

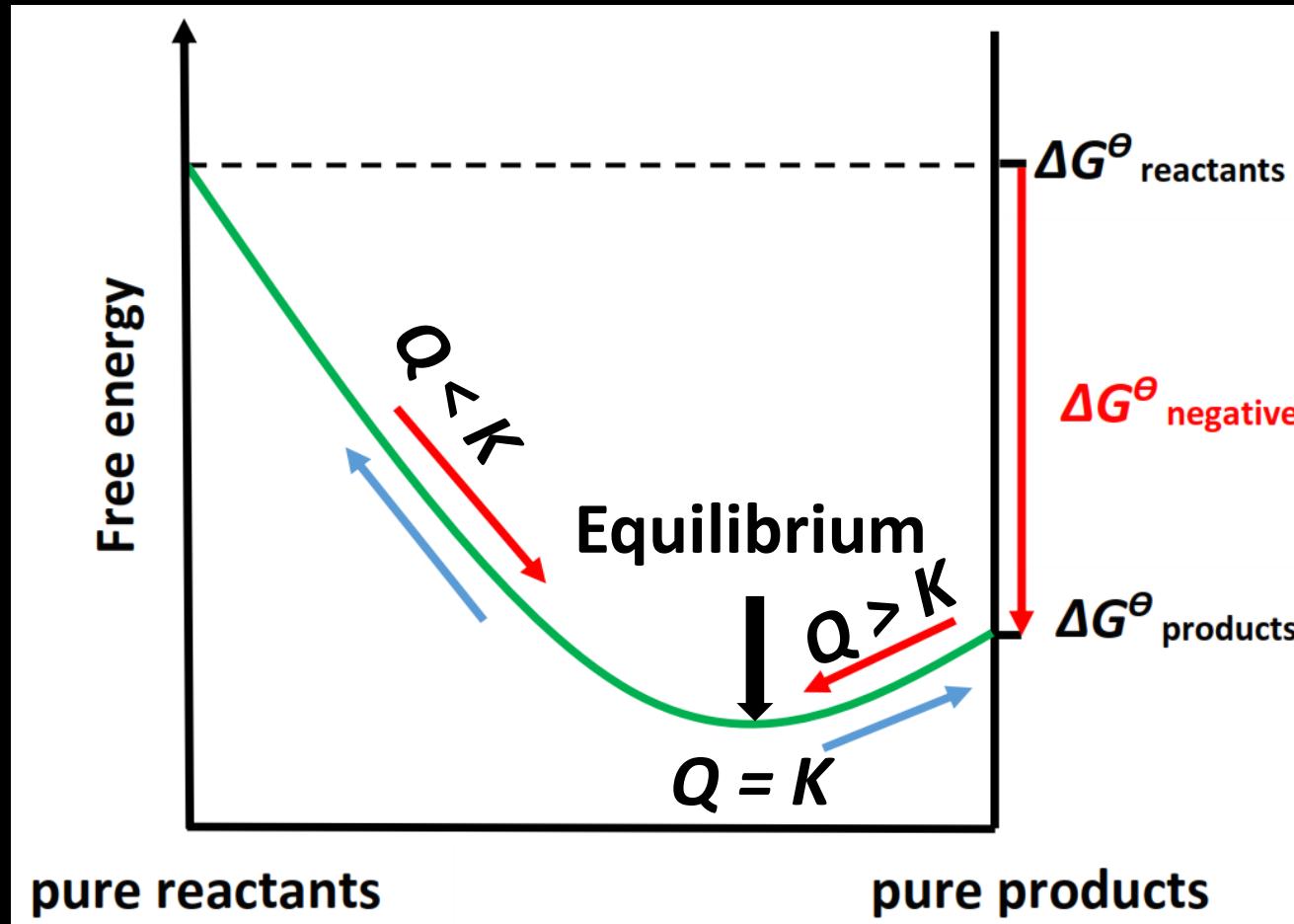
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Tutorials for IB Chemistry

**Gibbs free energy
and equilibrium**

This video will cover the following:

