

Unit 7
Thermochemistry
Chemistry 020, R. R. Martin

1. Thermochemistry

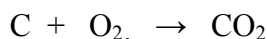
Heat is a form of energy - which may take many forms:

- 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:



stored chemical energy is liberated as heat

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



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 Distance² \times Time⁻²

In S.I. units kg m² s⁻²

and the **Joule is = 1 kg m² s⁻² = 1 N m**

e.g. the kinetic energy of a 2 kg mass moving at 1 ms⁻¹

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

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. ΔX) 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.

$$\text{i.e. } c = q/\Delta T \text{ per g of material in Joules (J)}$$

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

$$q = \text{mass(g)} \times c \text{ (J g}^{-1} \text{ }^\circ\text{C}^{-1}) \times T \text{ (}^\circ\text{C)}$$

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 (T) is the same in °C or in K

EXAMPLE

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

$$\begin{aligned} q &= m \times c \times T = 120 \text{ g} \times 0.902 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1} \times 75 \text{ }^\circ\text{C} \\ &= \mathbf{8118 \text{ J} = 8.118 \text{ kJ}} \end{aligned}$$

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

Call the final temp $T_f \text{ }^\circ\text{C}$ (for both water and Al)

Heat lost by Al = 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 $+q$)

Al: heat given out ($-ve$) = water: heat taken in ($+ve$)

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

and $T_f = 29.4 \text{ }^\circ\text{C}$.

The sign of the T is "automatically" taken care of in this approach.

In the above example, for the Al, $q = -1827 \text{ J}$ (heat energy lost); for the water, $q = +1827 \text{ J}$ (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? $c = 0.382 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$

$$\Delta T = T_f - T_i = (50 - 80)^{\circ}\text{C} = -30 \text{ }^{\circ}\text{C}$$

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

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 ΔT 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 ΔT 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)

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

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 (NH_4NO_3) is dissolved in 50 g water in a coffee cup calorimeter and the following reaction occurs



The temperature of the water, T , decreases from 25.00 to 23.32 $^\circ\text{C}$. Assuming that all the heat is absorbed by the water, calculate q for the reaction

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

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

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

$$q_{\text{reaction}} = \underline{+ 351 \text{ J}}$$

Note that this is a positive number and therefore the reaction is *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

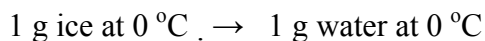
Heat energy may be consumed (produced) in **changes of state** at constant temperature (latent heat), where in this case, the state of the matter refers to the “phase” it is in: gas, liquid or solid.

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:*



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: $1 \text{ g H}_2\text{O}(\text{l}) \text{ at } 100 \text{ }^\circ\text{C} \rightarrow 1 \text{ g H}_2\text{O}(\text{g}) \text{ at } 100 \text{ }^\circ\text{C}$

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 $100\text{ }^{\circ}\text{C}$) 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 ΔE . We may increase this by adding either heat energy, q , or work energy, w (or both). The mechanical work is...

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

(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

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

at constant volume, $\Delta V = 0$ 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,

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

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.

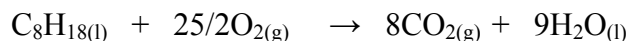
ΔH is usually defined at $T = 25.00 \text{ }^\circ\text{C}$ (298.15 K) and 1 bar and for a specified amount of substance/reactants etc.

For our purposes we will consider energy changes as manifested by ΔH and ignore the $P\Delta V$ term.

As we have defined earlier, if heat is evolved, ΔH is negative, and the reaction is said to be **EXOTHERMIC**.

If heat is gained by system, ΔH is positive, and the reaction is said to be **ENDOTHERMIC**.

e.g. for the combustion of octane:



$\Delta H = 5476 \text{ kJ}$, 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 ΔH 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 ΔH value is associated with one reactant only it would be "per mole", e.g. the heat of combustion of octane is $-5476 \text{ kJ mol}^{-1}$

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, ΔH is given by:

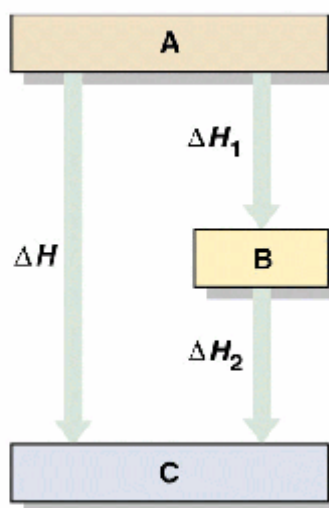
$$\Delta H = H_f - H_i$$

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** ΔH is the sum of the ΔH values of the component steps (sometimes called **Hess's Law**)

The value of ΔH for a reaction is the same whether it occurs in one step or in a series of steps.

