Entropy change, $\Delta S^\ominus$

a explain that entropy is a measure of the ‘disorder’ of a system, and that a system becomes more stable when its energy is spread out in a more disordered state ☐

b explain the entropy changes that occur:

   i during a change in state e.g. (s) → (l); (l) → (g); (s) → (aq) ☐

   ii during a temperature change ☐

   iii during a reaction in which there is a change in the number of gaseous molecules ☐

c predict whether the entropy change for a given process is positive or negative ☐

d calculate the entropy change for a reaction, $\Delta S^\ominus$, given the standard entropies, $S^\ominus$, of the reactants and products ☐

Gibbs free energy change, $\Delta G^\ominus$

a define standard Gibbs free energy change of reaction by means of the equation $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ ☐

b calculate $\Delta G^\ominus$ for a reaction using the equation $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ ☐

c state whether a reaction or process will be spontaneous by using the sign of $\Delta G^\ominus$ ☐

d predict the effect of temperature change on the spontaneity of a reaction, given standard enthalpy and entropy changes ☐

ENTROPY

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5 Chemical energetics

Enthalpy changes and entropy changes accompany chemical reactions. This topic demonstrates why some reactions and processes are spontaneous and others are not.

	Learning outcomes Candidates should be able to:
5.3 Entropy change, $\Delta S^\ominus$	**a) explain that entropy is a measure of the 'disorder' of a system, and that a system becomes more stable when its energy is spread out in a more disordered state** **b) explain the entropy changes that occur:** **(i) during a change in state e.g. (s) → (l); (l) → (g); (s) → (aq)** **(ii) during a temperature change** **(iii) during a reaction in which there is a change in the number of gaseous molecules** **c) predict whether the entropy change for a given process is positive or negative** **d) calculate the entropy change for a reaction, $\Delta S^\ominus$, given the standard entropies, $S^\ominus$, of the reactants and products**
5.4 Gibbs free energy change, $\Delta G^\ominus$	**a) define standard Gibbs free energy change of reaction by means of the equation $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$** **b) calculate $\Delta G^\ominus$ for a reaction using the equation $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$** **c) state whether a reaction or process will be spontaneous by using the sign of $\Delta G^\ominus$** **d) predict the effect of temperature change on the spontaneity of a reaction, given standard enthalpy and entropy changes**

ENTROPY

The dissolving of sodium chloride (common salt) in water is an example of an endothermic process that occurs spontaneously at room temperature.

The idea of an endothermic reaction occurring spontaneously goes against our experience from everyday life that things do not seem to move spontaneously from a lower to a higher energy state (a book does not jump from a lower shelf to a higher one but will fall to a lower shelf if the shelf it is on breaks).

This suggests that it is not just a consideration of the energy changes involved that can be used to predict whether a reaction occurs spontaneously.

ENTROPY

In a sodium chloride solution the Na^+ and Cl^- ions are dispersed throughout the solution and are moving around, which is a much more disordered, or random, arrangement than a separate crystal of sodium chloride and a beaker of pure water.

This property of disorder is called entropy, and it is possible to assign values to the entropy of a system and the entropy change for a reaction. An endothermic reaction can only occur if it involves an increase in entropy.

Entropy is given the symbol S. The units of entropy are $JK^{-1}mol^{-1}$.

ENTROPY CHANGE

It is possible to work out values for standard entropies for substances;

for example, the standard entropy of $H_2(g)$ is 131 J K^{-1} mol^{-1}, and the standard entropy of NaCl(s) is 72.4 J K^{-1} mol^{-1}.

An entropy change is represented by the symbol $\Delta S^\ominus$

A positive value for $\Delta S^\ominus$ indicates an increase in entropy, i.e. an increase in disorder.

For example, $\Delta S^\ominus$ for the process $H_2O(l) \longrightarrow H_2O(g)$ is +119 J K^{-1} mol^{-1}.

The disorder of the system has increased, as the molecules of water in the gas phase are moving around much more.

ENTROPY CHANGE

A negative value for $\Delta S^\ominus$ indicates an decrease in entropy, i.e. an decrease in disorder.

For example, $\Delta S^\ominus$ for the process $NH_3(g) + HCl \longrightarrow NH_4Cl$ is —285 J K^{-1} mol^{-1}.

Two molecules of gas being converted into a solid results in a decrease in disorder, i.e. a decrease in entropy.

