Enthalpy changes

EXOTHERMIC AND ENDOTHERMIC REACTIONS
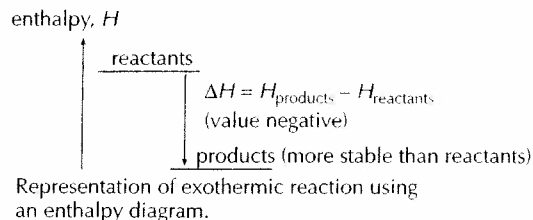
Energy is defined as the ability to do work, that is, move a force through a distance. It is measured in joules.

Energy = force × distance
(J)   (N   ×   m)

In a chemical reaction energy is required to break the bonds in the reactants, and energy is given out when new bonds are formed in the products. The most important type of energy in chemistry is heat. If the bonds in the products are stronger than the bonds in the reactants then the reaction is said to be **exothermic**, as heat is given out to the surroundings. Examples of exothermic processes include combustion and neutralization. In **endothermic** reactions heat is absorbed from the surroundings because the bonds in the reactants are stronger than the bonds in the products.
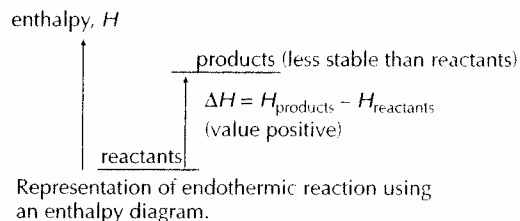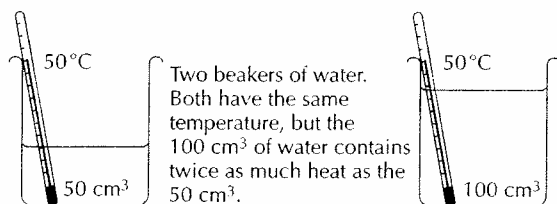
The internal energy stored in the reactants is known as its **enthalpy**, H. The absolute value of the enthalpy of the reactants cannot be known, nor can the enthalpy of the products, but what can be measured is the difference between them, ΔH. By convention ΔH has a negative value for exothermic reactions and a positive value for endothermic reactions. It is normally measured under standard conditions of 1 atm pressure at a temperature of 298 K. The **standard enthalpy change of a reaction** is denoted by $\Delta H^{\ominus}$.

enthalpy, H

reactants

$\Delta H = H_{products} - H_{reactants}$
(value negative)

products (more stable than reactants)

Representation of exothermic reaction using an enthalpy diagram.

enthalpy, H

products (less stable than reactants)

$\Delta H = H_{products} - H_{reactants}$
(value positive)

reactants

Representation of endothermic reaction using an enthalpy diagram.

TEMPERATURE AND HEAT

It is important to be able to distinguish between heat and temperature as the terms are often used loosely.

- Heat is a measure of the total energy in a given amount of substance and therefore depends on the amount of substance present.
- Temperature is a measure of the 'hotness' of a substance. It represents the average kinetic energy of the substance, but is independent of the amount of substance present.

50°C

50 cm³

Two beakers of water. Both have the same temperature, but the 100 cm³ of water contains twice as much heat as the 50 cm³.
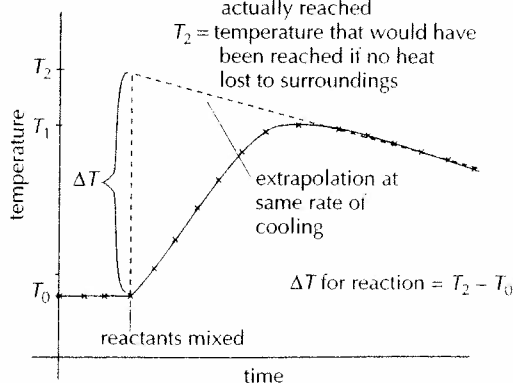
50°C

100 cm³

CALORIMETRY

The enthalpy change for a reaction can be measured experimentally by using a calorimeter. In a simple calorimeter all the heat evolved in an exothermic reaction is used to raise the temperature of a known mass of water. For endothermic reactions the heat transferred from the water to the reaction can be calculated by measuring the lowering of temperature of a known mass of water.

To compensate for heat lost by the water in exothermic reactions to the surroundings as the reaction proceeds a plot of temperature against time can be drawn. By extrapolating the graph, the temperature rise that would have taken place had the reaction been instantaneous can be calculated.

simple calorimeter

thermometer

lid

polystyrene

reaction mixture
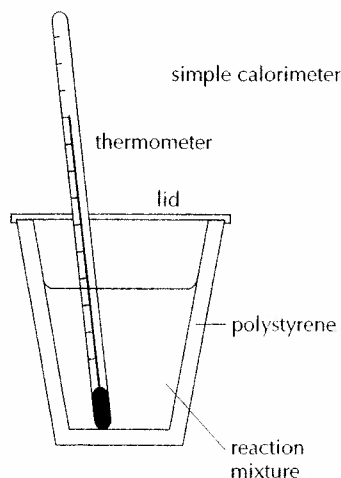
Compensating for heat lost
T_0 = initial temperature of reactants
T_1 = highest temperature actually reached
T_2 = temperature that would have been reached if no heat lost to surroundings

T_2
T_1
temperature
ΔT
T_0

extrapolation at same rate of cooling

ΔT for reaction = $T_2 - T_0$

reactants mixed

time

ΔH calculations

CALCULATION OF ENTHALPY CHANGES

The heat involved in changing the temperature of any substance can be calculated from the equation:

Heat energy = mass (m) × specific heat capacity (c) × temperature change (ΔT)

The specific heat capacity of water is 4.18 kJ kg^{-1} K^{-1}. That is, it requires 4.18 kilojoules of energy to raise the temperature of one kilogram of water by one kelvin.

