VICTORIA JUNIOR COLLEGE

CHEMISTRY DEPARTMENT

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Chemical Equilibrium

LECTURE OUTLINE

1 Introduction
- 1.1 Concept of Dynamic Equilibrium
- 1.2 Irreversible Reactions
- 1.3 Reversible Reactions

2 Position of Equilibrium and Equilibrium Constants - K_c and K_p
- 2.1 Definition of Equilibrium constant, K_c
- 2.2 Types of reaction mixtures
- 2.2 Rules for writing K_c and K_p expressions
- 2.3 Equilibrium constant in terms of partial pressure, K_p
- 2.4 Significance of the Equilibrium Constants, K_c and K_p
- 2.5 Use of Le Chatelier's Principle

3 Factors affecting Position of Equilibrium
- 3.1 Effect of Concentration changes
- 3.2 Effect of Pressure changes
- 3.3 Effect of adding Inert gases
- 3.4 Effect of Temperature changes
- 3.5 Effect of Catalyst

4 Calculations involving equilibrium constants K_c and K_p

5 Industrial Application of LCP: The Haber Process

6 Standard Gibbs Free Energy and Position of Equilibrium

LECTURE SCHEDULE

Lecture no.	Lecture contents	Tutorial Qs
1	1.1 to 1.3; 2.1 to 2.3	1 & 2
2	2.4 to 2.5; 3.1 to 3.5	3 to 6
3	4, 5 & 6	7 to 10

REFERENCE TEXTS

1. A-level Chemistry by E.N. Ramsden
2. Chemistry in Action by Michael Freemantle

ASSESSMENT OBJECTIVES

H2

Candidates should be able to:

1. Explain, in terms of rates of the forward and reverse reactions, what is meant by a reversible reaction and dynamic equilibrium

2. State Le Chatelier's Principle and apply it to deduce qualitatively (from appropriate information) the effects of changes in concentration, pressure or temperature, on a system at equilibrium

3. Deduce whether changes in concentration, pressure or temperature or the presence of a catalyst affect the value of the equilibrium constant for a reaction

4. Deduce expressions for equilibrium constants in terms of concentrations, K_c, and partial pressures, K_p
   [Treatment of the relationship between K_p and K_c is not required]

5. Calculate the values of equilibrium constants in terms of concentrations or partial pressures from appropriate data

6. Calculate the quantities present at equilibrium, given appropriate data (such calculations will not require the solving of quadratic equations)

7. Show understanding that the position of equilibrium is dependent on the standard Gibbs free energy change of reaction, ΔG^θ
   [Quantitative treatment is not required]

8. Describe and explain the conditions used in the Haber process, as an example of the importance of an understanding of chemical equilibrium in the chemical industry

H1

Candidates should be able to:

1. Explain, in terms of rates of the forward and reverse reactions, what is meant by a reversible reaction and dynamic equilibrium

2. State Le Chatelier's Principle and apply it to deduce qualitatively (from appropriate information) the effects of changes in concentration, pressure or temperature, on a system at equilibrium

3. Deduce whether changes in concentration, pressure or temperature or the presence of a catalyst affect the value of the equilibrium constant for a reaction

4. Deduce expressions for equilibrium constants in terms of concentrations, K_c

5. Calculate the value of K_c in terms of concentrations from appropriate data

6. Calculate the quantities present at equilibrium, given appropriate data (such calculations will not require the solving of quadratic equations)

7. Describe and explain the conditions used in the Haber process, as an example of the importance of an understanding of chemical equilibrium in the chemical industry

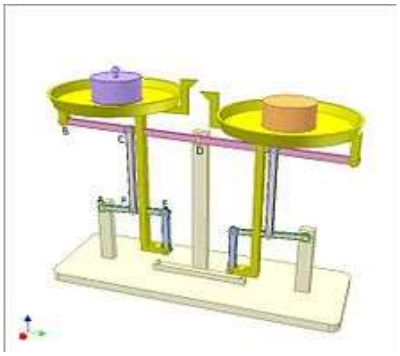
1 Introduction

LO: Explain, in terms of rates of the forward and reverse reactions, what is meant by a reversible reaction and dynamic equilibrium

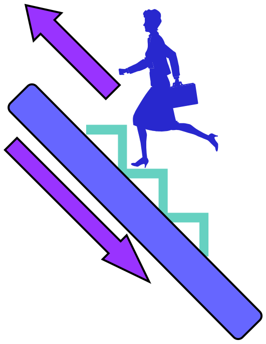
1.1 Concept of Dynamic Equilibrium

Static Equilibrium vs Dynamic Equilibrium

1. **Static** equilibrium is a state in which there is **no change** in **both macroscopic and microscopic** (molecular scale) properties in a system.
   E.g. two objects of equal mass on opposite sides of a balance.



static

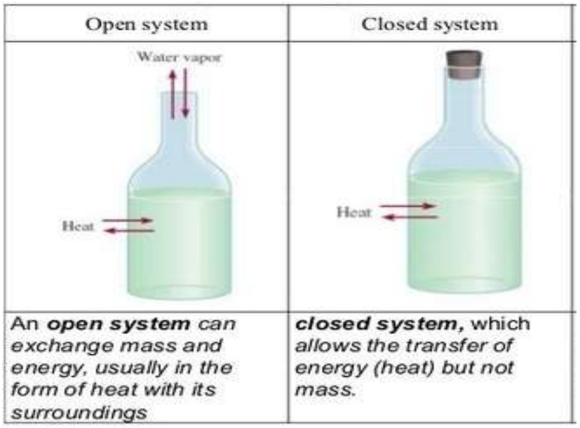


dynamic

2. On the other hand, for **dynamic** equilibrium, things are still happening. For example, the reactants are still **continually** forming products while the products are still **continually** forming reactants in a reversible reaction. This is why we say that the situation is **dynamic**. However, this cannot be deduced from observation as all macroscopic properties for a system at dynamic equilibrium are constant.

3. Dynamic equilibrium can only be achieved when the following 2 conditions are fulfilled:

   - The system is **closed, i.e.** one which does not allow matter to enter or leave but allows free transfer of energy.
   - The reaction is **reversible.**



Open system	Closed system
An ***open system*** *can exchange mass and energy, usually in the form of heat with its surroundings*	***closed system***, *which allows the transfer of energy (heat) but not mass.*

SLS QUIZ 1: True or false?

Questions	T or F
(1) When dynamic equilibrium is reached, both the forward and backward reactions stop and the composition of the equilibrium mixture remain unchanged.	
(2) When dynamic equilibrium is achieved, the concentrations of reactants are equal to the concentrations of products.	
(3) Dynamic equilibrium can be attained in both open and closed systems.	
(4) Dynamic equilibrium can only be attained if the reaction can take place in both directions (reversible).	
(5) Dynamic equilibrium is achieved when rate of forward reaction is the same as rate of backward reaction whereby there are no more changes to the concentration of both reactants and products.	

1.2 Irreversible Reactions

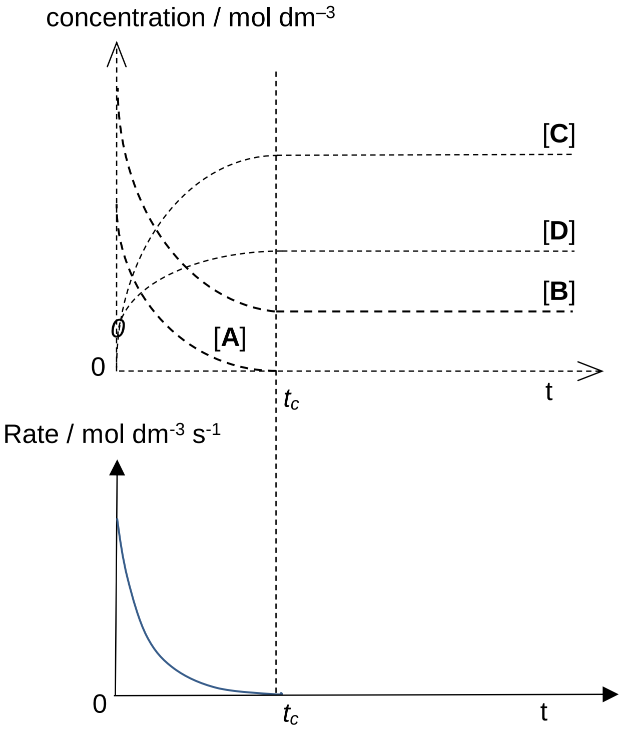
- Irreversible reactions are chemical reactions that proceed to **completion**. These chemical reactions take place in **one direction** almost exclusively and denoted by a **single–headed arrow** (→). The **limiting reagent** is **completely used up** in an irreversible reaction.

E.g. Burning of magnesium in air: $\mathbf{Mg(s) + O_2(g) \rightarrow 2MgO(s)}$

- Consider the **irreversible** reaction: $a\mathbf{A} + b\mathbf{B} \rightarrow c\mathbf{C} + d\mathbf{D}$

- t_c is time taken for the reaction to be completed.
- If **A** is the limiting reagent, **A** will be **consumed** at the end of the reaction, t_c
- [**B**], [**C**] and [**D**] remain **constant** after time t_c.

<u>Graph of Concentration against time</u>



SLS QUIZ 2: Fill in the blanks

1. Why does the curve plateau after t_c? Reaction has ……………..… because no more …..…. left.
2. Which reactant is present in excess? ……….……..
3. How does the rate of reaction change with time? Reaction rate ....with time until becoming …………….

1.3 Reversible Reactions

- Reversible reactions are reactions that proceed in **both the forward and backward directions** and denoted by a **double–headed arrow** ($\rightleftharpoons$). Reversible reactions are **incomplete** and reach a state of **dynamic equilibrium** containing a **mixture of both reactants and products**.