PREDICT THE SIGN OF AN ENTROPY CHANGE

Gases have higher entropy than liquids, which have higher entropy than solids.

The table below shows the values of standard entropies for elements across period 2 in the periodic table.

Lithium to carbon are all solid elements and have low entropy values at 298 K, but nitrogen to neon are all gases and have much higher entropy values.

Element	Li	Be	B	C	N_2	O_2	F_2	Ne
State	solid	solid	solid	solid	gas	gas	gas	gas
$S^{\ominus}$ **/ J K^{-1} mol^{-1}**	29	10	6	6	192	205	203	146

PREDICT THE SIGN OF AN ENTROPY CHANGE

Gases have higher entropy than liquids, which have higher entropy than solids.

This is an approximate rule of thumb, which is useful when considering the same substance in different states or similar substances. When considering very different substances, it must be used with caution.

For instance, $S^{\ominus}$ for $(NH_4)_2SO_4(s)$ is 220 J K^{-1} mol^{-1}, whereas that for $CCl_4(l)$ is 214 J K^{-1} mol^{-1} and that for HCl(g) is 187 J K^{-1} mol^{-1}.

PREDICT THE SIGN OF AN ENTROPY CHANGE

To predict the sign of the entropy change in a reaction, we must consider whether there is an increase or decrease in disorder in the system.

As gases have significantly higher entropy than solids and liquids, the most important factor in determining whether a chemical reaction involves an increase or decrease in entropy is whether there is an increase or decrease in the number of moles of **gas**.

Increase in number of moles of gas: **$\Delta S^\ominus$ +ve** (entropy increases).

Decrease in number of moles of gas: **$\Delta S^\ominus$ −ve** (entropy decreases).

ENTROPY CHANGES FOR SOME REACTIONS

If the number of moles of gas is the same on both sides of an equation, as in this one:

$$F_2(g) + Cl_2(g) \longrightarrow 2ClF(g)$$

the prediction could be made that the entropy change for this reaction would be approximately zero.

Reaction	**Entropy**	**$\Delta S^\ominus$**	**Explanation**
$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$	decrease	–	4 moles of gas on the left-hand side converted to 2 moles of gas on the right-hand side; a decrease in the number of moles of gas suggests a decrease in disorder and therefore a decrease in entropy
$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$	increase	+	1 mole of solid becomes 1 mole of solid and 1 mole of gas; therefore the number of moles of gas increases
$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$	decrease	–	3 moles of gas converted to 1 mole of gas
$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$	decrease	–	2 moles of gas converted to 1 mole of gas

SKILL CHECK

Work out whether each of the following processes involves an increase or decrease in entropy:

(a) $C_2H_2(g) + 2H_2(g) \longrightarrow C_2H_6(g)$

(b) $2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(l)$

(c) $COCl_2(g) \longrightarrow CO(g) + Cl_2(g)$

(d) $2C(s) + O_2(g) \longrightarrow 2CO(g)$

SKILL CHECK

Which of the following reactions has a $\Delta S^{\ominus}$ value that is negative?

A $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$
B $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
C $CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$
D $2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l)$

CALCULATING ENTROPY CHANGES

Values of **$\Delta S^\ominus$** may be worked out from standard entropies, **$S^\ominus$**:

entropy change = **total entropy of products — total entropy of reactants**

$$\Delta S^\ominus = \Sigma S_{products} - \Sigma S_{reactants}$$

CALCULATING ENTROPY CHANGES

Calculate the standard entropy change for the following reaction:

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

	$S^\ominus$/J K^{-1} mol^{-1}
N_2	192
H_2	131
NH_3	193

$\Delta S^\ominus = (2 \times 193) - [192 + (3 \times 131)]$

$\Delta S^\ominus = -199$ J K^{-1} mol^{-1}

SKILL CHECK

What is $\Delta S^\ominus$ for the following reactions?

