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2023 JC1 H2 CHEMISTRY (9729)
CORE IDEA 3 - TRANSFORMATION
Topic 7: CHEMICAL EQUILIBRIA

Name: ____ Civics Group: _________

Learning Outcomes

Students should be able to:

(a) explain, in terms of rates of the forward and reverse reactions, what is meant by a *reversible reaction* and *dynamic equilibrium*

(b) 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

(c) deduce whether changes in concentration, pressure or temperature or the presence of a catalyst affect the value of the equilibrium constant for a reaction

(d) 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]

(e) calculate the values of equilibrium constants in terms of concentrations or partial pressures from appropriate data

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

(g) show understanding that the position of equilibrium is dependent on the standard Gibbs free energy change of reaction, ΔG. [Quantitative treatment is **not** required]

(h) 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

Recommended References:

1.	**Chemistry (for CIE AS & A Level)** by Peter Cann & Peter Hughes	540 CAN
2.	**A-Level Chemistry** by E.N. Ramsden	540 RAM

Suggested Videos: (via URLs and QR codes provided or search using the titles)

1. What is Dynamic Equilibrium? The Chemistry Journey
(*Introductory video for chapter*)
URL:
https://youtu.be/wlD_ImYQAgQ

2. What is chemical equilibrium? George Zaidan and Charles Morton
(*Introductory video for chapter*)
URL:
https://youtu.be/dUMmoPdwBy4

3. NO_2 and N_2O_4 Equilibrium (Effect of Temperature)
URL:
http://www.youtube.com/watch?v=tlGrBcgANSY

4. Chemistry: Demo: Shifting Equilibrium of $[Fe(SCN)]^{2+}$ (Effect of Concentration)
URL:
https://www.youtube.com/watch?v=ZOYyCTvLa9E

Table of Contents

1 INTRODUCTION

1.1 Reversible Reaction

LO (a) explain, in terms of rates of the forward and reverse reactions, what is meant by a *reversible reaction* and *dynamic equilibrium*

Notation: A reversible reaction is denoted by using the $\rightleftharpoons$ sign in the equation.

1. A **reversible reaction** is a reaction where the **reactants form products that can react with each other to re-form the reactants**. In other words, the reaction proceeds in either direction.

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

   - Both forward and backward reactions occur.
   - As soon as NH_3 molecules are formed (***forward reaction***), some of the NH_3 molecules formed will decompose to form N_2 and H_2 (***backward reaction***).
   - Thus, in a reversible reaction, the reactants are ***never completely*** converted to the products. Instead, a mixture of products and reactants will be obtained.

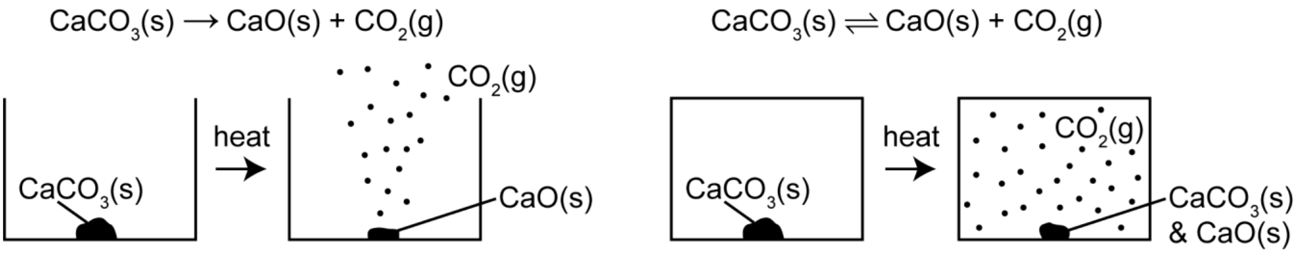
2. Convention: $\mathbf{A + B \rightleftharpoons C + D}$ ΔH = endothermic or exothermic

   - **A** & **B** are referred to as ***reactants*** and **C** & **D** as ***products of the forward reaction***.
   - $\mathbf{A + B \rightarrow C + D}$ is called the ***forward*** reaction.
   - $\mathbf{C + D \rightarrow A + B}$ is called the ***backward*** reaction.
   - ΔH indicates the enthalpy change of the ***forward*** reaction.
     - If ΔH is positive, the forward reaction is ***endothermic***.
     - If ΔH is negative, the forward reaction is ***exothermic***.

3. Some processes proceed in a *single direction* or are *irreversible* because they take place in an ***open*** system (see Fig. 1(a)), where some of the products can escape, making the backward reaction impossible.

   E.g. $Mg(s) + 2HC\ell(aq) \rightarrow MgC\ell_2(aq) + H_2(g)$

   Chemical reactions, in principle, are all reversible in a ***closed*** system, though some may appear to go to completion (see Fig. 1(b)).



(a) In an **open system**, CO_2 escapes, so the recombination of CO_2 and CaO to form $CaCO_3$ never occurs in an open container. The system does not reach equilibrium.

