

Reactivity 1.4 HL

IB CHEMISTRY HL

25 Mn Manganese 54.938045	16 S Sulfur 32.065	J	6 C Carbon 12.0107	2 He Helium 4.002602	25 Mn Manganese 54.938045
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Reactivity 1.4.1

Understandings:

- Entropy, S , is a measure of the dispersal or distribution of matter and/or energy in a system. The more ways the energy can be distributed, the higher the entropy.
- Under the same conditions, the entropy of a gas is greater than that of a liquid, which in turn is greater than that of a solid.

Learning outcomes:

- Predict whether a physical or chemical change will result in an increase or decrease in entropy of a system.
- Calculate standard entropy changes, ΔS^\ominus , from standard entropy values, S .

Additional notes:

- Standard entropy values are given in the data booklet.

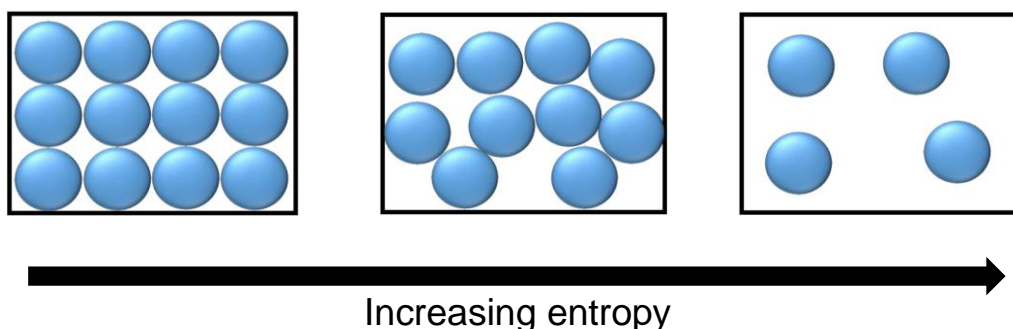
Linking questions:

- Structure 1.1 Why is the entropy of a perfect crystal at 0 K predicted to be zero?

Entropy (S)

- Entropy (S) refers to the distribution of available energy among the particles in a system.
- The more ways energy can be distributed, the greater the entropy.
- Gases have a higher entropy than liquids which have a higher entropy than solids.
- The table below has absolute entropy values for ice, liquid water and steam.
- The entropy increases from $\text{H}_2\text{O}(\text{s})$ to $\text{H}_2\text{O}(\text{g})$.

State of matter	Absolute entropy (S^\ominus) $\text{J K}^{-1} \text{mol}^{-1}$
$\text{H}_2\text{O}(\text{s})$	41.3
$\text{H}_2\text{O}(\text{l})$	70.0
$\text{H}_2\text{O}(\text{g})$	188



Predicting entropy changes

Factors that can change the entropy of a system include:

- changes in temperature
- changes of state (freezing, evaporating)
- dissolving (or crystallisation)
- changes in the amounts of gaseous reactants or products

Factors that increase entropy (positive entropy change, $+\Delta S$)

Dissolving	$\text{NaCl(s)} \rightarrow \text{Na}^{\text{(aq)}} \text{Cl}^{\text{(aq)}}$
Increase in mol of gas	$\text{CaCO}_3\text{(s)} \rightarrow \text{CaO(s)} + \text{CO}_2\text{(g)}$ $\text{C}_3\text{H}_8\text{(g)} + 5\text{O}_2\text{(g)} \rightarrow 3\text{CO}_2\text{(g)} + 4\text{H}_2\text{O(g)}$ $\text{CH}_4\text{(g)} + \text{H}_2\text{O(g)} \rightarrow 3\text{H}_2\text{(g)} + \text{CO(g)}$
Changes of state (melting, evaporation / boiling / vaporisation, sublimation)	$\text{H}_2\text{O(s)} \rightarrow \text{H}_2\text{O(l)}$

Factors that decrease entropy (negative entropy change, $-\Delta S$)

Crystallisation	$\text{Na}^{\text{(aq)}} \text{Cl}^{\text{(aq)}} \rightarrow \text{NaCl(s)}$
Decrease in mol of gas	$\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \rightleftharpoons 2\text{NH}_3\text{(g)}$ $\text{C}_2\text{H}_4\text{(g)} + \text{H}_2\text{(g)} \rightarrow \text{C}_2\text{H}_6\text{(g)}$ $2\text{Mg(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{MgO(s)}$
Changes of state (freezing, condensation, deposition)	$\text{H}_2\text{O(g)} \rightarrow \text{H}_2\text{O(l)}$

Exercise: Predict the entropy change in the following examples, giving a reason for your choice.