(a) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

[$\Delta S^\ominus$ /J mol^{-1} K^{-1}: $CaCO_3(s)$ 92.9; $CaO(s)$ 39.7; $CO_2(g)$ 213.6]

(b) $C_2H_4(g) + H_2O(l) \longrightarrow C_2H_5OH(l)$

[$\Delta S^\ominus$ /J mol^{-1} K^{-1}: $H_2O(l)$ 69.9; $C_2H_5OH(l)$ 160.7; $C_2H_4(g)$ 219.5]

SKILL CHECK

(c) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

[$\Delta S^\ominus$ /J mol^{-1} K^{-1}: $H_2(g)$ 130.6; $N_2(g)$ 191.6; $NH_3(g)$ 192.3]

SKILL CHECK

Use the entropy values in the table to calculate the standard entropy change in each of the following reactions:

(a) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

Substance	$S^\ominus$ / J K^{-1} mol^{-1}
$CH_4(g)$	186
$O_2(g)$	103
$CO_2(g)$	214
$H_2O(l)$	70
$Cu(NO_3)_2(s)$	193
$CuO(s)$	43
$NO_2(g)$	240
$BCl_3(l)$	206
$SF_4(g)$	292
$BF_3(g)$	254
$SCl_2(g)$	282
$Cl_2(g)$	83

SKILL CHECK - CONTINUED

(b) $2Cu(NO_3)_2(s) \longrightarrow 2CuO(s) + 4NO_2(g) + O_2(g)$

(c) $4BCl_3(l) + 3SF_4(g) \longrightarrow 4BF_3(g) + 3SCl_2(g) + 3Cl_2(g)$

Substance	$S^\ominus$ / J K^{-1} mol^{-1}
$CH_4(g)$	186
$O_2(g)$	103
$CO_2(g)$	214
$H_2O(l)$	70
$Cu(NO_3)_2(s)$	193
$CuO(s)$	43
$NO_2(g)$	240
$BCl_3(l)$	206
$SF_4(g)$	292
$BF_3(g)$	254
$SCl_2(g)$	282
$Cl_2(g)$	83

SPONTANEITY

Spontaneous reaction: one that occurs without any outside influence, i.e. no input of energy.

If sodium and oxygen are put together in an isolated container (one with no connection to the outside world) at 25 °C, they will react spontaneously to produce sodium oxide:

$$4Na(s) \quad + \quad O_2(g) \longrightarrow 2Na_2O(s)$$

This reaction will occur by itself – nothing has to be done to make the reaction occur.

This is an example of a spontaneous reaction.

SPONTANEITY

If methane and oxygen are put into an isolated container at 25 °C, they will react together spontaneously to form carbon dioxide and water.

This reaction, although it is spontaneous, is not a very fast reaction at room temperature (unless a spark is supplied) and would have to be left for a very long time before a significant amount of carbon dioxide and water could be detected.

Similarly, the conversion of diamond to graphite at room temperature is a spontaneous process, but luckily occurs immeasurably slowly!

A spontaneous reaction does not have to happen quickly.

SPONTANEITY

Whether a reaction will be spontaneous or not under a certain set of conditions can be deduced by looking at how the entropy of the Universe changes as the reaction occurs.

The second law of thermodynamics states that for a process to occur spontaneously it must result in an increase in the entropy of the Universe.

The Universe may be regarded as being composed of the system (the chemical reaction) and the surroundings.

The total entropy change (of the Universe) is given by:

$$\Delta S_{Total} = \Delta S_{surroundings} + \Delta S_{system}$$

If the value of ΔS_{Total} is positive, the total entropy increases and the reaction occurs spontaneously.

SPONTANEITY

The total entropy change is given by: $\Delta S_{total} = \Delta S_{surroundings} + \Delta S_{system}$

The entropy change of the system is given by: $\Delta S_{system} = \Sigma S_{products} - \Sigma S_{reactants}$

The entropy change of the surroundings is given by:

$$\Delta S_{surroundings} = \frac{-\Delta H_{reaction}}{T}$$

$$\Delta S_{total} = \Delta S_{surroundings} - \frac{\Delta H_{reaction}}{T}$$

GIBBS FREE ENERGY

There is a more straightforward way in which we can take account of both system and surroundings.

It involves a quantity called **Gibbs free energy** or, more simply, free energy.

The Gibbs free energy change is given by the relationship:

$$\Delta G = -T\Delta S_{total}$$

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

$$-\frac{\Delta G}{T} = -\frac{\Delta H_{reaction}}{T} + \Delta S_{system}$$

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

GIBBS FREE ENERGY

ΔG is called the change in Gibbs free energy, or just the free energy change. Or, under standard conditions, we have $\Delta G^\ominus$, which is the standard free energy change.