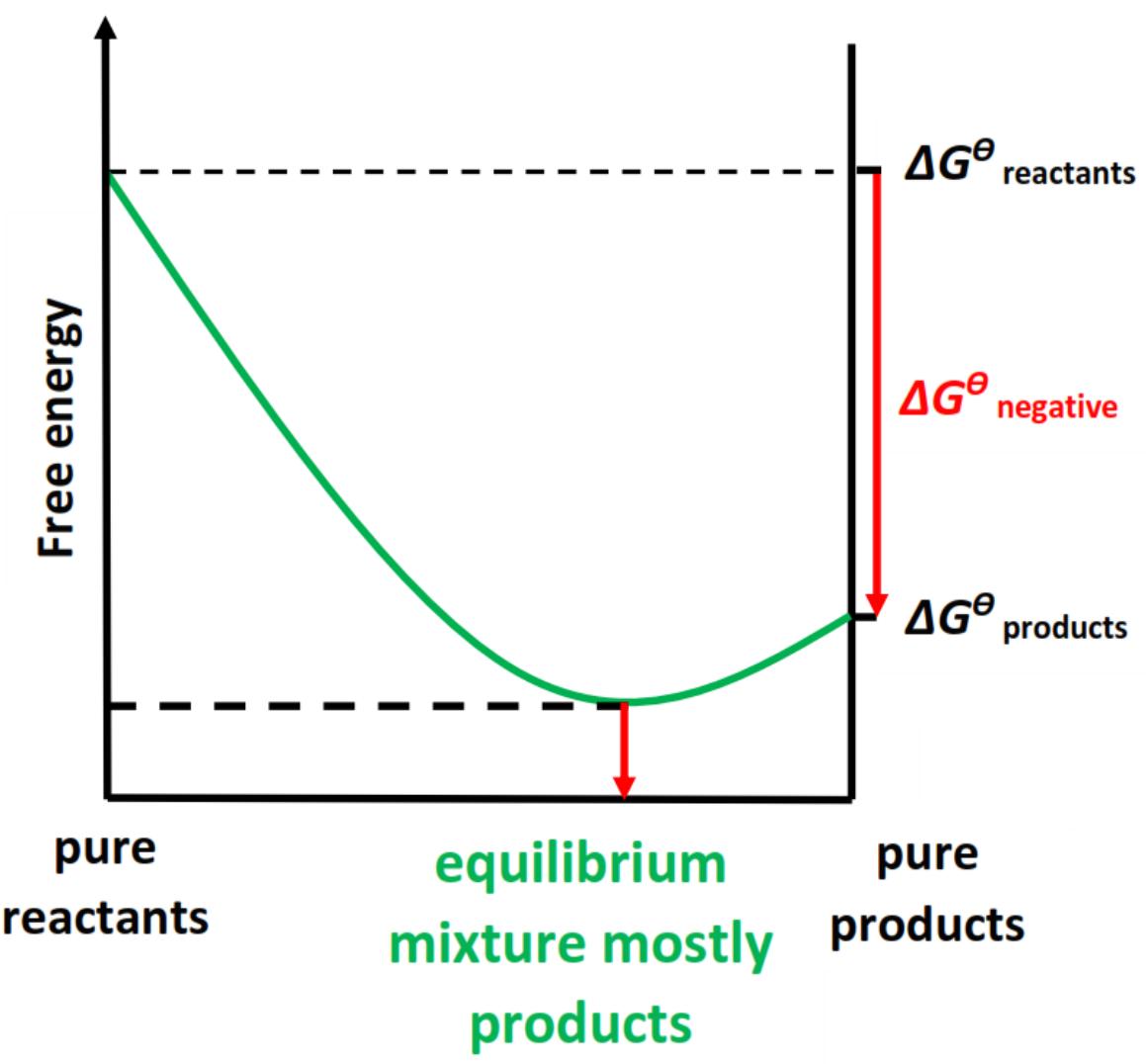
- how Gibbs free energy changes during the course of a reaction
- the relationship between the equilibrium constant, K , and the sign and magnitude of the ΔG°
- the value of ΔG at equilibrium



