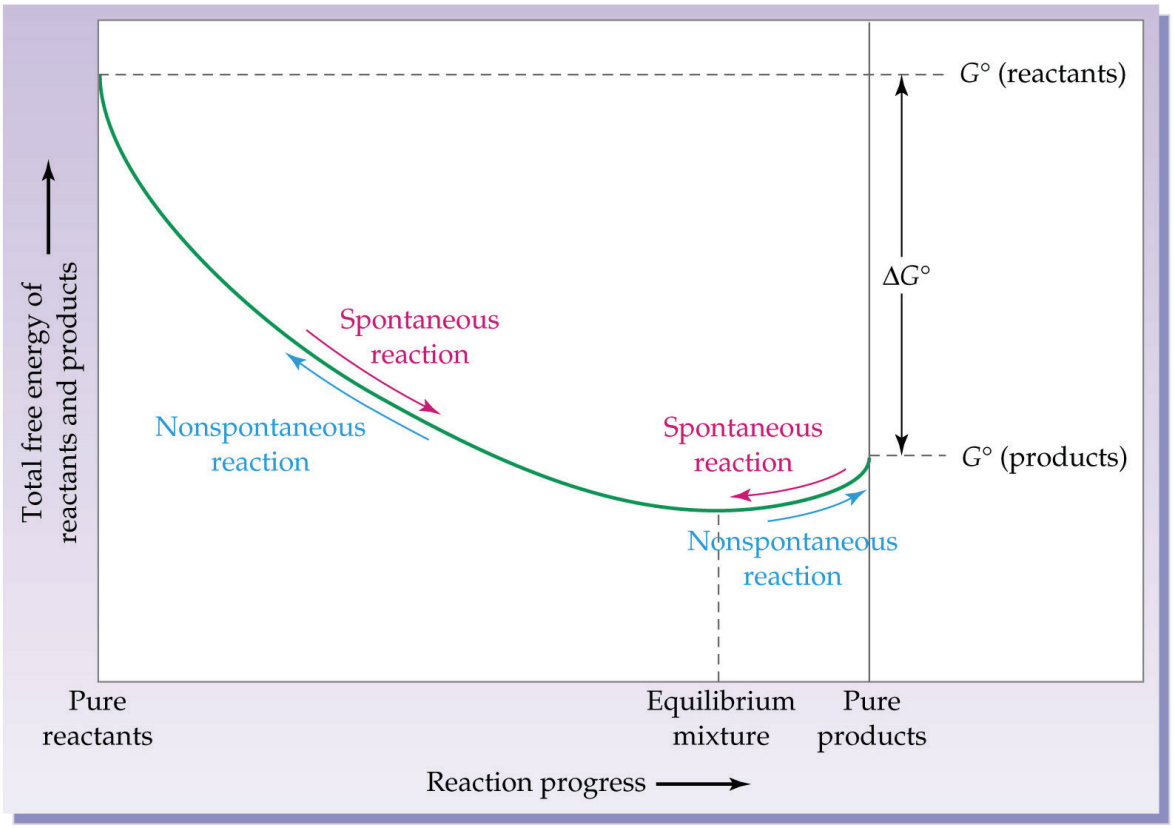
Unit 2 - Physical Chemistry

THERMOCHEMISTRY
(Enthalpy Changes)

THERMODYNAMICS
(Reaction Feasibility)



Pupil Notes
Learning Outcomes
Questions & Answers

SECTION 1

Enthalpy

Thermochemistry is the study of the changes in heat energy that occur during a chemical reaction. Energy is required to break bonds and is also released when bonds are formed. When a chemical reaction takes place these two processes occur and there is often an exchange of heat energy between the reaction and its surroundings. This is called the **enthalpy change** (ΔH). Every substance has an enthalpy (a chemical potential energy or heat content) that cannot be measured. Only when substances react can the enthalpy change be noted. In order that chemists worldwide can compare notes on thermochemical experiments, a series of special conditions have been agreed. Some of these are outlined in the following paragraphs.

Enthalpy changes are defined as the measured heat energy changes occurring during a reaction, usually per mole of product formed or reactant used up, depending on the particular enthalpy change being defined. The units are in kilojoules per mole, kJ mol^{-1}.

The **standard enthalpy change** is defined as the enthalpy change measured under standard conditions. **Standard conditions** are one mole of a substance at one atmosphere pressure and any specified temperature (in Kelvin). The symbol used is ΔH^{o}_{T}. The temperature specified is usually 298 K (25ºC) and ΔH^{o} is taken to mean ΔH^{o}_{298}.

The **standard enthalpy of formation (ΔH^{o}_{f})** of a compound is the enthalpy change when one mole of a compound is formed from its elements in their standard states. The **standard enthalpy of formation of elements** is by definition zero, giving a base line from which enthalpy changes can be measured.

The **standard state** of a substance is the most stable state of that substance under standard conditions. The **standard enthalpy of combustion (ΔH^{o}_{c})** of a substance is the enthalpy change (always energy released) when one mole of a substance is completely burned in excess oxygen. An excess of oxygen has to be used to ensure complete oxidation, e.g. for carbon to ensure that CO_2 is the only product and no CO is formed.

The enthalpy change for any reaction is defined as the sum of the enthalpy of the products minus the sum of the enthalpy of the reactants:

ΔH = Σenthalpy of products – Σenthalpy of reactants
Σ = the sum of

This means that exothermic reactions have a negative ΔH value as energy is lost to the surroundings, while endothermic processes have a positive ΔH value as energy is taken in by the reaction from the surroundings.

Hess's law

The **first law of thermodynamics** simply states that 'energy cannot be created or destroyed and can only be changed from one form to another.' Hess, in 1840, applied this law to chemical reactions and **Hess's law** states that 'the enthalpy change associated with converting reactants in a specified state into products in a specified state is independent of the route taken' e.g. for the oxidation of carbon:

$C(s) + O_2(g)$	$\rightarrow$	$CO_2(g)$	(a)	$\Delta H_a = -394$ kJ mol^{-1}
$C(s) + \frac{1}{2}O_2(g)$	$\rightarrow$	$CO(g)$	(b)	$\Delta H_b = -123$ kJ mol^{-1}
$CO(g) + \frac{1}{2}O_2(g)$	$\rightarrow$	$CO_2(g)$	(c)	$\Delta H_c = -271$ kJ mol^{-1}

equation (a) is the sum of equations (b) and (c):

$$\Delta H_a = \Delta H_b + \Delta H_c.$$

This law allows the calculation of enthalpy changes for reactions that are difficult or impossible to determine by experiment, e.g. the reaction is too slow or too fast or by-products are formed. There are two general methods of carrying out calculations based on Hess's law: the pictorial method and the algebraic method. The pictorial method requires a thermochemical cycle to be set up to show the energy changes between reactants and products. This method is easy to use when bond enthalpies (see page 41) and ionic compounds (Born–Haber cycle) are involved but may become cumbersome for other calculations. This method is illustrated in the bond enthalpy section (page 41) and the Born–Haber cycle section (page 45). The algebraic method can be used for any calculations and an example of this method follows.

Example 2
Calculate the standard enthalpy of formation of ethanoic acid given that its standard enthalpy of combustion is –876 kJ mol^{-1} and that the standard enthalpies of formation of carbon dioxide and water are –394 and –286 kJ mol^{-1} respectively.

Step 1: Write down the required equation:

$$2C(s) + 2H_2(g) + O_2(g) \rightarrow \quad CH_3COOH(l)$$

Step 2: Express all the information given in equation form:

(1)	$C(s) + O_2(g)$	$\rightarrow CO_2(g)$	$\Delta H^o = -394$ kJ mol^{-1}
(2)	$H_2(g) + \frac{1}{2}O_2(g)$	$\rightarrow H_2O(l)$	$\Delta H^o = -286$ kJ mol^{-1}
(3)	$CH_3COOH(l) + 2O_2(g)$	$\rightarrow 2CO_2(g) + 2H_2O(l)$	$\Delta H^o = -876$ kJ mol^{-1}

Step 3: Use the three equations to obtain the required balanced equation:

(1) × 2	$2C(s) + 2O_2(g)$	$\rightarrow 2CO_2(g)$	$\Delta H^o = -788$ kJ mol^{-1}
(2) × 2	$2H_2(g) + O_2(g)$	$\rightarrow 2H_2O(l)$	$\Delta H^o = -572$ kJ mol^{-1}
(3) reverse	$2CO_2(g) + 2H_2O(l)$	$\rightarrow CH_3COOH(l) + 2O_2(g)$	$\Delta H^o = +876$ kJ mol^{-1}

Step 4: Imagine that all three processes are going on at the same time in the same reaction container. To find the overall result, the three equations are added to give, after cancelling, the enthalpy change for the reaction:

$$2C(s) + 2H_2(g) + O_2(g) \rightarrow CH_3COOH(l) \qquad \Delta H^o = -484 \text{ kJ mol}^{-1}$$

Thus the standard enthalpy of formation of ethanoic acid is –484 kJ mol^{-1}.

The standard enthalpy change for any reaction can be calculated from the standard enthalpies of formation of the substances in the equilibrium using the equation:

$$\Delta H^o = \Sigma \Delta H^o_f \text{ products} - \Sigma \Delta H^o_f \text{ reactants}$$

Example 3

Calculate the standard enthalpy of reaction for the decomposition of copper(II) nitrate from the given standard enthalpies of formation.

Step 1: Write the equation with ΔH^o_f values beneath each substance:

$$Cu(NO_3)_2(s) \rightarrow CuO(s) + 2NO_2(g) + \tfrac{1}{2}O_2(g)$$

ΔH^o_f/kJ mol^{-1}	–307	–155	+34	0

Step 2: Multiply each ΔH^{o}_{f} value by its mole relationship:

$$Cu(NO_3)_2(s) \rightarrow CuO(s) + 2NO_2(g) + \tfrac{1}{2}O_2(g)$$

$$-307 \qquad -155 \quad +68 \quad 0$$

Step 3: Use the equation $\Delta H^{o} = \Sigma\Delta H^{o}_{f}$ products $- \Sigma\Delta H^{o}_{f}$ reactants:

$$\begin{aligned}\Delta H^{o} &= \Sigma\Delta H^{o}_{f} \text{ prod} - \Sigma\Delta H^{o}_{f} \text{ reactants} \\ &= -155 + 68 - (-307) \\ &= -87 + 307 \\ &= +220\end{aligned}$$

ΔH^{o} for the reaction = +220 kJ mol^{-1}

This method is just a shorthand way of carrying out the calculation using equations, as in Example 2, page 38:

Step 1: Write down the required equation:

$$Cu(NO_3)_2(s) \rightarrow CuO(s) + 2NO_2(g) + \tfrac{1}{2}O_2(g)$$

Step 2: Express all the information given in equation form:

(1)	$Cu(s) + \tfrac{1}{2}O_2(g)$	→	$CuO(s)$	$\Delta H^{o}_{f} = -155$ kJ mol^{-1}
(2)	$\tfrac{1}{2}N_2(g) + O_2(g)$	→	$NO_2(g)$	$\Delta H^{o}_{f} = +34$ kJ mol^{-1}
(3)	$Cu(g) + N_2(g) + 3O_2(g)$	→	$Cu(NO_3)_2(s)$	$\Delta H^{o}_{f} = -307$ kJ mol^{-1}

Step 3: Use the equations to obtain the required balanced equation:

				ΔH
(1) as written	$Cu(s) + \tfrac{1}{2}O_2(g)$	→	$CuO(s)$	–155 kJ mol^{-1}
(2) ×2	$N_2(g) + 2O_2(g)$	→	$2NO_2(g)$	+68 kJ mol^{-1}
(3) reverse	$Cu(NO_3)_2(g)$	→	$Cu(s) + N_2(g) + 3O_2(g)$	+307 kJ mol^{-1}

Step 4: Add the three equations to give the required equation and ΔH^{o}:

$$Cu(NO_3)_2(s) \rightarrow CuO(g) + 2NO_2(g) + \tfrac{1}{2}O_2(g) \qquad \Delta H^{o} = +220 \text{ kJ mol}^{-1}$$

Experimental methods of calculating ΔH values

In the laboratory simple experiments can be set up to measure some ΔH values of some reactions. These reactions are carried out in a vessel called a calorimeter (after the old heat unit the calorie, 4.18 J = 1 calorie). Calorimeters are used to measure quantitative heat changes during a chemical reaction and calorimetry is the term used for this type of determination.