(b) In a **closed system**, eventually, $CaCO_3$ is decomposing to form CaO and CO_2 at the same rate as CaO and CO_2 are reforming $CaCO_3$. Here, the pressure of the CO_2 gas inside the container remains constant as long as temperature remains constant.

Fig. 1 Thermal decomposition of calcium carbonate in **(a)** open and **(b)** closed systems.

Making Thinking Visible

Q: If a reaction is reversible and does not go to completion, wouldn't the reaction be useless in the chemical industry?

A: Not necessarily! We can still optimise the product yield of a reversible reaction by changing conditions such as concentration, pressure, temperature, and usage of a catalyst. This is what this chapter is all about.

Q: Does it matter whether the reaction is written as $A + B \rightleftharpoons C + D$ same as $C + D \rightleftharpoons A + B$?

A: No, they are not the same. This is because for $C + D \rightleftharpoons A + B$, the forward reaction is $C + D \rightarrow A + B$ while the backward reaction is $A + B \rightarrow C + D$. In addition, the enthalpy change of reaction for $C + D \rightleftharpoons A + B$ is the reversed of that for $A + B \rightleftharpoons C + D$.

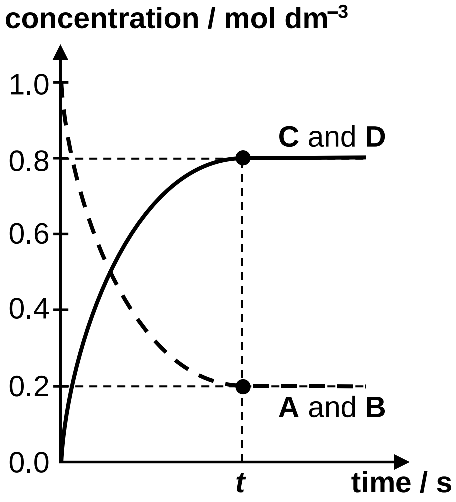
1.2 Dynamic Equilibrium

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

After some time, the reaction reaches a **state of equilibrium** in which both reactants and products are present, and there are no further changes in the amounts of reactants and products.

Macroscopically, the reaction will *appear* to have stopped. However, at the microscopic level, **A** and **B** are still reacting to form **C** and **D** (*i.e.* **forward reaction**), and at the same time, **C** and **D** are still reacting to form **A** and **B** (*i.e.* **backward reaction**) at the same rate.

	forward reaction	**backward reaction**
at the beginning of the reaction (time = 0)	• [**A**] and [**B**] are high, **rate of forward reaction is high**	• **C** and **D** are **not present**, **rate of backward reaction is zero**
as reaction proceeds, (time = 0 to ***t***)	• [**A**] and [**B**] decrease, hence **rate of forward reaction decreases**	• [**C**] and [**D**] increase, hence **rate of backward reaction increases**
time when equilibrium is reached (time = ***t***)	• **Forward and backward reactions are both taking place, where the rate of forward reaction = rate of backward reaction** Note: rates of forward and backward reactions are **NOT** zero. The forward and backward reactions are still taking place, even though no observable changes can be seen. • **Concentrations of reactants and products remain constant** (but are not necessarily equal) • [**A**] and [**B**] ≠ 0; [**C**] and [**D**] ≠ 0 **The system is in a state of dynamic equilibrium.**	



When dynamic equilibrium is established,
rate$_f$ = rate$_b$

For an elementary reversible reaction, this would hence imply:

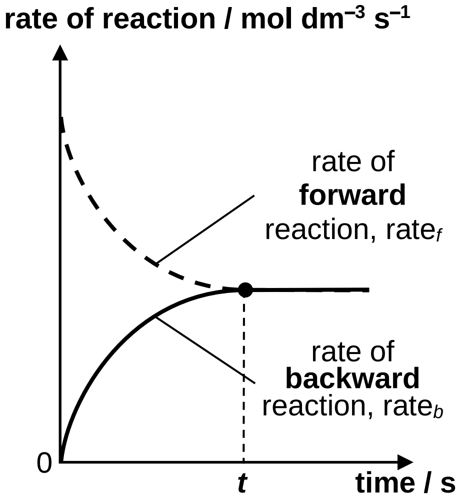
$$k_f[\mathrm{A}][\mathrm{B}] = k_b[\mathrm{C}][\mathrm{D}]$$

By re-arrangement,

$$K_c = \frac{k_f}{k_b} = \frac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]}$$

$$= \textbf{constant}$$

These ratios give us a sense of the extent of the reaction at equilibrium.



Dynamic equilibrium refers to a ***reversible process at equilibrium*** in which the ***rate of the forward reaction equals to the rate of backward reaction*** and the **concentrations of reactants and products do not change**.

Note: The term "dynamic" is opposite of static and is explained by the fact that the forward and backward reactions are still occurring. While the term "equilibrium" is explained by the fact that the concentrations of the reactants and products do not change.