  E.g. Contact Process: $\mathbf{2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)}$

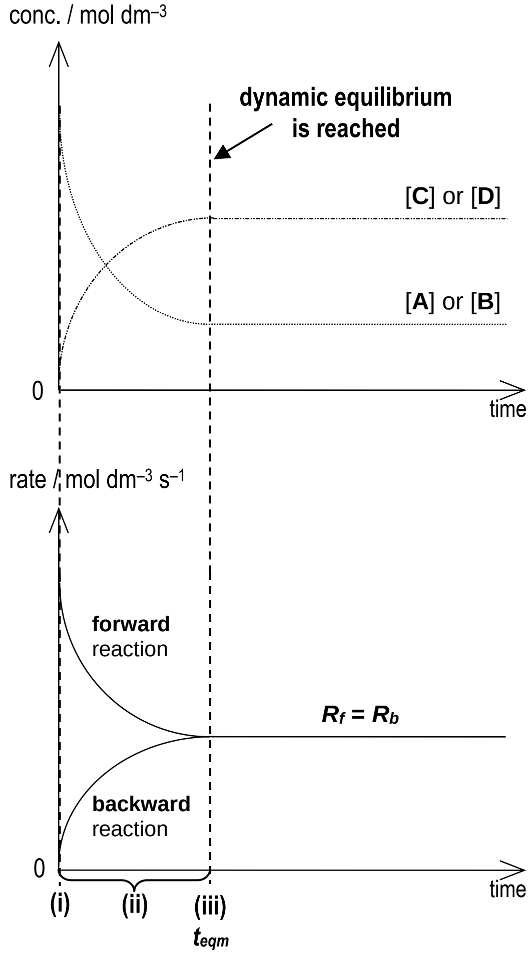
- **What is dynamic equilibrium?**

A state of **dynamic equilibrium** is said to have reached when **the rate of the forward reaction is <u>equal</u> to the rate of the backward reaction in a <u>reversible reaction</u>** and the concentrations of both reactants and products are **<u>constant</u>** (does not change).

➢ How is dynamic equilibrium achieved?

Consider the reversible reaction: $\mathbf{A + B \rightleftharpoons C + D}$

- At time = 0, the reactants **A** and **B** are allowed to mix in a **closed** container. The **forward reaction** occurs (i.e. from *left* to *right*) to form the products **C** and **D**.
- As **A** and **B** are turned into products, [**A**] and [**B**] **decreases** and rate of the forward reaction (R_f) **decreases.**
- Since **C** and **D** are formed, the **backward reaction** commences (i.e. from *right* to *left*) to form **A** and **B**. As [**C**] and [**D**] **increases** and so rate of the backward reaction (R_b) **increases.**
- At t_{eqm}, the forward and backward reactions are still occurring. The rate of **A** and **B** reacting to form **C** and **D** is **exactly equal** to the rate of **C** and **D** reacting to form **A** and **B**. A state of **<u>dynamic equilibrium</u>** is attained where $R_f = R_b$ = constant $\neq 0$.
- At this point, $[\mathbf{A}]_{eqm}$, $[\mathbf{B}]_{eqm}$, $[\mathbf{C}]_{eqm}$ and $[\mathbf{D}]_{eqm}$ become **constant**. In other words, **no net change** in the amount of reactants and products is observable.



- At equilibrium, the reaction is **incomplete** (i.e. not 100% conversion). In other words, **reactants** are still **present** in the system at equilibrium.

- Once equilibrium is reached, the system will **remain** in this state, until conditions (such as temperature, concentration or pressure) affecting the **rates of the forward and/or backward reactions** are introduced.

SLS QUIZ 3: Fill in the blanks

1. Why does the curve plateau after t_{eqm}? Reaction has reached a state of …………… ………………..
2. Which reactant is the limiting reagent? …………..
3. How does the rate of reaction change with time for a reversible reaction? Rate of forward reaction ....with time while rate of backward reaction …..……with time until both rates are …..….

2 Position of Equilibrium and Equilibrium Constants K_c and K_p

➢ What is Position of Equilibrium (POE)?

Consider this reversible reaction:

$$Cu^{2+}(aq) \quad + \quad 4Cl^{-}(aq) \quad \rightleftharpoons \quad CuCl_4^{2-}(aq) \quad + \quad 6H_2O(l)$$

Blue **Colourless** **Yellow**

A solution of Cu^{2+}(aq) is **blue** while a solution of $CuCl_4^{2-}$(aq) is **yellow**.

What would you expect to see when hydrochloric acid is add to Cu^{2+}(aq) followed by addition of water?

- The blue solution will turn ____________ when hydrochloric acid is added to it and it will turn __________ again when water is added to it.

Explain the observation.

- When HC*l* is added to the solution, the **forward** reaction between Cu^{2+} and Cl^{-} to form yellow $CuCl_4^{2-}$ will take place ***faster*** than the backward reaction.
- Hence, there will be an increase in the **proportion** of yellow $CuCl_4^{2-}$(aq) in the solution causing it to turn yellow.
- We can say that the **position of equilibrium (POE)** has shifted to the ________ when HC*l* is added to the solution. In other words, adding HC*l* *favours the forward reaction.*
- When water is added to the solution, the **backward** reaction between $CuCl_4^{2-}$ and water to form blue Cu^{2+} will take place **faster** than the forward reaction.
- Hence, there will be an increase in the **proportion** of blue Cu^{2+}(aq) in the solution causing it to turn blue again.
- We can say that the **position of equilibrium (POE)** has shifted to the _________ when water is added to the solution. In other words, adding H_2O *favours the backward reaction.*

➢ What is Reaction Quotient?

For a reversible reaction, the **ratio** of the concentrations of products to reactants raised to their stoichiometric coefficients in the balanced equation is known **Reaction quotient, Q_c**

Consider the reversible reaction:

$$mA(aq) \; + \; nB(aq) \; \rightleftharpoons \; pC(aq) \; + \; qD(aq)$$

Reaction quotient, $Q_c = \dfrac{[C]^p[D]^q}{[A]^m[B]^n}$

where [**X**] is the **concentration** of **X** in mol dm^{-3} at **any given time**.

Q_c is NOT constant; it changes with time until the reaction reaches equilibrium.

- **What is Equilibrium Constant?**
  At equilibrium (t = t_{eqm}), rate of forward reaction **equals** rate of backward reaction, and so concentration of both reactants and products are **constant**, and hence $\mathbf{Q_c}$ will be a constant, known as **Equilibrium Constant**, denoted by symbol $\mathbf{K_c}$.
  In other words, when the reaction is at equilibrium, $\mathbf{Q_c = K_c}$

  This is the law of equilibrium

  At equilibrium, $Q_c = \dfrac{[\mathrm{C}]^p[\mathrm{D}]^q}{[\mathrm{A}]^m[\mathrm{B}]^n} = K_c$

  When the reaction is not at equilibrium: $\mathbf{Q_c \neq K_c}$

- This **mathematical expression of** $\mathbf{K_c}$ relates the concentration of the species present in an equilibrium mixture and the $\mathbf{K_c}$ value can be found through experiments.

- The equilibrium constant, $\mathbf{K_c}$, for a reaction measures the **extent** to which reactants are converted to products at equilibrium at a given temperature.

- A reaction with a **higher** $\mathbf{K_c}$ value will contain a **higher** proportion of **products** relative to **reactants** in the equilibrium mixture compared with another reaction with a **lower** $\mathbf{K_c}$ value.

- The equilibrium constant, $\mathbf{K_c}$, is a **constant** value at a **given temperature.**

- The **units for** $\mathbf{K_c}$ is dependent on the balanced chemical equation of interest.

2.1 Definition of Equilibrium Constant

Here is the definition of equilibrium constant:

Consider the reversible reaction:

$$m\mathrm{A(aq)} + n\mathrm{B(aq)} \rightleftharpoons p\mathrm{C(aq)} + q\mathrm{D(aq)}$$

Equilibrium constant, $K_c = \dfrac{[\mathrm{C}]^p_{\mathrm{eqm}}[\mathrm{D}]^q_{\mathrm{eqm}}}{[\mathrm{A}]^m_{\mathrm{eqm}}[\mathrm{B}]^n_{\mathrm{eqm}}}$

where $[\mathbf{X}]_{\mathrm{eqm}}$ is the **concentration** of **X** in **mol dm^{-3}** in the equilibrium mixture.

Unit of K_c = **(mol dm^{-3})$^{(p+q)-(m+n)}$**

Only temperature can change the K_c value of a given reaction.

2.2 Types of reaction mixtures

- **Homogeneous mixtures**

The reaction mixtures contain reactants and products in the **same** phase or physical states:

E.g. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

E.g. $CH_3CO_2H(l) + CH_3OH(l) \rightleftharpoons CH_3CO_2CH_3(l) + H_2O(l)$

- **Heterogeneous mixtures**

The reaction mixtures contain reactants and product in **different** phases or physical states:

E.g. $I_2(s) \rightleftharpoons I_2(g)$

E.g. $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

E.g. $Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$

Rules for writing K_c and K_p expressions

The followings are **excluded** from the **K_c and K_p expressions**:

a) **Concentration of pure solids**
Exclude solids in **all** equilibrium expressions for all mixture because **concentration** of pure solids which are just their densities are **constants** and **independent** on the **mass of solid present.**
E.g.: $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$$K_c = [CO_2(g)] \quad \text{mol dm}^{-3}$$

b) **Concentration of pure liquids**
Exclude pure liquids in equilibrium expressions for **heterogeneous** equilibria because concentrations of pure liquids calculated from their densities are **constants** in heterogeneous mixtures.