1. $\text{Br}_2\text{(l)} \rightarrow \text{Br}_2\text{(g)}$ Entropy increases ($+\Delta S$) because gases have higher entropy than liquids.
2. $\text{Na}_2\text{CO}_3\text{(s)} + 2\text{HCl(aq)} \rightarrow \text{CO}_2\text{(g)} + 2\text{NaCl(aq)} + \text{H}_2\text{O(l)}$ Entropy increases ($+\Delta S$) because of the increase in mol of gas ($\text{CO}_2\text{(g)}$ in products).
3. $\text{AgNO}_3\text{(aq)} + \text{NaCl(aq)} \rightarrow \text{AgCl(s)} + \text{NaNO}_3\text{(aq)}$ Entropy decreases ($-\Delta S$) because of the formation of AgCl(s) in products.
4. $\text{NH}_3\text{(g)} + \text{HCl(g)} \rightarrow \text{NH}_4\text{Cl(s)}$ Entropy decreases ($-\Delta S$) because of the decrease in mol of gas (2 mol of gas in reactants, 1 mol of solid in products).

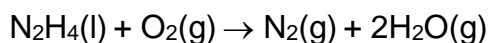
Standard entropy change (ΔS^\ominus)

- The standard entropy change of reaction (ΔS^\ominus) can be calculated using the equation:

$$\Delta S^\ominus = \sum S^\ominus_{\text{products}} - \sum S^\ominus_{\text{reactants}}$$

- A perfectly ordered crystal at zero kelvin has an entropy of zero.
- Absolute entropy values are always positive.

Example: Calculate the entropy change for this reaction:



Substance	S^\ominus ($\text{J K}^{-1} \text{mol}^{-1}$)
$\text{H}_2\text{O}(\text{g})$	188
$\text{O}_2(\text{g})$	205
$\text{N}_2(\text{g})$	192
$\text{N}_2\text{H}_4(\text{l})$	121

$$\Delta S^\ominus = (192 + 2 \times 188) - (205 + 121) = +242 \text{ J K}^{-1} \text{ mol}^{-1}$$

Exercises: Use the data in the table to answer the following questions.

Substance	S^\ominus ($\text{J K}^{-1} \text{mol}^{-1}$)	Substance	S^\ominus ($\text{J K}^{-1} \text{mol}^{-1}$)
$\text{H}_2\text{O}(\text{g})$	189	$\text{CO}_2(\text{g})$	214
$\text{H}_2\text{O}(\text{l})$	70	$\text{C}_3\text{H}_8(\text{g})$	270
$\text{H}_2(\text{g})$	131	$\text{O}_2(\text{g})$	205
$\text{Cl}_2(\text{g})$	223		
$\text{HCl}(\text{g})$	187		

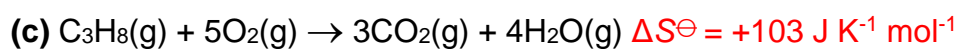
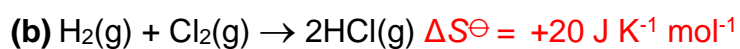
1. Predict the sign of ΔS^\ominus for the following reactions and explain your reasoning.

(a) $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$ **Negative ΔS^\ominus ; gases have higher entropy than liquids.**

(b) $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$ **Small change in entropy; same amount (in mol) of gas in reactants and products.**

(c) $\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$ **Positive ΔS^\ominus ; six moles of gas in reactants, seven moles of gas in products.**

2. Calculate ΔS^\ominus for the above reactions.



Spontaneity

- A spontaneous process is a process that occurs without adding energy (other than the energy required to overcome the energy barrier).



- According to the second law of thermodynamics, for a spontaneous process the change in entropy of the universe (ΔS_{total}) must be positive.

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

- For a spontaneous reaction $\Delta S_{\text{(total)}} > 0$.

