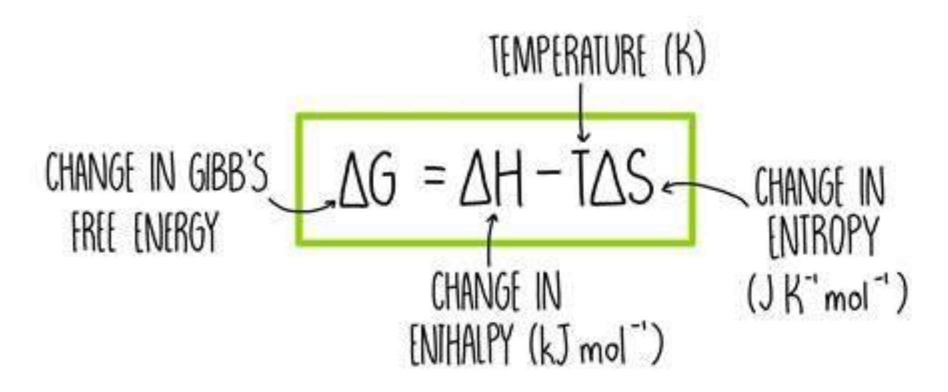
Cambridge
A2 Level
Chemistry
CODE: (9701)
Chapter 23
Entropy and Gibbs free energy



Introducing entropy

Entropy measures energy dispersal at a specific temperature and system randomness. Higher entropy indicates greater system disorder. In chemistry, entropy refers to the reaction between reactants, such as magnesium sulfate and hydrogen, releasing energy to the surroundings.

The surroundings include:
- The solvent (in this case water)
- The air around the test tube
- The test tube itself
- Anything dipping into the test tube (e.g. a thermometer).

Changes that tend to continue to happen naturally are called **spontaneous changes**

Chance and spontaneous change

Diffusion

Perfume spills in a closed room cause a gradual smell spread due to random movement of perfume vapor molecules. These molecules collide with air, other molecules, or room walls, causing them to change direction due to chance and probability laws.

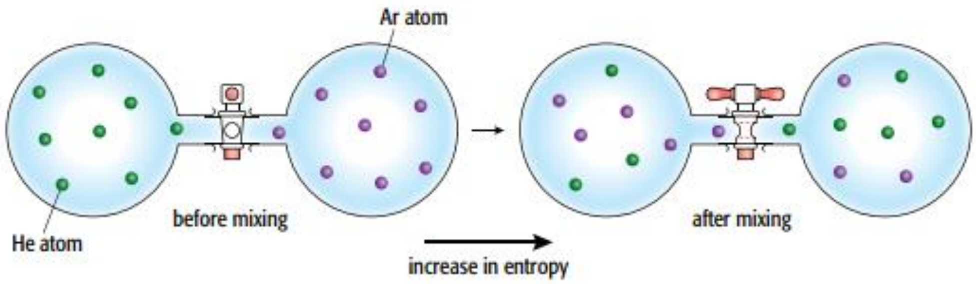
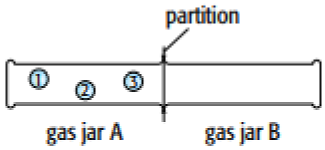


Figure 23.2 The spontaneous mixing of helium atoms (●) with argon atoms (●).

Diffusion and number of ways

We can show that the molecules in a vapour diffuse by chance by thinking about the probability of finding them at one place at any one time. Consider the simplified model shown below



The three molecules in gas jar A cannot move into gas jar B. In this model we assume that:
- There are only a few molecules in gas jar A
- There are no other particles present
- The molecules move randomly and change directions when they collide.

The number of ways of arranging the molecules after removing the partition is shown in Figure 23.3

There are eight different ways of arranging the three molecules between two gas jars. We can express this as:

$$2 \times 2 \times 2 = \underset{\substack{\uparrow \\ \text{two gas jars}}}{2}^{\overset{\text{number of molecules}}{\overset{\downarrow}{3}}} = 8$$

The probability of molecules settling in gas jars A and B is 1 in 8. The chance of a single molecule moving to gas jar B is 1 in 8. The number of ways molecules can be arranged is extremely large, with a million molecules between two jars. This overwhelming likelihood of diffusion occurs due to the large number of ways molecules can be arranged, which influences chemical reactions and physical processes like diffusion.

Comparing entropy values To make any comparison of entropy values fair, we must use standard conditions. These standard conditions are the same as those used for ΔH:

■A pressure of 105Pa
■A temperature of 298K (25 °C)
■Each substance involved in the reaction is in its normal physical state (solid, liquid or gas) at 105Pa and 298K.

Table 23.1 shows some values for some standard molar entropies. From the values in the table and other data we can make some generalisations:

■ Gases generally have much higher entropy values than liquids, and liquids have higher entropy values than solids. There are exceptions to this

■ Simpler substances with fewer atoms have lower entropy values than more complex substances with a greater number of atoms

■ For similar types of substances, harder substances have a lower entropy value

■ For a given substance the entropy increases as a solid melt and then changes to a vapour (see Figure 23.5).

