

INTERNATIONAL ADVANCED LEVEL

CHEMISTRY

TOPIC GUIDE

ENERGETICS: ENERGY AND ENTROPY

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Introduction

This guide is intended to help support teachers new to this specification and to provide some background information on the parts of the topic that are new – both from a teacher’s perspective to ensure clarity of what is expected, and from a student’s perspective when discussing transition from International GCSE/GCSE and addressing misconceptions.

This guide can be used as a reference document for teachers, and parts of it (such as the worked examples) could work as revision material for students.

Included in this guide are:

- some ideas on how to address common misconceptions in both new and previously included content
- possible teaching sequences for key specification points where there is new or challenging content
- worked examples which teachers could use to support students in developing their understanding.

George Facer

Enthalpy

First principles

A reaction vessel can be regarded as a thermodynamic system. If the amount of heat flowing in or out of the vessel during a chemical reaction is q , then q is negative if heat has left the system and has gone to the surroundings. This happens in an *exothermic* reaction. Likewise if q is positive, the system has gained heat from the surroundings and the reaction is *endothermic*.

Exothermic reaction: the system increases in temperature, so heat flows to the cooler surroundings. The system loses heat energy to the surroundings, so q is negative.

Endothermic reaction: the system gets colder, so heat flows from the warmer surroundings into the system. The system gains heat energy from the surroundings, so q is positive.

There are two distinct set of conditions – the reaction happening at constant pressure or at constant volume. In A level chemistry only changes that take place at constant pressure are considered. The heat change at constant pressure is called the enthalpy change, ΔH .

Exothermic reaction: ΔH is negative

Endothermic reaction: ΔH is positive

Any enthalpy change can be represented by

$$\Delta H = \Sigma H_{\text{products}} - \Sigma H_{\text{reactants}}$$

where Σ stands for 'the sum of'. This applies to chemical or physical changes.

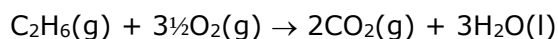
Definitions

All standard enthalpy changes must be quoted at 100 kPa pressure and a constant temperature, which is usually 298K (25°C). These conditions must be included in all definitions. You should be able to find a list of definitions of the enthalpy changes needed for A level chemistry in your textbook.

The definitions that students often get wrong are:

Enthalpy of combustion (of organic compounds), $\Delta_c H^\theta$

It is the enthalpy change when 1 mol of a substance is burnt in excess oxygen at 100 kPa pressure and a stated temperature (usually 298K). The equation representing this for ethane is:



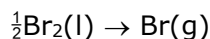
Note the following points:

Only 1 mol of the substance being burnt is on the left of the equation. This may, as here, result in a fractional number of oxygen molecules – don't double the equation in order to get whole numbers.

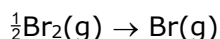
Water is in the liquid state, because at 298K and 100 kPa it is the stable form of water. When the experiment is carried out in the laboratory, water is normally produced as a gas, so the $\Delta_c H$ value obtained will be quite different from any data book's value.

Enthalpy of atomisation, $\Delta_{at} H^\theta$ (of an element)

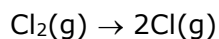
This is the enthalpy change under standard conditions of 100 kPa pressure and a temperature of 298K when 1 mol of gaseous atoms is formed from the element in its standard state. The equation representing this for bromine is:



The common errors are to start with the gaseous form of a liquid element or having 1 mol of a diatomic substance on the left of the equation. So it is *not* for

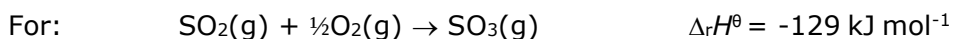


nor for



Enthalpy of reaction, $\Delta_r H^\theta$

This is the enthalpy change under standard conditions of 100 kPa and 298K when the *moles as in the equation written* completely react.



This means that all enthalpy of reaction data must be linked to an equation.

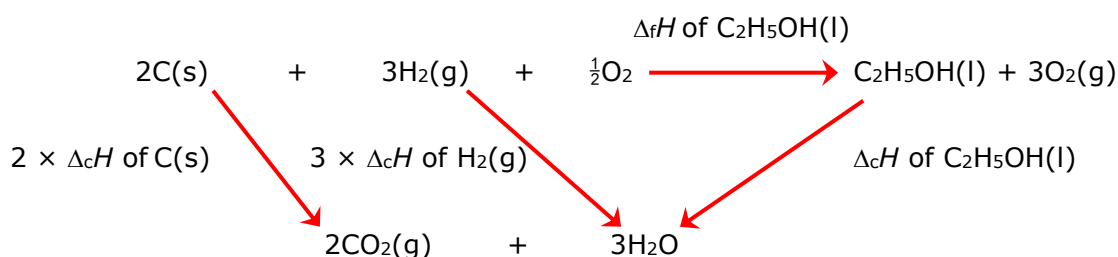
Hess's Law

The enthalpy of formation of almost all organic compounds cannot be measured directly – ethanol cannot be directly made from carbon, hydrogen and oxygen. However a table of such data is essential for calculating many enthalpies of reaction. Where a change cannot take place directly, then $\Delta_r H^\theta$ must be calculated by an indirect method. This uses Hess's Law.