Any calorimeter experiment requires all of the heat energy lost or gained by the reaction to be transferred to the calorimeter of known heat capacity, which is insulated so that no heat is lost to or gained from the surroundings. Polystyrene cups and vacuum flasks are good enough insulators for reactions carried out in solution, but combustion reactions are very difficult to undertake in the school laboratory since heat loss to the surroundings cannot be avoided when using spirit burners and metal beakers (see Higher Chemistry, PPA 3, Unit 1). Such experiments are carried out in a bomb calorimeter, in which known masses are burnt in excess oxygen.

Bond enthalpies

Bond enthalpies can be divided into two categories (see page 9 of the Data Booklet). The bond dissociation enthalpy is the energy required to break one mole of bonds and form two separate atoms, all species being in the gaseous state. These values are accurately known but it is only possible to calculate them for diatomic molecules, e.g.

$H_2(g)$	$\rightarrow$	$2H(g)$	$+432$ kJ mol^{-1}
$N_2(g)$	$\rightarrow$	$2N(g)$	$+941$ kJ mol^{-1}
$HCl(g)$	$\rightarrow$	$H(g) + Cl(g)$	$+428$ kJ mol^{-1}

For molecules with more than two atoms, such as methane, it is only possible to calculate the mean bond enthalpy since the situation is much more complex with the C–H bonds breaking off one after the other to form a different fragment of the original molecule.

The removal of the first hydrogen atom from CH_4 does not require the same energy as the removal of the second hydrogen from the CH_3 fragment and so on. The value obtained is the average or mean bond enthalpy for C–H, i.e.

$$CH_4(g) \rightarrow C(g) + 4H(g) \qquad \Delta H = 4 \times \text{C–H} = 1656 \text{ kJ mol}$$

therefore the mean bond enthalpy of C–H $= \dfrac{1656}{4} = 414$ kJ mol^{-1}

Mean bond enthalpies are quoted in data books for bonds of that type in any molecule but can also be calculated from other enthalpy changes, as shown in the following examples.

Example 4

Calculate the mean bond enthalpy of the C–H bond from the enthalpy of formation of methane and any other required data from the Data Booklet.

Step 1: Write down the required equation:

$CH_4 \rightarrow C(g) + 4H(g)$ $\quad \Delta H = 4 \times$ C–H

Step 2: Express all the information given in equation form:

(1)	$C(s) + 2H_2(g)$	→	$CH_4(g)$	$\Delta H = -75$ kJ mol^{-1}
(2)	$C(s)$	→	$C(g)$	$\Delta H = +715$ kJ mol^{-1}
(3)	$H_2(g)$	→	$2H(g)$	$\Delta H = +432$ kJ mol^{-1}

Step 3: Use the three equations to obtain the required balanced equation:

(1)	reverse	$CH_4(g)$	→	$C(s) + 2H_2(g)$	+75 kJ mol^{-1}
(2)		$C(s)$	→	$C(g)$	+715 kJ mol^{-1}
(3)	×2	$2H_2(g)$	→	$4H(g)$	+864 kJ mol^{-1}

Step 4: Add the three equations to give the required equation and ΔH:

$CH_4(g) \rightarrow C(g) + 4H(g)$ $\quad 1654$ kJ mol^{-1}

1654 kJ = 4 × C–H

$$\text{C–H} = \frac{1654}{4}$$

Mean bond enthalpy of C–H = 413.5 kJ mol^{-1}

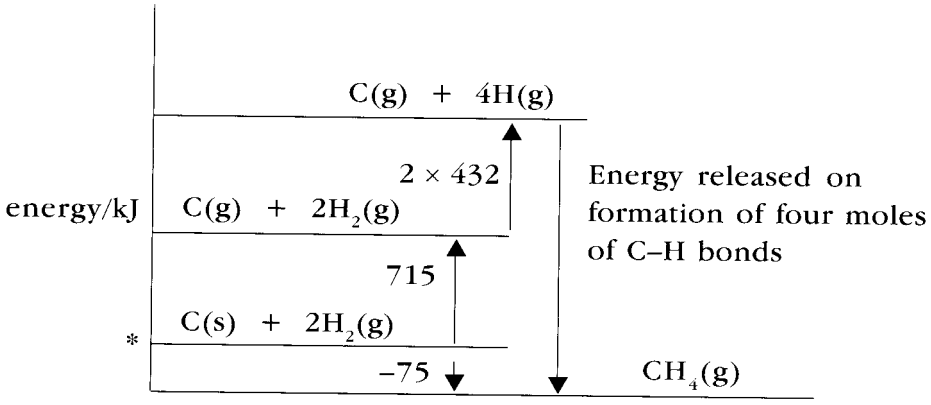
Example 4 can also be carried out in the form of a thermochemical cycle, as in Example 5.

Example 5

Calculate the mean C–H bond enthalpy in methane given that the standard enthalpy of formation is –75 kJ mol^{-1}, the enthalpy of sublimation of carbon is +715 kJ mol^{-1} and the bond enthalpy of an H–H bond is 432 kJ mol^{-1}.

From this information a thermochemical cycle can be drawn (Figure 13).

Figure 13



As long as the enthalpies are added in the cycle in the same direction then the sum of the enthalpies is zero, i.e. from * on the cycle going clockwise:

$$+715 + (2 \times (+432)) - (4 \times \text{C–H bond enthalpy}) + 75 = 0$$

(Note that the last two terms have had their sign reversed since they are quoted in the opposite direction.)

Rearranging $-4 \times$ C–H bond enthalpy $= -715 - 864 - 75$

$$\text{C–H bond enthalpy} = \frac{1654}{4} = 413.5 \text{ kJ mol}^{-1}$$

Example 6

Calculate the C–C bond enthalpy in ethane from the enthalpy of formation of ethane and data from page 9 of the Data Booklet. You may find it helpful to draw the full structural formulae of the substances to help work out the bonds that have to be broken and formed.

Step 1: Write down the required equation:

$$C_2H_6(g) \rightarrow 2C(g) + 6H(g) \quad \Delta H = 6 \times \text{C–H} + 1 \times \text{C–C}$$

Step 2: Express all the information given in equation form:

(1) $2C(s) + 3H_2(g) \rightarrow C_2H_6(g)$ $\Delta H = -85$ kJ mol^{-1}
(2) $C(s) \rightarrow C(g)$ $\Delta H = +715$ kJ mol^{-1}
(3) $H_2(g) \rightarrow 2H(g)$ $\Delta H = +432$ kJ mol^{-1}

Step 3: Use the three equations to obtain the required balanced equation and ΔH:

(1) reversed + (2 × (2)) + (3 × (3)) = +85 + 1430 + 1296
= +2811 kJ

However, this is (6 × C–H) + (1 × C–C) bonds.

C–H mean bond enthalpy = +414 kJ mol^{-1} (from the Data Booklet)
C–C bond enthalpy = ΔH required – (6 × C–H)
= 2811 – (6 × 414)
= +327 kJ
C–C bond enthalpy = + 327 kJ mol^{-1}

From Examples 5 and 6 it can be seen that the mean C–H bond enthalpy value and the C–C bond enthalpy values are different from the Data Booklet values. This is caused by them being calculated from different experimental data. Often different data booklets have slightly different values quoted for this reason.

It is possible to calculate ΔH values from mean bond enthalpies as ΔH values reflect the energy changes in bond breaking and bond making. The enthalpy of formation of ethane can be calculated from mean bond enthalpies either algebraically or by a thermochemical cycle, as shown in Example 7.

Example 7

C_2H_6 is made from 2C atoms and 6H atoms and the starting materials are C(s) and H_2(g):

$2C(s) + 3H_2(g) \rightarrow C_2H_6(g)$

Bond breaking:	$2C(s)$	→	$2C(g)$	= 2 × 715 kJ	= 1430 kJ
	$3H_2(g)$	→	$6H(g)$	= 3 × 432 kJ	= 1296 kJ
					2726 kJ
Bond making:	6 × C–H bonds	= 6 × –414 kJ			= –2484 kJ
	1 × C–C bond	= 1 × –346 kJ			= –346 kJ
					–2830 kJ

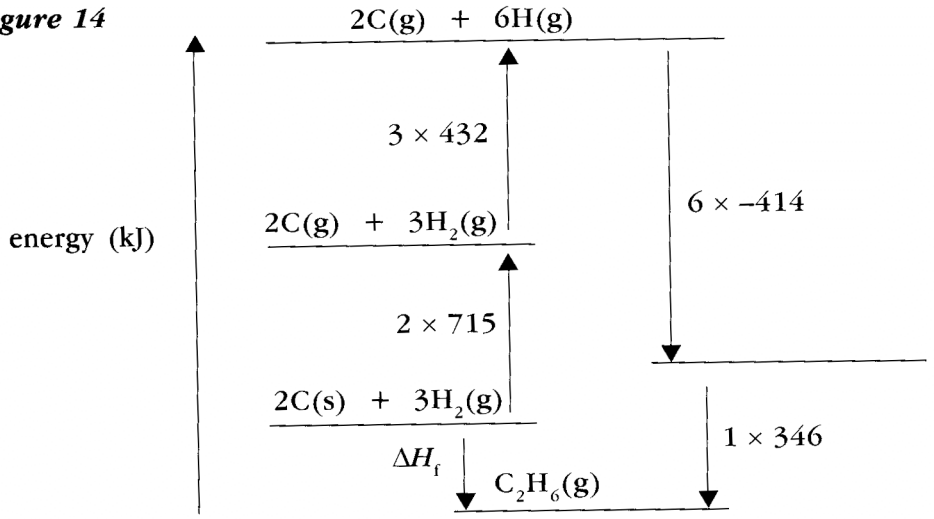
Energy for reaction = 2726 – 2830
= –104 kJ mol^{-1}

Therefore ΔH_f for C_2H_6 = –104 kJ mol^{-1}

The Data Booklet gives a value of –85 kJ mol^{-1}, which comes from experimental data rather than mean bond enthalpies, which may not be as accurate for the molecule concerned.

The thermochemical cycle method (Figure 14) gives the same result as that calculated above.

Figure 14



$(2 \times 715) + (3 \times 432) - (6 \times 414) - 346 - \Delta H_f = 0$

$\Delta H_f = 1430 + 1296 - 2484 - 346$

$= 2726 - 2830$

$= -104$ kJ mol^{-1}

The above calculations are all examples of the application of Hess's law and are therefore consistent with the first law of thermodynamics.

Hess's law applied to ionic substances

The Born–Haber cycle

The Born–Haber cycle is a special application of Hess's law applied to the formation of an ionic crystal. It can be used to calculate the enthalpy of lattice formation of an ionic substance, which cannot be found directly by experiment. The **standard molar enthalpy of lattice formation** is the enthalpy change when one mole of an ionic crystal is formed from its ions in their gaseous states under standard conditions.

Born and Haber drew up a cycle of the theoretical steps involved in the formation of an ionic crystal from its elements, even though the actual reaction may not follow this mechanism. The theoretical steps involved are

all named enthalpy changes, which have definitions. We have already come across enthalpy of formation, lattice enthalpy and bond enthalpy. The other enthalpy changes in a Born–Haber cycle are given below.

The **standard molar enthalpy of atomisation** of an element is the energy required to produce one mole of isolated gaseous atoms from an element in its standard state, e.g.

$$\tfrac{1}{2}I_2(s) \rightarrow I(g) \qquad \Delta H = 149 \text{ kJ mol}^{-1}$$

The **ionisation enthalpy** (ΔH^{o}_{IE}) of an element is the energy required to remove one mole of electrons from one mole of gaseous atoms (or ions) to form one mole of gaseous ions. This change can be represented by the following equations:

$X(g)$	$\rightarrow$	$X^+(g) + e^-$	first ionisation energy
$X^+(g)$	$\rightarrow$	$X^{2+}(g) + e^-$	second ionisation energy
$X^{2+}(g)$	$\rightarrow$	$X^{3+}(g) + e^-$	third ionisation energy

The **electron affinity** (ΔH^{o}_{EA}) of an element is the enthalpy change when one mole of electrons is added to one mole of isolated atoms (or ions) in the gaseous state. This can be represented by the following equations:

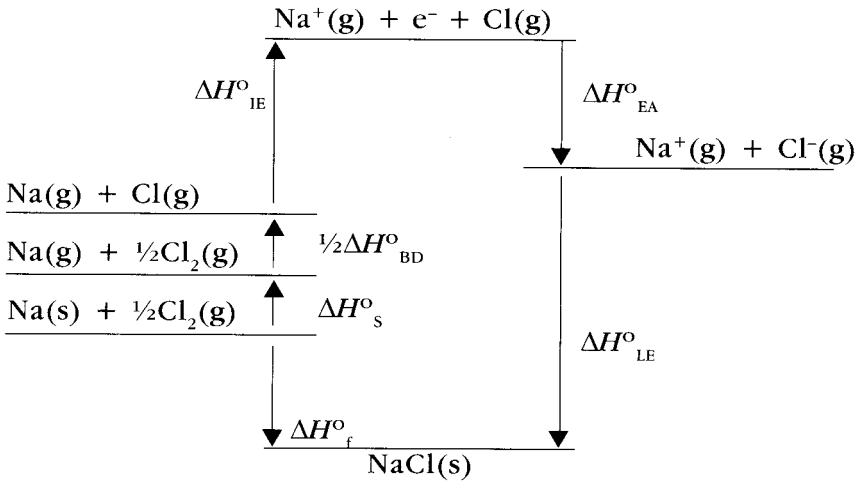
$X(g) + e^-$	$\rightarrow$	$X^-(g)$	first electron affinity
$X^-(g) + e^-$	$\rightarrow$	$X^{2-}(g)$	second electron affinity

Electron affinity is sometimes referred to as electron gain enthalpy.