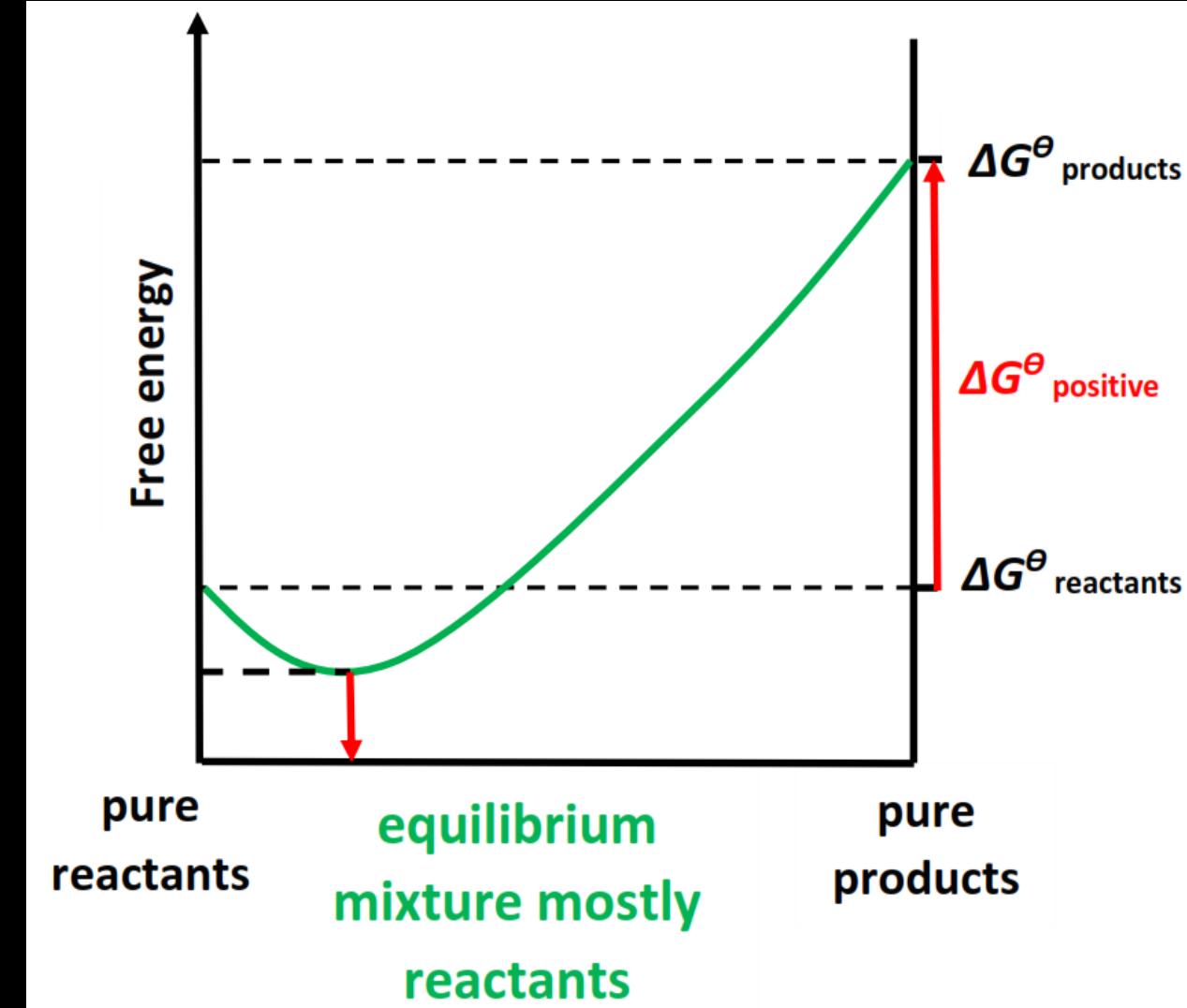
At the minimum value of Gibbs free energy, the reaction is at equilibrium.