Reactivity 1.4.2 and 1.4.3

Understandings:

- Change in Gibbs energy, ΔG , relates the energy that can be obtained from a chemical reaction to the change in enthalpy, ΔH , change in entropy, ΔS , and absolute temperature, T (1.4.2).
- At constant pressure, a change is spontaneous if the change in Gibbs energy, ΔG , is negative (1.4.2).
- Interpret the sign of ΔG calculated from thermodynamic data (1.4.3).
- Determine the temperature at which a reaction becomes spontaneous (1.4.3).

Learning outcomes:

- Apply the equation $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ to calculate unknown values of these terms (1.4.2).
- ΔG takes into account the direct entropy change resulting from the transformation of the chemicals and the indirect entropy change of the surroundings resulting from the transfer of heat energy (1.4.3).

Additional notes:

- Thermodynamic data values are given in the data booklet.
- Note the units: ΔH kJ mol⁻¹; ΔS J K⁻¹ mol⁻¹; ΔG kJ mol⁻¹.

Linking questions:

- Reactivity 3.2 How can electrochemical data also be used to predict the spontaneity of a reaction?

Gibbs free energy

- Gibbs free energy is the energy associated with a chemical reaction that can be used to do work.
- The Gibbs free energy change, ΔG , is negative for a spontaneous process and positive for a non-spontaneous process.
- The ΔG can be calculated using the following equation that is given in section one of the IB chemistry data booklet.

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

ΔG^\ominus – standard Gibbs free energy change (kJ mol^{-1})

ΔH^\ominus – change in enthalpy (kJ mol^{-1})

T – temperature in kelvin, K

ΔS^\ominus – change in entropy ($\text{J K}^{-1} \text{mol}^{-1}$)

Example: Calculate the ΔG , in kJ mol^{-1} , for this reaction at 500 K, using the data in the table. State and explain if the reaction is spontaneous at this temperature.



Compound	ΔH^\ominus (kJ mol^{-1})	S^\ominus ($\text{J K}^{-1} \text{mol}^{-1}$)
$\text{CaCO}_3(\text{s})$	-1207	92.9
$\text{CaO}(\text{s})$	-635	39.7
$\text{CO}_2(\text{g})$	-394	214

$$\Delta H = +178 \text{ kJ mol}^{-1}$$

$$\Delta S = +160.8 \text{ J K}^{-1} \text{mol}^{-1}$$

$$\Delta G = +178 - (500 \times 0.1608)$$

$$\Delta G = +97.6 \text{ kJ mol}^{-1}$$

Reaction is non-spontaneous at 500 K

Determine the temperature at which the reaction will be spontaneous.

$$<0 = +178 - (T \times 0.1608)$$

$$T = +178 \div 0.1608$$

$$T = \geq 1107 \text{ K}$$

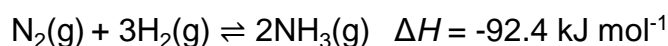
Exercises:

1. A reaction has a standard enthalpy change, ΔH^\ominus , of +10.00 kJ mol⁻¹ at 298 K. The standard entropy change, ΔS^\ominus , for the same reaction is +10.00 J K⁻¹ mol⁻¹. Calculate the value of ΔG^\ominus for the reaction in kJ mol⁻¹.

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus = 10000 - (298 \times 10.00) = 7020 \text{ J mol}^{-1}$$

$$\Delta G^\ominus = +7.02 \text{ kJ mol}^{-1}$$

2. Consider the following reaction:



- (a) The absolute entropy values, S , at 298 K for N₂(g), H₂(g) and NH₃(g) are 192, 131 and 193 J K⁻¹ mol⁻¹ respectively. Calculate the ΔS^\ominus for the reaction and explain the sign of ΔS^\ominus .

$$\Delta S^\ominus = [2 \times 193] - [192 + 3 \times 131] = -199 \text{ J K}^{-1} \text{ mol}^{-1}$$

ΔS^\ominus is negative; four moles of gas in reactants and two moles of gas in products.

- (b) Calculate ΔG^\ominus for the reaction at 298 K. State and explain whether the reaction is spontaneous.

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus = -92.4 - (298 \times -0.199) = -33.1 \text{ kJ mol}^{-1}$$

Reaction is spontaneous at 298 K (ΔG is negative).