ΔG is related to the entropy change of the Universe, and **for a reaction to be spontaneous, ΔG for the reaction must be negative.**

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

The units of ΔG are kJ mol^{-1} and T must be in K.

The subscripts are now omitted, as both ΔH and ΔS refer to the system, i.e. the chemical reaction.

CALCULATING ΔG

We can calculate ΔG for $C_2H_2(g) + 2H_2(g) \longrightarrow C_2H_6(g)$ given the following information:

ΔH = —313 kJ mol^{-1} and ΔS = −233JK^{-1} mol^{-1}

$$\Delta G = —313 — 298 \times (233/1000) = —244\ kJmol^{-1}$$

CALCULATING ΔG: EXAMPLE

Consider the decomposition of $Mg(NO_3)_2(s)$:

$$2Mg(NO_3)_2(s) \longrightarrow 2MgO(s) + 4NO_2(g) + O_2(g)$$

	$Mg(NO_3)_2(s)$	MgO(s)	$NO_2(g)$	$O_2(g)$
$\Delta H_f/kJmol^{-1}$	—790	—602	34	0
$S^{\ominus}$ / J K^{-1} mol^{-1}	164	27	240	205

CALCULATING ΔG: EXAMPLE

To calculate the enthalpy change, we have been given ΔH_f and so can use:

$$\Delta H = [(2 \times -602) + (4 \times 34) + 0] - [(2 \times -790)] = 512 \text{ kJmol}^{-1}$$

To calculate the entropy change we use:

$$\mathbf{\Delta S^{\ominus} = \Sigma S_{products} - \Sigma S_{reactants}}$$

$$\Delta S = [(2 \times 27) + (4 \times 240) + 205] - [(2 \times 164)] = 891 \text{ JK}^{-1}\text{ mol}^{-1}$$

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

$$\Delta G = 512 - 298 \times (891/1000) = 246 \text{ kJmol}^{-1}$$

Thus, at 298 K the reaction is not spontaneous because ΔG is positive.

SKILL CHECK

SKILL CHECK

SKILL CHECK

Calculate the Gibbs free energy change for the decomposition of zinc carbonate at 298 K.

$ZnCO_3(s) \longrightarrow ZnO(s) + CO_2(g) \quad \Delta H = +71.0\ kJ\ mol^{-1}$

Values for ΔS in $J\ K^{-1}\ mol^{-1}$: $CO_2(g) = +213.6$, $ZnCO_3(s) = +82.4$, $ZnO(s) = +43.6$

Answer: $+18.9\ kJ\ mol^{-1}$

CHANGING TEMPERATURE & ΔG

Consider a reaction for which ΔH is positive and ΔS is positive:

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

In this case, at low temperatures, the reaction is not spontaneous, as TΔS is smaller than ΔH, so ΔG is positive.

As the temperature is raised, TΔS becomes larger, and as this is being subtracted from ΔH, ΔG becomes smaller.

When TΔS is larger than ΔH, ΔG is negative, and the reaction becomes spontaneous.

Therefore, as the temperature is increased, this reaction becomes more spontaneous.

CHANGING TEMPERATURE & ΔG

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

Now consider a reaction for which ΔH is positive and ΔS is negative. In this case, at low temperatures, the reaction is not spontaneous.

However, as ΔS is negative —TΔS in the equation is positive, and this means that the value of ΔG will increase as the temperature is increased.

The consequence of —TΔS being positive is that this reaction will never be spontaneous.

CHANGING TEMPERATURE & ΔG

Both the reactions considered here so far have been endothermic reactions and it can be seen that:

an endothermic reaction can only occur spontaneously if it involves an increase in entropy (and the temperature is sufficiently high).

An exothermic reaction (ΔH negative) will always be spontaneous at some temperature.

And if an exothermic reaction involves an increase in entropy (ΔS positive) then $-T\Delta S$ will be negative. As ΔH is also negative, ΔG will always be negative, and the reaction will always be spontaneous.