Example 8

A Born–Haber cycle (Figure 15) for calculating the lattice enthalpy of sodium chloride is shown below.

Figure 15



ΔH^{o}_{BD} = bond dissociation enthalpy; ΔH^{o}_{LE} = lattice enthalpy

The use of the cycle is the same as before, i.e. the sum of the enthalpies round the cycle = 0. For the cycle in Figure 15:

$$\Delta H^{o}_{S} + \tfrac{1}{2}\Delta H^{o}_{BD} + \Delta H^{o}_{IE} + \Delta H^{o}_{EA} + \Delta H^{o}_{LE} - \Delta H^{o}_{f} = 0$$

Rearranging to calculate the lattice enthalpy:

$$\Delta H^{o}_{LE} = \Delta H^{o}_{f} - \Delta H^{o}_{S} - \tfrac{1}{2}\Delta H^{o}_{BD} - \Delta H^{o}_{IE} - \Delta H^{o}_{EA}$$

Substituting the values into this gives:

$$\Delta H^{o}_{LE} = -385.2 - 109 - 121.5 - 502 + 348.7 = -769 \text{ kJ mol}^{-1}$$

Enthalpy of solution

There are two enthalpy values associated with solutions: the enthalpy of solution and the hydration enthalpy. The **enthalpy of solution** is defined as the enthalpy change when one mole of a substance is dissolved in a large volume of water:

$$Na^{+}Cl^{-}(s) \rightarrow Na^{+}(aq) + Cl^{-}(aq)$$

The **enthalpy of hydration** is the energy released when a mole of isolated gaseous ions becomes hydrated, i.e.

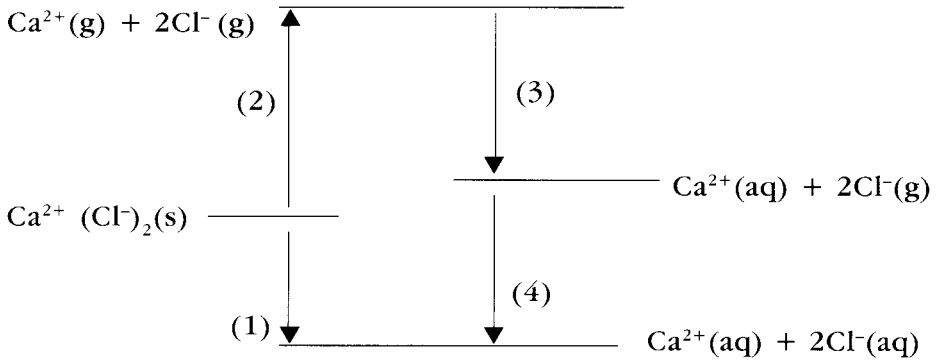
$$E^{n+}(g) \rightarrow E^{n+}(aq)$$
$$E^{n-}(g) \rightarrow E^{n-}(aq)$$

Enthalpies of solution are easily measured in the laboratory in simple experiments. The values obtained can be compared to those in data booklets or those calculated using thermochemical data in either the algebraic or the cyclic method.

Example 9

The enthalpy of solution of calcium chloride as calculated by the cyclic method is shown on the next page (Figure 16).

Figure 16



(1) $= \Delta H_{soln}$

(2) = reverse of lattice enthalpy of formation $= +2223$ kJ mol^{-1}

(3) $= \Delta H_{hydn}\ Ca^{2+} = -1653$ kJ mol^{-1}

(4) $= 2 \times \Delta H_{hydn}\ Cl^- = 2 \times -338$ kJ mol^{-1}

$(2) + (3) + (4) - (1) = 0$

$(1) = (2) + (3) + (4)$

$= 2223 - 1653 - 676$

$\Delta H_{soln} = -106$ kJ mol^{-1}

Questions

1. Calculate the enthalpy of formation of methane from the enthalpies of combustion on page 9 of the Data Booklet.

2. Calculate the enthalpy of formation of ethyne (C_2H_2) from the bond enthalpies and mean bond enthalpies on page 9 of the Data Booklet.

3. Set up a Born–Haber cycle to calculate the enthalpy of formation of lithium fluoride using the data on pages 9, 10 and 17 of the Data Booklet.

THERMOCHEMISTRY

Hess's Law

2.43 *Thermochemistry concerns the study of changes in energy which occur during chemical reactions.*

2.44 *The **First Law of Thermodynamics** states that energy is conserved.*

2.45 *Hess's law states that the overall reaction enthalpy is the sum of the reaction enthalpies of each step of the reaction. This is an application of the First Law of Thermodynamics.*

2.46 *A thermochemical cycle can be used to calculate an unknown enthalpy value.*

2.47 *The term 'standard enthalpy change' (ΔH^o) refers to an enthalpy change for a reaction in which the reactants and products are considered to be in their standard states at a specified temperature.*

2.48 *The standard state of a substance is the most stable state of the substance under standard conditions.*

2.49 *Standard conditions refer to a pressure of one atmosphere and a specified temperature, usually 298K (25°C).*

2.50 *The standard molar enthalpy of combustion refers to the enthalpy change which occurs when one mole of a substance is burned completely.*

2.51 *Calorimetry is the term used to describe the quantitative determination of the change in heat energy which occurs during a chemical reaction.*

2.52 *A calorimeter is used to measure the quantity of heat energy given out or taken in during a chemical reaction.*

2.53 *The standard molar enthalpy of formation refers to the enthalpy change which occurs when one mole of a substance is prepared from its elements in their standard states.*

2.54 *The standard enthalpy of formation of a substance can be calculated from standard enthalpy changes which are experimentally determined.*

2.55 *The standard enthalpy of a reaction can be calculated from tabulated standard molar enthalpies of formation using the relation:*

$$\Delta H^o = \Sigma \Delta H^o_f(\text{products}) - \Sigma \Delta H^o_f(\text{reactants})$$

Bond Enthalpies

2.56 *For a diatomic molecule, XY, the molar bond enthalpy is the energy required to break one mole of XY bonds, that is, for the process:*

$$X\text{-}Y_{(g)} \rightarrow X_{(g)} + Y_{(g)}$$

2.57 *Mean molar bond enthalpies are average values which are quoted for bonds which occur in different molecular environments.*

2.58 *Bond enthalpies may be calculated from data on enthalpy changes.*

2.59 *The enthalpy of a reaction can be estimated from a thermochemical cycle involving bond formation and bond dissociation.*

2.60 *Enthalpies of reaction estimated from bond enthalpies may differ from experimentally determined values.*

Hess's Law applied to ionic substances

Born-Haber cycle

2.61 *The Born-Haber cycle is a thermochemical cycle applied to the formation of an ionic crystal.*

2.62 *The Born-Haber cycle can be used to calculate the enthalpy of lattice formation, which cannot be determined directly by experiment.*

2.63 *The standard molar enthalpy change of lattice formation is the enthalpy change which occurs when one mole of an ionic crystal is formed from the ions in their gaseous states under standard conditions.*

2.64 *The cycle is a closed path which includes as steps the different enthalpy changes involved in the formation of an ionic crystal.*

2.65 *The different enthalpy changes include enthalpy of atomisation, ionisation energy, bond enthalpy, electron affinity, lattice enthalpy and enthalpy of formation.*

2.66 *The standard molar enthalpy of atomisation of an element is the energy required to produce one mole of isolated gaseous atoms from the element in its standard state.*

$$eg.\ ½\ I_{2(s)} \rightarrow I_{(g)}$$

2.67 *The electron affinity is usually defined as the enthalpy change for the process of adding one mole of electrons to one mole of isolated atoms in the gaseous state, ie, for the change represented by:*

$$E_{(g)} + e^- \rightarrow E^-_{(g)}$$

Enthalpy of solution

2.68 *A thermochemical cycle can represent the relation between enthalpy of solution, enthalpy of lattice formation and enthalpy of hydration for the solution of an ionic compound.*

2.69 *The hydration enthalpy is the energy released when one mole of individual gaseous ions becomes hydrated, ie, the changes represented by:*

$$E^{n+}_{(g)} \rightarrow E^{n+}_{(aq)} \text{ and } E^{n-}_{(g)} \rightarrow E^{n-}_{(aq)}$$

Q1 Solid magnesium chloride exists in two forms: anhydrous($MgCl_2$) and hydrated($MgCl_2.6H_2O$).

a) Calculate the enthalpy change for the process:

$$MgCl_{2(s)} \rightarrow Mg^{2+}_{(aq)} + 2Cl^-_{(aq)}$$

Use the following data:

$$Mg^{2+}_{(g)} \rightarrow Mg^{2+}_{(aq)} \quad \Delta H = -1920 \text{ kJ mol}^{-1}$$

$$Cl^-_{(g)} \rightarrow Cl^-_{(aq)} \quad \Delta H = -364 \text{ kJ mol}^{-1}$$

lattice enthalpy (anhydrous magnesium chloride) = 2493 kJ mol^{-1} **3**

b) Calculate the enthalpy change for converting anhydrous magnesium chloride to hydrated magnesium chloride, given the following enthalpies of formation:

ΔH^θ_f(hydrated magnesium chloride)	=	–2500 kJ mol^{-1}
ΔH^θ_f(anhydrous magnesium chloride)	=	–642 kJ mol^{-1}
ΔH^θ_f (water)	=	–286 kJ mol^{-1} **3**

(6)

Q2 Consider the following data:

Compound	***Lattice-breaking enthalpy/kJ mol^{-1}***	***Enthalpy of solution/kJ mol^{-1}***
KF	801	– 17.7
KCl	701	+ 17.2
KBr	670	+ 20.0

a) Why do the lattice-breaking enthalpies decrease down the series from KF to KBr? **1**

b) Calculate the enthalpy associated with the hydration of the ions in KCl. **1**

c) How would you expect the enthalpy associated with the hydration of the ions in calcium chloride to compare with that in potassium chloride? Explain your answer. **2**

(4)

Q3 Water gas is prepared by passing steam over white hot coke. The equation for the reaction is:

$$C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)}$$

The products of the reaction may be used to prepare methanol industrially, using chromium(III) oxide as a catalyst, a temperature of 300°C and a pressure of 300 atmospheres:

$$CO_{(g)} + 2H_{2(g)} \rightarrow CH_3OH_{(l)}$$

a) The enthalpy change for the reaction to produce water gas is 130 kJ mol^{-1}.

Use this value, with information on 'page 9' of the Data Booklet, to calculate the bond enthalpy for the C–O bond in carbon monoxide. **3**

b) The mean bond enthalpy for C–O is 331 kJ mol^{-1} and for C=O is 724 kJ mol^{-1}.

Use this information and your answer to **a)** to make a prediction about the nature of the bond in carbon monoxide. **1**

c) State two possible hazards associated with the industrial production of methanol. **2**

(6)

Q4 **a)** By referring to the Data Booklet write down the equation and the value for:

i) the enthalpy of formation of propane

ii) the enthalpy of combustion of carbon

iii) the enthalpy of combustion of hydrogen. **3**

b) Using the above data, calculate the enthalpy of combustion of propane. **2**

(5)

Q5 **a)** Name each of the changes shown by the equations ***i)*** to ***v)*** and beside each name write the value for the change as shown in the Data Booklet.

i) $Na_{(s)} \rightarrow Na_{(g)}$ **1**

ii) $\frac{1}{2}O_{2(g)} \rightarrow O_{(g)}$ **1**

iii) $Na_{(g)} \rightarrow Na^{+}_{(g)}$ **1**

iv) $O_{(g)} \rightarrow O^{2-}_{(g)}$ **1**

v) $2Na^{+}_{(g)} + O^{2-}_{(g)} \rightarrow (Na^{+})_2O^{2-}_{(s)}$ **1**

b) Write the equation for the enthalpy of formation of sodium oxide. **1**

c) ***i)*** Construct a Born–Haber cycle using all the information in **a)** and **b)**. **1**

ii) Calculate the enthalpy of formation of sodium oxide. **1**

(8)

Q6 **a)** Using bond enthalpy values from the Data Booklet, calculate the enthalpy change for the following reaction.

