products)

Suppose Reaction 1 all bonds in the reactant gases are broken to give gaseous atoms
Followed by Reaction 2 in which the gaseous atoms from reaction 1 react to give the gaseous products.
Gaseous reactants -------------> Gaseous products

\[ \Delta H^\circ = \Delta H_1 + \Delta H_2 \]

\[ \Delta H^\circ = \text{TBE(reactants)} - \text{TBE(products)} \]

This is easy to remember if we imagine a reaction such as:

\[ \text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g) \]

Suppose the reaction takes place in two steps, in the first we break up all the molecules to make gas phase atoms. The energy require (supplied therefore positive) will be equal to the total bond energy of the reactants ie:

1. \[ \text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{C}_{\text{atomic,g}} + 4\text{O}_{\text{atomic,g}} + 4\text{H}_{\text{atomic,g}} \quad \Delta H_1 = \text{TBE Reactants} \]

In step two we combine the gaseous atms to form the products…bond formation is exothermic.

2. \[ \text{C}_{\text{atomic,g}} + 4\text{O}_{\text{atomic,g}} + 4\text{H}_{\text{atomic,g}} \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g) \quad \Delta H_2 = -\text{TBE Products} \]

Adding the two steps yields our desired reaction and \[ \Delta H = \Delta H_1 + \Delta H_2 = \text{TBE Reactants} - \text{TBE Products} \]
Some examples:

EXAMPLE 1

Calculate

$\Delta H$ for:

$$\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}_2(g)$$

Given bond energies only (in kJ/mol) ie:

$E(\text{C-H}) = 411$

$E(\text{O-O})$ double bond $= 498$

$E(\text{C-O})$ double bond $= 714$

$E(\text{H-O}) = 464$

$\Delta H = \text{TBE Reactants -TBE Products}$

$= 4E(\text{C-H}) + 2E(\text{O-O}) - 2(\text{C-O}) - 4(\text{H-O})$

$= 4 \times 411 + 2 \times 498 - 2 \times 714 - 4 \times 464 = -644 \text{ kJ}$

Feb 2005 Exam Question

20. Calculate the standard heat of formation, $\Delta H^\circ$, of acetaldehyde, $\text{CH}_3\text{CHO}(g)$, in kJ mol$^{-1}$, using data provided on the data page

A) 251   B) -163   C) 381   D) -251   E) -878

Data page:
Standard enthalpies of formation, $\Delta H^\circ$, kJ mol$^{-1}$

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\Delta H^\circ$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NH}_3(g)$</td>
<td>-46</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}(g)$</td>
<td>-242</td>
</tr>
<tr>
<td>$\text{NO}(g)$</td>
<td>+90</td>
</tr>
<tr>
<td>$\text{N}_2\text{O}(g)$</td>
<td>+82</td>
</tr>
<tr>
<td>$\text{C}(g, at)$</td>
<td>+717</td>
</tr>
<tr>
<td>$\text{H}(g, at)$</td>
<td>+218</td>
</tr>
<tr>
<td>$\text{O}(g, at)$</td>
<td>+249</td>
</tr>
</tbody>
</table>

Bond Energies, kJ mol$^{-1}$

- $(\text{C-H})$ 414
- $(\text{C-C})$ 347
- $(\text{C}=\text{O})$ 715

We could use:

$$\text{CH}_3\text{CHO}(g) \rightarrow 2 \text{C}(g) + 4 \text{H(g)} + \text{O(g)}$$

We know:

$$\Delta H^\text{reaction} = \Sigma \Delta H^\circ_{\text{products}} - \Sigma \Delta H^\circ_{\text{reactants}} = \text{TBE reactants - TBE products}$$

(in this case TBE products = 0.0 since only atoms are formed.)

$$\Delta H^\text{reaction} = 2 \times 717 + 4 \times 218 + 249 - \Delta H^\circ_{\text{CH}_3\text{CHO}(g)} = 4 \times 414 + 715 + 347$$

$$\Delta H^\circ_{\text{CH}_3\text{CHO}(g)} = -163 \text{ kJ/mol}$$

Feb 2004 Exam Question

18. Which one of the following reactions, when carried out at 25 °C and 101.3 kPa pressure, has an enthalpy change corresponding to the standard molar enthalpy of formation, $\Delta H^\circ_r$, of $\text{C}_2\text{H}_5\text{OH}(l)$?

A) $\text{C}_2\text{H}_4(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{C}_2\text{H}_5\text{OH}(l)$

B) $\text{C}_2\text{H}_5\text{OH}(l) \rightarrow 2 \text{C}(g) + 6 \text{H(g)} + \text{O(g)}$

C) $4 \text{C}(s) + 6 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{C}_2\text{H}_5\text{OH}(l)$

D) $\text{C}_2\text{H}_5\text{OH}(l) + 3 \text{O}_2(g) \rightarrow 2 \text{CO}_2(g) + 3 \text{H}_2\text{O}(l)$

E) $2 \text{C}(s) + 3 \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{C}_2\text{H}_5\text{OH}(l)$