Enthalpy changes are normally quoted in kJ mol^{-1}, for either a reactant or a product, so it is also necessary to work out the number of moles involved in the reaction which produces the heat change in the water.

Worked example 1

50.0 cm^3 of 1.00 mol dm^{-3} hydrochloric acid solution was added to 50.0 cm^3 of 1.00 mol dm^{-3} sodium hydroxide solution in a polystyrene beaker. The initial temperature of both solutions was 16.7 °C. After stirring and accounting for heat loss the highest temperature reached was 23.5 °C. Calculate the enthalpy change for this reaction.

Step 1. Write equation for reaction

$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$
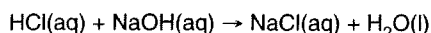
Step 2. Calculate molar quantities

Amount of HCl = $\dfrac{50.0}{1000}$ × 1.00 = 5.00 × 10^{-2} mol

Amount of NaOH = $\dfrac{50.0}{1000}$ × 1.00 = 5.00 × 10^{-2} mol

Therefore the heat evolved will be for 5.00 × 10^{-2} mol

Step 3. Calculate heat evolved

Total volume of solution = 50.0 + 50.0 = 100 cm^3
Assume the solution has the same density and specific heat capacity as water then
mass of 'water' = 100 g = 0.100 kg
Temperature change = 23.5 − 16.7 = 6.8 °C = 6.8 K
Heat evolved in reaction = 0.100 × 4.18 × 6.8 = 2.84 kJ
= 2.84 kJ (for 5.00 × 10^{-2} mol)

ΔH for reaction = − 2.84 × $\dfrac{1}{5.00 \times 10^{-2}}$ = −56.8 kJ mol^{-1}

(negative value as the reaction is exothermic)

Worked example 2

A student used a simple calorimeter to determine the enthalpy change for the combustion of ethanol.

$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$
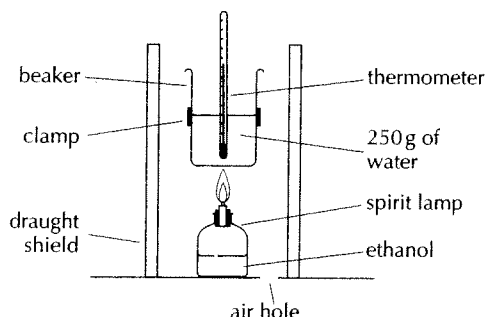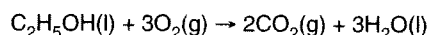
When 0.690 g (0.015 mol) of ethanol was burned it produced a temperature rise of 13.2 K in 250 g of water. Calculate ΔH for the reaction.

$\dfrac{\text{Heat evolved}}{\text{by 0.015 mol}} = \dfrac{250}{1000}$ × 4.18 × 13.2 = 13.79 kJ

$\Delta H = -13.79 \times \dfrac{1}{0.015} = -920$ kJ mol^{-1}

Note: the Data Book value is −1371 kJ mol^{-1}. Reasons for the discrepancy include the fact that not all the heat produced is transferred to the water, the water loses some heat to the surroundings, and there is incomplete combustion of the ethanol.

Worked example 3

50.0 cm^3 of 0.200 mol dm^{-3} copper(II) sulfate solution was placed in a polystyrene cup. After two minutes 1.20 g of powdered zinc was added. The temperature was taken every 30 seconds and the following graph obtained. Calculate the enthalpy change for the reaction taking place.

Step 1. Write the equation for the reaction

$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$

Step 2. Determine the limiting reagent

Amount of Cu^{2+}(aq) = 50.0/1000 × 0.200 = 0.0100 mol

Amount of Zn(s) = 1.20/65.37 = 0.0184 mol

∴ Cu^{2+}(aq) is the limiting reagent

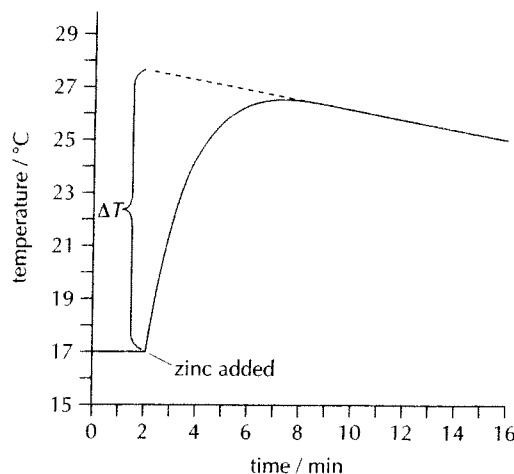**Step 3.** Extrapolate the graph (*already done*) to compensate for heat loss and determine ΔT