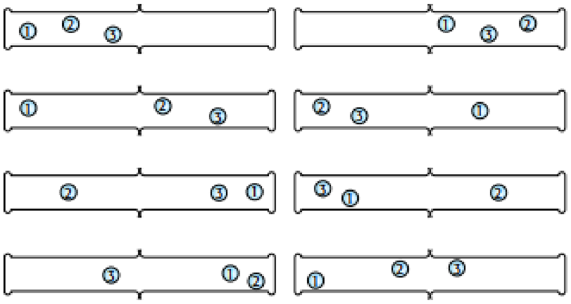


Figure 23.3 The eight possible arrangements of molecules after removing the partition between the gas jars.

Substance	$S^{\ominus}$ / $J K^{-1} mol^{-1}$	Substance	$S^{\ominus}$ / $J K^{-1} mol^{-1}$
diamond (s)	2.4	methanol (l)	239.7
graphite (s)	5.7	water (l)	69.9
calcium (s)	41.4	carbon monoxide (g)	197.6
lead (s)	64.8	hydrogen (g)	130.6
calcium oxide (s)	39.7	helium (g)	126.0
calcium carbonate (s)	92.9	ammonia (g)	192.3
mercury (l)	76.0	oxygen (g)	205.0
bromine (l)	151.6	carbon dioxide (g)	213.6

Table 23.1 Standard molar entropy values of some solids, liquids and gases. The states are shown as state symbols after each substance.

Figure 23.4 A diamond has a very low entropy value because it is a solid element with atoms regularly arranged. Bromine has a high entropy value because it tends to spread out.

When a solid changes to a liquid:
■The regularly arranged lattice of particles close together in the solid changes to
■ An irregular arrangement of particles, which are close together but rotate and slide over each other in the liquid.

When a liquid changes to a vapour:

- The irregular arrangement of particles in the liquid which are close together and rotating changes to
- An irregular arrangement of particles, which are free to move around rapidly because they are far apart from each other.

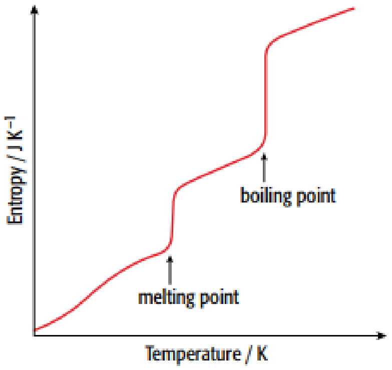


Figure 23.5 The change in entropy as a substance melts and then boils.

Entropy changes in reactions

In a chemical reaction, comparing entropies of reactants and products can explain the magnitude of entropy change. Gases have high entropy, while solids have low entropy. A significant entropy change is likely when the number of gaseous molecules changes.

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

there is an increase in entropy of the system because a gas is being produced (high entropy) but the reactant, calcium carbonate, is a solid (low entropy). In the reaction

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

The system's entropy increases due to the higher number of gas molecules in the products (5 molecules) and the greater disorder in the products, making it more energetically stable. In the reaction.

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

The system's entropy decreases due to a decrease in gas molecules, resulting in a negative change, with hydrogen and nitrogen being more stable than ammonia.

Calculating entropy changes

Entropy changes in exothermic and endothermic reactions

The surroundings are so large that when energy exchange takes place there is such a small change in temperature or pressure that we can ignore these.

- Exothermic reactions increase entropy and spontaneous chemical changes due to energy released from molecule rotation and translation, leading to a greater number of arrangements in the surroundings.

- Endothermic reactions result in a decrease in entropy and spontaneous chemical change probability due to the reduction in energy absorbed from the surroundings.

Total entropy change

Entropy values predict spontaneous chemical reactions by adjusting the entropy values of reactants and products. The standard entropy change symbol is $\Delta S^\ominus$, involving both the system and surroundings.

For the surroundings we write the entropy change as $\Delta S^\ominus_{\text{surroundings}}$.

The total entropy change is given by:

$$\Delta S^\ominus_{\text{total}} = \Delta S^\ominus_{\text{system}} + \Delta S^\ominus_{\text{surroundings}}$$

If the total entropy changes increases, the entropy change is positive. The reaction will then occur spontaneously. We say that the reaction is **feasible**

Calculating the entropy change of the system

In order to calculate the entropy, change of the system we use the relationship:

$$\Delta S^{\ominus}_{\text{system}} = S^{\ominus}_{\text{products}} - S^{\ominus}_{\text{reactants}}$$

Calculating the entropy change of the surroundings

The entropy change of the surroundings is calculated using the relationship:

$$\Delta S^{\ominus}_{\text{surroundings}} = \frac{-\Delta H^{\ominus}_{\text{reaction}}}{T}$$

where

- $\Delta H^{\ominus}_{\text{reaction}}$ is the standard enthalpy change of the reaction
- T is the temperature in kelvin. At standard temperature, this value is 298 K.

Calculating total entropy change

The total entropy change is given by:

$$\Delta S^{\ominus}_{\text{total}} = \Delta S^{\ominus}_{\text{system}} + \Delta S^{\ominus}_{\text{surroundings}}$$

We can also write this as:

$$\Delta S^{\ominus}_{\text{total}} = \Delta S^{\ominus}_{\text{system}} - \Delta H^{\ominus}_{\text{reaction}}/T$$

The total entropy changes for the examples given above for the reaction of calcium with oxygen and the combustion of methane are calculated by simply adding the entropy change of the system to the entropy change of the surroundings.

Entropy in equilibrium reactions

In equilibrium reactions, both products and reactants exist, causing a positive total entropy to change due to increased disorder and entropy.