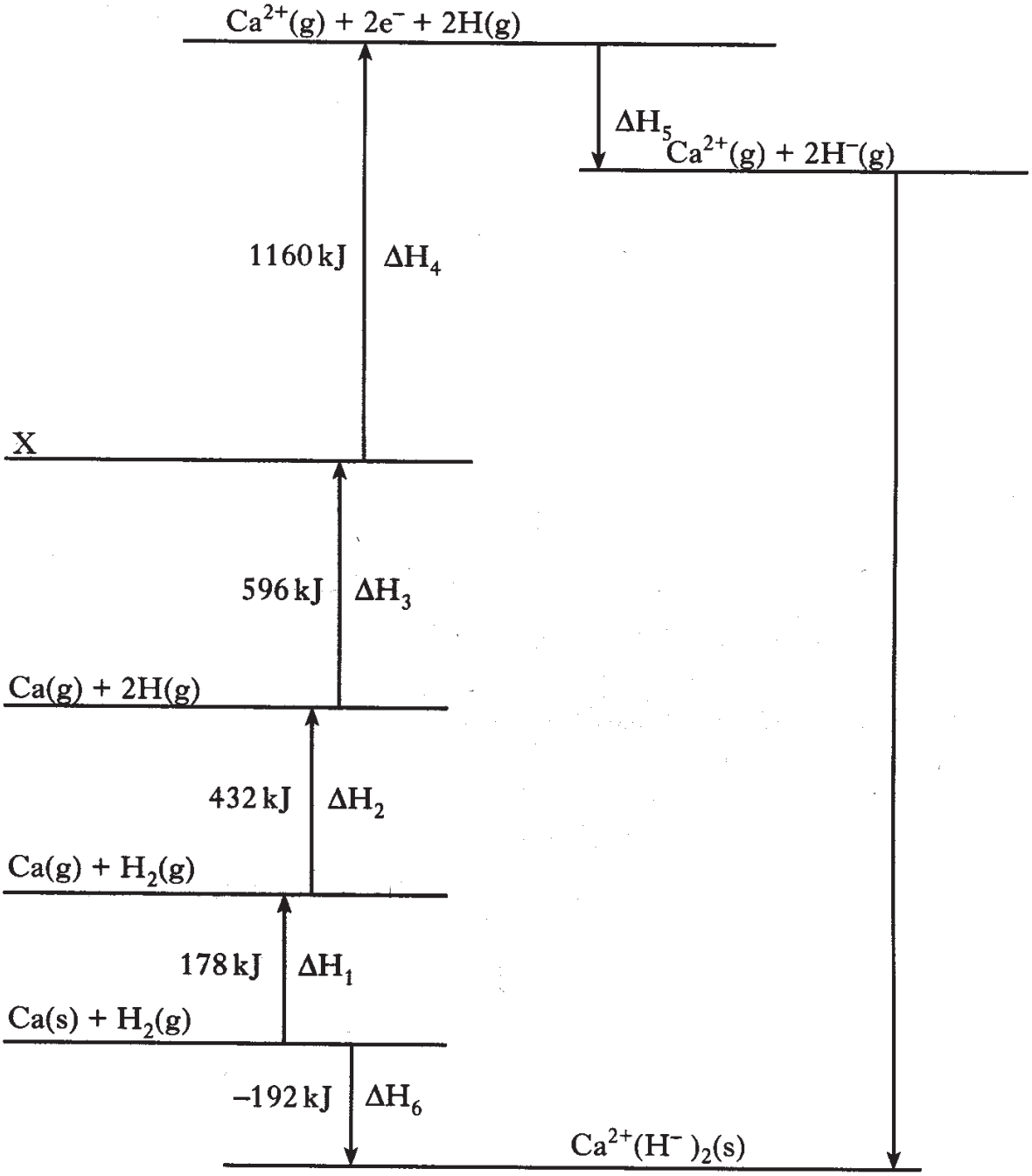
$$C_2H_{2\,(g)} + 2\,H_{2\,(g)} \rightarrow C_2H_{6\,(g)}$$ **3**

b) The enthalpy change for the reaction above can also be calculated using standard enthalpies of combustion.

Why might this value be different from the answer to **a)** ? **1**

(4)

Q7 Consider the following thermochemical cycle (which is not drawn to scale) describing the steps involved in the enthalpy of formation of calcium hydride.



a) What should be written on line X ? **1**

b) Calculate ΔH_5 using information from the Data Booklet **1**

c) Calculate the lattice enthalpy, in kJ mol^{-1}, of calcium hydride **1**

d) Identify the two products formed when calcium hydride reacts with water **1**

(4)

Answers

Q1 **a)** Find $MgCl_{2\,(s)} \rightarrow Mg^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$

Given
(1) $Mg^{2+}_{(g)} \rightarrow Mg^{2+}_{(aq)}$ $\Delta H_1 - 1923$
(2) $Cl^{-}_{(g)} \rightarrow Cl^{-}_{(aq)}$ $\Delta H_2 - 338$
(3) $Mg^{2+}_{(g)} + 2Cl^{-}_{(g)} \rightarrow Mg^{2+}(Cl^{-})_{2\,(s)}$ $\Delta H_3 - 2326$

$\Delta H = -\Delta H_3 + \Delta H_1 + 2\Delta H_2$ **1**
$= -(-2326) + (-1923) + 2(-338)$ **1**
$= -273$ kJ mol^{-1} **1**

b) $MgCl_{2(s)} + 6H_2O_{(l)} \rightarrow MgCl_2.6H_2O_{(s)}$

$\Delta H = \Sigma\Delta H_{products} - \Sigma\Delta H_{reactants}$ **1**
$= -2500 - (-642) + 6(-286)$ **1**
$= -142$ kJ mol^{-1} **1**
(6)

Q2 **a)** Ionic bonding becomes weaker going down the series.
or Halide ion increases in size going down the series (must mention ionic/ion). **1**

b) Enthalpy hydration = enthalpy solution – lattice enthalpy (breaking)
$= 17.2 - 701$
$= -683.8$ kJ mol^{-1} **1**

c) The hydration enthalpy for Ca^{2+} will be more negative. *(1)*
Ca^{2+} has a larger charge than K^+ and therefore there is stronger attraction between the Ca^{2+} and the water. *(1)* **2**
(4)

Q3. **a)** $C_{(s)} + H{-}O{-}H_{(g)} \rightarrow C{\sim}O_{(g)}) + H{-}H_{(g)}$ $\Delta H = 130$ kJ mol^{-1}

Bond breaking $C_{(s)} \rightarrow C_{(g)}$ = 715;
2 x O–H bonds = $2 \times 458 = 916$; ***total*** = 1631 kJ *(1)*

Bond making C~O = ***X***
H–H = –432; ***total*** = –432 + ***X*** kJ *(1)*

X = 130 –1631 + 432 = –1069 kJ mol^{-1}
Energy given out in forming one mole of C~O bonds = –1069 kJ *(1)*
3

Q3 contd

b) C–O = 358;

C=O = 798; therefore the bond in CO is C–O + C=O, i.e. C≡O **1**

c) CO poisonous; H_2 could be explosive; CH_3OH is flammable
(any two correct = 1+1) **2**

(6)

Q4 **a)** ***i)*** $3C_{(s)} + 4H_{2(g)} \rightarrow C_3H_{8(g)}$ – 140 *(1)*

ii) $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ – 394 *(1)*

iii) $H_{2(g)} + ½O_{2(g)} \rightarrow H_2O_{(g)}$ – 286 *(1)* **3**

b) Find $C_3H_{8(g)} + 5O_{2\,(g)} \rightarrow 3CO_{2(g)}$

$\Delta H = \Delta H_{(i)} + 4\,\Delta H_{(ii)} + 3\Delta H_{(iii)}$

$= -(-104) + (4 \times -286) + (3 \times -394)$ *(1)*

$= -2222$ kJ mol^{-1} *(1)* **2**

(5)

Q5 **a)** ***i)*** Sublimation enthalpy 109 kJ mol^{-1} **1**

ii) Bond dissociation enthalpy 248.5 kJ mol^{-1} **1**

iii) 1st ionisation energy 502 kJ mol^{-1} **1**

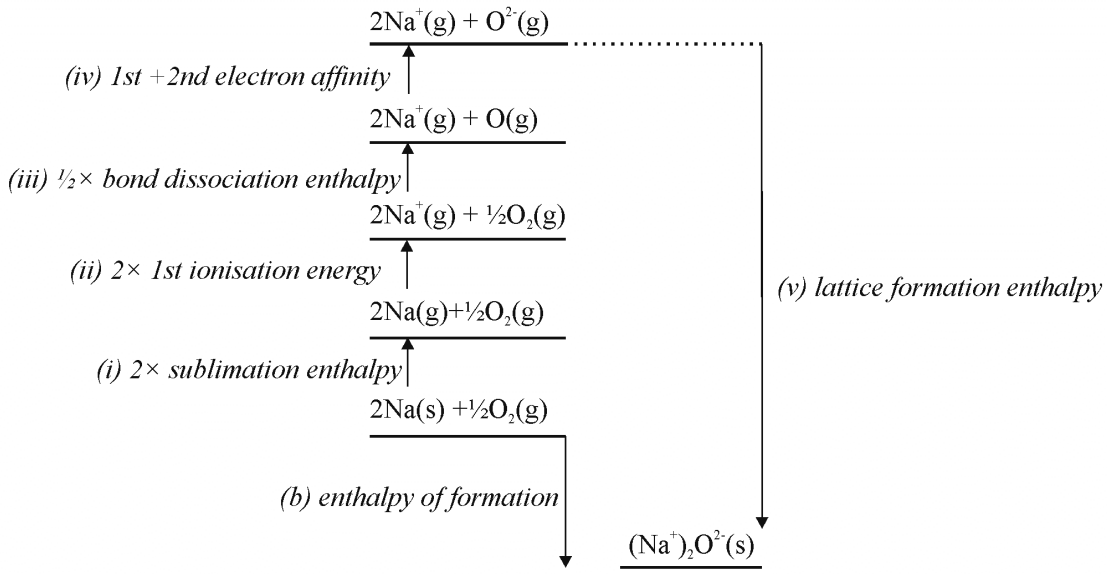
iv) 1st + 2nd electron affinity 703 kJ mol^{-1} **1**

v) Lattice formation enthalpy –2481 kJ mol^{-1} **1**

b) $2Na_{(s)} + ½O_{2(g)} \rightarrow (Na^+)_2O^{2-}{}_{(s)}$ **1**

Q5 contd

c) ***i)***



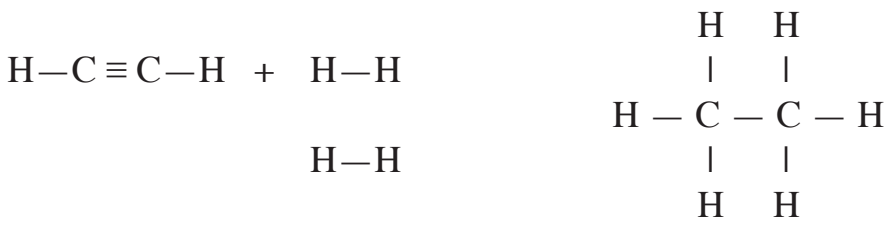
1

ii) $\Delta H_{(b)} = \Delta H_{(i)} + \Delta H_{(ii)} + \Delta H_{(iii)} + \Delta H_{(iv)} + \Delta H_{(v)}$

$= 2(109) + 2(502) + ½(497) + 703 + (–2481)$

$= –307.5$ kJ mol–1 **1**

Q6 **a)** ***Bonds broken*** ***Bonds Formed***



2 x H—H = 2 x 432 = 864 *1 x C—C = 1 x -346 = -346*
1 x C ≡ C = 1 x 835 = 835 *6 x C—H = 6 x -414 = -2484*
2 x C—H = 2 x 414 = 828