CHANGING TEMPERATURE & ΔG

ΔH	ΔS	$-T\Delta S$	ΔG	**Spontaneous?**
–	+	–	negative	at all temperatures
+	+	–	becomes **more** negative as temperature increases	becomes more spontaneous as temperature increases
–	–	+	becomes **less** negative as temperature increases	becomes less spontaneous as temperature increases
+	–	+	positive	never

SKILL CHECK

Using the data given below, calculate the value of $\Delta G^{\ominus}$, for the following reaction at 298 K:

$SO_2(g) + Cl_2(g) \rightarrow SO_2Cl_2(l)$
$\Delta H^{\ominus} = -97.3\,kJ\,mol^{-1}$ and $\Delta S^{\ominus} = -254.4\,J\,K^{-1}\,mol^{-1}$

SKILL CHECK

(a) Use the standard enthalpy change of combustion values given in the table to calculate the standard enthalpy change of formation of propan-1-ol.

Substance	**$\Delta H_c^{\ominus}$ / kJ mol^{-1}**
$CH_3CH_2CH_2OH(l)$	−2010
$C(s)$	−394
$H_2(g)$	−286

SKILL CHECK

(b) Use the standard entropy values in the table below to calculate the entropy change for the complete combustion of propan-1-ol and justify the sign of the entropy change.

Substance	$S^{\ominus}$/J K^{-1} mol^{-1}
$CH_3CH_2CH_2OH(l)$	196.6
$CO_2(g)$	214
$H_2O(l)$	69.9
$O_2(g)$	205

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SKILL CHECK

(c) Calculate the standard free energy change, $\Delta G^{\ominus}$, for the complete combustion of propan-1-ol and explain whether the reaction will be spontaneous at 25 °C.

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SKILL CHECK

For the reaction $C_2H_4(g) + HCl(g) \rightarrow C_2H_5Cl(g)$, at 298 K,
$\Delta H^\ominus = -96.7\,kJ\,mol^{-1}$ and $\Delta G^\ominus = -25.9\,kJ\,mol^{-1}$.
Calculate the value of $\Delta G^\ominus$ at 1000 K.

Calculate the temperature at which $\Delta G^\ominus$ for the addition of HCl to ethene becomes zero.

SKILL CHECK

SKILL CHECK

When KNO_3 dissolves in water at 298 K, $\Delta H^{\ominus} = +34.8\,\text{kJ mol}^{-1}$ and $\Delta G^{\ominus} = +0.3\,\text{kJ mol}^{-1}$.

a Calculate $\Delta S^{\ominus}$.

b Calculate $\Delta G^{\ominus}$ at 320 K.

c Comment on the effect of temperature on the solubility of KNO_3.

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SKILL CHECK

Graphite and diamond are both forms of carbon. Their standard molar entropies are:

$\Delta S^{\ominus}_{\text{graphite}} = 5.70\,\text{J K}^{-1}\,\text{mol}^{-1}$, $\Delta S^{\ominus}_{\text{diamond}} = 2.40\,\text{J K}^{-1}\,\text{mol}^{-1}$

a i Suggest why the standard molar entropy of graphite is greater than that of diamond.

ii Calculate the entropy change of the process $C_{\text{graphite}} \longrightarrow C_{\text{diamond}}$ at 298 K

iii Explain why you would be unlikely to make diamonds from graphite at atmospheric temperature and pressure.

b The standard molar enthalpy change for $C_{\text{graphite}} \longrightarrow C_{\text{diamond}}$ is $+2.00\,\text{kJ mol}^{-1}$.

i Calculate the total entropy change for this reaction at 25.0 °C.

ii Explain why you would be unlikely to make diamonds from graphite at atmospheric temperature and pressure.

c Graphite reacts with oxygen to form carbon dioxide. Would you expect the entropy of the products to be greater or less than the entropy of the reactants? Explain your answer.

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SKILL CHECK

3268 kJ are required to change 1 mole of ethanol into its gaseous atoms.

$C_2H_5OH(g) \longrightarrow 2C(g) + 6H(g) + O(g)$

a Calculate the entropy change of the surroundings during this process when it is carried out at 150 °C.

b Explain why the total entropy change of this reaction is likely to be negative.

c When ethanol undergoes combustion, carbon dioxide and water are formed.

$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l) \qquad \Delta H^{\ominus}_{\text{reaction}} = -1367\ \text{kJ mol}^{-1}$

Calculate the total standard entropy change for this reaction.

(Values for $S^{\ominus}$ in $\text{J K}^{-1}\,\text{mol}^{-1}$: $C_2H_5OH(l) = 160.7$, $CO_2 = 213.6$, $H_2O(l) = 69.90$, $O_2(g) = 205.0$)