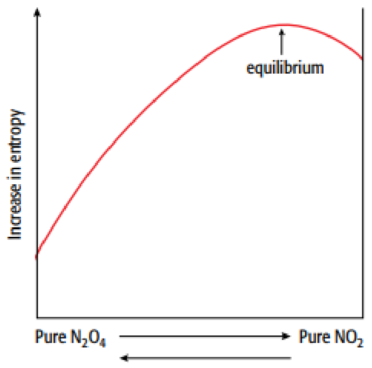


Figure 23.6 The total entropy change, $\Delta S^{\ominus}_{\text{total}}$, when N_2O_4 is converted to an equilibrium mixture of NO_2 and N_2O_4 and NO_2 is converted to the same equilibrium mixture.

Entropy and temperature

We have seen that the entropy change of the surroundings is given by;

$$\Delta S^{\ominus}_{\text{surroundings}} = \frac{-\Delta H^{\ominus}_{\text{reaction}}}{T}$$

The entropy changes of surroundings changes with temperature, with an increase in temperature making it less negative or more positive, and a decrease in temperature making it more negative or less positive. This relationship assumes that $\Delta H^{\ominus}_{\text{reaction}}$ doesn't significantly change with temperature.

$$ZnCO_3(s) \longrightarrow ZnO(s) + CO_2(g)$$

$$\Delta H^{\ominus}_{\text{reaction}} = +72.3\ \text{kJ mol}^{-1}$$

For this reaction $S^{\ominus}_{\text{system}} = +174.8\ \text{J K}^{-1}\ \text{mol}^{-1}$ (the same for both temperatures).

Reaction at 298 K

$$\Delta S^{\ominus}_{\text{surroundings}} = \frac{-72\,300}{298}$$

$$= -242.6\ \text{J K}^{-1}\,\text{mol}^{-1}$$

$$\Delta S^{\ominus}_{\text{total}} = +174.8 - 242.6\ \text{J K}^{-1}\,\text{mol}^{-1}$$

$$\Delta S^{\ominus}_{\text{total}} = -67.8\ \text{J K}^{-1}\,\text{mol}^{-1}$$

Reaction at 550 K

$$\Delta S^{\ominus}_{\text{surroundings}} = \frac{-72\,300}{550}$$

$$= -131.5\ \text{J K}^{-1}\,\text{mol}^{-1}$$

$$\Delta S^{\ominus}_{\text{total}} = +174.8 - 131.5\ \text{J K}^{-1}\,\text{mol}^{-1}$$

$$\Delta S^{\ominus}_{\text{total}} = +43.3\ \text{J K}^{-1}\,\text{mol}^{-1}$$

You can see that at 298 K the total entropy change is negative, so the reaction does not occur at this temperature. At 550 K the total entropy change is positive, so the reaction is spontaneous at this temperature.

- When the total entropy change in a reaction shows a large increase, e.g. $+200\ \text{J K}^{-1}\,\text{mol}^{-1}$, the reaction can be regarded as going to completion. It is definitely spontaneous.
- When the total entropy change shows a large decrease, e.g. $-600\ \text{J K}^{-1}\,\text{mol}^{-1}$, we can deduce that there is very little likelihood of a reaction occurring.

Entropy, enthalpy changes and free energy

For an exothermic reaction such as:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g) \qquad \Delta H^{\ominus}_{\text{reaction}} = -890.3\ \text{kJ mol}^{-1}$$

The entropy change in a system is negative, but a large negative value compensates for it by causing a positive value in the term $-\Delta H^{\theta}_{\text{reaction}}/T$. This results in a spontaneous reaction. In highly exothermic reactions, the enthalpy change is the driving force. In endothermic reactions, the entropy term is more important. Gibbs free energy, also known as **Gibbs free energy** or Gibbs function, allows for a more straightforward approach to considering both system and surroundings.

Gibbs free energy

What is Gibbs free energy?
In determining whether a chemical reaction is likely to be spontaneous we use the quantity Gibbs free energy change, ΔG. The Gibbs free energy change is given by the relationship:

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

We can also write the expression without having to consider the entropy changes of the surroundings:

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

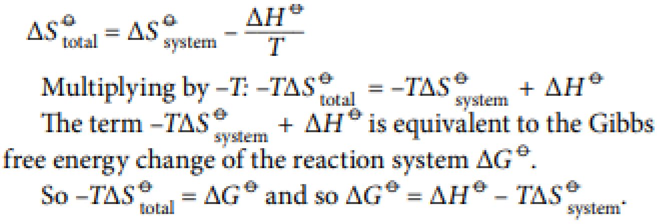
Gibbs free energy, a useful concept encompassing enthalpy and entropy change, requires standard conditions for fair comparison, similar to those used for ΔH and ΔS.

- Pressure of 105 Pa
- Temperature of 298K (25 °C)
- Each substance involved in the reaction is in its normal physical state (solid, liquid or gas) at 105 Pa and 298K.

The **standard molar Gibbs free energy of formation** is the free energy change that accompanies the formation of one mole of a compound from its elements in their standard state.