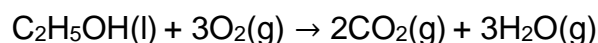
Standard change in Gibbs free energy (ΔG^\ominus)

- The standard change in Gibbs free energy (ΔG^\ominus) is the change in Gibbs free energy measured under standard conditions (298 K and 100 kPa).

$$\Delta G^\ominus = \sum \Delta G_{f^\ominus}^{\text{products}} - \sum \Delta G_{f^\ominus}^{\text{reactants}}$$

- ΔG_{f^\ominus} – the standard Gibbs free energy of formation is the change in Gibbs free energy when one mole of a compound is formed from its elements in their standard states under standard conditions (100 kPa and 298 K).

Example: Calculate the ΔG^\ominus for the following reaction. State and explain if the reaction is spontaneous at 298 K.



Compound	ΔG_{f^\ominus} (kJ mol ⁻¹)
C ₂ H ₅ OH(l)	-175
CO ₂ (g)	-394
H ₂ O(g)	-229

$$\Delta G^\ominus = (3 \times -229 + 2 \times -394) - (-175)$$

$$\Delta G^\ominus = -1300 \text{ kJ mol}^{-1}$$

Reaction is spontaneous at 298 K (ΔG^\ominus is negative).

The effect of ΔH , ΔS and T on the spontaneity of a chemical reaction

Exothermic reactions

ΔH	ΔS	T	ΔG	spontaneity
negative < 0	positive > 0	any temperature	Negative	Spontaneous

- ΔH is negative and ΔS is positive, therefore ΔG will be negative at any temperature.
- An exothermic reaction with an increase in entropy will be spontaneous at any temperature.

ΔH	ΔS	T	ΔG	spontaneity
negative < 0	negative < 0	high	Positive	Non-spontaneous

ΔH	ΔS	T	ΔG	spontaneity
negative < 0	negative < 0	low	Negative	Spontaneous

- ΔG will be negative only at low temperatures; at high T, $(T\Delta S)$ makes ΔG positive.

Endothermic reactions

ΔH	ΔS	T	ΔG	spontaneity
positive > 0	negative 0 <	any temperature	Positive	Non-spontaneous

- ΔH is positive and ΔS is negative, therefore ΔG will be positive at any temperature.
- An endothermic reaction with a decrease in entropy will be non-spontaneous at any temperature.

ΔH	ΔS	T	ΔG	spontaneity
positive > 0	positive > 0	high	Negative	Spontaneous

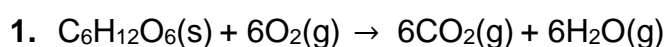
ΔH	ΔS	T	ΔG	spontaneity
positive > 0	positive > 0	low	Positive	Non-spontaneous

- ΔG will be negative only at high temperatures ($T\Delta S > \Delta H$); at low temperatures $\Delta H > T\Delta S$ ($+\Delta G$).

Summary:

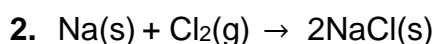
ΔS		
$\Delta H < 0 \quad \Delta S > 0$ Spontaneous at any temperature		$\Delta H > 0 \quad \Delta S > 0$ Spontaneous at high temperatures
		ΔH
$\Delta H < 0 \quad \Delta S < 0$ Spontaneous at low temperatures		$\Delta H > 0 \quad \Delta S < 0$ Non-spontaneous at any temperature

Exercise: Determine the spontaneity of the following reactions, giving a reason for your answer.



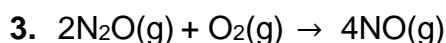
$$\Delta H < 0 \quad \Delta S > 0$$

Reaction is spontaneous at any temperature because reaction is exothermic with increase in entropy.



$$\Delta H < 0 \quad \Delta S < 0$$

Reaction is spontaneous at low temperatures because reaction is exothermic with decrease in entropy. Low temperatures mean that when the product of $T\Delta S$ is subtracted from the negative ΔH , ΔG will be negative.



$$\Delta H > 0 \quad \Delta S > 0$$

Reaction is spontaneous at high temperatures because reaction is endothermic with increase in entropy. High temperatures mean that when the product of $T\Delta S$ is subtracted from the positive ΔH , ΔG will be negative.

Reactivity 1.4.4

Understandings:

- As a reaction approaches equilibrium, ΔG becomes less negative and finally reaches zero.