$\Delta T = 10.4$ °C

Step 4. Calculate the heat evolved in the experiment for 0.0100 mol of reactants
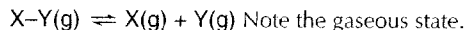
Heat evolved = 50.0/1000 × 4.18 × 10.4 °C = 2.17 kJ

Step 5. Express this as the enthalpy change for the reaction $\Delta H = -2.17 \times \dfrac{1}{0.0100} = -217$ kJ mol^{-1}

Bond enthalpies and Hess' law

BOND ENTHALPIES

Enthalpy changes can also be calculated directly from bond enthalpies.
For a diatomic molecule the bond enthalpy is defined as the enthalpy change for the process

$$X–Y(g) \rightleftharpoons X(g) + Y(g) \text{ Note the gaseous state.}$$

For bond formation the value is negative and for bond breaking the value is positive. If the bond enthalpy values are known for all the bonds in the reactants and products then the overall enthalpy change can be calculated.
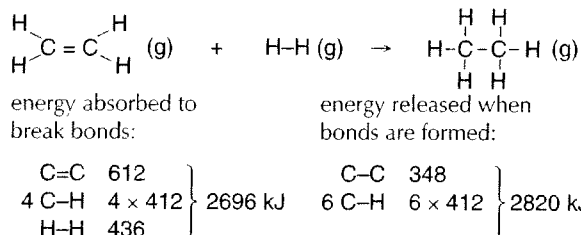
Some average bond enthalpies
All values in $kJ\ mol^{-1}$

H–H	436	C=C	612	C≡C	837
C–C	348	O=O	496	N≡N	944
C–H	412				
O–H	463				
N–H	388				
N–N	163				

Worked example 1
Hydrogenation of ethene

$$\underset{H}{\overset{H}{C}} = \underset{H}{\overset{H}{C}} \text{ (g)} + \text{H–H (g)} \rightarrow \text{H–}\underset{H}{\overset{H}{C}}\text{–}\underset{H}{\overset{H}{C}}\text{–H (g)}$$

energy absorbed to break bonds:

C=C	612	
4 C–H	4 × 412	} 2696 kJ
H–H	436	

energy released when bonds are formed:

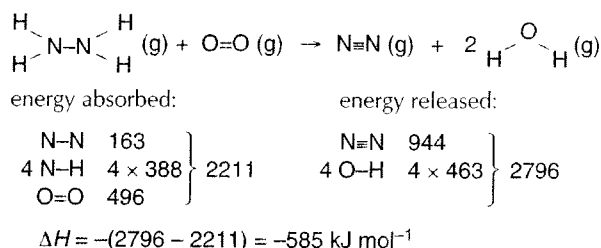| C–C	348	
6 C–H	6 × 412	} 2820 kJ

There is more energy released than absorbed so the reaction is exothermic.

$$\Delta H = -(2820 - 2696) = -124\ kJ\ mol^{-1}$$

Worked example 2
Combustion of hydrazine in oxygen (this reaction has been used to power spacecraft)

$$\underset{H}{\overset{H}{N}}\text{–}\underset{H}{\overset{H}{N}} \text{ (g)} + \text{O=O (g)} \rightarrow \text{N≡N (g)} + 2\ \underset{H}{\overset{O}{}}\text{H (g)}$$

energy absorbed:

N–N	163	
4 N–H	4 × 388	} 2211
O=O	496	

energy released:

N≡N	944	
4 O–H	4 × 463	} 2796

$$\Delta H = -(2796 - 2211) = -585\ kJ\ mol^{-1}$$

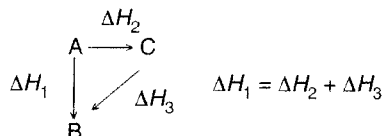## LIMITATIONS OF USING AVERAGE BOND ENTHALPIES

Average bond enthalpies can only be used if all the reactants and products are in the gaseous state. If water were a liquid product in the above example then even more heat would be evolved since the enthalpy change of vaporization of water would also need to be included in the calculation.

In the above calculations **average** bond enthalpies have been used. These have been obtained by considering a number of similar compounds. In practice the energy of a particular bond will vary slightly in different compounds, as it will be affected by neighbouring atoms. So ΔH values obtained from using average bond enthalpies will not necessarily be very accurate.
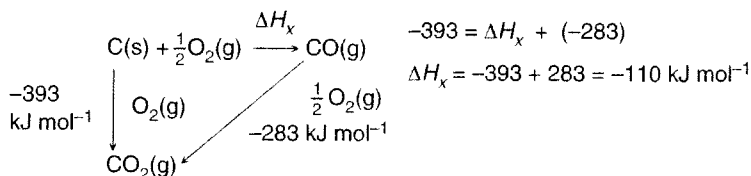

HESS' LAW

Hess' law states that the enthalpy change for a reaction depends only on the difference between the enthalpy of the products and the enthalpy of the reactants. It is independent of the reaction pathway.