The position of equilibrium corresponds to the maximum value of entropy.

Spontaneous reaction



Non-spontaneous reaction



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

ΔG° – standard Gibbs free energy change

R – universal gas constant ($8.31 \text{ J K}^{-1} \text{ mol}^{-1}$)

T – temperature in kelvin (K)

$\ln K$ – natural log of K

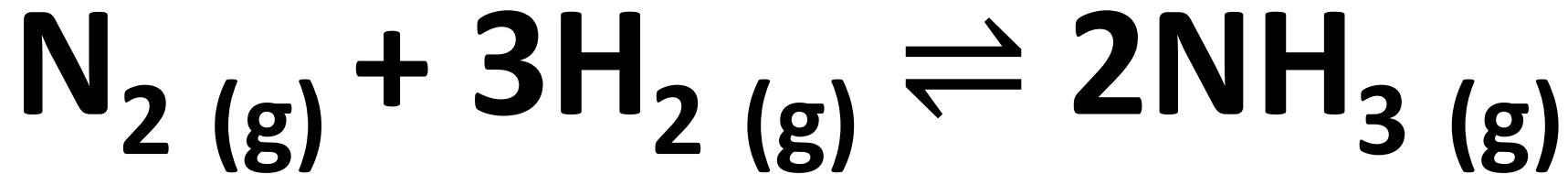
$$\Delta G^\Theta = -RT \ln K$$

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

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

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

Calculate the value of ΔG° at 298 K for the following reaction, given that the equilibrium constant, K , has a value of 5.8×10^5



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

Calculate the value of ΔG^\ominus at 298 K for the following reaction, given that the equilibrium constant, K , has a value of 5.8×10^5

$$\Delta G^\ominus = -8.31 \times 298 \times \ln 5.8 \times 10^5$$

$$\Delta G^\ominus = -32864 \text{ J mol}^{-1}$$

$$\Delta G^\ominus = -32.9 \text{ kJ mol}^{-1}$$

If the value of $K = 1$, then $\Delta G^\circ = \text{zero}$.

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

$$\Delta G^\circ = -RT \ln 1$$

$$\Delta G^\circ = 0$$

Gibbs free energy and equilibrium

Reaction (298 K)	ΔG^\ominus (kJ mol ⁻¹)	K
$2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$	+141.7	1.4×10^{-25}
$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$	+79.9	1.0×10^{-14}
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$	-32.9	5.8×10^5
$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$	-211	1.4×10^{37}

Standard Gibbs free energy change (ΔG^\ominus)	Equilibrium constant (K)	Equilibrium mixture
$\Delta G^\ominus < 0$ (negative)	$K > 1$	Equilibrium lies to the right - products favoured
$\Delta G^\ominus > 0$ (positive)	$K < 1$	Equilibrium lies to the left - reactants favoured
$\Delta G^\ominus = 0$	$K = 1$	neither reactants nor products favoured

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

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

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

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

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

Q/K	$\ln Q/K$	ΔG
<1	<0	negative – reaction will proceed to right
>1	>0	positive – reaction will proceed to left
1	0	zero – reaction is at equilibrium

At equilibrium, $Q = K$, therefore $Q/K = 1$

$$\Delta G = RT \ln \frac{Q}{K}$$
$$\Delta G = RT \ln 1$$

$$\Delta G = 0$$

At equilibrium, ΔG is zero.

A reaction at equilibrium has the minimum value of Gibbs free energy and a maximum value of entropy.

The ΔG° for a reaction can be calculated from the equilibrium constant, K , and vice versa.

The ΔG° also gives us information about the position of equilibrium for a reaction.

At equilibrium, ΔG for a reaction is zero.

The standard Gibbs free energy change (ΔG°) is the change in Gibbs free energy for a reaction under standard conditions.