E.g.: $2HBr(g) \rightleftharpoons H_2(g) + Br_2(l)$

$$K_c = \frac{[H_2]}{[HBr]^2} \quad \text{mol}^{-1}\text{ dm}^{3}$$

c) **Concentration of solvents**
Exclude solvents in **all** equilibrium expressions as they are present in ***excess*** so their concentrations are relatively constants. In addition, being pure liquids, their concentrations calculated from their densities would be **constant.**

SLS QUIZ 4: **Yes or No**

Physical state of species	Heterogeneous mixtures	Homogeneous mixtures
Solid		
Liquid		
Gaseous		
Aqueous **(solvent is H_2O)**		

2.3 Equilibrium Constant in terms of Partial Pressures, K_p [for H2 only]

1. The equilibrium constant can also be defined in terms of **partial pressures,** K_p
2. The use of K_p is only useful for systems involving **gases**.
3. For a reversible gaseous system in dynamic equilibrium:

$$A(g) + nB(g) \rightleftharpoons qC(g)$$

equilibrium constant, $K_p = \dfrac{p_C^q}{p_A^m p_B^n}$; unit of K_p = (Pa or atm)$^{q-(m+n)}$

where p_Z is the **<u>equilibrium</u> partial pressure** of gas **Z** in Pa, kPa or atm.

[Recall: $p_A = \dfrac{n_A}{n_T} \times p_T$ and Dalton's Law of Partial Pressure $p_T = p_A + p_B + \ldots$]

4. The equilibrium constant, K_p, is a **<u>constant</u>** value at a **<u>given temperature</u>.**
5. The **units for K_p** are dependent on the balanced chemical equation of interest.

E.g.: $2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$

$$K_p = \frac{p_{H_2} p_{Br_2}}{p2_{HBr}} \quad \text{(no units)}$$

__Exercise__

Write down the equilibrium constant expressions and their units for the following:

	Equation	K_c (or K_p)	Unit for K_c (or K_p)
(a)	$I_2(aq) + 2Fe^{2+}(aq) \rightleftharpoons 2I^-(aq) + 2Fe^{3+}(aq)$	K_c =	
(b)	$BiCl_3(aq) + H_2O(l) \rightleftharpoons BiClO(s) + 2HCl(aq)$	K_c =	
(c)	$CH_3CO_2CH_2CH_3(l) + H_2O(l)$ $\rightleftharpoons CH_3CO_2H(l) + CH_3CH_2OH(l)$	K_c =	
[For H2 only]			
(d)	$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$	K_p =	

Enrichment: Relationship between K_c and K_p [Not in syllabus]

- For ideal gases, $pV = nRT$

  Concentration of a gas: $\frac{n}{V} = \frac{p}{RT}$

- Consider a reversible reaction: $a\text{A(g)} + b\text{B(g)} \rightleftharpoons c\text{C(g)} + d\text{D(g)}$

$$K_c = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b} = \frac{\left(\frac{p_C}{RT}\right)^c\left(\frac{p_D}{RT}\right)^d}{\left(\frac{p_A}{RT}\right)^a\left(\frac{p_B}{RT}\right)^b} = \frac{p_C{}^c p_D{}^d}{p_A{}^a p_B{}^b}(RT)^{(a+b)-(c+d)} = K_p \times (RT)^{(a+b)-(c+d)}$$

2.4 Significance of the Equilibrium Constants, K_c or K_p

- As K_c (or K_p) is sensitive to the stoichiometric coefficients of the chemical equation, it must be accompanied by the chemical equation of interest.
- Units of K_c and K_p vary and should always be stated (unless otherwise stated).
- K_c (or K_p) is **constant** only when **temperature remains <u>constant</u>**. It varies with temperature.
- The **value of K_c (or K_p)** indicates the **<u>extent</u>** of the forward reaction at equilibrium at a given temperature.
  - If K_c is **<u>large</u>** (eg.10^5) ⇒ conversion of reactants to products would be high i.e. forward reaction is almost complete.
  - If K_c is **<u>small</u>** (eg.10^{-5}) ⇒ conversion of reactants to products would be low i.e. forward reaction does not proceed to any appreciable extent.
- The value of K_c (or K_p) is **<u>unaffected</u> by changes in the concentrations or pressure of either reactants or products**. K_c (or K_p) value is affected by temperature only.

2.5 Use of Le Chatelier's Principle (LCP)

LO: State Le Chatelier's Principle and apply it to deduce qualitatively (from appropriate information) the effects of changes in concentration, pressure or temperature, on a system at equilibrium

- Le Chatelier's Principle states that when a system **at equilibrium** is **disturbed,** the system will **counteract** by **shifting its position of equilibrium** in a direction that will **reduce** that disturbance in order to **re-establish** the equilibrium.
- These disturbances could be changes in concentration, partial pressure, temperature or the use of a catalyst.

3 Factors affecting Position of Equilibrium of Reversible reactions

3.1 Effect of Concentration changes

- If a substance is **added** to a system (i.e. its concentration increases) at equilibrium, the system will adjust itself so as to **remove** the substance added.

- If a substance is **removed** from a system (i.e. its concentration decreases) at equilibrium, the system will adjust itself so as to **replace** the substance removed.

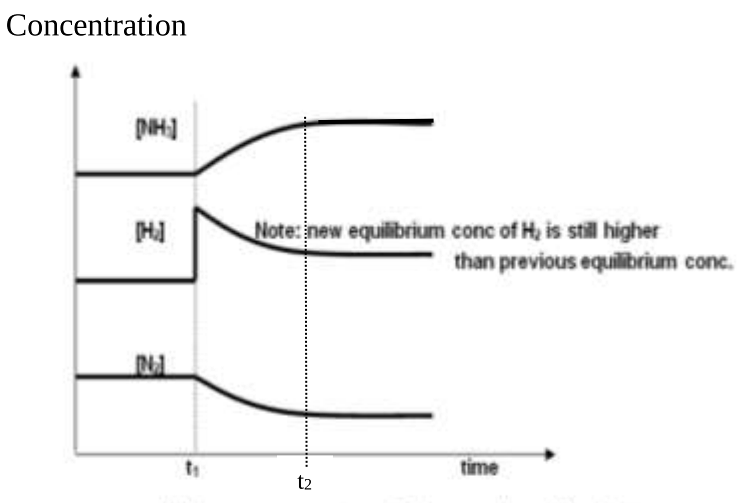
E.g. For $\mathbf{N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)}$, predict what happens if more H_2 is introduced.

<u>Prediction using LCP</u>:

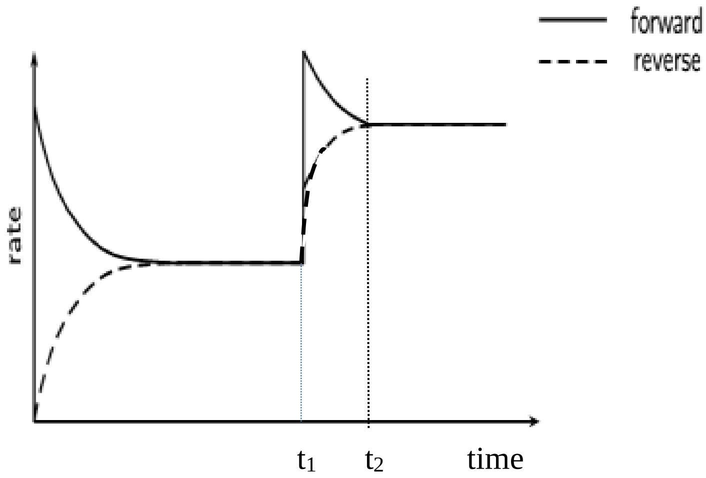
- By Le Chatelier's Principle, the system will **counteract** the increase in amount of H_2 by favouring the **forward** reaction, so the position of equilibrium will shift to the **right**.
- In the new equilibrium mixture, the concentration of NH_3 and H_2 would be **higher** than the previous one, while that of N_2 would be **lower** than the previous one (see graph below).

<u>Effect on rates of forward and backward reactions</u>:

- When more H_2 is added (i.e. $[H_2]$ increases) at t_1 (see graph below), the system will **adjust to reduce** the concentration of H_2.
- Rate of forward reaction will i**ncrease** leading to formation of more NH_3.
- The forward rate will then start to **decrease** while the backward rate starts to **increase** with time until both are **equal** again. At this stage, the system is said to have re-established its equilibrium (refer to t_1 in the graph)
- Position of equilibrium is said to have shifted to the **RIGHT**.



conc of H_2 increase at time t_1 equilibrium position shifts right



- New equilibrium $[H_2]$ is still **higher** than the initial equilibrium $[H_2]$.
- The new equilibrium mixture will contain **more** H_2 and NH_3 but **less** N_2.
- There is **no change** to the value of K_c.

WHY?

- When the system is **at equilibrium**, $Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = K_c$
- Adding H_2 will cause $[H_2]$ to increase, so value of Q_c will drop at the start.
  $\Rightarrow Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3} < K_c$, the system is no longer at equilibrium
- At the same time, forward rate will spike, causing more N_2 to react and more NH_3 formed.
- $[N_2]$ will start to decrease while $[NH_3]$ will start to increase. Hence, Q_c will start to increase until it is equal to the K_c value again.
- When H_2 is added, forward rate will spike and then drop as concentration of H_2 and N_2 start to fall. Backward rate will increase as concentration of NH_3 start to increase. The system will re-establish its equilibrium when the forward rate and backward rate are the same again. At this stage, value of Q_c is equal to the value of K_c.
- Hence changes in concentration of species will not change K_c value.

1.2 Effect of changes in Partial Pressure of gases

Since pressure has a **negligible** effect on the volumes of **solids and liquids**, pressure changes only affect those reactions in which **gases** are involved.