The enthalpy change going from A to B is the same whether the reaction proceeds directly to A or whether it goes via an intermediate.

$$\begin{array}{ccc} & \Delta H_2 & \\ A & \longrightarrow & C \\ \Delta H_1 \downarrow & \swarrow \Delta H_3 & \\ B & & \end{array} \quad \Delta H_1 = \Delta H_2 + \Delta H_3$$

This law is a statement of the law of conservation of energy. It can be used to determine enthalpy changes, which cannot be measured directly. For example, the enthalpy of combustion of both carbon and carbon monoxide to form carbon dioxide can easily be measured directly, but the combustion of carbon to carbon monoxide cannot. This can be represented by an energy cycle.

$$\begin{array}{ccc} & \Delta H_x & \\ C(s) + \tfrac{1}{2}O_2(g) & \longrightarrow & CO(g) \\ -393\ kJ\ mol^{-1} \downarrow O_2(g) & \swarrow \tfrac{1}{2}O_2(g) & \\ & -283\ kJ\ mol^{-1} & \\ CO_2(g) & & \end{array}$$

$$-393 = \Delta H_x + (-283)$$
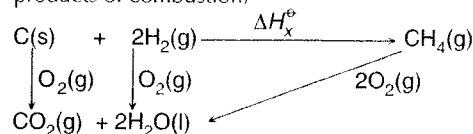$$\Delta H_x = -393 + 283 = -110\ kJ\ mol^{-1}$$

Worked example 3
Calculate the standard enthalpy change when one mole of methane is formed from its elements in their standard states. The standard enthalpies of combustion $\Delta H_c^{\ominus}$ of carbon, hydrogen, and methane are –393, –286, and –890 $kJ\ mol^{-1}$ respectively.

Step 1. Write the equation for the enthalpy change with the unknown $\Delta H^{\ominus}$ value. Call this value $\Delta H_x^{\ominus}$.

$$C(s) + 2H_2(g) \xrightarrow{\Delta H_x^{\ominus}} CH_4(g)$$
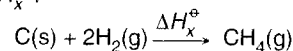
Step 2. Construct an energy cycle showing the different routes to the products (in this case the products of combustion)

$$\begin{array}{ccc} & \Delta H_x^{\ominus} & \\ C(s) + 2H_2(g) & \longrightarrow & CH_4(g) \\ \downarrow O_2(g) \quad \downarrow O_2(g) & \swarrow 2O_2(g) & \\ CO_2(g) + 2H_2O(l) & \swarrow & \end{array}$$

Step 3. Use Hess' law to equate the energy changes for the two different routes

$$\underbrace{\Delta H_c^{\ominus}(C) + 2\Delta H_c^{\ominus}(H_2)}_{\text{direct route}} = \underbrace{\Delta H_x^{\ominus} + \Delta H_c^{\ominus}(CH_4)}_{\text{route via methane}}$$

Step 4. Rearrange the equation and substitute the values to give the answer

$$\Delta H_x^{\ominus} = \Delta H_c^{\ominus}(C) + 2\Delta H_c^{\ominus}(H_2) - \Delta H_c^{\ominus}(CH_4)$$
$$= -393 + (2 \times -286) - (-890)\ kJ\ mol^{-1}$$

(HL) Energy cycles

STANDARD ENTHALPY CHANGE OF FORMATION $\Delta H_f^\ominus$

The standard enthalpy change of formation of a compound is the enthalpy change when one mole of the compound is formed from its elements in their standard states at 298 K and 1 atm pressure. From this it follows that $\Delta H_f^\ominus$ for an element in its standard state will be zero. The standard enthalpy change of combution, $\Delta H_c^\ominus$, is the enthalpy change when one mole of a substance is completely combusted in oxygen under standard conditions, An accurate value for the standard enthalpy change of formation of ethanol can be determined from the following cycle.
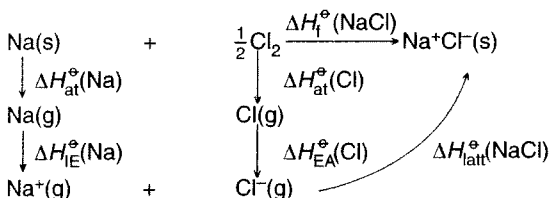
$$2C(s) \quad + \quad 3H_2(g) \quad + \quad \tfrac{1}{2}O_2(g) \xrightarrow{\Delta H_f^\ominus (C_2H_5OH)} C_2H_5OH(l)$$