A reaction carried out under standard conditions only has **one value for its ΔG°**

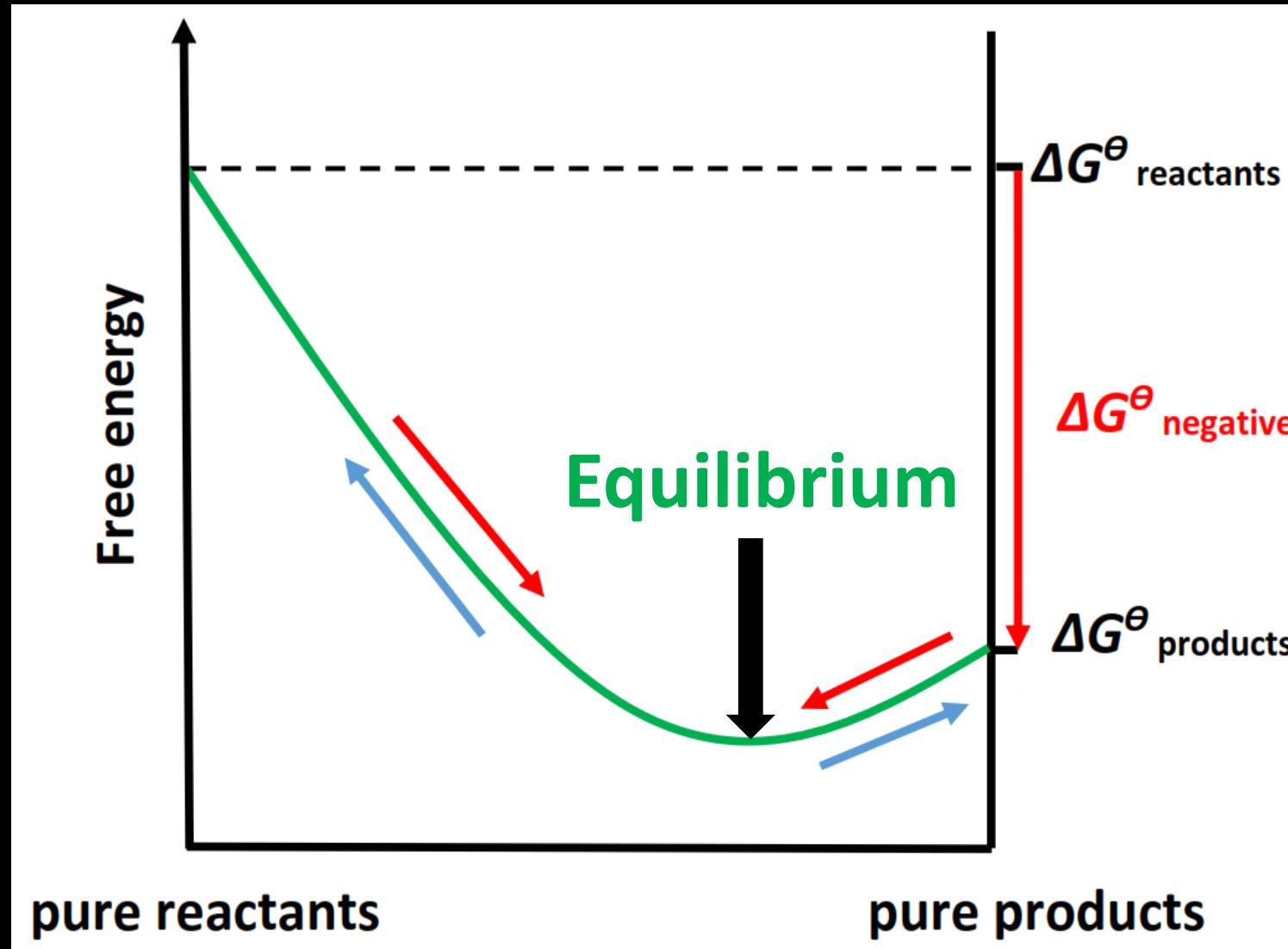
The Gibbs free energy change (ΔG) is the change in Gibbs free energy at any point in the reaction and can have an **infinite number of values**.

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**Gibbs free energy
and equilibrium**

Gibbs free energy and equilibrium



At the minimum value of Gibbs free energy, the reaction is at equilibrium.