Derivation

Gibbs free energy can easily be derived from the equation relating total entropy to the entropy changes of system and surroundings. As:



$$\Delta S^{\ominus}_{\text{total}} = \Delta S^{\ominus}_{\text{system}} - \frac{\Delta H^{\ominus}}{T}$$

Multiplying by $-T$: $-T\Delta S^{\ominus}_{\text{total}} = -T\Delta S^{\ominus}_{\text{system}} + \Delta H^{\ominus}$

The term $-T\Delta S^{\ominus}_{\text{system}} + \Delta H^{\ominus}$ is equivalent to the Gibbs free energy change of the reaction system $\Delta G^{\ominus}$.

So $-T\Delta S^{\ominus}_{\text{total}} = \Delta G^{\ominus}$ and so $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}_{\text{system}}$.

Gibbs free energy and spontaneous reactions

A spontaneous reaction requires a positive $\Delta S^{\Theta}_{\text{total}}$ and a negative $\Delta G^{\Theta}_{\text{value}}$, resulting in a decrease in Gibbs free energy at constant temperature and pressure, while a positive ΔG is not spontaneous.

Applying the equation

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

We can calculate the Gibbs free energy change for a reaction if we know:

■The entropy change of the system in $\text{JK}^{-1}\text{mol}^{-1}$

■The enthalpy change of the system in Jmol^{-1}; we have to multiply the value of the enthalpy change by 1000 because the entropy change is in joules per kelvin per mol

■The temperature; under standard conditions, this is 298K.

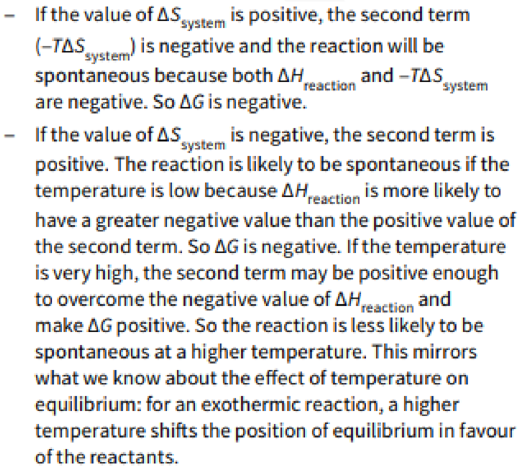
Temperature change and reaction spontaneity

For a reaction to be spontaneous, ΔG must be negative. The temperature can influence the spontaneity of a reaction. We can deduce this by considering the Gibbs free energy as a combination of two terms in the relationship

$$\Delta G = \underbrace{\Delta H_{\text{reaction}}}_{\text{first term}} - \underbrace{T\Delta S_{\text{system}}}_{\text{second term}}$$

If the value of ΔH reaction does not change much with temperature, we can see that the value of $T\Delta S_{\text{system}}$ may influence the value of ΔG.

■For an exothermic reaction, the first term ($\Delta H_{\text{reaction}}$) has a negative value.



- If the value of ΔS_{system} is positive, the second term ($-T\Delta S_{\text{system}}$) is negative and the reaction will be spontaneous because both $\Delta H_{\text{reaction}}$ and $-T\Delta S_{\text{system}}$ are negative. So ΔG is negative.
- If the value of ΔS_{system} is negative, the second term is positive. The reaction is likely to be spontaneous if the temperature is low because $\Delta H_{\text{reaction}}$ is more likely to have a greater negative value than the positive value of the second term. So ΔG is negative. If the temperature is very high, the second term may be positive enough to overcome the negative value of $\Delta H_{\text{reaction}}$ and make ΔG positive. So the reaction is less likely to be spontaneous at a higher temperature. This mirrors what we know about the effect of temperature on equilibrium: for an exothermic reaction, a higher temperature shifts the position of equilibrium in favour of the reactants.

- For an endothermic reaction, the first term ($\Delta H_{\text{reaction}}$) has a positive value.
  - If the value of ΔS_{system} is negative, the second term is positive. The reaction will not occur because both terms are positive, making the value of ΔG positive.
  - If the value of ΔS_{system} is positive, the second term is negative. The reaction is unlikely to be spontaneous if the temperature is low because $\Delta H_{\text{reaction}}$ is more likely to have a greater positive value than the negative value of the second term. So ΔG is positive. If the temperature is very high, the second term may be negative enough to overcome the positive value of $\Delta H_{\text{reaction}}$ and make ΔG negative. So the reaction is more likely to be spontaneous at a higher temperature. This mirrors what we know about the effect of temperature on equilibrium: for an endothermic reaction, a higher temperature shifts the position of equilibrium in favour of the products.

Comparing Gibbs free energy values

Table 23.2 displays standard molar Gibbs free energy changes of formation, which are zero for all elements. Some compounds have negative values, while others, like ethene, have positive values. The standard Gibbs free energy change also depends on the state, with -237.2 kJmol^{-1} for l and -228.6 kJmol^{-1} for g.

Gibbs free energy calculations

Gibbs free energy change of reaction

The **standard Gibbs free energy change of reaction** is the Gibbs free energy change when the amounts of the reactants shown in the stoichiometric equation react under standard conditions to give products. The reactants and products must be in their standard states.

The method of calculating Gibbs free energy change of reaction uses an energy cycle similar to the enthalpy cycles you used to calculate the enthalpy change of reaction in Chapter 6 (see Figure 23.8).