- A change in **partial pressure** of gases in the reaction will affect position of equilibrium in the **same way** as concentration changes as they are **directly proportional** to each other.
- For gas A, $p_A V = n_A RT \Rightarrow p_A = \frac{n_A}{V} RT = [A] \times RT$

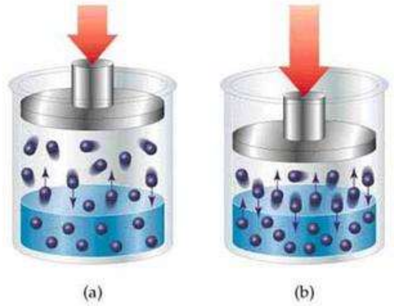
  Hence, $p_A \propto [A]$
  ⇨ Effect of changing partial pressure of A on POE is the same as changing concentration of A.
- There are **2 ways** to change the partial pressure of gases:

(i) Adding or removing any of the gaseous components at constant temperature

Eg 1: For $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, predict what happens if some NH_3 is removed.

Prediction using LCP:
- Removal of some NH_3 will **lower the partial pressure** of NH_3.
- By **Le Chatelier's Principle**, the system will counteract by favouring the **forward reaction** in order to **increase** the partial pressure of NH_3.
- So position of equilibrium will shift to the **right**.

(ii) Change the **volume** of the vessel at constant temperature



- **Compression** (i.e. **decreasing volume of vessel**) to **increase** partial pressure of all gases
- **Expansion** (i.e. **increasing volume of vessel**) to **decrease** partial pressure of all gases

The **stoichiometry** of a gaseous reaction will influence the effect of changing partial pressure of **all** gases on the **Position of Equilibrium** of the reaction.

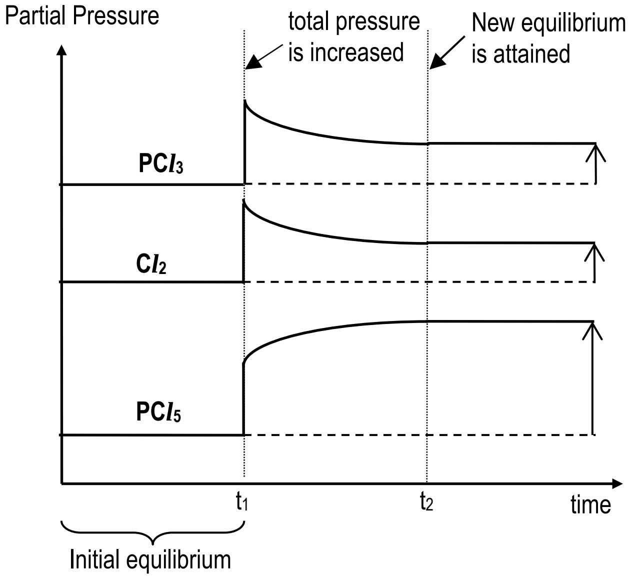
There are **2 types of stoichiometry:**

❶ Reactions with different amount of gaseous reactants and products

Eg 2: $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$, predict what happens if volume of vessel is decreased.

Prediction using LCP:

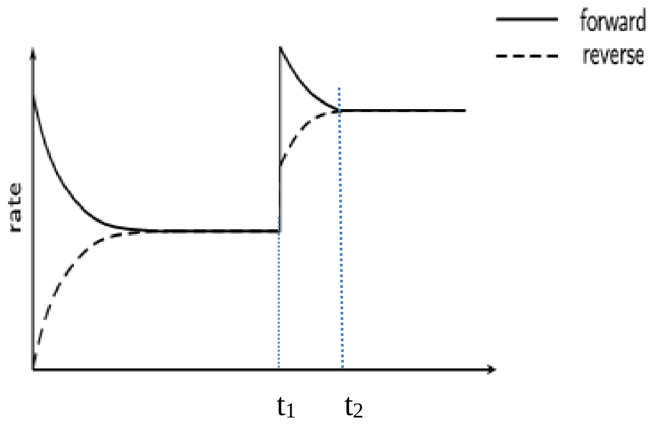
- When the volume of the vessel is **decreased**, the partial pressure of **all** gases will **increase.**
- By **Le Chatelier's Principle**, the system will counteract the increase in pressure by favouring the **forward** reaction to **reduce** the total amount of gas particles in the system.
- Hence, the position of equilibrium will shift to the **right.**
- Partial pressure of PCl_3 and Cl_2 will fall while partial pressure of PCl_5 will rise until new equilibrium is attained at t_2.
- At the new equilibrium, the partial pressure of all species are **higher** than in the previous equilibrium**.**



New equilibrium partial pressures of PCl_3, Cl_2 and PCl_5 will be **higher** than their initial equilibrium partial pressures.

Note: *The above graphs are not drawn to exact scale.*

Effect on rates of forward and backward reactions:

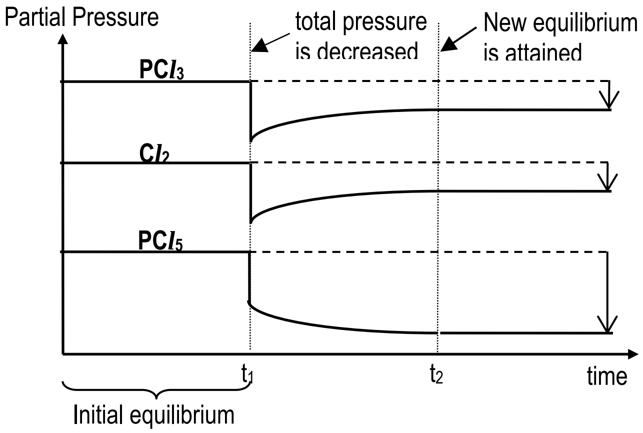


- When the volume of the vessel is **decreased** (t_1), partial pressure of all gases will **increase** and so both forward and backward rates will **spike**. The system will counteract by **reducing** the total amount of gas particles in the system and so the forward rate will spike more.
- As more PCl_5 formed, the backward rate will rise while the forward rate fall until they are **equal** again.
- At this stage (t_2), a new equilibrium position is attained.

Eg 3: $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$, predict what happens if volume of vessel is increased.

Prediction using LCP:

- When the volume of the vessel is **increased**, the partial pressure of **all** gases will **decrease at t_1.**
- By **Le Chatelier's Principle**, the system will counteract the decrease in pressure by favouring the **backward** reaction to **increase** the total amount of gas particles in the system.
- Hence, the position of equilibrium will shift to the **left.**
- Partial pressure of PCl_3 and Cl_2 will rise while partial pressure of PCl_5 will fall until new equilibrium is attained at t_2.
- At the new equilibrium, the partial pressure of all species are **lower** than in the previous equilibrium**.**

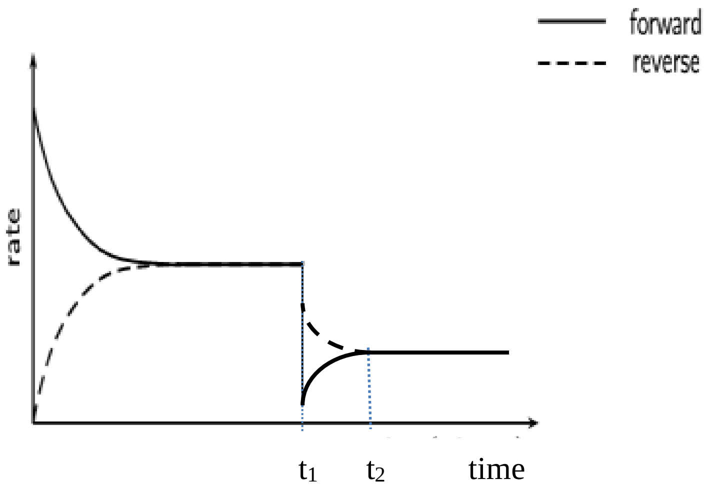


New equilibrium partial pressures of PCl_3, Cl_2 and PCl_5 will be **lower** than their initial equilibrium partial pressures.

Note: *The above graphs are not drawn to exact scale*

Effect on **rates** of forward and backward reactions:

- When the volume of the vessel is **increased** (t_1), partial pressure of all gases will **decrease** and so both forward and backward rates will **drop**. The system will counteract by **increasing** the amount of gas particles in the system and so the backward rate will drop less and hence faster than the forward reaction.
- As **more** Cl_2 and PCl_3 formed, the forward rate will **rise** while the backward rate will **fall** until they are **equal** again.
- At this stage (t_2), a new equilibrium position is attained.



❷ Reactions with equal amount of gaseous reactants and products

Eg 4: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

- Since the number of gaseous particles on both sides of the system is **equal**, changes in partial pressure of gases favour **neither** the forward nor the backward reaction
- Position of equilibrium is **unaffected** and the **system remains at equilibrium**.
- There will be **no change** to the **composition** of the equilibrium mixture (i.e. amount of H_2, I_2 and HI remain unchanged).

1.3 Effect of adding an Inert Gas

- An inert gas is a gas that does not react with any of the species involved in the equilibrium.
- The inert gas can be added to an equilibrium system under two separate conditions:
  ❶ Constant volume or ❷ Constant total pressure.

E.g. Adding Ne gas to the closed system $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at:

❶ At constant volume

- The **partial pressures** (**or concentration**) of the reactants and products **do not change** though there is an increase in total pressure.

- Hence, the reaction is **not disturbed** and the **equilibrium position is unchanged**.

❷ **At constant pressure** (refers to total pressure of system)

- The **volume** of the system must **increase** to keep total pressure constant when an inert gas is added. Hence, the **partial pressures** of the reactants and products will **decrease.**

$$P_T = P_{reactant} + P_{product} + P_{inert\ gas}$$

- By Le Chatelier's Principle, the system will counteract by shifting the equilibrium position to the **side** with **more gas particles** are present to **raise** the partial pressures in order to overcome the stress.

Note: The effect of adding inert gas at constant pressure on the equilibrium position is the **same** as **increasing the volume of vessel**.

Tickle your Brains

Why does partial pressure of gaseous reactants and products remain the same when an inert gas is added at constant volume?

Partial pressure of a gas A
= mole fraction of A x P_T

$$= \downarrow \frac{n_A}{n_T \uparrow} \times P_T \uparrow$$

Since decrease in mole fraction of gas is matched by increase in total pressure of the system, the two effects cancel each other. Hence, partial pressure remains the same.