Masterton/Hurley, Chemistry: Principles and Reactions, 4e
Figure 8.6



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A consequence of the fact that the ΔH values are functions of state is that the ΔH value for the **reverse** of a given process or reaction has the **opposite** sign.

E.g.

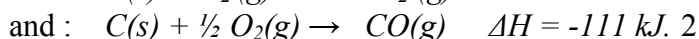


6. Combining Reactions and combining ΔH values.

When equations are added, ΔH values are added.

This permits us to compute ΔH values for reactions that would otherwise be difficult or impossible to measure

Example. What is ΔH for $\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$?

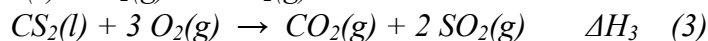
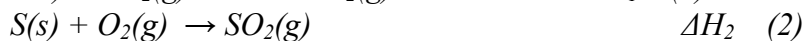
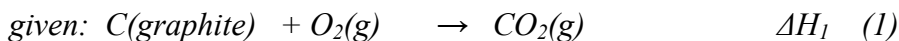
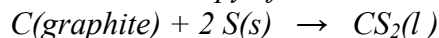


Our task is to devise a set of equations that when added together, yield the desired reaction. This can involve rewriting a particular reaction in the reverse direction. If we do this we have to reverse the sign of the ΔH value.

Thus:



Example: Calculate the enthalpy of the reaction



Since we need to derive the first equation with $\text{CS}_2(l)$ on the rhs of the equation we should rewrite equation 3 in the reverse direction:



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



adding **a) + b) + c)**

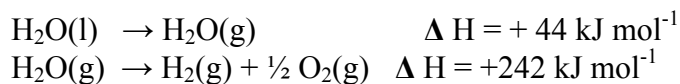


OR:

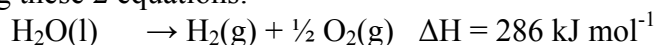


Thus stoichiometrically balanced reaction equations can be treated like algebra, and can be added and subtracted to yield a desired equation for a reaction. Similarly the ΔH values can be added together taking into account the appropriate signs for each reaction. These rules are summarized in the next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

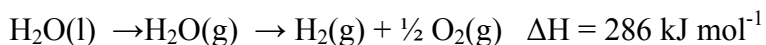
For example, suppose we wish to know the ΔH for the process of converting $\text{H}_2\text{O}(l)$ to $\text{H}_2(g)$ and $\text{O}_2(g)$ and are given the ΔH values for the vaporization of liquid water and for the conversion of gaseous water to H_2 and O_2



Adding these 2 equations:



and schematically what we are describing is:

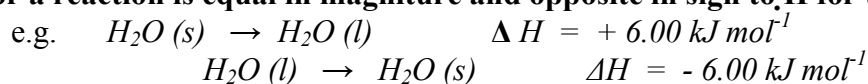


Thermochemistry rules for reactions

1. The magnitude of ΔH is directly proportional to the amount of reactant or product

Enthalpies, H or changes of enthalpy, ΔH 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. ΔH 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. ΔH for a reaction is equal in magnitude and opposite in sign to ΔH for the reverse reaction.



3. The value of ΔH 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 ΔH .



... is a thermochemical equation.

- The sign of ΔH indicates whether the reaction produces heat (exothermic, ΔH negative), or absorbs heat (endothermic, ΔH positive).
- The value of ΔH 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 ΔH value, ($\Delta H_1, \Delta H_2, \dots$ etc.), Then the ΔH for the overall reaction is the sum of the ΔH 's for the individual reactions as defined by their appropriate balanced stoichiometric equations

$$\text{i.e. } \Delta H = \Delta H_1 + \Delta H_2 + \dots$$

Example of independence of the value of ΔH of a reaction upon the route

Combustion reactions are very important (eg gasoline engine). *The heat of combustion is the enthalpy change ΔH 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 $CO_2(g)$**