Hess's Law: When reactants are converted into products, the enthalpy change is the same whether the reaction takes place in one step or in a series of steps.

The enthalpy of formation of ethanol can thus be calculated knowing the enthalpies of combustion of ethanol, carbon and hydrogen. (Note that the enthalpies of combustion of these two elements are the same as the enthalpies of formation of water and carbon dioxide)

Figure 1



$$\Delta_f H \text{ of C}_2\text{H}_5\text{OH(l)} = 2 \times \Delta_c H \text{ of C(s)} + 3 \times \Delta_c H \text{ of H}_2 - \Delta_c H \text{ of C}_2\text{H}_5\text{OH}$$

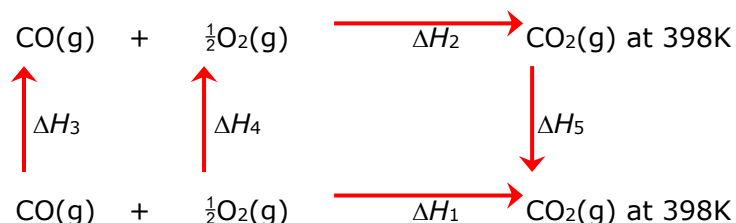
The arrow for the combustion of ethanol could be drawn from $2\text{CO}_2 + 3\text{H}_2\text{O}$ towards $\text{C}_2\text{H}_5\text{OH}$ but then the label would be $-\Delta_c H \text{ of C}_2\text{H}_5\text{OH(l)}$.

It is essential to have the arrows properly labelled, either as in Figure 1 or with their numerical values.

Effect of temperature on the value of ΔH

It is assumed, at A level, that a change in temperature will not alter the value of an enthalpy change. This is an oversimplification as can be seen from a Hess's Law diagram.

Figure 2



ΔH_1 is the enthalpy change of the reaction at 298K

ΔH_2 is the enthalpy change of the reaction at 398K

ΔH_3 is the heat change when 1 mol of CO is heated from 298 to 398K

$$= 100 \times \text{molar heat capacity of CO} = +2860 \text{ J}$$

ΔH_4 is the heat change when $\frac{1}{2}$ mol of O_2 is heated from 298 to 398K

$$= 100 \times \frac{1}{2} \times \text{molar heat capacity of O}_2 = +1470 \text{ J}$$

ΔH_5 is the heat change when 1 mol of CO_2 is cooled from 398 to 298K

$$= -100 \times \text{molar heat capacity of CO}_2 = -3710 \text{ J}$$

$$\Delta H_1 = \Delta H_3 + \Delta H_4 + \Delta H_2 + \Delta H_5$$

$$\Delta H_1 - \Delta H_2 = +2860 + 1470 - 3710 = +670 \text{ J or } 0.7 \text{ kJ}$$

The conversion of CO to CO_2 is exothermic, but the value at 398K is 0.670 kJ more exothermic per mole of CO reacting. The value at 298K = $-283.0 \text{ kJ mol}^{-1}$ whereas that at 398K is $-283.7 \text{ kJ mol}^{-1}$.

Thus it is fair, at A level, to regard an enthalpy change as being independent of temperature, unless the change in temperature results in a change of state.

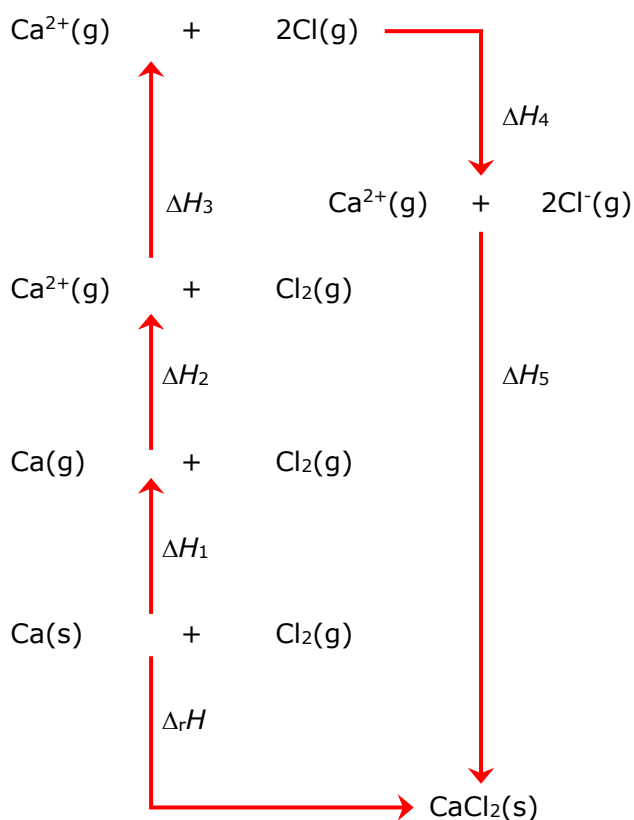
Born-Haber cycles

These are specific examples of Hess's Law and relate the enthalpy of formation of an ionic compound with a number of other quantities. It assumes that the alternative pathway is:

element in normal state $\rightarrow$ gaseous atoms $\rightarrow$ gaseous ions $\rightarrow$ solid ionic compound

The example below is the cycle for calcium chloride.