1.4 Effect of Temperature changes

➢ Direction of POE shift will depend on **enthalpy change** of reaction.

Eg 1: Consider an equilibrium system with an exothermic forward reaction:

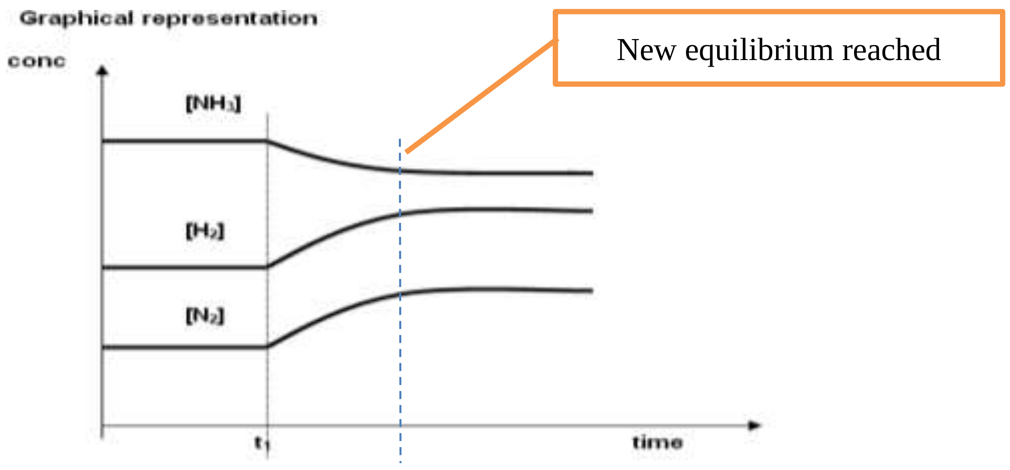
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92\ kJ\ mol^{-1}$$

Predict what happens if temperature of the system is changed.

❶ When the temperature is **increased**:

Prediction using LCP:

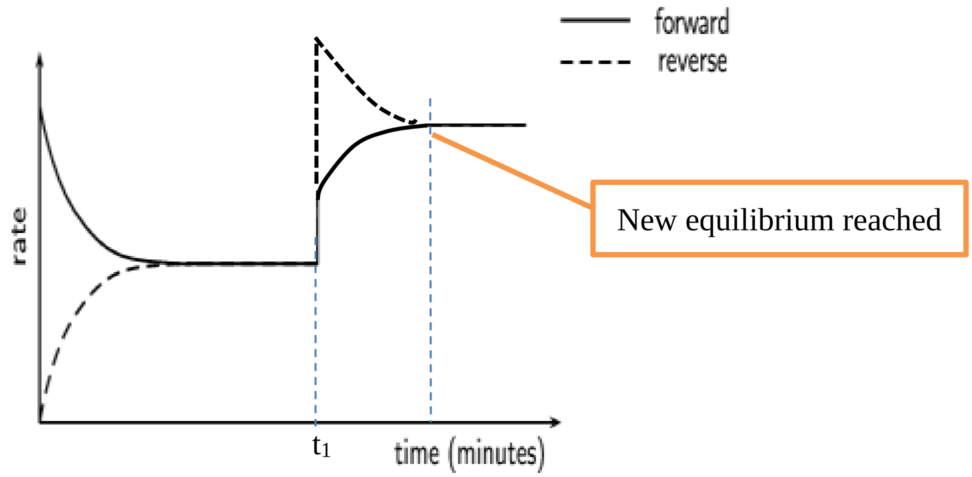
- By Le Chatelier's Principle, the system will **counteract** the increase in temperature by favouring the **backward endothermic** reaction to **lower temperature** by **removing** heat, so the position of equilibrium will shift to the **left**.
- In the new equilibrium mixture, the concentration of N_2 and H_2 would be **higher** than the previous one while that of NH_3 would be **lower** than the previous one (see graph below).
- Hence, K_c value will **decrease.** $\downarrow K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$



temp increase at time t_1, equilibrium position shifts left

<u>Effect on rates of forward and backward reactions</u>:

- Increasing temperature at time **t_1** will increase the kinetic energy of both reactants and products in the system. Hence <u>both</u> forward and backward reactions will become **faster**.
- However, rate of backward reaction increases **<u>more than</u>** forward reaction as backward endothermic reaction is favoured in order to remove heat.
- More H_2 and N_2 formed and so the forward rate will start to **increase** while the backward rate will **decrease** until both rates are the **equal**.
- At this stage, a new equilibrium is reached.
- Since the **rates of both** forward and backward reactions **increase**, equilibrium is reached **faster**.



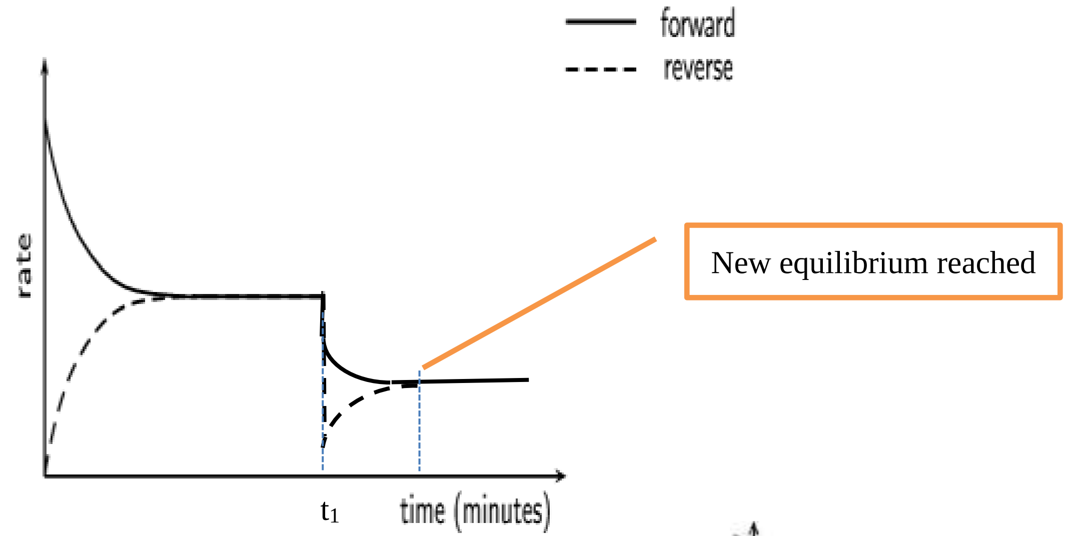
❷ When the temperature is **lowered:**

<u>Prediction using LCP</u>:

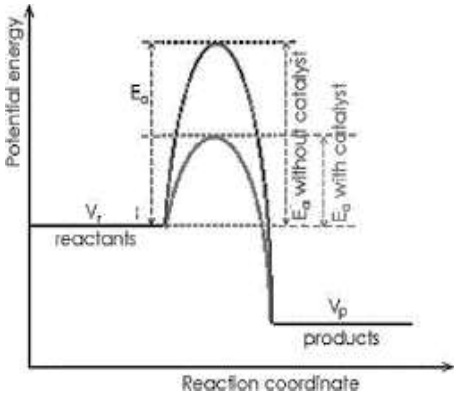
- By Le Chatelier's Principle, the system will **counteract** the decrease in temperature by favouring the **forward exothermic** reaction to **increase temperature** by **releasing** heat, so the position of equilibrium will shift to the **right**.
- In the new equilibrium mixture, the concentration of N_2 and H_2 would be **lower** than the previous one while that of NH_3 would be **higher** than the previous one (see graph below).
- Hence, K_c value will **increase.** $\uparrow K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$
- The numerical value of K_c (or K_p) will only change **<u>if and only if</u>** temperature changes.

Effect on rates of forward and backward reactions:

- Decreasing temperature at time **t_1** will **lower** the kinetic energy of both reactants and products in the system. Hence both forward and backward reactions will become **slower**.
- However, rate of forward reaction decreases **less than** backward reaction as the forward exothermic reaction is favoured in order to release heat.
- More NH_3 formed and so the backward rate will start to **increase** while the forward rate **decrease** until both rates are the **equal**.
- At this stage, a new equilibrium is reached.
- Since the **rates of both** forward and backward reactions **decrease**, equilibrium is reached **at a longer time**.



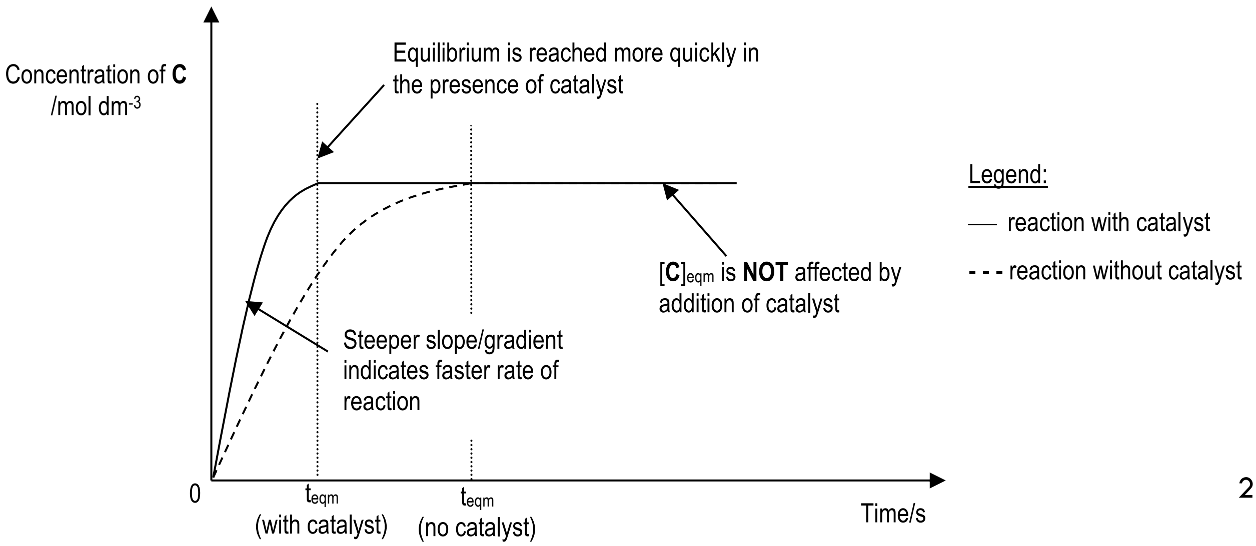
1.5 Effect of Catalyst



- Catalyst **increases both** the **rates** of the forward and backward reactions to the **same extent** by lowering the activation energy of both reactions by the **same amount.**
- Hence, it will **not** affect equilibrium position but it will allow equilibrium to reach ***faster***.
- It has **no effect** on equilibrium composition and **no effect** on K_c (or K_p)