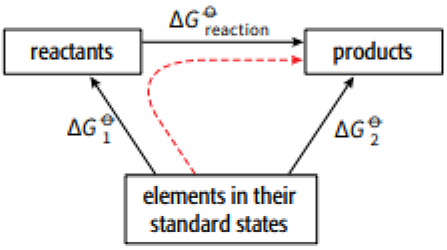


Figure 23.8 A free energy cycle for calculating the standard Gibbs free energy of reaction. The dashed line shows the indirect (two-step) route.

Substance	$\Delta G^{\ominus}_{f}$ / kJ mol^{-1}	Substance	$\Delta G^{\ominus}_{f}$ / kJ mol^{-1}
carbon (s)	0	water (l)	−237.2
calcium (s)	0	methanol (l)	−166.4
bromine (l)	0	chlorobenzene (l)	+93.6
helium (g)	0	water (g)	−228.6
calcium oxide (s)	−604.0	ethane (g)	+68.2
calcium carbonate (s)	−1128.8	ammonia (g)	−16.5
magnesium oxide (s)	−569.4	magnesium ion, Mg^{2+} (aq)	−454.8
zinc sulfide (s)	−201.3	carbonate ion, CO_3^{2-} (aq)	−527.9

Table 23.2 Standard molar Gibbs free energy changes of some solids, liquids, gases and aqueous ions. The states are shown as state symbols after each substance.

Using the same ideas as in Hess's law, we see that:

$$\Delta G_2^\ominus = \Delta G_1^\ominus + \Delta G_{\text{reaction}}^\ominus$$

So:

$$\Delta G_{\text{reaction}}^\ominus = \Delta G_2^\ominus - \Delta G_1^\ominus$$

Another way of writing this is:

$$\Delta G_{\text{reaction}}^\ominus = \Delta G_{\text{products}}^\ominus - \Delta G_{\text{reactants}}^\ominus$$

To calculate the Gibbs free energy change of reaction from an energy cycle like this, we use the following procedure:

- Write the balanced equation at the top
- Draw the cycle with the elements at the bottom
- Draw in all arrows making sure that they go in the correct directions
- calculate $\Delta G_{\text{reaction}}^\ominus = \Delta G_2^\ominus - \Delta G_1^\ominus$ taking into account the number of moles of reactants and products.

Gibbs free energy and work

Gibbs free energy change is part of the enthalpy change needed for work, with the +TΔS part unavailable due to system disorder, and the ΔG part available for work, like driving charge in electrochemical cells.

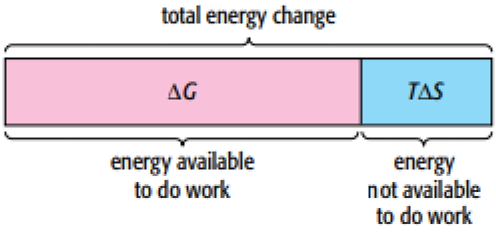


Figure 23.10 The enthalpy change of a reaction at constant temperature can be split into two parts.

Gibbs free energy change and direction of chemical change

Gibbs free energy of formation is a measure of the stability of a compound. The more negative the value of $\Delta G^\ominus{}_f$ the greater the stability of the compound. It is unlikely to decompose. If $\Delta G^\ominus{}_f$ is positive, the compound islikely to be unstable with respect to its elements.

The Gibbs free energy change of reaction is also a measure of the feasibility of a reaction. Reactions with negative values of $\Delta G^\ominus$ reaction are likely to be feasible (spontaneous), whereas those with positive values are less likely to be spontaneous.

- When a system is in chemical equilibrium and the amounts of products and reactants balance, the value of $\Delta G_{\text{reaction}}^\ominus$ is zero ($\Delta G_{\text{reaction}}^\ominus = 0$).
- The products predominate if the value of $\Delta G_{\text{reaction}}^\ominus$ has a fairly low negative value, e.g. $-10\,\text{kJ mol}^{-1}$.
- The reactants predominate if the value of $\Delta G_{\text{reaction}}^\ominus$ has a slightly positive value, e.g. $+10\,\text{kJ mol}^{-1}$.
- The reaction can be regarded as complete if the value of $\Delta G_{\text{reaction}}^\ominus$ is high and negative, e.g. $-60\,\text{kJ mol}^{-1}$.

- The reaction can be regarded as not being feasible (spontaneous) at all if the value of $\Delta G_{\text{reaction}}^\ominus$ is high and positive, e.g. $+60\,\text{kJ mol}^{-1}$.

Revision questions

1) (a) Silver carbonate, $Ag2CO_3$, is sparingly soluble in water. The numerical value of the solubility product, Ksp, for silver carbonate is 6.3×10^{-12} at 25◦C.

(i) Write an expression for the solubility product, Ksp, of $Ag2CO_3$, and state its units.

(ii) Calculate the equilibrium concentration of Ag^+ in a saturated solution of Ag_2CO_3 at 25°C.

$[Ag^+] = moldm^{-3}$ [1]

$[Ag^+] = moldm^{-3}$ [1]

(iii) Solid Ag_2CO_3 is stirred at 25°C with $0.050 moldm^{-3} AgNO_3$ until no more Ag_2CO_3 dissolves. Calculate the concentration of carbonate ions, $[CO_3{}^{2-}]$, in this solution.