Figure 3



$\Delta_r H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5$ where

ΔH_1 = enthalpy of atomisation of calcium

ΔH_2 = 1st + 2nd ionisation energies of calcium

ΔH_3 = 2 $\times$ enthalpy of atomisation of chlorine

ΔH_4 = 2 $\times$ electron affinity of chlorine

ΔH_5 = the lattice energy of calcium chloride.

Points to note are:

Lattice energies are defined as the energy change when the gaseous ions (infinitely far apart) form a mole of ionic solid, and so is exothermic and hence is a negative number.

ΔH_2 is the sum of the 1st and 2nd ionisation energies, not just the 2nd ionisation energy of calcium.

The enthalpy of atomisation is that for the formation of 1 mol of gaseous atoms not the enthalpy change for the atomisation of 1 mol of the diatomic molecule, thus

$$\Delta H_3 = 2 \times \Delta_{\text{at}}H \text{ of chlorine.}$$

The change from Ca(g) to $\text{Ca}^{2+}(\text{g})$ is often written as two separate steps.

This cycle is used to find the experimental lattice energy of an ionic compound. The theoretical value can be worked out. The energy change when one ion pair is formed can be calculated from Coulomb's Law and using integral calculus and is:

$$\text{Energy} \propto \frac{\text{the product of the charges on the ions}}{\text{the distance between the centre of the ions}}$$

This theoretical value assumes that the solid is 100% ionic. In many ionic compounds this is not true as the cation polarises the anion to some extent. The difference between the theoretical and the experimental values depends on the extent of polarisation. The process representing the actual (experimental) lattice energy can be regarded as:



Step 1 is the exothermic process of bringing the gaseous ions together to form a perfect lattice and is equal to the theoretical lattice energy. Step 2 is moving the electron cloud around the anion closer to the polarising cation and is also exothermic. The sum of steps 1 and 2 is the experimental lattice energy. As each step is exothermic the experimental lattice energy will be *more exothermic* than the theoretical value. The greater the difference, the more the anion has been polarised.

Cations with a 2+ charge are more polarising than those with a 1+ charge and those with a smaller ionic radius are more polarising. Likewise anions with a 2- charge are more polarisable than those with a 1- charge and larger anions are more polarisable than smaller anions – see Table 1.

Table 1

• Substance	• Radius of cation / nm	• Radius of anion / nm	• Difference between experimental and theoretical lattice energies • / kJ mol^{-1}
NaCl	0.095	0.181	10
NaI	0.095	0.216	18
CsCl	0.169	0.181	18
CsI	0.169	0.216	21
MgCl_2	0.065	0.181	100
MgI_2	0.065	0.216	383

The extent of polarisation is sometimes called the extent of covalency.

Entropy, S

The first law of thermodynamics states that energy cannot be created or destroyed. This concept was encountered earlier in both Hess's Law and Born-Haber cycles.

In chemical and physical changes there is almost always a change in enthalpy, but some endothermic changes happen and some exothermic ones do not. When solid ammonium carbonate is added to liquid ethanoic acid, the reaction is rapid with the evolution of carbon dioxide but the mixture becomes much colder. So this endothermic reaction is spontaneous. Water at 25°C does not spontaneously freeze even though the process of a liquid turning to a solid is exothermic.

Entropy is a measure of disorder

It is the second law that predicts whether a change is spontaneous or not.

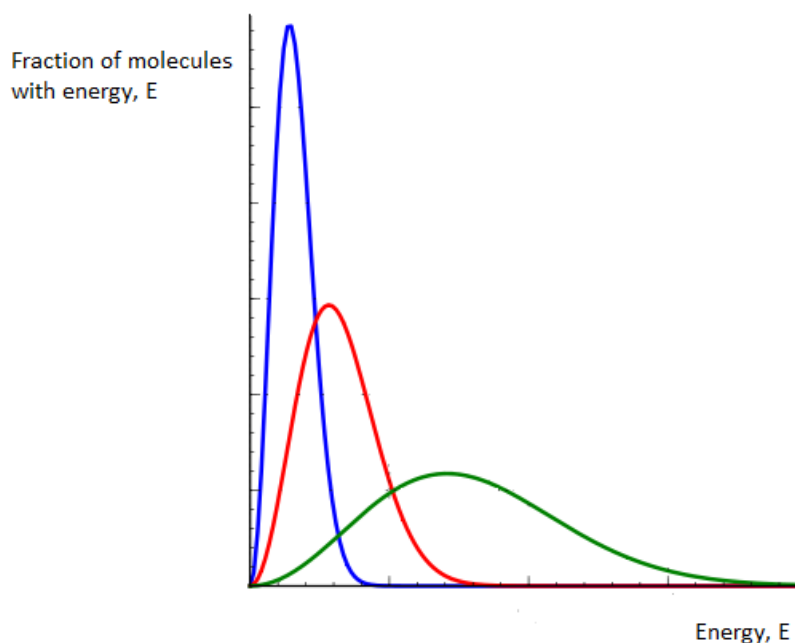
A spontaneous change is one that has a natural tendency to occur without the needing to be driven by an external factor.