$2 \times \Delta H_f^\ominus (CO_2)\Big\downarrow 2O_2(g) \quad 3 \times \Delta H_f^\ominus (H_2O) \Big\downarrow 1\tfrac{1}{2}O_2(g) \qquad 3O_2(g)$

$$\xrightarrow{\Delta H_c^\ominus (C_2H_5OH)}$$

$$2CO_2(g) \quad + \quad 3H_2O(l)$$
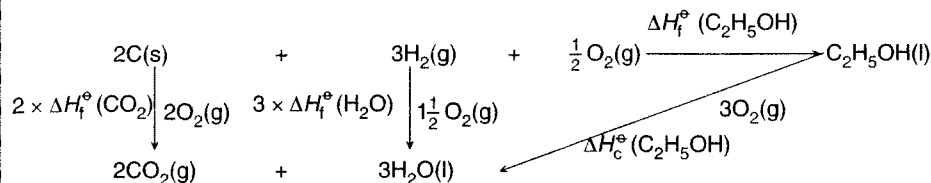
By Hess' law: $\Delta H_f^\ominus(C_2H_5OH) = 2 \times \Delta H_f^\ominus(CO_2) + 3 \times \Delta H_f^\ominus(H_2O) - \Delta H_c^\ominus(C_2H_5OH)$

Substituting the relevant values $\Delta H_f^\ominus(C_2H_5OH) = (2 \times -393.5) + (3 \times -285.8) - (-1371) = -273.4$ kJ mol^{-1}

BORN–HABER CYCLES

Born–Haber cycles are simply energy cycles for the formation of ionic compounds. The enthalpy change of formation of sodium chloride can be considered to occur through a number of separate steps.

$$Na(s) \quad + \quad \tfrac{1}{2}Cl_2 \xrightarrow{\Delta H_f^\ominus (NaCl)} Na^+Cl^-(s)$$

$\Big\downarrow \Delta H_{at}^\ominus(Na) \qquad\qquad \Big\downarrow \Delta H_{at}^\ominus(Cl)$

$$Na(g) \qquad\qquad\qquad Cl(g)$$

$\Big\downarrow \Delta H_{IE}^\ominus(Na) \qquad \Big\downarrow \Delta H_{EA}^\ominus(Cl) \quad \nearrow \Delta H_{latt}^\ominus(NaCl)$

$$Na^+(g) \quad + \quad Cl^-(g)$$

Using Hess' law:

$\Delta H_f^\ominus(NaCl) = \Delta H_{at}^\ominus(Na) + \Delta H_{IE}^\ominus(Na) + \Delta H_{at}^\ominus(Cl) + \Delta H_{EA}^\ominus(Cl)$
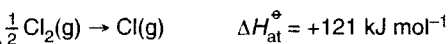$+ \Delta H_{latt}^\ominus(NaCl)$

Substituting the relevant values:
$\Delta H_f^\ominus(NaCl) = +108 + 494 + 121 - 364 - 771 = -412$ kJ mol^{-1}

Note: it is the large lattice enthalpy that mainly compensates for the endothermic processes and leads to the enthalpy of formation of ionic compounds having a negative value.
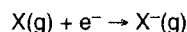
LATTICE ENTHALPY $\Delta H_{latt}^\ominus$

The lattice enthalpy relates either to the endothermic process of turning a crystalline solid into its gaseous ions or to the exothermic process of turning gaseous ions into a crystalline solid.

$$MX(s) \rightleftharpoons M^+(g) + X^-(g)$$
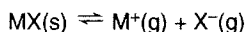
The sign of the lattice enthalpy indicates whether the lattice is being formed (−) or broken (+).

The size of the lattice enthalpy depends both on the size of the ions and on the charge carried by the ions.

cation size increasing			anion size increasing		
LiCl	NaCl	KCl	NaCl	NaBr	NaI
Lattice enthalpy / kJ mol^{-1}					
846	771	701	771	733	684

charge on cation increasing		charge on anion increasing	
NaCl	MgCl$_2$	MgCl$_2$	MgO
Lattice enthalpy / kJ mol^{-1}			
771	2493	2493	3889

ENTHALPY OF ATOMIZATION $\Delta H_{at}^\ominus$

The standard enthalpy of atomization is the standard enthalpy change when one mole of gaseous atoms is formed from the element in its standard state under standard conditions. For diatomic molecules this is equal to half the bond dissociation enthalpy.
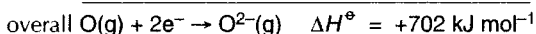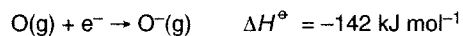
$\tfrac{1}{2}Cl_2(g) \rightarrow Cl(g) \qquad \Delta H_{at}^\ominus = +121$ kJ mol^{-1}

ELECTRON AFFINITY $\Delta H_{EA}^\ominus$

The electron affinity is the enthalpy change when an electron is added to an isolated atom in the gaseous state, i.e.

$$X(g) + e^- \rightarrow X^-(g)$$

Atoms 'want' an extra electron so electron affinity values are negative for the first electron. However, when oxygen forms the O^{2-} ion the overall process is endothermic:

$O(g) + e^- \rightarrow O^-(g)$	$\Delta H^\ominus = -142$ kJ mol^{-1}
$O^-(g) + e^- \rightarrow O^{2-}(g)$	$\Delta H^\ominus = +844$ kJ mol^{-1}
overall $O(g) + 2e^- \rightarrow O^{2-}(g)$	$\Delta H^\ominus = +702$ kJ mol^{-1}

USE OF BORN–HABER CYCLES

Like any energy cycle Born–Haber cycles can be used to find the value of an unknown. They can also be used to assess how ionic a substance is. The lattice enthalpy can be calculated theoretically by considering the charge and size of the constituent ions. It can also be obtained indirectly from the Born–Haber cycle. If there is good agreement between the two values then it is reasonable to assume that there is a high degree of ionic character, e.g. NaCl. However, if there is a big difference between the two values then it is because the compounds possesses a considerable degree of covalent character, e.g. AgCl.