$\Delta H = 2527 - 2830 = -303$ kJ mol^{-1} **3**

b) C ≡ C, C—C and C—H are mean (average) bond energies

or Enthalpies of combustion can be measured directly (wheras bond energies are calculated values). **1**

Q7 **a)** $Ca^{+}_{(g)} + e^{-} + 2\,H_{(g)}$ (states must be present) **1**

b) -145.6 kJ mol^{-1} or -145.6 kJ or -146 kJ or -146 kJ mol^{-1} **1**

no mark for -72.8 kJ no mark if KJ used no mark if no units shown

c) -2412.4 (kJ mol^{-1}) - no units required as given in question **1**

Following on from -72.8 kJ in **b)** would give -2458.2

d) calcium hydroxide and hydrogen or $Ca(OH)_2$ and H_2 **1**

SECTION 2

Chemical reactions can be used to provide energy to do work. In the engine of a car (petrol or diesel) and in a rocket engine, chemicals are burned and their energy is converted into work. One basic fact of thermodynamics is that the conversion of energy into work is never 100% efficient and the work energy derived from a chemical reaction is **always** less than the heat energy (ΔH) that is used. A small part of the heat change is never converted into work and is referred to as 'unavailable' energy. It is therefore possible to write the equation:

ΔH = work energy + 'unavailable' energy

In thermodynamic terms this is changed into:

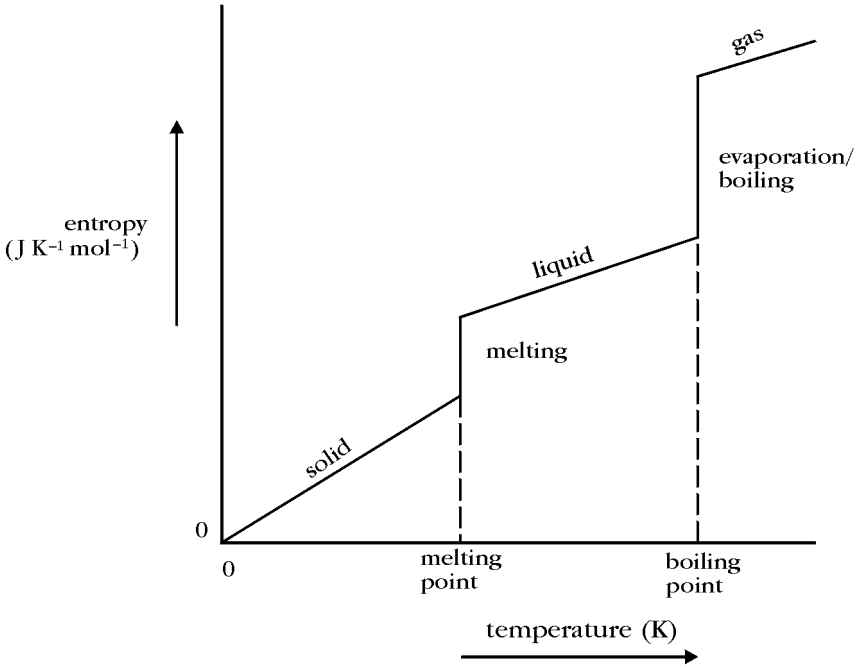
ΔH = free energy + entropy energy

These two terms are explained in the following sections.

Entropy

In nature there is a tendency towards disorder. A brick wall changes into a disordered heap of bricks either with age or the demolition squad, but the reverse process does not take place spontaneously, i.e. without outside help. More widely, an untended garden, diffusion, corrosion and the dispersion of sewage into the sea are all examples of systems naturally tending towards disorder. In thermodynamic terms disorder is called **entropy**. The degree of disorder in a system is called the entropy of that system. The greater the disorder, the greater the entropy. The molecular motion of any substance depends on its state. Solids only have vibrational motion while gases have vibration, rotation and translational motion. It therefore follows that entropy increases as temperature increases and that changes in state, such as melting and evaporation, involve large changes in entropy. When a state change occurs there is a change in entropy without a change in temperature and this is linked to the concept of latent heat. This is shown in Figure 17, which relates to no specific substance.

Figure 17



At absolute zero (0 K) a crystal lattice has perfect order and therefore zero entropy. This is one version of the **third law of thermodynamics**. As the solid is heated it gains more kinetic energy and the entropy increases slowly. There is a rapid increase in entropy at the melting point and boiling point, with a greater increase at the boiling point than at the melting point. In other words, the entropy of a system is temperature dependent.

The **second law of thermodynamics** states that the total entropy of a reaction system and its surroundings always increases for a **spontaneous process**. A spontaneous process is a process that is **thermodynamically possible** and this means that it can take place on its own irrespective of how long this requires.

It should now become clearer why spontaneous endothermic processes take place. Consider the following endothermic reactions:

$CoCl_2.6H_2O(s) + 6SOCl_2(l) \rightarrow CoCl_2(s) + 12HCl(g) + 6SO_2(g)$

$Ba(OH)_2.8H_2O(s) + 2NH_4CNS(s) \rightarrow Ba(CNS)_2(aq) + 2NH_3(g) + 8H_2O(l)$

$(NH_4)_2CO_3(s) + 2C_2H_5COOH(l) \rightarrow 2NH_4^+C_2H_5COO^-(aq) + H_2O(l) + CO_2(g)$

It is clear that the entropy of the system increases just by looking at the changes in state from reactants to products.

The entropy increase is so large that it more than counter balances the unfavourable enthalpy changes and the reactions are spontaneous. We can see that the second law requires that both system and surroundings be taken into account. Heat energy released by a reaction into the surroundings increases the entropy of the surroundings while heat absorbed by a reaction system from the surroundings decreases the entropy of the surroundings. The change in entropy of the surroundings that occurs as a result of such a reaction can be calculated from the temperature and entropy change during the reaction. Some examples are given in Table 5.

Table 5

	Entropy change		
Process	**System**	**Surroundings**	**Overall**
Mixing/expansion	Increase	No change	Increase
Crystallisation	Decrease	Increase	Increase
Polymerisation	Decrease	Increase	Increase
Evolution of life	Decrease	Increase	Increase
Combustion of fuels	Increase	Increase	Increase

The standard entropy of a substance is the entropy for that substance in its standard state and is given the symbol $S°$ (standard conditions are one mole of a substance at one atmosphere pressure and any specified temperature in Kelvin). These values can be used to calculate the standard entropy change for a reaction given that:

$$\Delta S° = \Sigma S° \text{ products} - \Sigma S° \text{ reactants}$$

The unit of entropy change is joules per Kelvin ($J\ K^{-1}$) or joules per Kelvin per mole ($J\ K^{-1}\ mol^{-1}$).

Free energy

We have now established that, in a thermodynamically feasible endothermic reaction, there is a favourable entropy change **inside** the reaction mixture. An endothermic reaction can only take place if its entropy change is sufficiently favourable to 'overcome' the unfavourable enthalpy change. How can these two factors be balanced against each other?

Entropy changes are expressed in joules per Kelvin per mole whereas enthalpy changes are expressed in kilojoules per mole. To convert the entropy into energy units per mole, it has to be multiplied by the absolute temperature. Thus, $T\Delta S$ has units of joules per mole and can be combined with ΔH, allowing for the use of joules and kilojoules. In fact, the combination must involve a subtraction. A negative enthalpy change is favourable, whereas a positive entropy change is favourable. Thus, a combination of enthalpy and entropy gives the expression:

$$\Delta H - T\Delta S \text{ or } T\Delta S - \Delta H$$

It is a matter of choice and history that decided that the former expression is the one that is used to describe the energy available to do work.

The combination of enthalpy and entropy changes is known as the **free energy change** and is given the symbol ΔG:

$$\Delta G = \Delta H - T\Delta S$$

The sign of the free energy change obtained can be used to predict the possibility of the reaction proceeding. This can be summarised by saying that a **negative** value for the change in free energy shows that the reaction is likely to happen spontaneously. On the other hand, a positive value for ΔG shows that the reaction is unlikely to happen unless external energy is available to do work on the system (e.g. the reaction is heated).

If the values for the enthalpy and entropy changes are known for a reaction, it is possible to calculate the value of the free energy change at any temperature.

If the measurements are all made under standard conditions, then:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Although a negative ΔG or ΔG° value allows one to predict that the reaction is feasible, i.e. the reaction will go in the direction of the products, it does not imply anything about the rate of the reaction. The activation energy for the reaction has to be overcome for the reaction to occur and this could be very high and so the reaction could be very slow. For example, if hydrogen and oxygen gases are mixed, the standard free energy change for the formation of 1 mole of water at 298 K is about –237 kJ mol^{-1}. However, virtually no

reaction occurs until energy is supplied to overcome the activation energy or a suitable catalyst is added.

The standard free energy change for a reaction can be calculated from tabulated data of standard enthalpy and standard entropy changes for that reaction. In the same way as standard enthalpies of formation can be used to calculate the standard enthalpy change for a reaction, the standard free energy for a reaction can be calculated from the standard free energies of formation.

Example 10

Using the $\Delta G°_f$ values given, we can calculate the standard free energy change for the reaction:

$$\begin{array}{rcl} 2NO_2 & \rightleftharpoons & N_2O_4 \\ \Delta G°_f \;\; 2 \times (+52) & & (+98) \end{array}$$

At 298 K, $\Delta G° = +98 - (2 \times 52)$
$= -6 \text{ kJ mol}^{-1}$

It is important to appreciate the difference between $\Delta G°$ and ΔG, as the former refers to standard conditions. When discussing a reaction, $\Delta G°$ and ΔG have entirely different meanings. $\Delta G°$ applies only to the initial and final states in the reaction, i.e. when reactants and products are under standard conditions. We can picture this by standing **outside** the reaction and observing the difference in free energy under standard conditions between pure reactants and pure products. From the value of $\Delta G°$, we can predict whether the products or reactants will be favoured after equilibrium has been established. As soon as the reaction has started, standard conditions no longer apply and ΔG is needed rather than $\Delta G°$.

Only when the free energy of the reactants has fallen (by the reactants being used up) to the same value as the products (i.e. $\Delta G = 0$) do we reach equilibrium. This is considered in the following section.

Question

Using the data given below, calculate $\Delta G°$ at 298 K and 1 atmosphere pressure for the reaction:

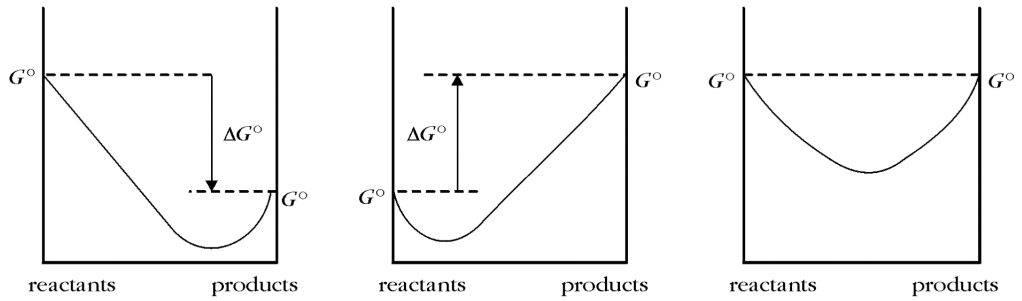
$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l)$$

	$\Delta H°$ (kJ mol^{-1})	$S°$ (J K^{-1} mol^{-1})
$H_2(g)$	0	131
$O_2(g)$	0	205
$H_2O(l)$	–286	70

Free energy and equilibrium

At equilibrium, the free energy of the system has reached its minimum value under the given conditions. At this point, the free energy of the products formed is equal to the free energy of the reactants left. This can be pictured by considering the graphs in Figure 18 which show how the free energy varies with the composition of the reaction mixture.

Figure 18



In any chemical system once the reaction has started G will be lower than G° since:

- there is a change from standard conditions
- there is an increased entropy due to the mixing of reactant and product.

The minimum point of the free energy curve corresponds to the position of equilibrium and at this point $\Delta G = 0$.

When equilibrium is established, the concentrations of the various species will not be of unit molarity and therefore standard conditions are not applicable. When equilibrium is attained (and the time is not determined by thermodynamic considerations), the free energy of the reactants (at equilibrium) is equal to the free energy of the products (at equilibrium). This can be seen by considering the following illustration.

Suppose a mole of ethanoic acid is placed in water to give a litre of solution at 298 K. The following ionisation takes place:

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

The standard free energy of dissociation $\Delta G°$ is 25 kJ mol^{-1}.