Eg: Concentration of **C** against time graph for the catalysed and uncatalysed reaction:

$$a\mathbf{A} + b\mathbf{B} \rightleftharpoons c\mathbf{C} + d\mathbf{D}$$



SLS QUIZ 5

1. YES or NO

Factors	**Any effect on POE?**	***Any effect on K_c or K_p?***
Concentration		
Pressure		
Temperature		
Catalyst		
Inert gas (constant P)		
Inert gas (constant V)		

2. Silver chlorate(V) reacts with chlorine in a 1 dm^3 container as follows:

$$2AgClO_3(s) + Cl_2(g) \rightleftharpoons 2AgCl(s) + 2ClO_2(g) + O_2(g) \qquad \Delta H > 0$$

Which one of the following changes would affect the equilibrium position of the above reaction?

A Addition of an inert gas
B Increase in temperature
C Addition of a suitable catalyst
D Removal of some silver chloride

3. The key stage in the manufacture of sulfuric acid is the reaction between sulfur dioxide and oxygen.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -197 \text{ kJ mol}^{-1}$$

Which of the following statements are correct for an increase in temperature?

1 The equilibrium constant increases.

2 The rate for the forward reaction increases.

3 The rate for the backward reaction increases.

4 The activation energy for the forward reaction decreases.

A **1**, **2**, **3** and **4** **B** **2**, **3** and **4** only

C **2** and **3** only **D** **3** only

4 Calculations involving K_c and K_p

LO: Calculate the quantities present at equilibrium, given appropriate data (such calculations will not require the solving of quadratic equations)

Worked Example 1

The reaction 2**D**(aq) + **E**(aq) $\rightleftharpoons$ **F**(aq) was allowed to reach equilibrium. The initial amounts of the reactants present in a 3 dm^3 solution were 3.00 mol **D** and 2.25 mol **E**. At equilibrium, there were 0.60 mol **F**.

Calculate the equilibrium constant, K_c.

Solution:

		2**D**(aq)	+ **E**(aq)	$\rightleftharpoons$ **F**(aq)
I	**I**nitial amount / mol			
C	**C**hange in amount / mol			
E	**E**quilibrium amount / mol			
Equilibrium concentration / mol dm^{-3}				

Ans: **1.01 mol^{-2} dm^6**

Worked Example 2

The system **B**(aq) $\rightleftharpoons$ **C**(aq) has an equilibrium constant, K_c of 0.50 at 50 °C. Initially there is 0.0150 mol dm^{-3} of **B** which is allowed to reach equilibrium at 50 °C.

(i) Calculate the equilibrium concentrations of **B** and **C**.
(ii) If the concentration of **B** in the equilibrium mixture is increased by 0.0075 mol dm^{-3} at time = t_1, what will be the concentrations of **B** and **C** when the equilibrium is established again at the same temperature at time = t_2?
(iii) Sketch the concentration-time graph for the reaction from time = 0 to time = t_2.

Solution:

(i) Let **x** be the concentration of B be reacted.

		B(aq) $\rightleftharpoons$	**C**(aq)
I	Initial concentration / mol dm^{-3}		
C	Change in concentration / mol dm^{-3}		
E	Equilibrium concentration / mol dm^{-3}		

Ans: $[C]_{eqm}$ = **0.00500 mol dm^{-3}**

$[B]_{eqm}$ = **0.0100 mol dm^{-3}**

(ii) **<u>Method 1:</u>**

Let the change in concentration of **C** be **y** from **t_1**

mol dm^{-3}	**B**(aq)	$\rightleftharpoons$	**C**(aq)
[I] at t_1			
[C]			
[E]			

Ans: [**B**]$_{eqm}$ = **0.0150 mol dm^{-3}**

[**C**]$_{eqm}$ = **0.00750 mol dm^{-3}**

Method 2:

Start from the beginning with no C in the system,

Let **y** be the equilibrium concentration of **C** at t_2.

mol dm^{-3}	**B**(aq)	$\rightleftharpoons$	**C**(aq)
[I]			
[C]			
[E]			

$$K_c = \frac{[C]}{[B]}$$

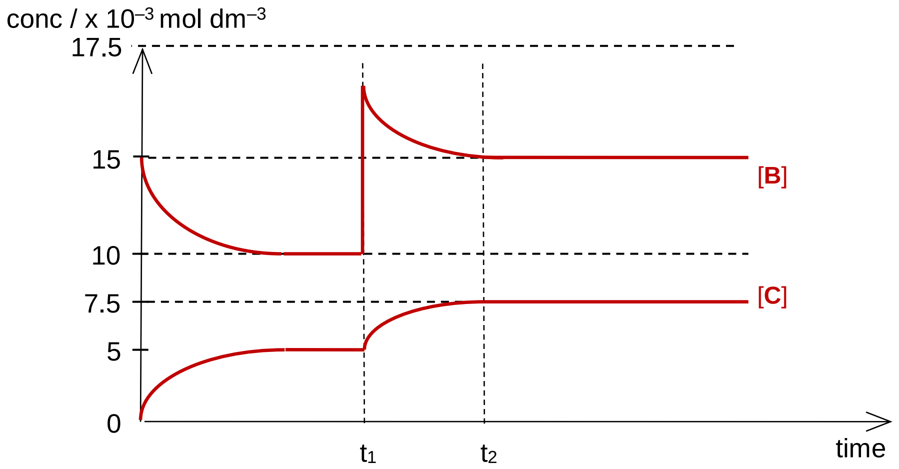
0.5 = y / (0.0225 –y)

y = 0.00750

[**C**]$_{eqm}$ = y = **<u>0.00750 mol dm^{-3}</u>**

[**B**]$_{eqm}$ = 0.0225 – y = 0.0225 – 0.0075 = **<u>0.0150 mol dm^{-3}</u>**

(iii)



Worked Example 3 [For H2 only]

At 1100 K, $K_p = 0.13\ \text{atm}^{-1}$ for the system $\mathbf{2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)}$

If 2.00 mol of SO_2 and 3.00 mol of O_2 are mixed and allowed to react in a vessel, what would be the final total pressure to give 90% yield of SO_3?

Solution:

Limiting reagent is SO_2 => 90% of SO_2 reacted will give 90% yield of SO_3

mol	$2SO_2(g)$	+	$O_2(g)$	$\rightleftharpoons$	$2SO_3(g)$
I					
C	- 90% x 2 = 1.80				
E					

n_{total} = 0.20 + 2.10 + 1.80 = **4.10 mol**

Let the total pressure required be P_T

Recall:

P_T = Sum of partial pressure of all gases in the system

P_A = mole fraction of A x Total Pressure

$= (\mathbf{n_A / n_T})\, P_T = \mathbf{X_A P_T}$

Ans: P_T = **1220 atm** (too high for economic production).

Worked Example 4 [For H2 only]

At 50 °C and 1.01 x 10^5 N m^{-2}, the degree of dissociation of N_2O_4 is 0.53.
Find the equilibrium constant, K_p, for the dissociation $N_2O_4(g) \rightleftharpoons 2NO_2(g)$.

Solution:

Degree of dissociation, α, is the **fraction** of **reactant** that has dissociated at a particular temperature. It can be expressed as fraction or percentage.

$$\boxed{\text{Degree of dissociation, } \alpha = \frac{\text{amount dissociated}}{\textbf{initial}\text{ amount}}}$$

Let the initial amount of N_2O_4 be **y**

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
Initial amount / mol	y		
Change in amount / mol			
Equilibrium amount / mol			
Equilibrium mole fraction, **X**			
Partial pressure at equilibrium / N m^{-2} = mole fraction x P_T			

Total amount of gases at equilibrium = 0.47y + 1.06y = 1.53y

P_T = 1.01 x 10^5 **Nm^{-2}**

Ans: K_p = **1.58 x 10^5 Nm^{-2}**

SLS QUIZ 6:

1 On heating, nitrogen dioxide decomposes as follows:

$$2NO_2\,(g) \rightleftharpoons 2NO\,(g) + O_2\,(g)$$

When 4 mol of nitrogen dioxide (in a V dm^3 vessel) is heated to a constant temperature, the equilibrium mixture is found to contain x mol of oxygen.
Which one of the following shows the correct K_c for this reaction?

A $\dfrac{x^3}{V(4-x)^2}$

B $\dfrac{4x^3}{V(4-2x)^2}$

C $\dfrac{(4-2x)^2}{4Vx^3}$

D $\dfrac{4Vx^3}{(4-2x)^2}$

Industrial Application of LCP: The Haber Process

LO: Describe and explain the conditions used in the Haber process, as an example of the importance of an understanding of chemical equilibrium in the chemical industry

The **Haber Process for production of NH_3** is an example of an important industrial reaction which is **reversible** and involves equilibrium mixtures:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H^\ominus(298\text{ K}) = -92\text{ kJ mol}^{-1}$$

3 important principles in industrial reactions are:

1. Reaction must be **fast**
2. Yield is **high**
3. Cost is **low**

The desired reaction should take place **quickly** to produce the required product in **high yield**. The process should **minimise cost** by making the reaction as fast as possible such as ensuring that the temperature is not too low, avoiding very high pressures and making use of catalysts if possible.