Learning outcomes:

- Perform calculations using the equation $\Delta G = \Delta G^\ominus + RT \ln Q$ and its application to a system at equilibrium $\Delta G^\ominus = -RT \ln K$.

Additional notes:

- The equations are given in the data booklet.

Linking questions:

- Reactivity 2.3 What is the likely composition of an equilibrium mixture when ΔG^\ominus is positive?

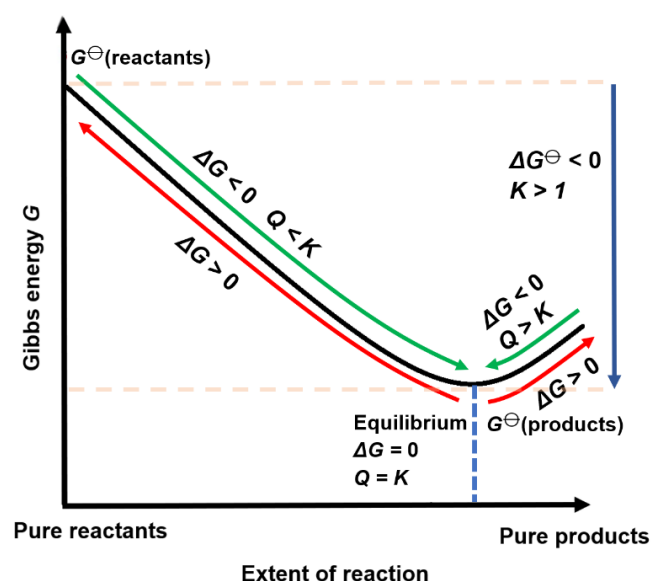
Gibbs free energy and equilibrium

- A system not at equilibrium (where $Q \neq K$) will proceed spontaneously in the direction necessary to reach equilibrium (where $Q = K$).
- As a reaction approaches equilibrium, the Gibbs free energy change, ΔG , becomes less negative and eventually reaches zero at equilibrium.
- The equilibrium position occurs where the free energy is at its minimum and entropy is at its maximum.

Plots of free energy against extent of reaction

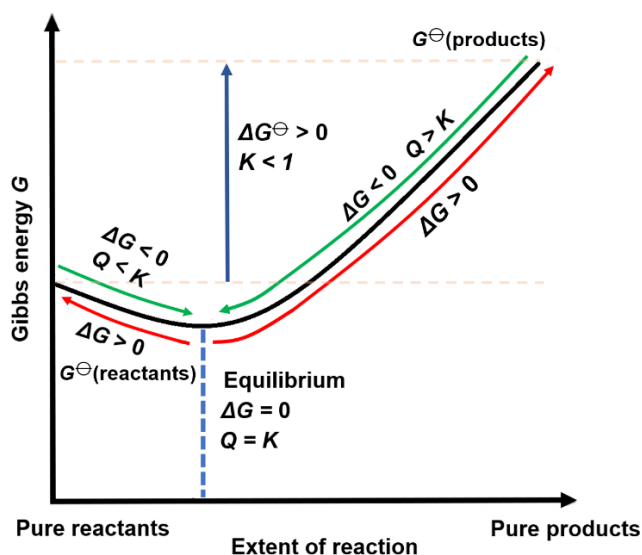
- The reaction proceeds spontaneously from either pure reactants or pure products to the equilibrium position where $\Delta G = 0$ and $Q = K$ (shown by the green arrows).
- The reaction away from the equilibrium position is non-spontaneous (shown by the red arrows).

Spontaneous reaction



For a spontaneous reaction, the equilibrium position lies further towards pure products meaning that at equilibrium $[\text{products}] > [\text{reactants}]$ and $K > 1$.
 $G^\ominus(\text{products}) < G^\ominus(\text{reactants})$ so $\Delta G^\ominus < 0$ (spontaneous).

Non-spontaneous reaction



For a non-spontaneous reaction, the equilibrium position lies further towards pure reactants meaning that at equilibrium $[\text{reactants}] > [\text{products}]$ and $K < 1$.
 $G^\ominus(\text{products}) > G^\ominus(\text{reactants})$ so $\Delta G^\ominus > 0$ (non-spontaneous).