The **second law of thermodynamics** states that every natural thermodynamic process proceeds in the direction in which the total entropy is increased.

Examples of changes which result in an **increase** in entropy are:

The increase in temperature of a gas. This can be seen by looking at the Maxwell-Boltzmann distribution of a gas at two or more temperatures. The spread of energies is much greater at a higher temperature meaning that the disorder or randomness of the hot gas is greater than that of the cooler gas.

Figure 4



The blue line is for a lower temperature than the red line and the green line represents the distribution at a much higher temperature.

A solid melting or a liquid boiling. The ordered arrangement of molecules in the solid become random as it melts. The close packed molecules in the liquid become dispersed in the gas phase.

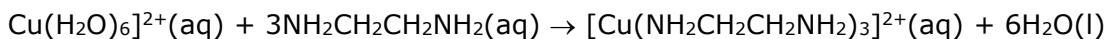
$$S_{\text{ice}} = 43 \text{ J K}^{-1} \text{ mol}^{-1}; S_{\text{water}} = 70 \text{ J K}^{-1} \text{ mol}^{-1}; S_{\text{vapour}} = 189 \text{ J K}^{-1} \text{ mol}^{-1}$$

A reaction in which a gas is produced from a solid and a liquid



$$\Delta S_{\text{system}} > 0$$

A reaction in which there is an increase in the number of moles in the same physical state.



The change is from four moles to seven moles, so $\Delta S_{\text{system}} > 0$.

Total entropy change

The total entropy involved in a change, ΔS_{total} , is made up of the entropy change of the system, ΔS_{system} and that of the surroundings, $\Delta S_{\text{surroundings}}$.

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

At A level, the system is normally considered to be the substances reacting; and the surroundings the air in the room in which the reaction is taking place.

For a spontaneous change, ΔS_{total} must be positive.

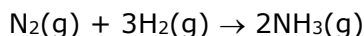
Thus it is possible for either ΔS_{system} or $\Delta S_{\text{surroundings}}$ to be negative, as long as their sum is positive.

Entropy change of the system, ΔS_{system}

This is equal to the sum of all the molar entropies of the products – the sum of those of the reactants.

$$\Delta S_{\text{system}} = S_{\text{products}} - S_{\text{reactants}}$$

So for the reaction



it is

$$\Delta S_{\text{system}} = 2 \times S_{\text{NH}_3} - (S_{\text{N}_2} + 3 \times S_{\text{H}_2})$$

Calculation of ΔS_{system} requires a table of entropies. At A level, these will always be standard entropies which is the entropy value at a pressure of 100 kPa and a temperature of 298K (25°C). The units are $\text{J K}^{-1} \text{mol}^{-1}$.

Table 2 Standard entropies of some substances

• Physical state	• Substance	• Standard entropy, $S^\ominus$ / J K ⁻¹ mol ⁻¹
Solid	Calcium carbonate, CaCO ₃	93
	Calcium oxide, CaO	40
	Magnesium carbonate, MgCO ₃	66
Liquid	Ethanol, C ₂ H ₅ OH	161
	Propan-1-ol, C ₂ H ₅ CH ₂ OH	197
	Benzene, C ₆ H ₆	173
Gas	Hydrogen, H ₂	131
	Nitrogen, N ₂	192
	Ammonia, NH ₃	193
	Carbon monoxide, CO	191
	Carbon dioxide, CO ₂	214
	Hydrogen chloride, HCl	187
	Chlorine, Cl ₂	223
	Ethene, C ₂ H ₄	219
	Ethane, C ₂ H ₆	230
	Propane, C ₃ H ₈	270

Notice the following things:

- 1 The entropies of gases, except for the simplest gases, are generally larger than those of liquids which are larger than those of solids: $S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$

The more atoms there are in a species (in a given physical state), the larger the entropy: $S(\text{CaCO}_3(\text{s})) > S(\text{CaO}(\text{s}))$ and $S(\text{C}_6\text{H}_6(\text{l})) > S(\text{C}_2\text{H}_5\text{OH}(\text{l}))$

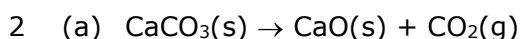
For species with a similar number of atoms, the larger the number of electrons, the larger the entropy: $S(\text{CaCO}_3(\text{s})) > S(\text{MgCO}_3(\text{s}))$ and $S(\text{Cl}_2(\text{g})) > S(\text{CO}(\text{g}))$

Points 2 and 3 can be summarised as: the more complex the substance, the larger is its entropy.