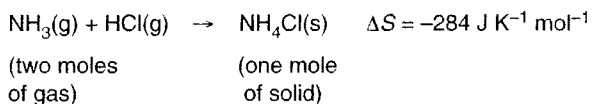|	NaCl	AgCl
Theoretical value / kJ mol^{-1}	766	770
Experimental value / kJ mol^{-1}	771	905

⚓ Entropy and spontaneity

DISORDER

In nature systems naturally tend towards disorder. An increase in disorder can result from:

- mixing different types of particles, e.g. the dissolving of sugar in water
- a change in state where the distance between the particles increases, e.g. liquid water → steam
- the increased movement of particles, e.g. heating a liquid or gas
- increasing the number of particles, e.g.
  $2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$.

The greatest increase in disorder is usually found where the number of particles in the gaseous state increases.

The change in the disorder of a system is known as the entropy change, ΔS. The more disordered the system becomes the more positive the value of ΔS becomes. Systems which become more ordered will have negative ΔS values.

$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s) \quad \Delta S = -284 \text{ J K}^{-1}\text{ mol}^{-1}$

(two moles   (one mole
of gas)   of solid)

ABSOLUTE ENTROPY VALUES

The standard entropy of a substance is the entropy change per mole that results from heating the substance from 0 K to the standard temperature of 298 K. Unlike enthalpy, absolute values of entropy can be measured. The standard entropy change for a reaction can then be determined by calculating the difference between the entropy of the products and the reactants.

$\Delta S^{\ominus} = S^{\ominus} \text{ (products)} - S^{\ominus} \text{ (reactants)}$

e.g. for the formation of ammonia

$3H_2(g) + N_2(g) \quad 2NH_3(g)$
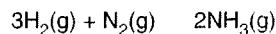
the standard entropies of hydrogen, nitrogen, and ammonia are respectively 131, 192, and 192 J K^{-1} mol^{-1}.

Therefore per mole of reaction

$\Delta S^{\ominus} = 2 \times 192 - [(3 \times 131) + 192] = -201 \text{ J K}^{-1}\text{mol}^{-1}$

(or per mole of ammonia $\Delta S^{\ominus} = \dfrac{-201}{2} = -101 \text{ J K}^{-1}\text{mol}^{-1}$)

SPONTANEITY

A reaction is said to be spontaneous if it causes a system to move from a less stable to a more stable state. This will depend both upon the enthalpy change and the entropy change. These two factors can be combined and expressed as the Gibbs energy change ΔG, often known as the 'free energy change'.

The standard free energy change $\Delta G^{\ominus}$ is defined as:

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

Where all the values are measured under standard conditions. For a reaction to be spontaneous it must be able to do work, that is $\Delta G^{\ominus}$ must have a negative value.

Note: the fact that a reaction is spontaneous does not necessarily mean that it will proceed without any input of energy. For example, the combustion of coal is a spontaneous reaction and yet coal is stable in air. It will only burn on its own accord after it has received some initial energy so that some of the molecules have the necessary activation energy for the reaction to occur.

⑪ Spontaneity of a reaction

POSSIBLE COMBINATIONS FOR FREE ENERGY CHANGES

Some reactions will always be spontaneous. If $\Delta H^{\ominus}$ is negative or zero and $\Delta S^{\ominus}$ is positive then $\Delta G^{\ominus}$ must always have a negative value. Conversely if $\Delta H^{\ominus}$ is positive or zero and $\Delta S^{\ominus}$ is negative then $\Delta G^{\ominus}$ must always be positive and the reaction will never be spontaneous.

For some reactions whether or not they will be spontaneous depends upon the temperature. If $\Delta H^{\ominus}$ is positive or zero and $\Delta S^{\ominus}$ is positive, then $\Delta G^{\ominus}$ will only become negative at high temperatures when the value of $T\Delta S^{\ominus}$ exceeds the value of $\Delta H^{\ominus}$.

Type	$\Delta H^{\ominus}$	$\Delta S^{\ominus}$	$T\Delta S^{\ominus}$	$\Delta H^{\ominus} - T\Delta S^{\ominus}$	$\Delta G^{\ominus}$
1	0	+	+	(0) – (+)	–
2	0	–	–	(0) – (–)	+
3	–	+	+	(–) – (+)	–
4	+	–	–	(+) – (–)	+
5	+	+	+	(+) – (+)	– or +
6	–	–	–	(–) – (–)	+ or –

Type 1. Mixing two gases. $\Delta G^{\ominus}$ is negative so gases will mix of their own accord. Gases do not unmix of their own accord (Type 2) as $\Delta G^{\ominus}$ is positive.

Type 3. $(NH_4)_2Cr_2O_7(s) \rightarrow N_2(g) + Cr_2O_3(s) + 4H_2O(g)$

The decomposition of ammonium dichromate is spontaneous at all temperatures.