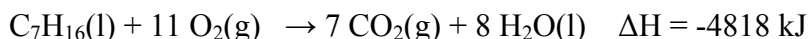
For hydrogen: **most stable oxide is $H_2O(l)$ not $H_2O(g)$**

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

Eg:



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



This can be produced by the following reaction schemes:

A)



and

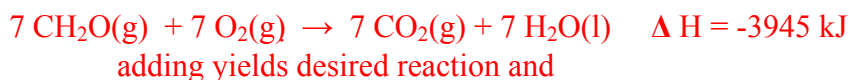


Add these two reactions, get desired reaction with $\Delta H = -2832 + (-1986) \text{ kJ mol}^{-1} = -4818 \text{ kJ}$

B)



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 ΔH values for a huge number of reactions. This is not desirable or practical and it would be much better to tabulate ΔH values of individual compounds which could be used in any hypothetical reaction to obtain ΔH_{rxn} . This has been achieved through the use of *standard enthalpies of formation*, ΔH_f°

The standard Molar Enthalpy of Formation is ΔH of reaction when 1 mol of compound (in standard state) is formed from its component elements in their standard states. Symbol ΔH_f°

“**Standard State**” is the physical state in which an element is found at 25 °C and 1 atm pressure. e.g. H_2 , O_2 , N_2 , Cl_2 are gaseous, Br_2 a liquid, C a solid, etc.

In the case of an element known in more than one form (**allotropy**) the standard state is that of **lowest energy**
e.g. C(graphite), not diamond.

It follows from this definition that

$$\Delta H_f^\circ \text{ of an element in its standard state is zero}$$

and that ΔH_f° for other forms (allotropes) of the element must be positive.

By Hess' Law :

$$\Delta H \text{ of Reaction} =$$
$$(\text{Total } \Delta H_f^\circ \text{ of all Products}) + (- \text{Total } \Delta H_f^\circ \text{ of all Reactants})$$

On this basis we can write:

ΔH 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 ΔH_f° = heat of formation for any substance is defined as the ΔH for the reaction in which 1 mol of substance is produced from its constituent elements in their standard states:

ΔH (for any reaction) = sum of ΔH_f° 's of products minus the sum of the ΔH_f° 's of the reactants

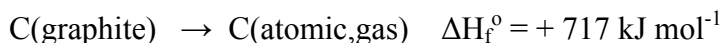
$$= \Sigma \Delta H_f^\circ \text{'s (products)} - \Sigma \Delta H_f^\circ \text{'s (reactants)}$$

This works for all reactions including **enthalpy of atomization of the elements:**



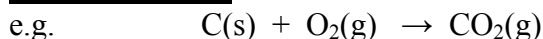
So: $\Delta H_f^\circ (\text{H, atomic}) = 432/2 = 216 \text{ kJ mol}^{-1}$

Note that the value of 432 kJ mol⁻¹ is called the bond dissociation energy of H₂(g). Note also that it is by definition 2 x ΔH_f^o (H-atom)



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

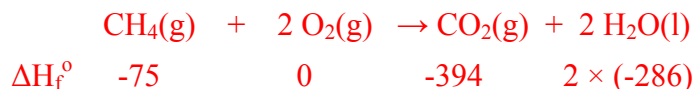
For compounds.



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

Reactions

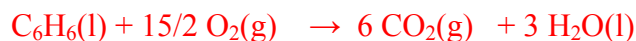
Example. Using ΔH_f^o values calculate the enthalpy of combustion of methane, CH₄(g)



$$\begin{aligned} \Delta H_{\text{reaction}} &= [-394 + 2 \times (-286)] - [(-75)] \\ &= - 891 \text{ kJ per mol of CH}_4 \end{aligned}$$

Example. Benzene, C₆H₆(l) has enthalpy of combustion of -3271 kJ mol⁻¹. What is its ΔH_f^o ?