$[CO_3{}^{2-}] =$
$moldm^{-3}$ [1]

(iv) An electrochemical cell is set up to measure the electrode potential, E, for the Ag+/Ag half-cell using the saturated Ag_2CO_3(aq) with a standard hydrogen electrode

Use the Data Booklet, your answer to (a)(ii), and the Nernst equation to calculate the electrode potential, E, for this Ag+/Ag half-cell.
E for Ag+/Ag half-cell = V [S]

(b) Silver chloride, AgCl, is sparingly soluble in water. The equation for the enthalpy change of solution is shown.

$AgCl(s) \rightarrow Ag^+(aq) + Cl^-(aq) \quad \Delta H^\ominus_{sol} = +65.5\ kJ\ mol^{-1}$

Standard entropies are shown in the table.

species	$AgCl(s)$	$Ag^+(aq)$	$Cl^-(aq)$
$S^\ominus / J K^{-1} mol^{-1}$	+96.2	+72.7	+56.5

(i) Calculate the standard entropy change of solution, ΔS^θ.

$\Delta S^\ominus =$ .... $JK^{-1}\ mol^{-1}$[1]

(ii) Explain, with the aid of a calculation, why AgCl is insoluble in water at 25°C.
You should use data from this question and your answer to (b)(i).

(ii) Explain, with the aid of a calculation, why AgCl is insoluble in water at 25°C. You should use data from this question and your answer to (b)(i).
[3] [Total: 10]

2) One method of producing hydrogen from natural gas is the reaction between hydrogen sulfide and methane.

$$2H_2S(g) + CH_4(g) \rightleftharpoons CS_2(g) + 4H_2(g)$$

(a) Write the expression for K_p for this reaction, and state its units
b) The initial partial pressures of the two gases in a mixture at 1000 K are recorded.

$H_2S(g)$ 200 atm $CH_4(g)$ 100 atm

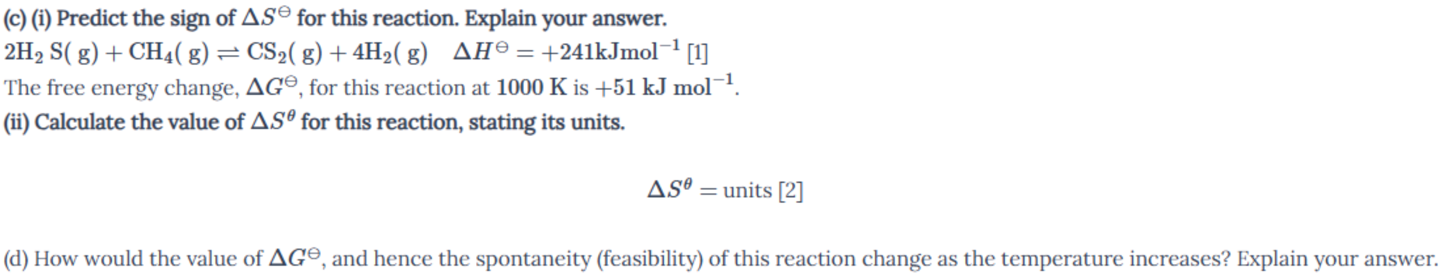
The mixture is left to reach equilibrium.

It is found that the equilibrium partial pressure of $CS_2(g)$ is 2 atm and that of the remaining $CH_4(g)$ is 98 atm.

(i) Calculate the equilibrium partial pressures of $H_2S(g)$ and H2(g).

ii) Calculate the value of Kp at this temperature.

3)



(c) (i) Predict the sign of $\Delta S^{\ominus}$ for this reaction. Explain your answer.

$2H_2S(g) + CH_4(g) \rightleftharpoons CS_2(g) + 4H_2(g) \quad \Delta H^{\ominus} = +241\,\text{kJmol}^{-1}$ [1]

The free energy change, $\Delta G^{\ominus}$, for this reaction at **1000 K** is **+51 kJ mol^{-1}**.

(ii) Calculate the value of ΔS^{θ} for this reaction, stating its units.

$\Delta S^{\theta} =$ units [2]

(d) How would the value of $\Delta G^{\ominus}$, and hence the spontaneity (feasibility) of this reaction change as the temperature increases? Explain your answer.

4) One method of producing hydrogen from natural gas is the reaction between hydrogen sulfide and methane.

$$2H_2S(g) + CH_4(g) \rightleftharpoons CS_2(g) + 4H_2(g)$$

(a) Write the expression for Kp for this reaction, and state its units.

(b) The initial partial pressures of the two gases in a mixture at 1000 K are recorded.

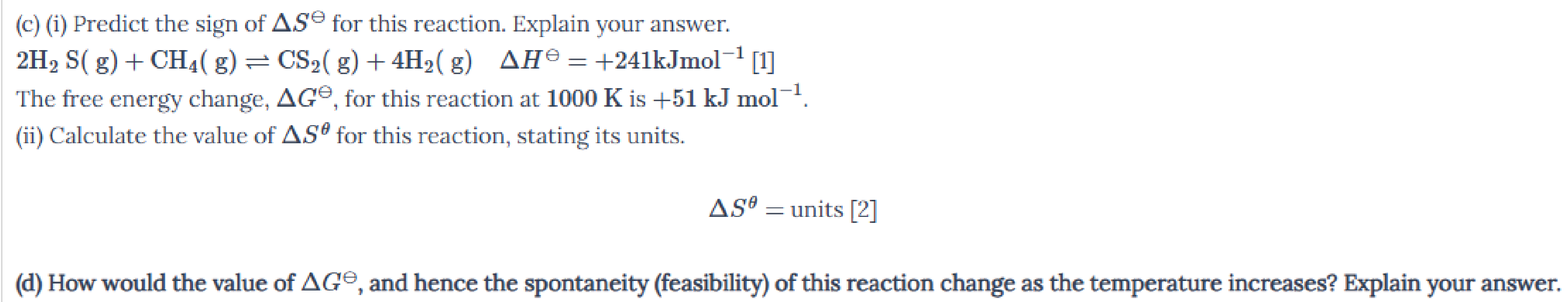
$H_2S(g)$ 200 atm $CH_4(g)$ 100 atm

The mixture is left to reach equilibrium.