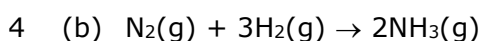
It is often stated that the entropy of gases are always bigger than those of a liquid. This is an oversimplification as liquid benzene has a higher entropy than gaseous hydrogen. The reason is that benzene has many more atoms in a molecule and so more ways of arranging energy in terms of vibration and rotation.

Example 1

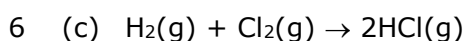
1 Use **Table 2** to calculate ΔS_{system} for:



3



5



Answers for Example 1

7 (a) $\Delta S_{\text{system}} = 40 + 214 - 93 = +161 \text{ J K}^{-1} \text{ mol}^{-1}$

8

9 (b) $\Delta S_{\text{system}} = 2 \times 193 - (192 + 3 \times 131) = -199 \text{ J K}^{-1} \text{ mol}^{-1}$

10

11 (c) $\Delta S_{\text{system}} = 2 \times 187 - (131 + 223) = +20 \text{ J K}^{-1} \text{ mol}^{-1}$

These ΔS_{system} values show the following general rules:

If there are more gas moles on the right than on the left of an equation, ΔS_{system} will be positive and large

If there are fewer gas moles on the right than on the left of an equation, ΔS_{system} will be a large negative number

If there are the same number of gas moles on each side, ΔS_{system} may be positive or negative and will be small.

Entropy change of the surroundings, $\Delta S_{\text{surroundings}}$

In an exothermic reaction heat is transferred to the surroundings. This increases the variety of energies of the surrounding air molecules and so increases their disorder. This is clearly shown in the Maxwell-Boltzmann curves at different temperatures (see page 9). The result is that the transfer of heat to the surroundings causes $S_{\text{surroundings}}$ to increase. Conversely if heat is transferred from the surroundings to the reaction vessel, $S_{\text{surroundings}}$ will decrease.

Exothermic: $\Delta S_{\text{surroundings}}$ positive **Endothermic:** $\Delta S_{\text{surroundings}}$ negative

The magnitude of $\Delta S_{\text{surroundings}}$ depends upon two factors:

2 The enthalpy of reaction, $\Delta_r H$

If the value of $\Delta_r H$ for an exothermic reaction is large, there will be a large increase in the disorder of the surrounding air molecules and so the value of $\Delta S_{\text{surroundings}}$ will also be large.

$\Delta S_{\text{surroundings}}$ is proportional to $-\Delta_r H$ and is positive for an exothermic reaction.

The temperature, T

If the temperature in the surrounding air is high, the air molecules will already be in a high state of disorder and so an input of heat energy will only make a small difference to its extent of disorder. This means that $\Delta S_{\text{surroundings}}$ only increases by a small amount. However if the temperature is low, an input of energy will cause a much bigger increase in disorder and so $\Delta S_{\text{surroundings}}$ will increase to a greater extent.

$\Delta S_{\text{surroundings}}$ is inversely proportional to an increase in temperature.

When these two are combined the following relationship is obtained:

$$\Delta S_{\text{surroundings}} = - \frac{\Delta_r H}{T}$$

Spontaneity

$$\begin{aligned}\Delta S_{\text{total}} &= \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \\ &= \Delta S_{\text{system}} - \frac{\Delta_r H}{T}\end{aligned}$$

For a spontaneous change ΔS_{total} must be positive.

Table 3

• ΔS_{system}	• Enthalpy change	• Spontaneity
Positive	Negative (so $-\frac{\Delta_r H}{T}$ positive)	At all temperatures
Negative	Negative	Only if $-\frac{\Delta_r H}{T} > \Delta S_{\text{system}}$
Positive	Positive (so $-\frac{\Delta_r H}{T}$ negative)	Only if $\Delta S_{\text{system}} > -\frac{\Delta_r H}{T}$
Negative	Positive	Never

Example 2

12 Calculate whether the following changes are spontaneous or not at a temperature of 298K.

13

14 (a) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$

15 $\Delta_r H = -92.2 \text{ kJ mol}^{-1}$ $\Delta S_{\text{system}} = -199 \text{ J K}^{-1} \text{ mol}^{-1}$

16

17 (b) $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

18 $\Delta_r H = +178 \text{ kJ mol}^{-1}$ $\Delta S_{\text{system}} = +164 \text{ J K}^{-1} \text{ mol}^{-1}$

19

20 **Note that ΔS_{system} is measured in J units whereas $\Delta_r H$ is measured in kJ units, so the latter has to be multiplied by 1000 so as to get both in joules.**