This value shows that the standard free energy of the products (each at a concentration of 1 mole per litre) is much greater than that of the reactant (at 1 mole per litre). In other words, there is little reason for the reaction to move to form products and the position of equilibrium lies well to the left.

However, by ionising slightly the free energy of the system falls. At equilibrium, the free energy of the unionised ethanoic acid is the same as the combined free energy of the ions formed. Note that we cannot use standard free energy because at equilibrium there is no longer the standard concentration of 1 mole per litre. This means that, at equilibrium, $\Delta G = 0$.

We can now provide an even clearer picture of the difference between $\Delta G°$ and ΔG. The value of $\Delta G°$ tells the observer (outside the reaction) whether the equilibrium position will favour reactants or products. When that equilibrium has been established, the ΔG value (inside the reaction) will be zero. Thus, at equilibrium, the free energy of reactants will be equal to the free energy of products and this is why there is no further change in the composition of the reaction with time.

When $\Delta G° = 0$, neither products nor reactants are favoured. This is called the balance point, i.e. products and reactants are equally favoured. It is often possible to calculate the conditions at which the $\Delta G°$ value changes from being positive to being negative (which is when $\Delta G° = 0$). This is done by considering **only** the standard free energies of the reactants and products. This can inform the observer about the conditions at which a reaction is just

becoming feasible, i.e. when products are just slightly more favoured than reactants. Some examples follow which illustrate this situation:

Example 11

At what temperature does the Haber process become feasible?

	$N_2(g)$	+ $3H_2(g)$ $\rightleftharpoons$	$2NH_3(g)$
$\Delta H°_f$	0	0	2×-46.4
$S°$	191.6	3×130.7	2×193.2

$\Delta H°$ (reaction) = –92.8 kJ mol^{-1} = –92 800 J mol^{-1}
$\Delta S°$ (reaction) = –197.3 J K^{-1} mol^{-1}

When products are favoured as much as reactants, $\Delta G° = 0$.

Thus from the equation:

$$\Delta G° = \Delta H° - T\Delta S°$$
$$T = \Delta H°/\Delta S° = -92\,800/-197.3$$
$$= 470 \text{ K}$$
$$= 197°C$$

This result can be interpreted as meaning that at 470 K, the reactants and products are equally favoured. By considering the sign of $\Delta S°$, we can work out whether the reaction is feasible at a temperature higher or lower than 470 K. Since $\Delta S°$ is negative, $-T\Delta S°$ is positive. At low temperatures, $\Delta H°$ will dominate and $\Delta G°$ will be negative. Hence, the Haber process becomes feasible at temperatures **below** 470 K.

By calculating $\Delta G°$ at temperatures slightly above and below 470 K, it is possible to see that $\Delta G°$ is positive at temperatures above 470 K and negative at temperatures below 470 K. Therefore, ammonia production is feasible at temperatures **below** 470 K. Unfortunately, the industrial reaction cannot be carried out at such a low temperature as a suitable catalyst has not yet been found. It is interesting to note that leguminous plants can bring about this reaction. Current research is trying to identify the enzymes responsible to see if they could be used on an industrial scale.

Example 12

At what temperature does the decomposition of magnesium carbonate become feasible?

The reaction is:

	$MgCO_3$	→	$MgO + CO_2$	
$\Delta H°_f$	–1117.2		–604.1	–394
$S°$	65.9		26.9	213.8
	$\Delta H°$ (reaction)		= +119.1 kJ mol^{-1}	
			= +119100 J mol^{-1}	
	$\Delta S°$ (reaction)		= +174.8 J K^{-1} mol^{-1}	

When the reaction becomes feasible:

$\Delta G° = 0$
$T = \Delta H°/\Delta S°$
$T = 119100/174.8$
$= 681.35$ K
$= 408°C$

Therefore, at 408°C the decomposition becomes feasible and above this temperature decomposition is favoured. It must be stressed that these calculations depend on a knowledge of the standard enthalpies and standard entropies of reactants and products (obtained from data tables). The calculation does not depend in any way on the route taken by the reaction. The calculation does not say anything about either the reaction pathway or the reaction rate. Thermodynamics tells us only how far a reaction will proceed (given enough time), it can never tell us how fast a reaction will take place or by which route.

The fact that the standard free energy change is greater than zero does not mean that no reaction takes place. It means that the products are less favoured than the reactants. In industry, equilibrium is rarely allowed to occur. Removal of a product can make a reaction with an unfavourable equilibrium position move in the desired direction.

Ellingham diagrams

In Example 12 the temperature at which $\Delta G°$ of a reaction is 0 was calculated, this being the temperature when the products just become favoured. This calculation assumes that enthalpy and entropy values do not alter with temperature. Consider the reduction of iron(III) oxide to iron using carbon:

$$2Fe_2O_3(s) + 3C(s) \rightarrow 4Fe(s) + 3CO_2(g)$$

This reaction can be considered to be a combination of two reactions:

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s) \quad \text{reversed}$$
$$\text{and} \quad 3C(s) + 3O_2(g) \rightarrow 3CO_2(g)$$

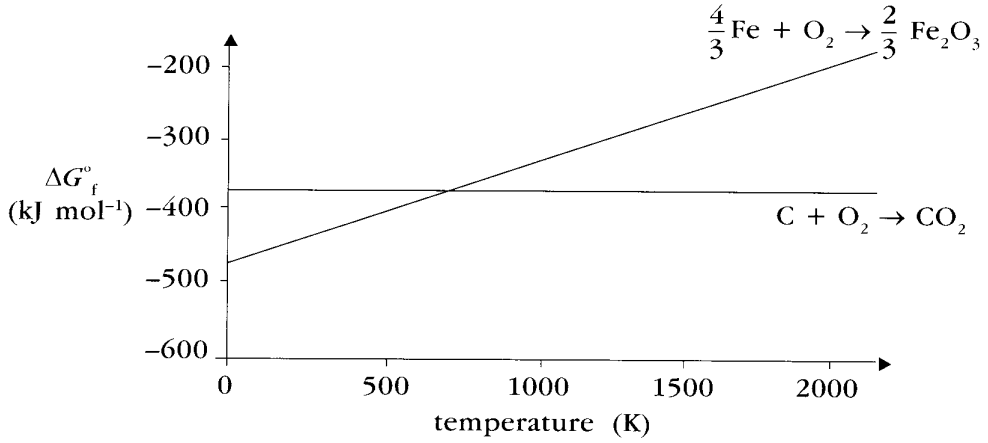
If $\Delta H°$ and $\Delta S°$ are fairly constant over a range of temperatures, it is possible to calculate $\Delta G°$ for each reaction at a range of temperatures using $\Delta G° = \Delta H° - T\Delta S°$. Once this is done, a graph of $\Delta G°$ against T for each reaction can be drawn. Rearranging the free energy equation to:

$$\Delta G° = -T\Delta S° + \Delta H°$$

gives a recognisable straight line graph of the form $y = mx + c$, where the gradient is $-\Delta S°$ and the intercept on the y-axis is $\Delta H°$.

Both graphs can be combined on one set of axes if the values are adjusted to be per mole of oxygen used. This combined graph is called an Ellingham diagram (Figure 19).

Figure 19



The Ellingham diagram provides much more information than the calculation of the temperature at which the reaction becomes feasible and gives a visual understanding of the nature of a reaction over a temperature range.

When using Ellingham diagrams the reaction that corresponds to the lower of the two lines will operate as written while the reaction corresponding to the upper line will be reversed at a given temperature. Combining the equations and taking this into account shows at which temperature, if any, a reaction becomes thermodynamically feasible. The point of intersection of the two lines represents the temperature at which the overall standard free energy

change is zero. This is the point at which the products (iron and carbon dioxide) just become more favoured than the reactants (iron oxide and carbon). Above the temperature of intersection of the two graphs, the reduction of iron(III) oxide is thermodynamically feasible.

Ellingham diagrams can be used to plan the reaction conditions required for metal extraction from ores. There are three general methods for the extraction of metals from their ores:

- reduction by a non-metal (usually carbon)
- reduction by another metal
- electrolytic reduction.

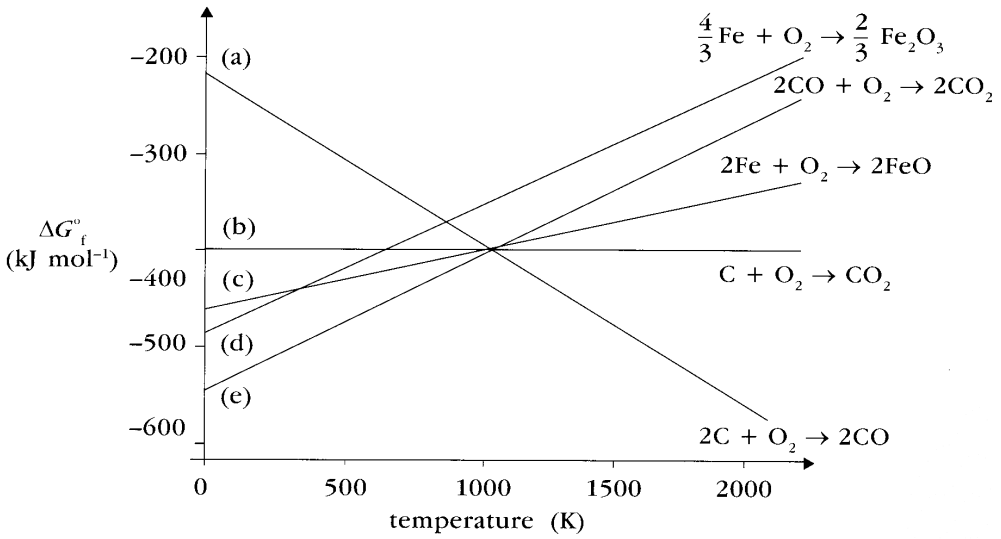
The method adopted for each metal depends on relative costs. All three methods are possible for many metals, but the temperatures required for the first two methods may be impracticable. Only a general appreciation of the relative costs can be attempted since accurate information can be difficult to obtain, and is quickly out of date. There are many factors that affect costs:

- carbon is a cheap raw material
- the use of high temperatures is expensive, both because of the fuels required and the equipment required to withstand the temperature
- the use of high temperatures requires longer cooling times before furnaces can be tapped and consequently slows down the process
- electricity for electrolytic reduction is expensive, but this may be the only practical method
- electrolysis is often of a melt that requires fuel and equipment for high temperatures
- reduction by another metal necessarily makes the metal obtained more expensive than that consumed, although regeneration of the metal consumed may be possible (but will probably be expensive)
- reactions involving two solids are generally slower than reactions involving a solid and a gas.

From this general information, it is clear that non-metal reduction is much the cheapest method as long as the required temperature is not too high. A very high temperature causes chemical as well as economic problems: most metals form carbides at high temperatures, furnace linings may react with the metal being made, the reaction to produce the metal is reversible and cooling must be carried out under controlled conditions to prevent the reverse reaction.

The conditions for the extraction of iron in a blast furnace can be predicted from an Ellingham diagram of all the possible reactions (Figure 20).

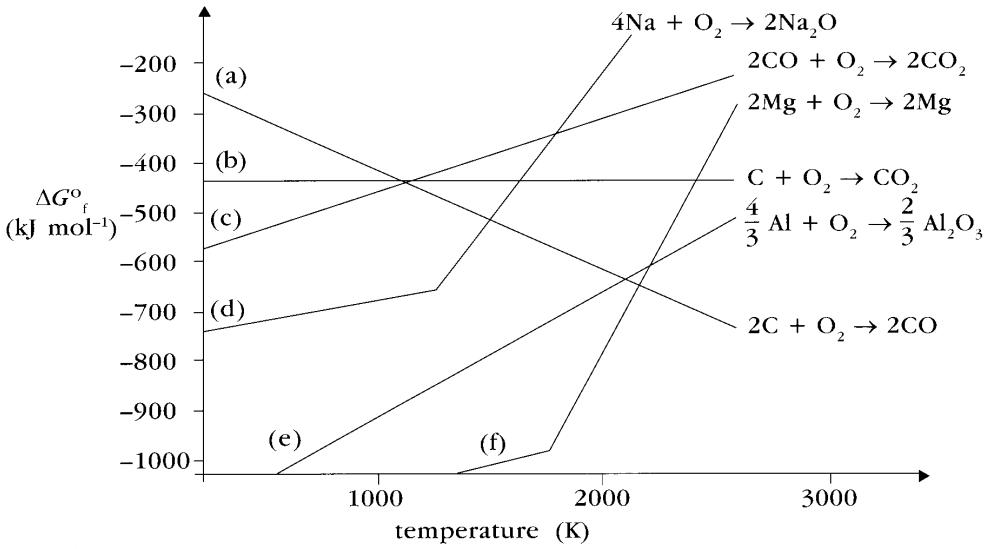
Figure 20



Iron ore is a mixture of Fe_2O_3 and FeO. The ore is mixed with coke (carbon) and limestone ($CaCO_3$) and then added to the furnace. Preheated air is blown in at the bottom of the furnace and a temperature of about 2000 K is reached. At this temperature the calcium carbonate decomposes to give calcium oxide and carbon dioxide, which combines with carbon to form carbon monoxide (see lines (a) and (b) in Figure 20). The carbon monoxide rises within the furnace to a cooler area that has a temperature just below 1000 K. Here the carbon monoxide reduces both oxides of iron to the metal (see lines (c) and (e), and (d) and (e) in Figure 20). In addition to these reactions, in areas of the furnace where the temperature is above 900 K the carbon will also reduce Fe_2O_3 to iron (see lines (a) and (d) in Figure 20). The temperature within a blast furnace must be carefully controlled to achieve the best rate of reduction. It is found that carbon monoxide is more efficient than carbon as a reducing agent since it is a gas and mixes much more intimately with the iron ore.