It is found that the equilibrium partial pressure of $CS_2(g)$ is 2 atm and that of the remaining $CH_4(g)$ is 98 atm.

(i) Calculate the equilibrium partial pressures of $H_2S(g)$ and $H_2(g)$.

(ii) Calculate the value of Kp at this temperature.



(c) (i) Predict the sign of $\Delta S^{\ominus}$ for this reaction. Explain your answer.

$2H_2S(g) + CH_4(g) \rightleftharpoons CS_2(g) + 4H_2(g) \quad \Delta H^{\ominus} = +241\,\text{kJmol}^{-1}$ [1]

The free energy change, $\Delta G^{\ominus}$, for this reaction at **1000 K** is **+51 kJ mol^{-1}**.

(ii) Calculate the value of ΔS^{θ} for this reaction, stating its units.

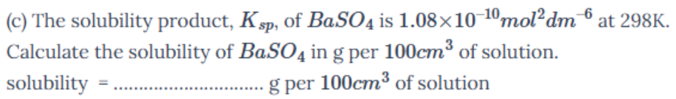
$\Delta S^{\theta} =$ units [2]

(d) How would the value of $\Delta G^{\ominus}$, and hence the spontaneity (feasibility) of this reaction change as the temperature increases? Explain your answer.

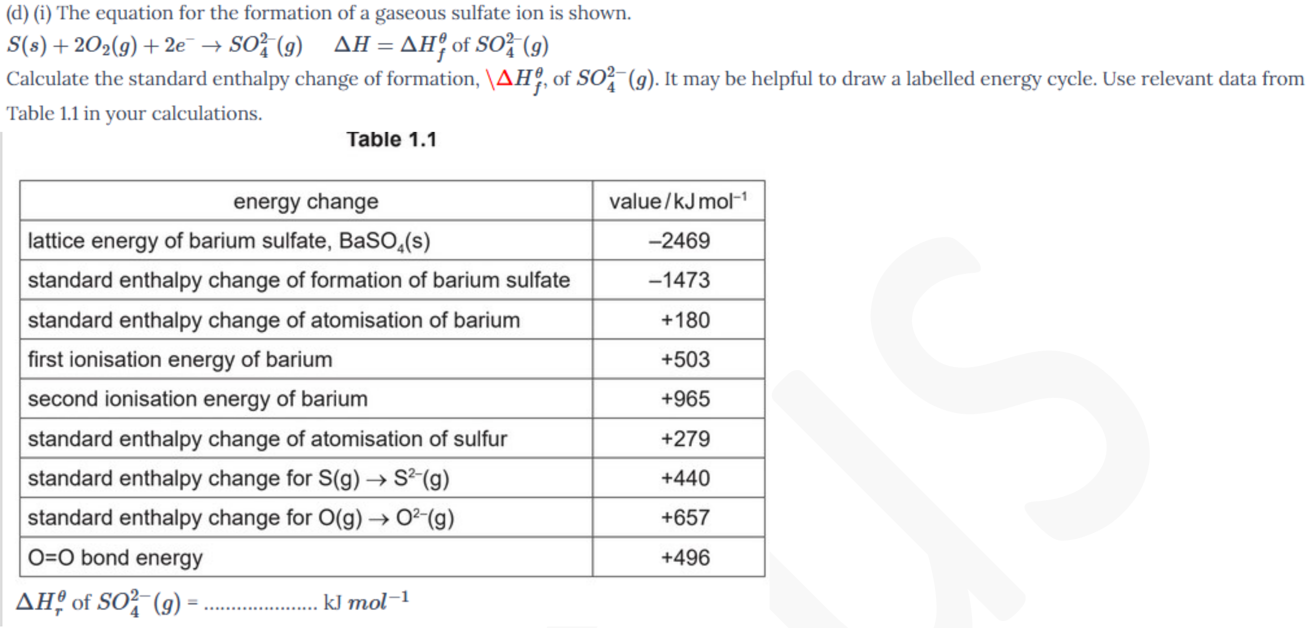
5) (a) The solubility of the Group 2 sulfates decreases down the group.

Explain this trend.

(b) Describe what is observed when magnesium and barium are reacted separately with an excess of dilute sulfuric acid.



(c) The solubility product, K_{sp}, of $BaSO_4$ is $1.08\times10^{-10}mol^2dm^{-6}$ at 298K.
Calculate the solubility of $BaSO_4$ in g per $100cm^3$ of solution.
solubility = ... g per $100cm^3$ of solution



(d) (i) The equation for the formation of a gaseous sulfate ion is shown.