Answers for Example 2

21 (a) $\Delta S_{\text{total}} = \Delta S_{\text{system}} - \frac{\Delta_r H}{T} = -199 - (-92200 \div 298) = +110 \text{ J K}^{-1} \text{ mol}^{-1}$

22

23 This is positive so the reaction is spontaneous at a temperature of 298 K.

24 The favourable $\Delta S_{\text{surroundings}} (-\frac{\Delta_r H}{T})$ outweighs the unfavourable ΔS_{system} .

25 This reaction is thermodynamically spontaneous but a mixture of nitrogen and hydrogen can be left for years and there will be no sign of any ammonia. The reason is that the reaction has a very high activation energy and so is said to be kinetically stable. For this reason the word 'feasible' or the phrase 'thermodynamically spontaneous' is sometimes used in place of 'spontaneous', the latter implying that it happens automatically.

26

27 (b) $\Delta S_{\text{total}} = +164 - (+178000 \div 298) = -433 \text{ J K}^{-1} \text{ mol}^{-1}$

28

29 This is negative, so the reaction is not spontaneous at a temperature of 298K.

30 The unfavourable $\Delta S_{\text{surroundings}} (-\frac{\Delta_r H}{T})$ outweighs the favourable ΔS_{system} .

Change in spontaneity

For reactions where ΔS_{system} and $\Delta S_{\text{surroundings}}$ have different signs, there will be a unique temperature at which the reaction changes from being spontaneous to be non-spontaneous or vice versa. This happens at the temperature when $\Delta S_{\text{total}} = \text{zero}$.

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} - \frac{\Delta_r H}{T} = 0$$

$$\Delta S_{\text{system}} = \frac{\Delta_r H}{T}$$

The temperature at which this happens is given by

$$T = \frac{\Delta_r H}{\Delta S_{\text{system}}}$$

Example 3

31 Use the data from Example 2 (b) to calculate the temperature at which the decomposition of calcium carbonate becomes thermodynamically feasible.

Answer for Example 3

32 $\Delta_r H = +178 \text{ kJ mol}^{-1}$ $\Delta S_{\text{system}} = +164 \text{ J K}^{-1} \text{ mol}^{-1}$

33 $T = \frac{\Delta_r H}{\Delta S_{\text{system}}} = \frac{+178000 \text{ J mol}^{-1}}{+164 \text{ J K}^{-1} \text{ mol}^{-1}} = 1085 \text{ K} = 812^\circ \text{C}$

Effect of temperature on entropy values

As a solid is heated, the motion of its molecules increases and so its entropy increases. This is a gradual process until the melting temperature is reached, when a large increase in entropy occurs. There is a further gradual increase in entropy as the liquid is heated and then a large increase as the liquid boils. Finally there is another gradual increase in entropy as the gas is heated. This happens with all substances.

For a reaction in a given physical state



both $S(A)$ and $S(B)$ increase as the temperature is increased. It is an acceptable approximation to state that both $S(A)$ and $S(B)$ increase by the same amount and so ΔS_{system} will not change in value if the temperature is altered.

This is not true if the temperature change causes a change of physical state. Consider the combustion of hydrogen. At 25°C the product water is a liquid but at 125°C it is a gas. ΔS_{system} at 125°C is much greater than ΔS_{system} at 25°C but very similar to ΔS_{system} at 225°C.

It is also assumed that $\Delta_r H$ is also independent on temperature (see page 6). It is a fair assumption that neither ΔS_{system} nor $\Delta_r H$ varies with temperature, but ΔS_{total} will alter as the temperature is changed because $\Delta S_{\text{total}} = \Delta S_{\text{system}} - \Delta_r H / T$. This is an important point when considering how the equilibrium constant changes with temperature (page 19).

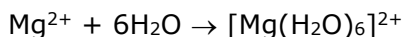
Entropy changes on dissolving

It is often thought that the dissolving of an ionic solid always results in an increase of ΔS_{system} . This is true for solids with singly charged cations such as Na^+ and NH_4^+ . But with doubly and triply charged anions this is not the case.

When an anhydrous ionic solid dissolves in water there are two contributions to ΔS_{system} :

- 3 The increased disorder caused by the highly ordered solid spreading out into the solvent. The entropy change here is always positive.

The ions, and especially the cations, become hydrated. In magnesium chloride, the magnesium ions gather six water molecules around them.



These hydrated ions then gather a second sphere of water molecules around them, thus the water solvent becomes significantly ordered. In this process the entropy change is negative and often outweighs the positive entropy change caused by the solid becoming dispersed through the solvent. For small and highly charged cations this decrease in entropy can be quite large and the solid will only dissolve if $\Delta H_{\text{solution}}$ is highly exothermic.

Gibbs Free Energy, G

Not that the Gibbs free energy is not expected by the IAL specification, but is included here as teachers may wish to use it as an alternative approach to entropy.