ΔG at equilibrium

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

$$\Delta G = \Delta G^\ominus + RT \ln Q$$

$$\Delta G = -RT \ln K + RT \ln Q$$

$$\Delta G = RT \ln \frac{Q}{K}$$

- At equilibrium $Q = K$, therefore $\frac{Q}{K} = 1$

$$\Delta G = RT \ln(1)$$

$$\Delta G = 0$$

- At equilibrium $\Delta G = 0$, but ΔG^\ominus is not necessarily zero unless $K=1$.

Calculating ΔG for a reaction under non-standard conditions

- The ΔG for a reaction under non-standard conditions can be calculated using the equation shown which is given in section one of the IB chemistry data booklet.

$$\Delta G = \Delta G^\ominus + RT \ln Q$$

- ΔG^\ominus is the Gibbs free energy change under standard conditions.
- ΔG is the Gibbs free energy change under non-standard conditions.
- Q is the reaction quotient.

Exercise: A reaction has a ΔG^\ominus value of -142 kJ mol^{-1} and a Q value of 452. Calculate the ΔG for the reaction at 1455 K. Comment on the spontaneity of the reaction at this temperature and in which direction the reaction will proceed to reach equilibrium.

$$\Delta G = \Delta G^\ominus + RT \ln Q$$

$$\Delta G = -142 + 8.31 \times 1455 (\ln 452)$$

$$\Delta G = 73778 \text{ J mol}^{-1} = 73.8 \text{ kJ mol}^{-1}$$

Reaction is non-spontaneous and will proceed to the left to reach equilibrium.

ΔG , Q versus K and direction of reaction

- If a system is not at equilibrium, ΔG and Q can be used to tell us in which direction the reaction will proceed to reach equilibrium.
- For a spontaneous reaction, ΔG is negative, $Q < K$ and the reaction will proceed in the forward direction until equilibrium is reached.
- For a non-spontaneous reaction, ΔG is positive, $Q > K$ and the reaction will proceed in the reverse direction until equilibrium is reached.

Summary:

	ΔG	Q versus K	Direction of reaction
Spontaneous reaction	$\Delta G < 0$	$Q < K$	Reaction proceeds to right
Non-spontaneous reaction	$\Delta G > 0$	$Q > K$	Reaction proceeds to left
Reaction at equilibrium	$\Delta G = 0$	$Q = K$	No change

Relationship between ΔG^\ominus and K

- The relationship between ΔG^\ominus and K is given by the following equation which can be found in section one of the IB chemistry data booklet.
- In this equation, temperature is in kelvin and ΔG^\ominus in J mol^{-1} .
- R is the universal gas constant, $8.31 \text{ J K}^{-1} \text{ mol}^{-1}$.

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

- This equation can be rearranged to solve for K .

$$K = e^{-\frac{\Delta G}{RT}}$$

Exercises:

1. Calculate the value of K at 298 K for a reaction given that $\Delta G^\ominus = -33.0 \text{ kJ mol}^{-1}$

$$K = e^{-(-32960 \div (8.31 \times 298))}$$

$$K = e^{13.3}$$

$$K = 5.98 \times 10^5$$

2. Calculate the ΔG^\ominus for a reaction given that the K is 45.6 at 298 K.

$$\Delta G^\ominus = -8.31 \times 298 \times \ln 45.6$$

$$\Delta G^\ominus = -9.46 \text{ kJ mol}^{-1}$$

- The table below shows values of the ΔG^\ominus and K for some chemical reactions.

Reaction	ΔG^\ominus (kJ mol ⁻¹)	K
$2\text{SO}_3(\text{g}) \rightleftharpoons 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$	+141.7	1.4×10^{-25}
$\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$	+79.9	1.0×10^{-14}
$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$	-32.9	5.8×10^5
$\text{Zn}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu}(\text{s})$	-211	1.4×10^{37}

- Reactions that have a more positive ΔG^\ominus have a smaller K and reactions that have a more negative ΔG^\ominus have a larger K .
- For a spontaneous reaction, $K > 1$ and the equilibrium mixture will contain a higher concentration of products.
- For a non-spontaneous reaction, $K < 1$ and the equilibrium mixture will contain a higher concentration of reactants.

Summary:

Gibbs free energy change (ΔG^\ominus)	Equilibrium constant, K	Composition of equilibrium mixture
< 0 (negative)	> 1	Higher concentration of products
> 0 (positive)	< 1	Higher concentration of reactants
0	1	Neither reactants nor products favoured