First write down the balanced combustion reaction:

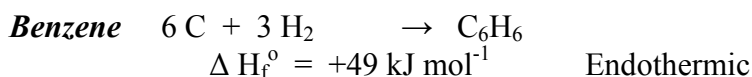
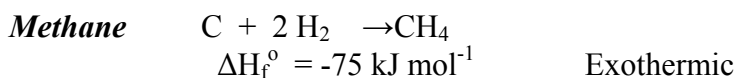


$$\Delta H_f^\circ \quad 0 \quad 6 \times (-394) \quad 3 \times (-286)$$

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

$$\begin{aligned} 3 \times (-286) + 6 \times (-394) - \Delta H_f^\circ(\text{benzene}) - 0 &= -3271 \text{ kJ mol}^{-1} \\ \Delta H_f^\circ(\text{benzene}) &= + 49 \text{ kJ mol}^{-1} \end{aligned}$$

Note the difference in the ΔH_f° values:



Benzene is less stable than its component elements. It is an endothermic compound. Most compounds have a negative ΔH_f° 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.

$$\text{Heat evolved in reaction} = \\ \text{Heat absorbed by water} + \text{heat absorbed by “bomb”}$$

Example. 1.00 g of sucrose, $C_{12}H_{22}O_{11}$ is burnt, and the temperature rises from 25.00 °C to 27.32 °C. The mass of water is 1.50×10^3 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.

$$\text{Heat of reaction} + \text{heat gained (or lost) by water} + \text{heat gained (or lost) by the calorimeter} = 0$$

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

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

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

$$\text{Heat of reaction} = -16502 \text{ J} = -16.5 \text{ kJ g}^{-1}$$

$$\text{Total heat produced by combustion of 1 g sucrose} \\ = -16.5 \text{ kJ g}^{-1} \quad (\text{Exothermic})$$

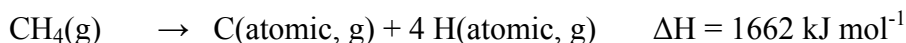
$$\text{heat evolved per mole of sucrose, } C_{12}H_{22}O_{11} \text{ is} \\ (-16.5 \text{ kJ g}^{-1}) \times (342.3 \text{ g mol}^{-1}) = -5650 \text{ kJ mol}^{-1}$$

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.

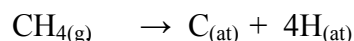


Important: all reactants and products must be gases

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 =



$$\Delta H = \Delta H_f^\circ (\text{C, atomic, g}) + 4\Delta H_f^\circ (\text{H, atomic, g}) - \Delta H_f^\circ (\text{CH}_4, \text{g})$$

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

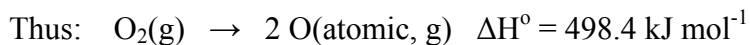
$$\square 4 \times \text{BE}(\text{C-H}) = 1662 \text{ and } \text{BE}(\text{C-H}) = 1662/4 = 415.5 \text{ kJ mol}^{-1} \text{ of C-H bonds}$$

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



and this is TBE of O₂ 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 ΔH for this reaction in terms of ΔH_f°

$$\Delta H^\circ = 2 \Delta H_f^\circ (\text{O, atomic, g}) - \Delta H_f^\circ (\text{O}_2, \text{g})$$

$$= 2 \times 249.2 - 0 \text{ kJ mol}^{-1}$$

$$\text{O}_2(\text{g}) = 498.4 \text{ kJ mol}^{-1}$$

Note that the ΔH_f° of an O-atom is half the ΔH_f° of an O₂(g) molecule

bond energy, since 2 O-atoms are produced per

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

H,

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: CH₄, methane

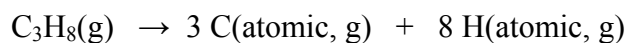
n = 2: C₂H₆, ethane

n = 3: C₃H₈, propane

We can compute C-C and C-H BE's from enthalpy of atomization data

Propane C₃H₈, 2 C-C bonds, 8 C-H bonds

$$\Delta H_f^\circ (\text{C}_3\text{H}_8, \text{g}) = -103.9 \text{ kJ mol}^{-1}$$



ΔH° for this reaction is the TBE by definition, and

$$\Delta H^\circ = 3 \Delta H_f^\circ(\text{C}, \text{atomic}, \text{g}) + 8 \Delta H_f^\circ(\text{H}, \text{atomic}, \text{g}) - \Delta H_f^\circ (\text{C}_3\text{H}_8, \text{g})$$

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

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

However while we have TBE for C₃H₈(g), the molecule has two sorts of bonds (C-C and C-H) and we cannot deduce the individual energies. *Need further information*