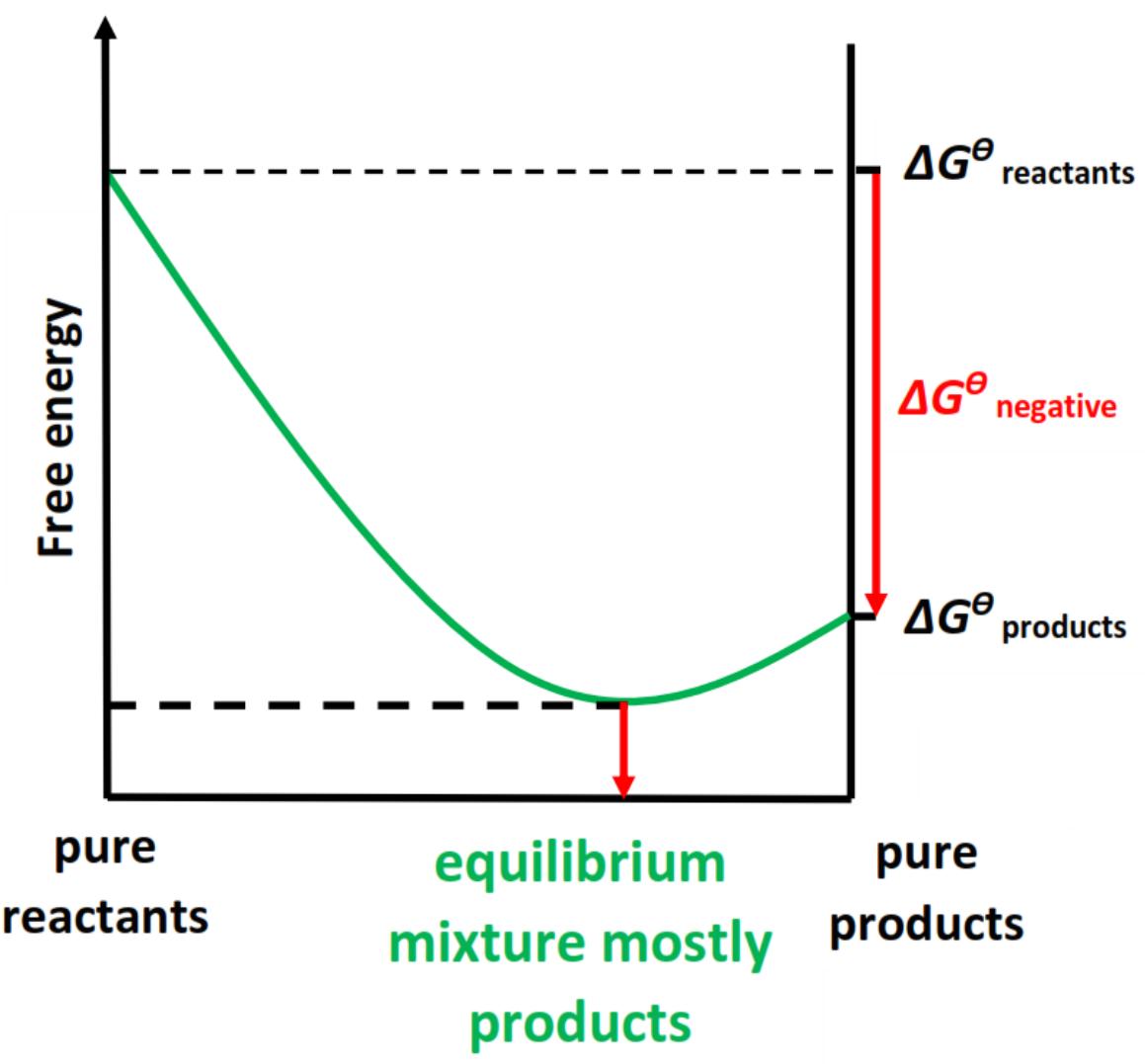
ΔG can be calculated at any point in a reaction using this equation:

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

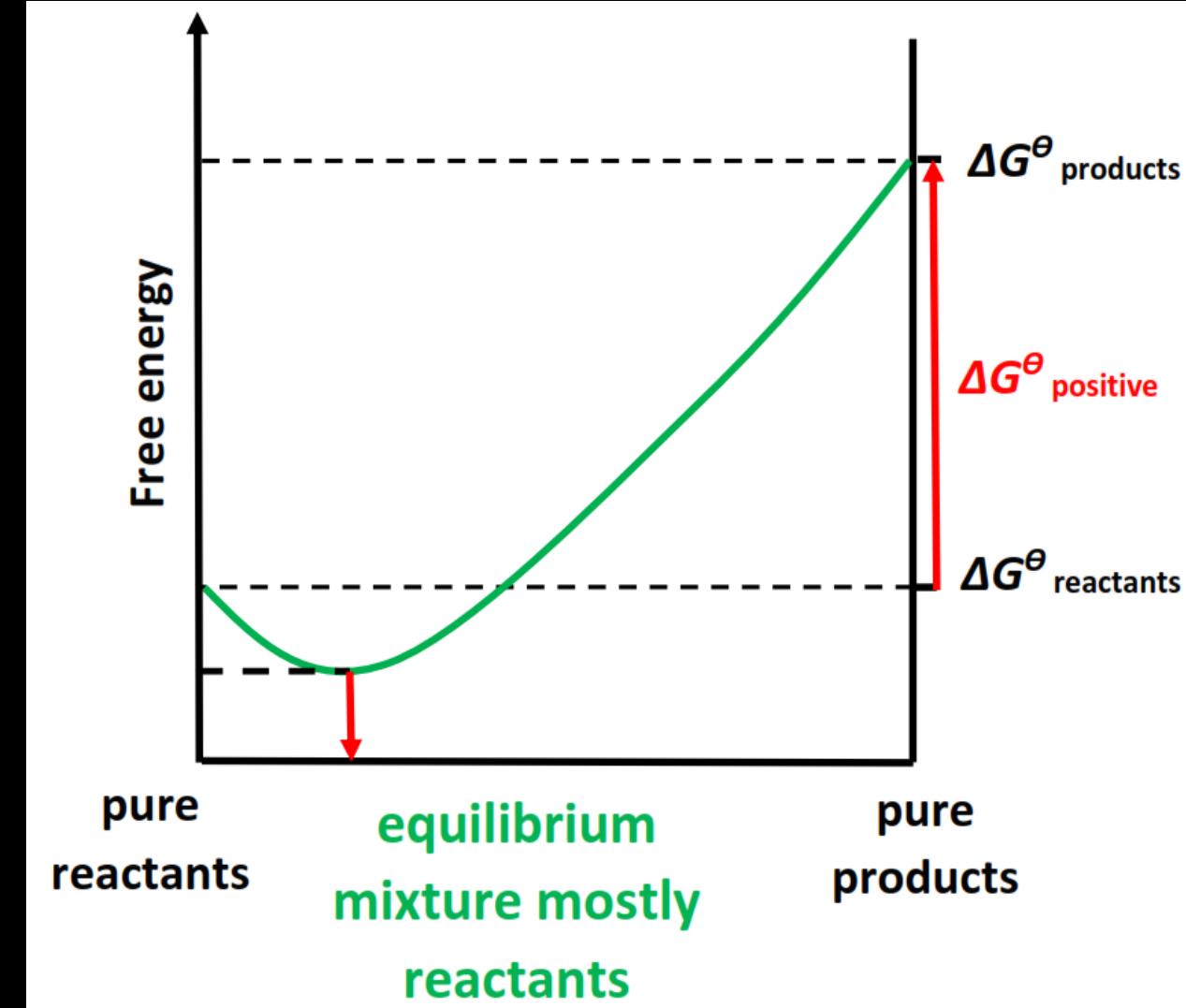
At equilibrium $\Delta G = 0$ and $Q = K$, therefore:

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

Spontaneous reaction



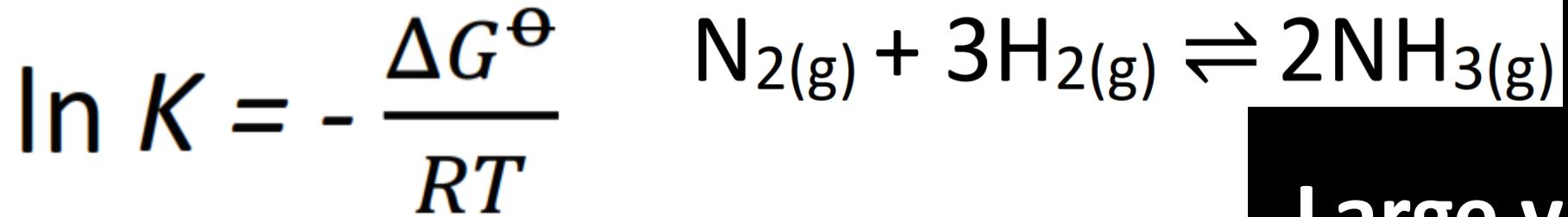
Non-spontaneous reaction



Gibbs free energy and equilibrium

Entropy and the second law of thermodynamics provide the key to understanding equilibrium. An isolated system, free from all other influences, may undergo various spontaneous changes, some of which will increase its entropy. If the total entropy *increases* during a process, as it usually does, the process is irreversible - it is impossible to return to the starting point, leaving no other traces, since that would require a decrease in the total entropy, which is impossible. Once the entropy has increased, it cannot decrease again. An isolated system therefore approaches a state in which the entropy has the highest possible value. This is a state of equilibrium. In equilibrium, the entropy of the system cannot increase (because it is already at a maximum) and it cannot decrease (because that would violate the second law of thermodynamics). The only changes allowed are those in which the entropy remains constant.

Calculate the value of K at 298 K for the following reaction given that $\Delta G^\ominus = -32.96 \text{ kJ mol}^{-1}$



$$\ln K = -\frac{-32960}{8.31 \times 298} = 13.3$$

$$K = e^{13.3}$$

$$K = 5.97 \times 10^5$$

Large value for K means the equilibrium lies to the right (favours the products) at 298 K.

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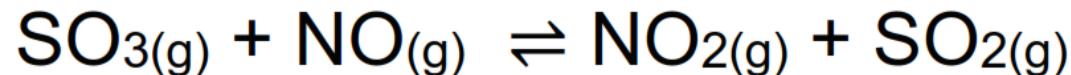
**Calculating equilibrium
concentrations from K_c and
initial concentrations**

Equilibrium law

The K_c for the following reaction is 6.78 at a certain temperature.

The initial concentrations of NO and SO_3 were both $0.0300 \text{ mol dm}^{-3}$

Calculate the equilibrium concentration of each reactant.



	$\text{SO}_3(\text{g})$	$\text{NO}(\text{g})$	$\text{NO}_2(\text{g})$	$\text{SO}_2(\text{g})$
Initial (mol dm^{-3})	0.0300	0.0300	0.00	0.00
Change (mol dm^{-3})	$-x$	$-x$	$+x$	$+x$
Equilibrium (mol dm^{-3})	$0.0300 - x$	$0.0300 - x$	x	x

Equilibrium law

$$K_c = \frac{[NO_2][SO_2]}{[SO_3][NO]} = \frac{x^2}{(0.0300-x)^2} = 6.78$$

Take the square root of both sides of the equation

$$2.60 = \frac{x}{0.0300-x}$$

$$x = \frac{0.078}{3.60} = 0.0217$$

Equilibrium law

$$[\text{SO}_3] = 0.0300 - 0.0217 = 0.00830 \text{ moldm}^{-3}$$

$$[\text{NO}] = 0.0300 - 0.0217 = 0.00830 \text{ moldm}^{-3}$$

$$[\text{NO}_2] = 0.0217 \text{ moldm}^{-3}$$

$$[\text{SO}_2] = 0.0217 \text{ moldm}^{-3}$$