Type 4. $N_2(g) + 2H_2(g) \rightarrow N_2H_4(g)$

The formation of hydrazine from its elements will never be spontaneous.

Type 5. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

The decomposition of calcium carbonate is only spontaneous at high temperatures.

Type 6. $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$

Above a certain temperature this reaction will cease to be spontaneous.

DETERMINING THE VALUE OF $\Delta G^{\ominus}$

The precise value of $\Delta G^{\ominus}$ for a reaction can be determined from $\Delta G_f^{\ominus}$ values using an energy cycle, e.g. to find the standard free energy of combustion of methane given the standard free energies of formation of methane, carbon dioxide, water, and oxygen.

$$CH_4(g) + 2O_2 \xrightarrow{\Delta G_x^{\ominus}} CO_2(g) + 2H_2O(l)$$
$$C(s) + 2O_2(g) + 2H_2(g)$$
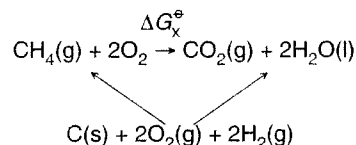
By Hess' law

$\Delta G_x^{\ominus} = [\Delta G_x^{\ominus}(CO_2) + 2\Delta G_f^{\ominus}(H_2O)] - [\Delta G_f^{\ominus}(CH_4) + 2\Delta G_f^{\ominus}(O_2)]$

Substituting the actual values

$\Delta G_x^{\ominus} = [-394 + 2 \times (-237)] - [-50 + 2 \times 0] = -818$ kJ mol^{-1}

$\Delta G^{\ominus}$ values can also be calculated from using the equation $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$. For example, in Type 5 in the adjacent list the values for $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ for the thermal decomposition of calcium carbonate are +178 kJ mol^{-1} and +165.3 J K^{-1} mol^{-1} respectively. Note that the units of $\Delta S^{\ominus}$ are different to those of $\Delta H^{\ominus}$.

At 25 °C (298 K) the value for $\Delta G^{\ominus} = 178 - 298 \times \dfrac{165.3}{1000}$

$$= +129 \text{ kJ mol}^{-1}$$

which means that the reaction is not spontaneous.

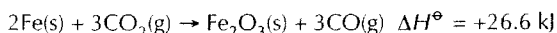The reaction will become spontaneous when $T\Delta S^{\ominus} > \Delta H^{\ominus}$.

$T\Delta S^{\ominus} = \Delta H^{\ominus}$ when $T = \dfrac{\Delta H^{\ominus}}{\Delta S^{\ominus}} = \dfrac{178}{165.3/1000} = 1077$ K (804 °C)

Therefore above 804 °C the reaction will be spontaneous.

Note: this calculation assumes that the entropy value is independent of temperature, which is not strictly true.

IB QUESTIONS – ENERGETICS

1. Which statement about this reaction is correct?

   $2Fe(s) + 3CO_2(g) \rightarrow Fe_2O_3(s) + 3CO(g) \quad \Delta H^{\ominus} = +26.6$ kJ

   A. 26.6 kJ of energy are released for every mole of Fe reacted

   B. 26.6 kJ of energy are absorbed for every mole of Fe reacted

   C. 53.2 kJ of energy are released for every mole of Fe reacted

   D. 13.3 kJ of energy are absorbed for every mole of Fe reacted

2. When solutions of HCl and NaOH are mixed the temperature increases. The reaction:

   $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$
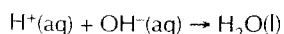
   A. is endothermic with a positive $\Delta H^{\ominus}$.

   B. is endothermic with a negative $\Delta H^{\ominus}$.

   C. is exothermic with a positive $\Delta H^{\ominus}$.

   D. is exothermic with a negative $\Delta H^{\ominus}$.

3.

reactants

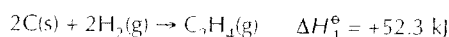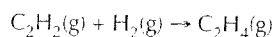$\Delta H^{\ominus}$
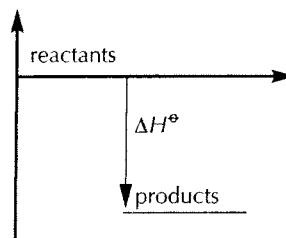
products

What can be deduced about the relative stability of the reactants and products and the sign of $\Delta H^{\ominus}$, from the enthalpy level diagram above?

	Relative stability	Sign of $\Delta H^{\ominus}$
A.	Products more stable	–
B.	Products more stable	+
C.	Reactants more stable	–
D.	Reactants more stable	+

4. For the reaction:

$$2C(s) + 2H_2(g) \rightarrow C_2H_4(g) \qquad \Delta H_1^\ominus = +52.3 \text{ kJ}$$

If $\Delta H_2^\ominus = -174.4$ kJ for the reaction:

$$C_2H_2(g) + H_2(g) \rightarrow C_2H_4(g)$$

what can be said about the value of $\Delta H_3^\ominus$ for the reaction below?

$$2C(s) + H_2(g) \rightarrow C_2H_2(g)$$
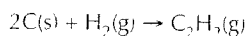
A. $\Delta H_3^\ominus$ must be negative.