Butane C₄H₁₀; 3 C-C bonds, 10 C-H bonds

$$\Delta H_f^\circ (\text{C}_4\text{H}_{10}, \text{g}) = -127 \text{ kJ mol}^{-1}$$



$$\begin{aligned} \Delta H^\circ &= 4 \Delta H_f^\circ(\text{C}, \text{atomic}, \text{g}) + 10 \Delta H_f^\circ(\text{H}, \text{atomic}, \text{g}) - \Delta H_f^\circ (\text{C}_4\text{H}_{10}, \text{g}) \\ &= 4 \times 715 + 10 \times 218 - (-127) = 5167 \text{ kJ mol}^{-1} = \text{TBE} \end{aligned}$$

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

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

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

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

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

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

$$\text{and} \quad \text{BE(C-C)} = 351.7 \text{ kJ mol}^{-1} \text{ of C-C bonds}$$

Note that the value for BE(C-H) is slightly different from the value obtained from atomizing CH₄(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:



Bond strength is increasing $1 < 2 < 3$.

Similarly with diatomic molecules :

F-F	O=O	$\text{N}\equiv\text{N}$	
153	498	941	kJ

A selection of Bond Dissociation Energies, kJ mol⁻¹

	H	C	N	O	S	F	C□
H	436	414(411)	389	464	339	565	431
C		347(352)	293	351	259	485	331
N			159	222			272
O					138		201
S						184	205
F					226	285	255
C□						153	255
							243

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

$\tilde{\text{C}}\text{C}$	820	$\tilde{\text{C}}\text{N}$	890	$\tilde{\text{N}}\text{N}$	941
C=C	612	C=O	715	C=N	615
C=S	477	N=N	418	O=O	498
S=O	498	N=O	607	(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

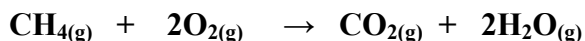
Followed by Reaction 2 in which the gaseous atoms from reaction 1 react to give the gaseous products.

Gaseous reactants -----> Gaseous products

$$\Delta H^{\circ} = \Delta H_1 + \Delta H_2$$

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

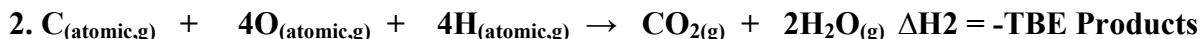
This is easy to remember if we imagine a reaction such as:



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:



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



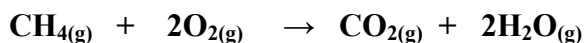
Adding the two steps yields our desired reaction and $\Delta H = \Delta H_1 + \Delta H_2 = \text{TBE Reactants} - \text{TBE Products}$

Some examples:

EXAMPLE 1

Calculate

ΔH for:



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

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

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

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

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

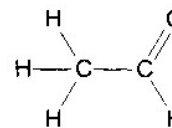
$$\Delta H = \text{TBE Reactants} - \text{TBE Products}$$

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

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

Feb 2005 Exam Question

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



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

Data page:

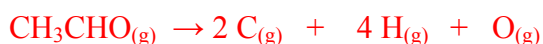
Standard enthalpies of formation, ΔH_f° , kJ mol^{-1}

$\text{NH}_3(\text{g})$	-46	$\text{H}_2\text{O}(\text{g})$	-242	$\text{NO}(\text{g})$	+90	$\text{N}_2\text{O}(\text{g})$	+82
$\text{C}(\text{g,at})$	+717	$\text{H}(\text{g,at})$	+218	$\text{O}(\text{g,at})$	+249		

Bond Energies, kJ mol^{-1}

(C-H)	414	(C-C)	347	(C=O)	715
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We could use:



We know :

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

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

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

$$\Delta H_{\text{f}}^{\circ} \text{CH}_3\text{CHO}(\text{g}) = -163 \text{ kJ/mol}$$

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, ΔH_f° , of $\text{C}_2\text{H}_5\text{OH}(\text{l})$?

- A) $\text{C}_2\text{H}_6(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{l})$
- B) $\text{C}_2\text{H}_5\text{OH}(\text{l}) \rightarrow 2 \text{C}(\text{g}) + 6 \text{H}(\text{g}) + \text{O}(\text{g})$
- C) $4 \text{C}(\text{s}) + 6 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{C}_2\text{H}_5\text{OH}(\text{l})$
- D) $\text{C}_2\text{H}_5\text{OH}(\text{l}) + 3 \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g}) + 3 \text{H}_2\text{O}(\text{l})$
- E) $2 \text{C}(\text{s}) + 3 \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{l})$