The free energy measured at constant pressure is called the Gibbs free energy (or Gibbs function), symbol G , and is named after the American scientist J. Willard Gibbs. It is a measure of the chemical potential, μ , that a mole of a substance has when on its own. It is the energy that is available to do work in the same way that water at a higher potential energy can run downhill and drive a machine.

Gibbs free energy is defined as:

$$G = H - TS$$

where H is the enthalpy of the substance and S its entropy. T is the temperature, measured in kelvin.

The Gibbs free energy can be thought of as the enthalpy content minus TS which represents the substance's energy that is already disordered. This difference is the energy that is available to become disordered by doing work.

When 1 mol of substance A reacts to form 1 mol of substance B, the change in free energy is given by:

$$\Delta_r G^\theta = G_B^\theta - G_A^\theta = (H_B^\theta - TS_B^\theta) - (H_A^\theta - TS_A^\theta)$$

Thus
$$\Delta_r G^\theta = \Delta_r H^\theta - T\Delta S^\theta$$

As all these quantities refer to the system, the subscript system need not be used for the entropy change.

The expression for the total entropy change has been seen earlier.

$$\Delta S_{\text{total}}^\theta = \Delta S_{\text{system}}^\theta - \frac{\Delta_r H^\theta}{T}$$

If this is multiplied by $-T$, it becomes

$$-T\Delta S_{\text{total}}^\theta = \Delta_r H^\theta - T\Delta S_{\text{system}}^\theta$$

This is identical to the expression for ΔG^θ , so the relationship between ΔG^θ and $\Delta S_{\text{total}}^\theta$ is

$$\Delta_r G^\theta = -T\Delta S_{\text{total}}^\theta$$

or
$$\Delta S_{\text{total}}^\theta = -\frac{\Delta_r G^\theta}{T}$$

Feasibility in terms of ΔG

The criterion for a process being thermodynamically spontaneous is that ΔS_{total} must be positive. This means that ΔG must be negative for a spontaneous change.

A reaction changes spontaneity at a temperature such that $\Delta G = 0$.

$$\Delta G = \Delta H - T\Delta S = 0$$
$$T = \frac{\Delta H}{\Delta S}$$

This is identical to the expression on page 14.

Calculation of $\Delta G^\ominus$ for a reaction

This calculation is similar to that for calculating $\Delta_r H$ given a table of standard enthalpies of formation.

$$\Delta_r G^\ominus = \Sigma(\Delta_f G^\ominus \text{ of products}) - \Sigma(\Delta_f G^\ominus \text{ of reactants})$$

(Taking into account the number of moles of each substance in the equation.)

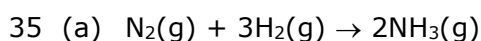
Table 4 Standard free energy of formation, $\Delta_f G^\ominus$, of some substances

• Substance	• $\Delta_f G^\ominus / \text{kJ mol}^{-1}$
Nitrogen, $\text{N}_2(\text{g})$	0
Hydrogen, $\text{H}_2(\text{g})$	0
Ammonia, $\text{NH}_3(\text{g})$	-27
Ethanoic acid, $\text{CH}_3\text{COOH}(\text{l})$	-390
Ethanol, $\text{C}_2\text{H}_5\text{OH}(\text{l})$	-175
Ethyl ethanoate, $\text{CH}_3\text{COOC}_2\text{H}_5(\text{l})$	-326
Water, $\text{H}_2\text{O}(\text{l})$	-237

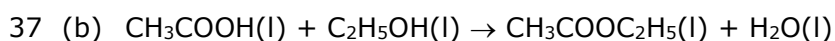
Note that, as with $\Delta_r H$ data, the standard free energy of formation of elements in their standard states is zero. This means that $\Delta_r H^\ominus$ and $\Delta_r G^\ominus$ data for elements will not be given in an A level question.

Example 4

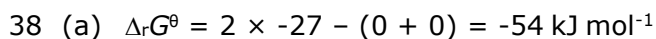
34 Calculate the standard free energy change for the following reactions:



36

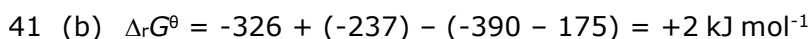


Answers for Example 4



39 As this value is negative, the reaction is (thermodynamically) spontaneous at 298K.

40



42 As this value is positive, the reaction is (just) non-spontaneous at 298K.

43

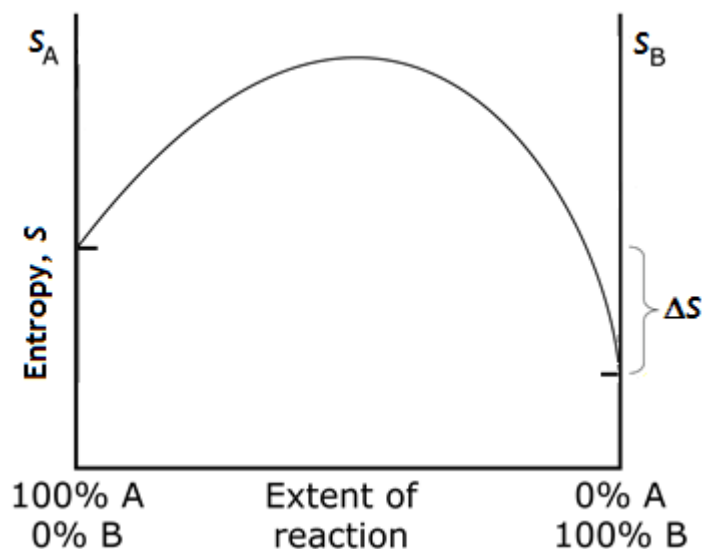
Equilibrium, ΔS_{total} and $\Delta_r G^\theta$

In terms of $\Delta S_{\text{total}}^\theta$

As an equilibrium reaction proceeds from reactants towards products, the total entropy of the mixture increases, reaching a maximum when equilibrium is reached. This is shown in Figure 5 for the equilibrium reaction



Figure 5



The relationship between the total entropy change, $\Delta S_{\text{total}}^\theta$, and the equilibrium constant, K , is given by the expression

$$\Delta S_{\text{total}}^\theta = R \ln K$$

In this expression K_p must be used for gaseous equilibria and K_c for equilibria in solution. Also partial pressures must be in atm. The reason for this is that the partial pressure term of $A(g)$ in the expression for K_p is really the partial pressure of $A(g)$ divided by the standard pressure. So for a gas with a mole fraction of 0.25 at 1 atm, the value that should be substituted into the expression for K_p is $0.25 \text{ atm} \div 1 \text{ atm} = 0.25$. If kPa had been used the value should be $0.25 \times 100 \text{ kPa} \div 100 \text{ kPa} = 0.25$. The resulting value will be the same as long as the partial pressures are divided by the standard pressure.

For this reason Edexcel will always use atm as the unit for pressure in all K_p questions, so that failure to divide by 1 will not alter the value of K_p .

In terms of $\Delta_r G^\ominus$

The relationship between $\Delta_r G^\ominus$ and $\Delta S_{\text{total}}^\ominus$ is

$$\Delta_r G^\ominus = -T \Delta S_{\text{total}}^\ominus$$

So the relationship between $\Delta_r G^\ominus$ and K is

$$\Delta_r G^\ominus = RT \ln K$$

Effect of temperature on the value of K

For an exothermic reaction, it is usual to state that, because $\Delta_r H$ is negative, an increase in temperature will cause the value of K to decrease. This, in turn, lowers the equilibrium yield (drives the position of equilibrium to the left). This can be explained in terms of the total entropy change.

$$\Delta S_{\text{total}}^\ominus = R \ln K \quad \text{and} \quad \Delta S_{\text{total}}^\ominus = \Delta S_{\text{system}}^\ominus - \frac{\Delta_r H^\ominus}{T}$$

$$\ln K = \frac{\Delta S_{\text{total}}^\ominus}{R} = \frac{\Delta S_{\text{system}}^\ominus}{R} - \frac{\Delta_r H^\ominus}{RT}$$

For an exothermic reaction $\Delta_r H$ is negative and so $-\frac{\Delta_r H^\ominus}{RT}$ is positive.

An increase in temperature will cause this positive number to decrease in value making $\ln K$ a smaller number. This means that K will also be a smaller number.

Note that this assumes that neither $\Delta S_{\text{system}}^\ominus$ nor $\Delta_r H^\ominus$ change in value as the temperature is altered (see page 15).

It also can be explained in terms of $\Delta_r G^\ominus$.

$$\Delta_r G^\ominus = -RT \ln K$$

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T \Delta S_{\text{system}}^\ominus$$

$$\ln K = \frac{-\Delta_r G^\ominus}{RT} = \frac{T \Delta S_{\text{system}}^\ominus}{RT} - \frac{\Delta_r H^\ominus}{RT} = \frac{\Delta S_{\text{system}}^\ominus}{R} - \frac{\Delta_r H^\ominus}{RT}$$

This is the same expression as that derived from $\Delta S_{\text{total}}^\ominus$ and so the reasoning for the change in the value of K is the same as that from $\Delta S_{\text{total}}^\ominus$.

Points to remember

Entropies and the gas constant R are always quoted in joules, whereas free energy and enthalpy values are quoted in kilojoules.

A positive value for $\Delta S_{\text{total}}^\ominus$ means that the forward reaction is thermodynamically feasible and so there will be more product than reactant in the equilibrium mixture.

A negative value for $\Delta_r G^\ominus$ also means that the forward reaction is thermodynamically feasible and so there will be more product than reactant in the equilibrium mixture.

The temperature at which feasibility changes is given by the expression

$$T = \frac{\Delta_r H^\ominus}{\Delta S_{\text{system}}^\ominus}$$