The Haber process provides a good example to show how an understanding of LCP can be applied in the chemical industry to achieve the aim of producing the **maximum amount of product** in the **shortest time** and at the **minimum cost**.

Condition	Explanation
Temperature: **450 ºC**	▪ Since the forward reaction is exothermic, a **lower** temperature would result in a **higher yield** of NH_3. ▪ However, the rate of reaction is **too slow at low temperature** and it takes a long time to establish equilibrium. ▪ On the other hand, a **high** temperature increases the rate of production but results in **lower** yield and **higher** production cost. ▪ Thus, a compromise is needed and a moderately high temperature of 450 ºC is used to ensure a reasonable rate of production and yield.
Pressure: **200 atm**	▪ The forward reaction takes place with a reduction in the number of gaseous particles. ▪ A **high** pressure will favour the desired reaction (increase yield). ▪ However, too high a pressure **increases cost** of production (more expensive and stronger equipment that could withstand the high pressure need to be used).
Catalyst: Finely divided Fe catalyst with Al_2O_3 as promoter	▪ This increases the rate of production. **Note:** The catalyst does not affect the percentage of NH_3 in the equilibrium mixture.
Continuous removal of NH_3	▪ The removal of NH_3 as it forms shifts the position of equilibrium to the right, thereby **increasing** the **yield** of NH_3.
Molar ratio of $N_2 : H_2$ = 1 : 3	▪ The molar ratio used is similar to that of the stoichiometric ratio to **minimise excess**.

SLS QUIZ 7:

1 Ammonia is manufactured industrially via the Haber process.

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g), \qquad \Delta H < 0$$

Which statements are true about the Haber process?

1 Iron catalyst is used to increase yield of ammonia.
2 A pressure of 250 atm is used to increase yield of ammonia.
3 A temperature of 450 °C is used to increase rate of reaction.

A 1, 2 and 3 only
B 1 and 2 only
C 2 and 3 only
D 3 only

Additional Information: Applications of Equilibrium

Carbon monoxide poisoning

Haemoglobin is a complex molecule that transports oxygen in the blood system. The binding process can be represented by the equilibrium:

$$\text{haemoglobin} + O_2 \rightleftharpoons \text{oxyhaemoglobin}$$

The equilibrium position will shift to the left when oxygen is used in the body to maintain the state of equilibrium.

Carbon monoxide, a by–product of “incomplete” oxidation (burning) of hydrocarbons, poses a major pollution problem. It is dangerous to life because it also binds to haemoglobin:

$$\text{haemoglobin} + CO \rightleftharpoons \text{carboxyhaemoglobin}$$

This equilibrium has a much greater equilibrium constant than the haemoglobin–O_2 reaction, i.e. CO binds much more strongly to haemoglobin than O_2. Consequently, less haemoglobin is available to transport oxygen and the victim of CO poisoning suffocates. The treatment for CO poisoning is to supply pure oxygen to the victim. This helps by shifting equilibrium position to the left, thus reversing the binding of CO to haemoglobin and increasing the concentration of oxyhaemoglobin in blood plasma.

DID YOU KNOW….

Ammonia, World War I and Haber...

Fritz Haber 1868-1934

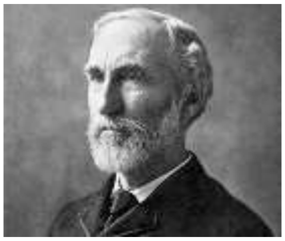
A march in support of Hitler for president.

Ammonia, which can be converted into nitrates, is an indispensable ingredient in gunpowder. Before the Haber Process, nature supplied the nitrates needed. Plants such as pea and peanut plants harbor bacteria in their roots that can convert nitrogen gas in air into nitrogen compounds. Animals eat the plants and nitrates form in their nitrogen rich manure. Large amounts of manure, such as those found in seasonal roosting areas for large flocks of birds used to be harvested for nitrates. In Europe prior to World War I, such nitrates had to be imported, which meant the importing countries were vulnerable to blockade. German chemist Fritz Haber was the first to develop a practical industrial process that could manufacture ammonia on large scales. He won the Nobel prize in 1918 for his efforts. He also helped the Germany government to develop various chemical weapons, including mustard gas, during the war. However, though he received much adulation, his life was not without tragedies. During the War, his wife committed suicide. We all know Germany eventually lost the war. Due to his Jewish roots, Haber, was later forced to leave his homeland when the Nazis came into power. After a grave illness, Haber died on January 29, 1934, at Basle, on his way from England to convalesce in Switzerland, his spirit was broken by his rejection by the Germany he had served so well.

6 Gibbs Free Energy and the Position of Equilibrium [For H2 only]

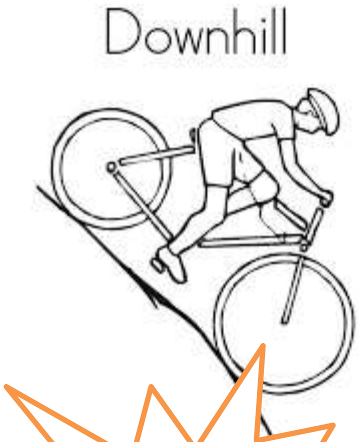
LO: Show understanding that the position of equilibrium is dependent on the standard Gibbs free energy change of reaction, ΔG^θ *[Quantitative treatment is not required]*

- **J. Willard Gibbs** is a professor of mathematical Physics at Yale University. In 1878, he wrote a 323-page paper that virtually established the major principles governing chemical equilibria. He has given us another perspective in understanding chemical equilibrium based on free energy consideration.

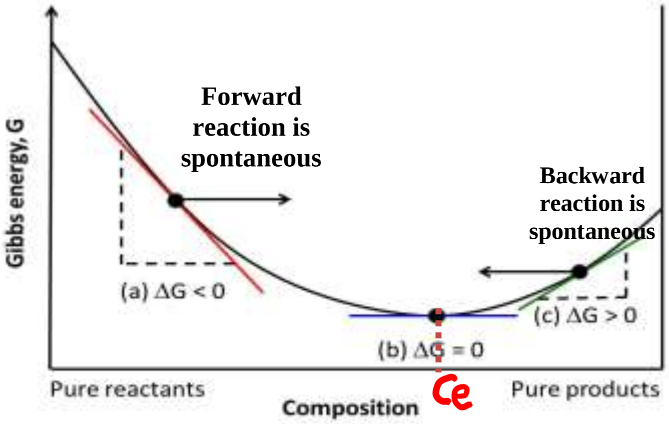


Significance of *Gibbs free energy, G*

- **G** is not a constant**.** Its value will change with **temperature and pressure** of the system**.**
  - The **lower** the **G** value, the **more stable** is the system.
  - At a given temperature and pressure, chemical reactions will change its **composition** in a direction to **reduce the value** of the **G** until it reaches the **minimum** value. At this stage, the reaction reaches **equilibrium**.
  - When **minimum G** is obtained, there will be **no more changes** in the **composition** of the mixture and so **G** remains constant, hence **ΔG** is **zero**. The reaction reaches **dynamic equilibrium** and the rate of forward reaction and rate of backward reaction are now **equal**.



The road to ***equilibrium*** is downhill



(a) Forward reaction is spontaneous; (b) system is at equilibrium; (c) backward reaction is spontaneous

C_e: Composition of mixture at equilibrium

- Reaction will shift its POE to change its composition towards **Ce** so as to obtain minimum **G**.
- **Sign of ΔG** gives information about the **spontaneity** of the reaction.
  - When the reaction has a **high proportion of reactants**, **ΔG** is **negative**. Hence **forward** reaction will be **spontaneous** and is **faster** than backward reaction.
  - When the reaction has a **low proportion of reactants**, **ΔG** is **positive.** Hence **backward** reaction will be **spontaneous** and is **faster** than forward reaction.
  - When the reaction has **equilibrium composition**, Ce, **ΔG** is **zero.** Hence both forward and backward reactions will be **spontaneous** and occurring at the **same rate**.

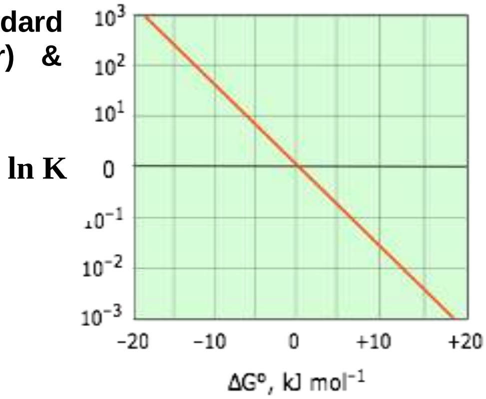
Summary of information from sign of ΔG

Reactants $\rightleftharpoons$ Products **ΔG = + or 0 or —** **(depend on the reaction composition)**

Reaction composition	**Sign of ΔG**	**Which direction is spontaneous?**
High proportion of reactants	Negative	**Forward** reaction is spontaneous; faster than backward reaction.
C_e (equilibrium composition)	Zero	**Both** reactions are spontaneous and occurring at an equal rate. Reaction is at **equilibrium.**
Low proportion of reactants	Positive	**Backward** reaction is spontaneous; faster than forward reaction.