B. $\Delta H_3^\ominus$ must be a positive number smaller than 52.3 kJ.

C. $\Delta H_3^\ominus$ must be a positive number larger than 52.3 kJ.

D. No conclusion can be made about $\Delta H_3^\ominus$ without the value of H for $H_2(g)$.

5. The enthalpy changes for two different hydrogenation reactions of C_2H_2 are:

$$C_2H_2 + H_2 \rightarrow C_2H_4 \quad \Delta H_1^\ominus$$
$$C_2H_2 + 2H_2 \rightarrow C_2H_6 \quad \Delta H_2^\ominus$$
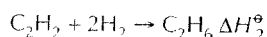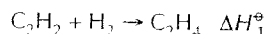
Which expression represents the enthalpy change for the reaction below?

$$C_2H_4 + H_2 \rightarrow C_2H_6 \quad \Delta H^\ominus = ?$$

A. $\Delta H_1^\ominus + \Delta H_2^\ominus$

B. $\Delta H_1^\ominus - \Delta H_2^\ominus$

C. $\Delta H_2^\ominus - \Delta H_1^\ominus$

D. $-\Delta H_1^\ominus - \Delta H_2^\ominus$

6.
$$2KHCO_3(s) \xrightarrow{\Delta H^\ominus} K_2CO_3(s) + CO_2(g) + H_2O(l)$$

$$+2HCl(aq) \searrow \quad \Delta H_2^\ominus \nearrow +2HCl(aq)$$

$$\Delta H_1^\ominus$$

$$2KCl(aq) + 2CO_2(g) + 2H_2O(l)$$

This cycle may be used to determine $\Delta H^\ominus$ for the decomposition of potassium hydrogencarbonate. Which expression can be used to calculate $\Delta H^\ominus$?

A. $\Delta H^\ominus = \Delta H_1^\ominus + \Delta H_2^\ominus$

B. $\Delta H^\ominus = \Delta H_1^\ominus - \Delta H_2^\ominus$

C. $\Delta H^\ominus = \frac{1}{2}\Delta H_1^\ominus - \Delta H_2^\ominus$

D. $\Delta H^\ominus = \Delta H_2^\ominus - \Delta H_1^\ominus$

7. Use the bond energies for H–H (436 kJ mol^{-1}), Br–Br (193 kJ mol^{-1}) and H–Br (366 kJ mol^{-1}) to calculate $\Delta H^\ominus$ (in kJ mol^{-1}) for the reaction:

$$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$$
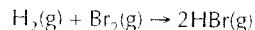
A. 263   C. –103

B. 103   D. –263

8. The average bond enthalpy for the C–H bond is 412 kJ mol^{-1}. Which process has an enthalpy change closest to this value?

A. $CH_4(g) \rightarrow C(s) + 2H_2(g)$

B. $CH_4(g) \rightarrow C(g) + 2H_2(g)$

C. $CH_4(g) \rightarrow C(s) + 4H(g)$

D. $CH_4(g) \rightarrow CH_3(g) + H(g)$

(HL) ───

9. Which of the changes below occurs with the greatest increase in entropy?

A. $Na_2O(s) + H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq)$

B. $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$

C. $H_2(g) + I_2(g) \rightarrow 2HI(g)$

D. $C(s) + CO_2(g) \rightarrow 2CO(g)$

10. How would this reaction at 298 K be described in thermodynamic terms?

$$2H_2O(g) \rightarrow 2H_2(g) + O_2(g)$$

A. Endothermic with a significant increase in entropy

B. Endothermic with a significant decrease in entropy

C. Exothermic with a significant increase in entropy

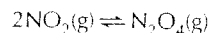D. Exothermic with a significant decrease in entropy

11. The enthalpy change, $\Delta H^\ominus$, for a chemical reaction is –10 kJ mol^{-1} and the entropy change, $\Delta S^\ominus$, is –10 JK^{-1} mol^{-1} at 27 °C. What is the value of $\Delta G^\ominus$ (in J) for this reaction?

A. –260

B. –7000

C. –9730

D. –13000

12. At 0 °C, the mixture formed when the following reaction reaches equilibrium consists mostly of $N_2O_4(g)$.

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

What are the signs of ΔG, ΔH, ΔS at this temperature?

	ΔG	ΔH	ΔS
A.	+	+	+
B.	–	–	–
C.	–	+	+
D.	+	+	–

13. Which substance has the largest lattice energy?

A. NaF   C. MgO

B. KCl   D. CaS

14. Which factor(s) will cause the lattice enthalpy of ionic compounds to increase in magnitude?

I. an increase in the charge on the ions

II. an increase in the size of ions

A. I only   C. Both I and II

B. II only   D. Neither I nor II

15. The Born–Haber cycle for the formation of potassium chloride includes the steps below:

I. $K(g) \rightarrow K^+(g) + e^-$ III. $Cl(g) + e^- \rightarrow Cl^-(g)$

II. $\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$ IV. $K^+(g) + Cl^-(g) \rightarrow KCl(s)$

Which of these steps are exothermic?

A. I and II only   C. I, II and II only

B. III and IV only   D. I, III and IV only