Similarly, the conditions for the extraction of aluminium from aluminium oxide (bauxite) can be deduced from an Ellingham diagram (Figure 21).

Figure 21



It can be seen that reduction with carbon or carbon monoxide is not possible (from lines (a), (b) and (e) in Figure 21) at reasonable temperatures (up to 2000 K) but displacement by magnesium is possible at lower temperatures (see lines (e) and (f) in Figure 21). Unfortunately, the high cost of magnesium makes this process more expensive than electrolytic reduction for the production of aluminium.

Questions

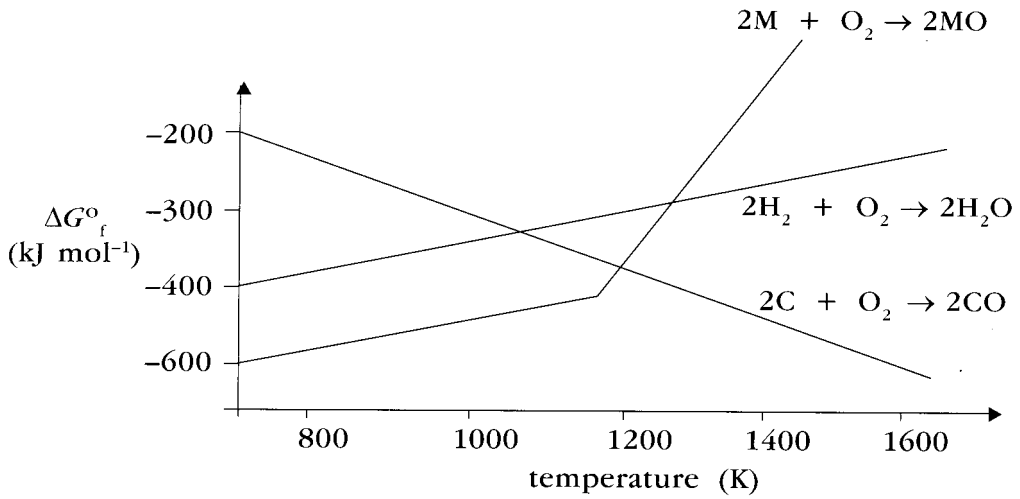
1. Calculate the temperature at which the decomposition of barium carbonate becomes feasible.

   $\Delta H^\circ = 268$ kJ mol^{-1} $\Delta S^\circ = 168$ J K^{-1} mol^{-1}

   Is decomposition more favourable above or below this temperature?

2. The reaction of carbon with steam to produce carbon monoxide and hydrogen is endothermic ($\Delta H^\circ = 131$ kJ mol^{-1}).
   The reaction is successful at 1500 K when $\Delta G^\circ = -71.5$ kJ mol^{-1}
   (a) Calculate the entropy change for the above reaction at 1500 K.
   (b) Is the reaction feasible at 25°C?
   (c) At which temperature does the reaction just become feasible?

3.



What is the minimum temperature at which the metal oxide, MO, can be reduced by:
(a) hydrogen
(b) carbon?

THERMODYNAMICS (Reaction Feasibility)

Entropy

2.70 *The **entropy** (S) of a system is the **degree of disorder** of the system. The greater the disorder, the greater the entropy.*

2.71 *Entropy increases as temperature increases.*

2.72 ***Changes of state** involve changes in entropy. Melting and evaporation are accompanied by increases in entropy.*

2.73 *One version of the **Third Law of Thermodynamics** states that the entropy of a perfect crystal at O K is zero.*

2.74 *The standard entropy of a substance is the entropy value for the standard state of the substance.*

2.75 *The change in standard entropy for a reaction system can be calculated from the standard entropy values for the reactants and products.*

Free energy

2.76 *One version of the **Second Law of Thermodynamics** states that the **total** entropy of a reaction system **and** its surroundings always **increases** for a **spontaneous** process.*

2.77 *Heat energy released by the reaction system into the surroundings increases the entropy of the surroundings, whereas heat absorbed by the reaction system from the surroundings decreases the entropy of the surroundings.*

2.78 *The change in entropy of the surroundings that occurs as a result of a chemical reaction can be calculated from the temperature and from the enthalpy change for the reaction system.*

2.79 *The total entropy change is normally expressed in terms of **Gibbs free energy** (G). The direction of **spontaneous** change is in the direction of **decreasing free energy.***

2.80 *The change in standard free energy for a reaction is related to the standard enthalpy and entropy changes by:*

$$\Delta G^\circ = \Delta H^\circ - T\Delta S$$

2.81 *The standard free energy change of a reaction can be calculated from the standard enthalpy and standard entropy changes for the reaction.*

2.82 *The standard free energy change of a reaction can be calculated from the standard free energies of formation of the reactants and products.*

2.83 *A reaction is **feasible** under standard conditions if the change in **standard free energy** between reactants and products is **negative**. This means that the equilibrium composition favours the products over the reactants.*

2.84 *Under non-standard conditions any reaction is feasible if ΔG is negative.*

2.85 *At **equilibrium** $\Delta G = O$.*

2.86 *A reaction will proceed spontaneously in the forward direction until the composition is reached where $\Delta G = O$*

Applications of the concept of free energy

2.87 *The feasibility of a chemical reaction under standard conditions can be predicted from the calculated value of the change in standard free energy ($\Delta G°$).*

2.88 *The **temperature** at which the reaction becomes feasible can be calculated for a reaction for which both $\Delta H°$ and $\Delta S°$ have positive values.*

2.89 ***Ellingham diagrams** are plots of variation of free energy change with temperature and can be used to predict the conditions under which a reaction can occur.*

2.90 *Ellingham diagrams can be used to **predict the conditions** required to extract a metal from its ores.*

Q1 1,2-dichloroethane has been used as a solvent for lacquers and oils. One proposed method of production is the addition of hydrogen chloride to ethyne:

$$C_2H_2 + 2HCl \rightarrow CH_2ClCH_2Cl$$

Compound	S^θ/J K^{-1} mol^{-1}	ΔH^θ_f/kJ mol^{-1}
C_2H_2	201	227
HCl	187	–92.3
CH_2ClCH_2Cl	208	–166

a) Using the data given in the table above,

i) calculate the standard entropy change, in J K mol^{-1}, for the reaction. **1**

ii) calculate the standard enthalpy change, in kJ mol^{-1}, for the reaction. **1**

b) The reaction is thermodynamically feasible at room temperature. Above which temperature will this reaction no longer be feasible? **2**

(4)

Q2 Consider the following reactions and their values for ΔG^θ and ΔH^θ at 298K:

Reaction		ΔG^θ/kJ mol^{-1}	ΔH^θ/kJ mol^{-1}
i)	$\frac{1}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)} \rightarrow HCl_{(g)}$	–95	–92
ii)	$2Al_{(s)} + 11\frac{1}{2}O_{2(g)} \rightarrow Al_2O_{3(s)}$	–1576	–1669
iii)	$NH_4Cl_{(s)} \rightarrow NH_4^+{}_{(aq)} + Cl^-_{(aq)}$	–7	+16

a) Reaction ***ii)*** has the greatest difference in the values of ΔG^θ and ΔH^θ.

Suggest a reason for this difference. **1**

b) From the values given for reaction ***iii)***, it can be concluded that ammonium chloride dissolves spontaneously in water under standard conditions with a drop in temperature.

Why can we come to these two conclusions? **2**

c) Calculate the entropy change for reaction ***i)*** at 298K. **2**

(5)

Q3 In a catalytic reformer, straight-chain alkanes are converted to branched chains, cycloalkanes and aromatic hydrocarbons. Consider the sequence shown below.

Octane

A

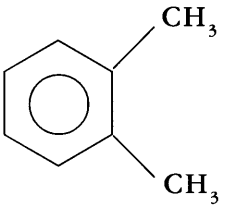
2,3-dimethylhexane

B

1,2-dimethylcyclohexane + hydrogen

C

1,2-dimethylbenzene (*o*-xylene) + hydrogen



a) Use the data in the table below to calculate ΔS^{θ} for the conversion of octane to o-xylene and hydrogen at 298K.

Compound	S^{θ}***/J K^{-1} mol^{-1}***
Octane	463
o-xylene	352
Hydrogen	131

3

b) Calculate the minimum temperature at which the conversion in ***a)*** becomes thermodynamically feasible, given that

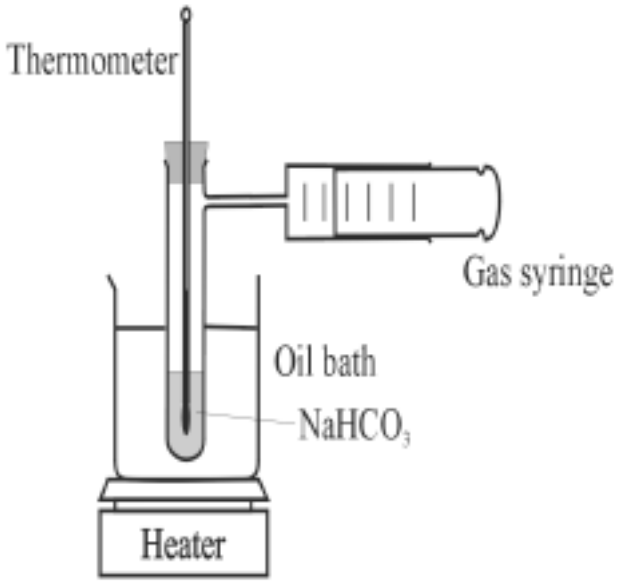
$\Delta H^{\theta} = 227$ kJ mol^{-1}. **3**

c) Explain why the conversion in ***a)*** can be achieved at or above the temperature calculated in ***b)***, despite the fact that the equilibrium constant for reaction A is very much less than 1 at this temperature.

1

(7)

Q4 The apparatus shown in the diagram below can be used to find the decomposition temperature of sodium hydrogencarbonate.