> Note: Under Energetics, you have also learned that **ΔG** can be calculated from **enthalpy change and entropy change at a given temperature.**
>
> $$\Delta G = \Delta H - T\Delta S$$

- ○ **ΔG^θ** is known as **Standard Gibbs Free energy change.**
  - ❖ **ΔG^θ** has a **<u>constant</u> value** for a given reaction
  - ❖ It refers to the free energy change of a reaction under **standard conditions** which refer to **25°C, 10^5 Pa (or 1 bar) & concentration of 1 mol dm^{-3}**
  - ❖ **ΔG^θ** is related to equilibrium constant **K**



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

At equilibrium under a given temperature, **ΔG = 0** and **Q = K**

$$0 = \Delta G^\theta + RT\ln K$$

⇨ $\Delta G^\theta = -RT\ln K$ *[no need to remember]*

where **R** is the Gas constant and **K** is the **thermodynamic equilibrium constant** (has no units).

- ○ Since **ΔG^θ** is related to **K**, we can look at the **sign** of **ΔG^θ** of a reaction to gather information about its **K value**, **position of equilibrium** and its **composition at equilibrium**.

❶ **When ΔG^θ** has a **negative sign**, **K** would be **greater than 1** and **<u>very big</u>** (K >>1).

⇨ The position of **equilibrium** (i.e. position of **minimum G**) lies very much to the **right**, and the reaction should be **almost complete**; there would be a **high** proportion of **products** in such a reaction mixture.

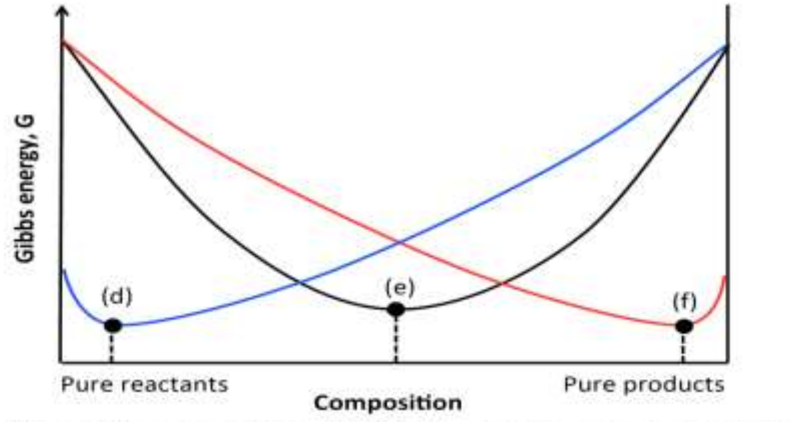
⇨ **Ratio** of **[Products] / [Reactants] > 1**

❷ **When ΔG^θ** has a **positive sign, K** would be **<u>small</u>** and **less than 1** (0 < K < 1).

⇨ The position of **equilibrium or minimum G** lies very much to the **left**, and most of the reactants are left **unreacted**; there would be a **low** proportion of products in such a reaction mixture.

⇨ **Ratio** of **[Products] / [Reactants] < 1**

❸ How about a reaction with **ΔG^θ = 0**? *[Refer to summary on page 33 for answers]*
  - ⇨ What would be its **K value**?
  - ⇨ Where is the **position of equilibrium**?
  - ⇨ And what would be the **ratio of [Products] / [Reactants]** at equilibrium?



- We can also look at the position of the **minimum G** of a reaction to gather information about its **position of equilibrium**, its **composition at equilibrium** and **sign** of its ΔG^θ.

Position of minimum G	**Composition of mixture at equilibrium and its position of equilibrium**	**Sign of ΔG^θ**
Reaction (d) Close to reactants	• **High** proportion of **reactants** at equilibrium. • **[Products] / [Reactants] < 1** • Position of equilibrium lies very much to the **left,** so reaction is **rather incomplete.**	Forward reaction is **non-spontaneous ,** so ΔG^θ has a **positive** sign
Reaction (f) Close to products	• **High** proportion of **products** at equilibrium. • **[Products] / [Reactants] > 1** • Position of equilibrium lies very much to the **right**, so reaction is **almost complete**.	Forward reaction is **spontaneous, so** ΔG^θ has **negative** sign
Reaction (e) At about equal amount of reactants and products	• About **equal** amount of products and reactants at equilibrium. • **[Products] / [Reactants] ≈** 1 • Position of equilibrium lies at about **midway** of reaction.	$\Delta G^\theta \approx 0$ Reaction is almost reaching equilibrium.

SLS QUIZ 8: True/False

1	A reversible reaction has the lowest free energy when it is in a state of equilibrium	
2	A reversible reaction is not in equilibrium if its free energy is not the minimum.	
3	A reversible reaction will change its composition until it has zero free energy.	
4	A reversible reaction will adjust its composition so as to achieve minimum free energy.	
5	A reaction with **negative** ΔG^θ would contain a high proportion of products at equilibrium.	

Summary of Factors Affecting Position of Equilibria

$$aA + bB \rightleftharpoons cC + dD$$

Change	Shift in Position of Equilibrium	K_c (or K_p)	Rate Constant		Remarks
			k_f	k_b	
↑ [A] or [B] ↓ [C] or [D]	To right	No change	No change		For **gaseous** components, the effect of ↑ or ↓ partial pressure is similar to that of ↑ or ↓ concentrations.
↓ [A] or [B] ↑ [C] or [D]	To left	No change	No change		
↓P_T or ↑V	▪ To left if (a+b) **>** (c+d) ▪ To right if (a+b) **<** (c+d) ▪ No change if (a+b) **=** (c+d)	No change	No change		Only **gaseous** system is affected.
↑P_T or ↓V	▪ To right if (a+b) **>** (c+d) ▪ To left if (a+b) **<** (c+d) ▪ No change if (a+b) **=** (c+d)	No change	No change		
↑T	For ΔH > 0 (endothermic forward reaction) ▪ To right	↑	↑	↑	Equilibrium is achieved in a shorter time.
	For ΔH < 0 (exothermic forward reaction) ▪ To left	↓	↑	↑	
↓T	For ΔH > 0 (endothermic forward reaction ▪ To left	↓	↓	↓	Equilibrium is achieved in a longer time.
	For ΔH < 0 (exothermic forward reaction) ▪ To right	↑	↓	↓	
Addition of a catalyst	No change	No change	Increase to **same** extent		Equilibrium is achieved in a shorter time.
Addition of inert gas at constant *pressure* *(increase volume of vessel)*	▪ To left if (a+b) **>** (c+d) ▪ To right if (a+b) **<** (c+d) ▪ No change if (a+b) **=** (c+d)	No change	No change		Only **gaseous** system is affected. Total volume of system is increased. Reaction that produces **more** molecules is favoured.
Addition of inert gas at constant volume	No change	No change	No change		Only **gaseous** system is affected. Total pressure of system is increased but partial pressures unchanged.

Summary of ΔG, ΔG^{θ} & Position of Equilibirum (For H2 Only)

1. The **sign of Gibbs free energy change, ΔG** gives information about the **spontaneity** of a process; it provides information on the relative rates of the forward or backward reaction as well as the **state of equilibrium** of the reaction.

ΔG is **negative**	**Forward** reaction is occurring faster than backward reaction.	Reaction is **not** at equilibrium; the backward reaction will catch up as the concentration of products increase until both rates are equal whereby a state of equilibrium is achieved.
ΔG is **positive**	**Backward** reaction is occurring faster than backward reaction.	Reaction is **not** at equilibrium; the forward reaction will catch up as the concentration of reactants increase until both rates are equal whereby a state of equilibrium is achieved.
ΔG = **0**	Forward rate and backward rate are **equal**.	Reaction is **at equilibrium**

2. **Standard Gibbs free energy change, ΔG^{θ}** is a **constant**. The **sign of ΔG^{θ}** provides information on the **K value**, **position of equilibrium** and the **composition** of the reaction mixture at equilibrium, i.e. **[Products] / [Reactants]** ratio.

$$\Delta G^{\theta} = -RT\ln K$$ *(don't need to remember)*

Sign of ΔG^{θ}	**K value**	**Position** & **Composition of mixture at equilibrium**
ΔG^{θ} has **negative** sign	K would be **very big** (K >> 1)	• There would be a **high** proportion of products in the reaction mixture. • **[Products] / [Reactants] > 1** • Position of equilibrium lies very much to the **right**, and the reaction should be **almost complete.** • **Position of minimum G** lies close to **products.**
ΔG^{θ} has **positive** sign	K would be **small** ($0 < K < 1$)	• There would be a **low** proportion of products in the reaction mixture. • **[Products] / [Reactants] < 1** • Position of equilibrium lies very much to the **left**, and most of the reactants are **left unreacted.** • **Position of minimum G** lies close to **reactants.**
ΔG^{θ} = 0	K = 1 $\Delta G^{\theta} = -RT\ln K$ $0 = -RT\ln K$ $K = 1$	• There would be **equal** proportion of products and reactants in the reaction mixture. • **[Products] / [Reactants] = 1** • Position of equilibrium lies at **mid-point** and the reaction is half completed. • **Position of minimum G** is at **equal amount** of reactants and products**.**

3. **Position of minimum G** of a reaction provides information about its **position of equilibrium**, its **composition at equilibrium** and **sign** of its ΔG^{θ}.

Position of minimum G	**Composition of mixture at equilibrium** and its **position of equilibrium**	**Sign of ΔG^{θ}**
Close to reactants	• **High** proportion of **reactants** at equilibrium. • **[Products] / [Reactants] < 1** • Position of equilibrium lies very much to the **left,** so reaction is **rather incomplete.**	Forward reaction is **non-spontaneous ,** so ΔG^{θ} has a **positive** sign
Close to products	• **High** proportion of **products** at equilibrium. • **[Products] / [Reactants] > 1** • Position of equilibrium lies very much to the **right**, so reaction is **almost complete**.	Forward reaction is **spontaneous, so** ΔG^{θ} has **negative** sign
At about equal amount of reactants and products	• About **equal** amount of products and reactants at equilibrium. • **[Products] / [Reactants] ≈** 1 • Position of equilibrium lies at about **midway** of reaction.	$\Delta G^{\theta} \approx 0$ Reaction is almost reaching equilibrium.