$S(s) + 2O_2(g) + 2e^- \rightarrow SO_4^{2-}(g) \quad \Delta H = \Delta H_f^\theta$ of $SO_4^{2-}(g)$

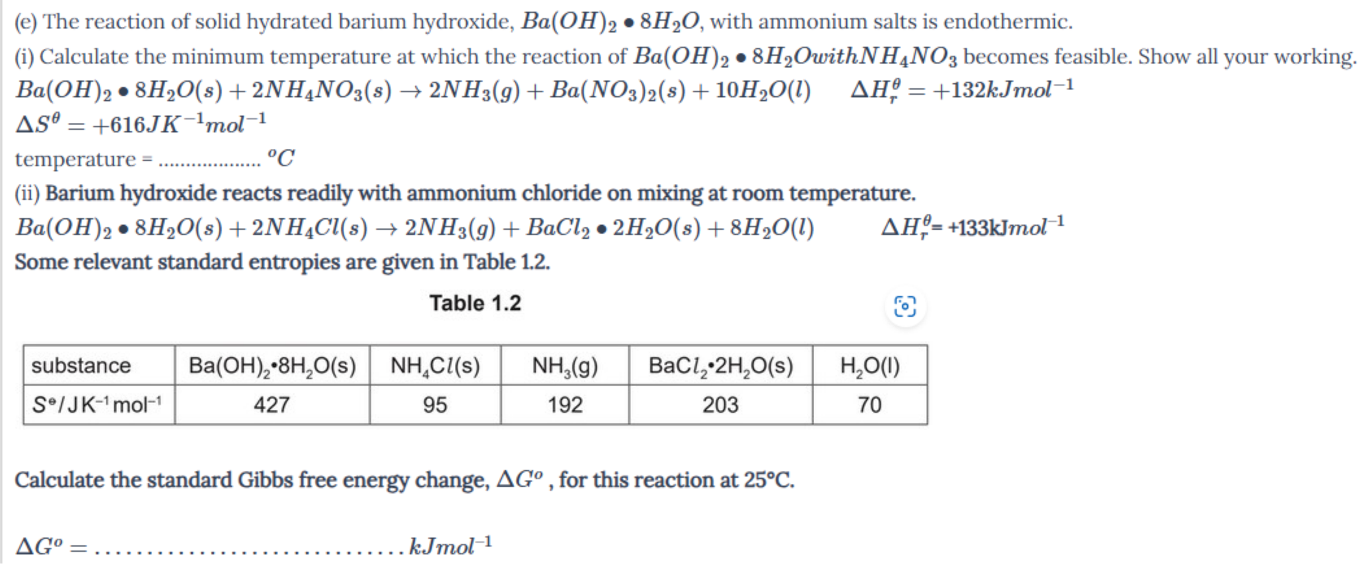
Calculate the standard enthalpy change of formation, \ ΔH_f^θ, of $SO_4^{2-}(g)$. It may be helpful to draw a labelled energy cycle. Use relevant data from Table 1.1 in your calculations.

Table 1.1

energy change	value / kJ mol^{-1}
lattice energy of barium sulfate, $BaSO_4(s)$	–2469
standard enthalpy change of formation of barium sulfate	–1473
standard enthalpy change of atomisation of barium	+180
first ionisation energy of barium	+503
second ionisation energy of barium	+965
standard enthalpy change of atomisation of sulfur	+279
standard enthalpy change for $S(g) \rightarrow S^{2-}(g)$	+440
standard enthalpy change for $O(g) \rightarrow O^{2-}(g)$	+657
O=O bond energy	+496

ΔH_r^θ of $SO_4^{2-}(g)$ = ... kJ mol^{-1}

(ii) Suggest how the lattice energy of $BaSO_4(s)$ differs from the lattice energy of $C_s2SO_4(s)$.
Explain your answer



(e) The reaction of solid hydrated barium hydroxide, $Ba(OH)_2 \bullet 8H_2O$, with ammonium salts is endothermic.

(i) Calculate the minimum temperature at which the reaction of $Ba(OH)_2 \bullet 8H_2O with NH_4NO_3$ becomes feasible. Show all your working.

$Ba(OH)_2 \bullet 8H_2O(s) + 2NH_4NO_3(s) \rightarrow 2NH_3(g) + Ba(NO_3)_2(s) + 10H_2O(l) \qquad \Delta H_r^\theta = +132kJmol^{-1}$

$\Delta S^\theta = +616JK^{-1}mol^{-1}$

temperature = ... ^oC

(ii) Barium hydroxide reacts readily with ammonium chloride on mixing at room temperature.

$Ba(OH)_2 \bullet 8H_2O(s) + 2NH_4Cl(s) \rightarrow 2NH_3(g) + BaCl_2 \bullet 2H_2O(s) + 8H_2O(l) \qquad \Delta H_r^\theta = +133kJmol^{-1}$

Some relevant standard entropies are given in Table 1.2.

Table 1.2

substance	$Ba(OH)_2\bullet8H_2O(s)$	$NH_4Cl(s)$	$NH_3(g)$	$BaCl_2\bullet2H_2O(s)$	$H_2O(l)$
S^θ / J K^{-1} mol^{-1}	427	95	192	203	70

Calculate the standard Gibbs free energy change, ΔG^o, for this reaction at 25°C.

$\Delta G^o = ...kJmol^{-1}$