The equation for the decomposition is:

$$2NaHCO_{3(s)} \rightarrow Na_2CO_{3(s)} + H_2O_{(g)} + CO_{2(g)} \qquad \Delta H^{\theta} = +129 \text{ kJ mol}^{-1}$$

Substance	***S^{θ}/J K^{-1} mol^{-1}***
$NaHCO_{3(s)}$	102.1
$Na_2CO_{3(s)}$	136.0
$H_2O_{(g)}$	188.7
$CO_{2(g)}$	213.6

a) Calculate ΔS^{θ} for the reaction. **2**

b) Calculate the temperature at which the decomposition becomes thermodynamically feasible. **3**

c) As the temperature of the oil bath is increased, the volume of gas in the syringe increases. Sketch the shape of the graph you would expect to obtain if the volume of gas is plotted against temperature. Graph paper is not required. Start at room temperature and mark clearly the decomposition temperature on your graph. **2**

(7)

Q5 The table below shows how the standard free energy change varies with temperature for the following reactions:

reaction A: $2Zn_{(s)} + O_{2(g)} \rightarrow 2ZnO_{(s)}$

reaction B: $2C_{(s)} + O_{2(g)} \rightarrow 2CO(g)$

Temperature/K	***ΔG^{θ}, reaction A/ kJ mol^{-1}***	***ΔG^{θ}, reaction B/ kJ mol^{-1}***
400	–615	–300
600	–595	–335
800	–555	–370
1000	–495	–405
1200	–425	–440
1400	–40	–475
1600	–260	–505
1800	–165	–540

a) For each reaction, plot the graph of the standard free energy change against temperature. **3**

b) Use your graph to:

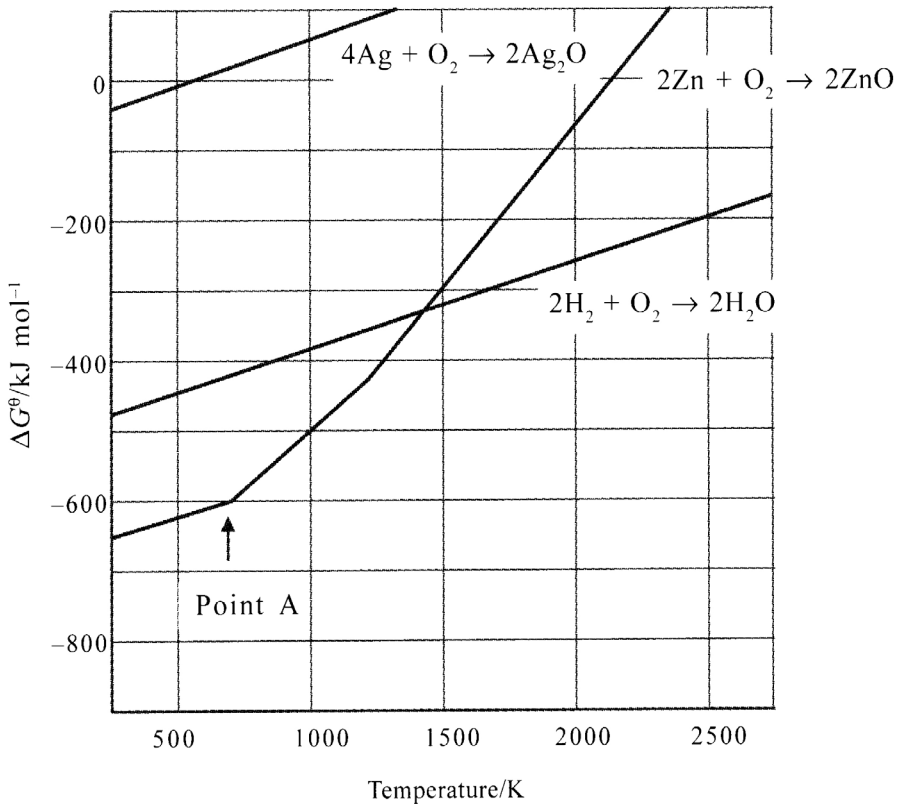
i) determine the minimum temperature at which carbon can reduce zinc oxide **1**

ii) calculate the standard free energy change for this reaction at 1500K. **2**

c) Give one advantage and one disadvantage of using carbon for this reduction on an industrial scale. **2**

(8)

Q6 Examine the Ellingham diagram below and answer the questions that follow.



a) At what temperature does the thermal decomposition of zinc oxide become thermodynamically feasible? **1**

b) Write the balanced chemical equation for the reduction of zinc oxide using hydrogen. **1**

c) At what temperature does it become thermodynamically feasible to reduce zinc oxide using hydrogen? **1**

d) The melting point of zinc is approximately 700K.

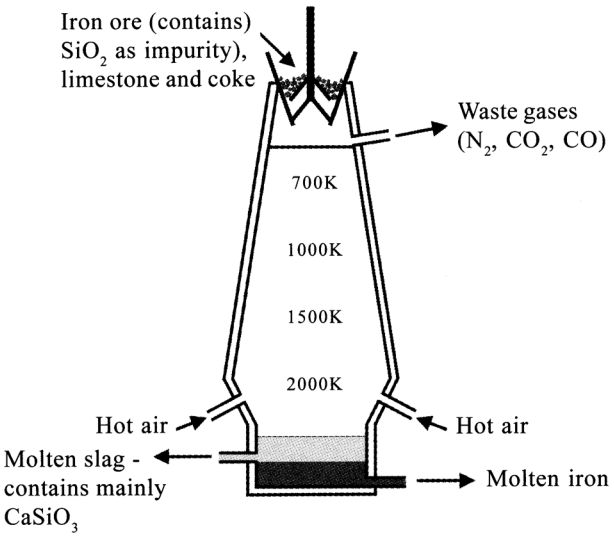
Explain, in terms of entropy, why the gradient of the graph changes at point A. **2**

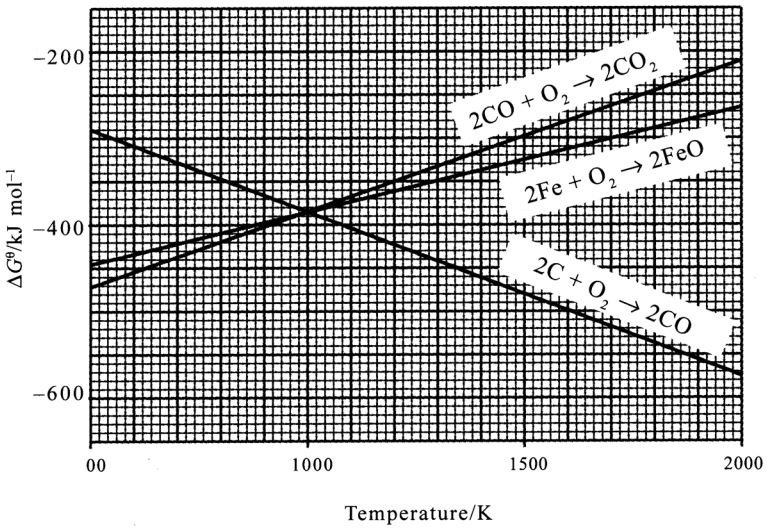
e) From the graph, it is thermodynamically feasible to use hydrogen to reduce silver(I) oxide at all temperatures shown.

Suggest why this reaction does not occur at room temperature. **1**

(6)

Q7 The diagram below shows the blast furnace for the extraction of iron from iron ore. An appropriate Ellingham diagram is also shown.





a) Calculate the standard free energy change for the reduction of iron(II) oxide by carbon at 1900K. **2**

b) At what temperature will it be thermodynamically feasible for carbon monoxide to reduce iron(II) oxide? **1**

c) Explain why the reduction by carbon monoxide is more efficient than by carbon. **1**

d) Give a reason for adding limestone to the furnace. **1**

e) To achieve maximum economy, suggest a use for the waste gases. **1**

(6)

Answers

Q1 ***a)*** ***i)*** $\Delta S = \Sigma Sp - \Sigma Sr = 208 - (201 + 2(187))$

$= -367 \text{ J K}^{-1} \text{ mol}^{-1}$ **1**

ii) $\Delta H = \Sigma \Delta Hp - \Sigma \Delta Hr = (-166 - (227 + 2(-92.3)))$

$= -209.4 \text{ kJ mol}^{-1}$ **1**

b) $T = \Delta H/\Delta S = 209.4/0.367$ (1)

$= 570.6K$ (1) **2**

(4)

Q2 ***a)*** Large entropy change or gas to solid **1**

b) Spontaneous ΔG^{θ} –ve (1)

ΔH^{θ} +ve or endothermic, therefore drop in temperature (1) **2**

c) $\Delta G = \Delta H - T\Delta S \rightarrow \Delta S = (\Delta H - \Delta G)/T = (-92 - (-95))/298$ (1)

$= 10 \text{ J K}^{-1} \text{ mol}^{-1}$ (1) **2**

(5)

Q3. ***a)*** $C_8H_{18} \rightarrow C_8H_{10} + 4H_2$ (1)

$\Delta S = \Sigma Sp - \Sigma Sr = (352 + 4(131)) - 463$ (1)

$= 413$ J K–1 mol–1 (1) **3**

b) At this temperature $\Delta G = 0$

$T = \Delta H/\Delta S$ (1)

$= 227/0.413$ (1)

$= 550$ K (1) **3**

c) A small quantity of 2,3-dimethylhexane will form even if $K << 1$. Removal of 2,3-dimethylhexane in reaction B disturbs the equilibrium in reaction A, promoting the forward reaction. **1**

(7)

Q4 ***a)*** $\Delta S = \Sigma Sp - \Sigma Sr = (136 + 188.7 + 2213.8) - 2(102.1)$ (1)

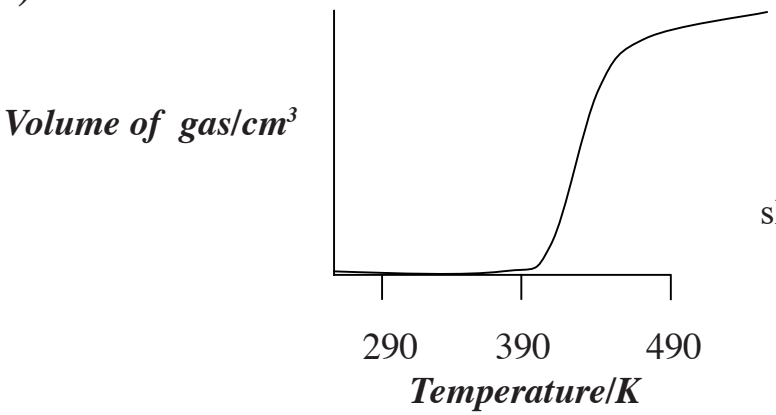
$= 334.1 \text{ J K}^{-1} \text{ mol}^{-1}$ (1) **2**

b) $T = \Delta H/\Delta S$ (1)

$= 129/0.3341$ (1)

$= 386.1\text{K}$ (1) **3**

c)



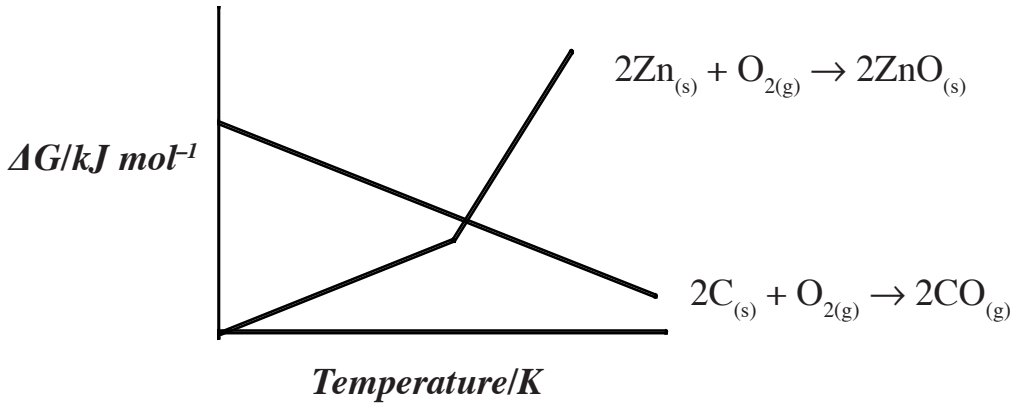
labels (1)

shape at correct point (1)

2

(7)

Q5 ***a)***



scale (1) labels (1) accurate points (1) **3**

b) ***i)*** Minimum temperature (where graphs cross) 1160K **1**

ii) ΔG for A +300; ΔG for B –490 (1)

ΔG for reaction = –190 kJ mol^{-1} (1) **2**

c) Advantage – carbon is cheap and readily available. (1)
Disadvantage – it is a solid therefore the reaction is slower. (1) **2**

(8)

Q6 ***a)*** At temperatures above 2250 K **1**

b) $ZnO + H_2 \rightarrow Zn + H_2O$ **1**

c) 1400 K (above) **1**

d) Below A solid + gas → solid
Above A liquid + gas → solid (1)
therefore there is a greater decrease in entropy,
i.e. ΔS –ve. (1)

(As gradient is –ΔS then an increase in gradient means that ΔS is more –ve.) **2**

e) Although the reaction is feasible at room temperature it does not occur in practice because the activation energy for the reaction is too high.

or The rate of the reaction at room temperature is too slow for the reaction to occur at a measurable rate. **1**

(6)

Q7 ***a)*** ΔG = (275 to 280) – 555 (1)

= –270 to –280 kJ

or –135 to –140 kJ mol^{-1} (1) **2**

b) Accept between 950 and 1020 K **1**

c) Gas/solid reaction better than solid/solid reaction. **1**

d) To remove impurities (silicates) or forming slag or to produce more CO_2 (any one) **1**

e) CO could be burned to (pre)heat the air. **1**

(6)