1.3 Characteristics of a State of Dynamic Equilibrium

1. When a system is at a state of equilibrium, the ***concentration of all reactants and products remain constant*** and an equilibrium mixture is obtained.

2. At equilibrium, the ***rate of forward reaction is equal to the rate of the backward reaction***.

3. ***Equilibrium can only be achieved in a closed system,*** where there is no loss or gain of substances to and from the surroundings.

4. ***Equilibrium can be established from either direction***.

   A state of equilibrium can be established from any initial system *e.g.*
   - reactants only (Fig. 2(a))
   - products only (Fig. 2(b))
   - a mixture of reactants and products (Fig. 2(c))

   When the equilibrium for each of the systems is reached, you can observe a certain ratio between the equilibrium concentration for the reactant and product species. However, the concentration of each species present at equilibrium will depend on how much of each species was present in the system initially (*this will be discussed in detail in the later part of the notes*).

In an equilibrium mixture, all species are present and there is no change in its properties (*i.e.* density and colour, etc) with respect to time.

(a) System comprises reactants only initially

	A $\rightleftharpoons$	**C**
initial conc /mol dm^{-3}	**1.0**	0
eqm conc / mol dm^{-3}	0.2	0.8

(b) System comprises products only initially

	A $\rightleftharpoons$	**C**
initial conc / mol dm^{-3}	0	**0.5**
eqm conc / mol dm^{-3}	0.1	0.4

(c) System comprises mixture of reactants and products

	A $\rightleftharpoons$	**C**
initial conc / mol dm^{-3}	**1.0**	**0.5**
eqm conc / mol dm^{-3}	0.3	1.2

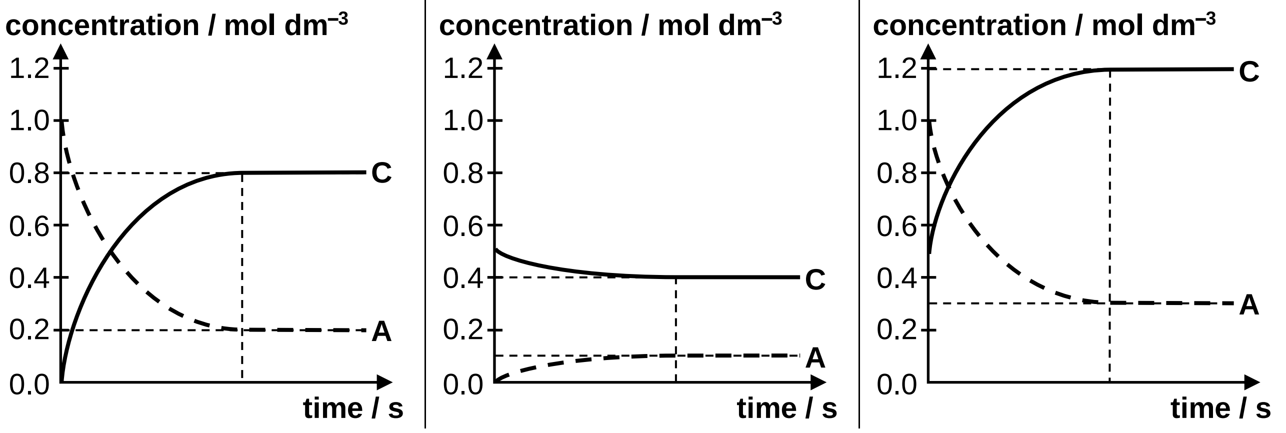


Fig. 2 Equilibrium **A** $\rightleftharpoons$ **C** is established **(a)** from only **A**, **(b)** only **C** **(c)** a mixture of **A** and **C**

Important concepts to remember:

(i) ***I need to know how to explain, in terms of rates of the forward and backward reactions, what is meant by a reversible reaction and dynamic equilibrium.***

(ii) ***I need to understand that at dynamic equilibrium both forward and backward reactions are still happening and the concentrations of reactants and products do not change.***

(iii) ***I need to know that there are many different ways to reach the same state of equilibrium.***

2 EQUILIBRIUM CONSTANTS, K_c and K_p

The **equilibrium constant indicates the proportion of products to reactants in an equilibrium mixture**. It applies only to a system in equilibrium and is written based on the given chemical equation.

2.1 Equilibrium Constant K_c

Consider the following general reversible reaction:

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

A series of experiments can be carried out using different initial amounts of **A** and **B** and allowing the reaction to reach equilibrium at the same temperature. For each experiment, the **equilibrium concentrations** of reactants and products can be measured to determine the ***equilibrium constant*** **(K_c)**.

$$\boxed{K_c = \frac{[\mathbf{C}]^c_{eqm}[\mathbf{D}]^d_{eqm}}{[\mathbf{A}]^a_{eqm}[\mathbf{B}]^b_{eqm}}}$$

where $[\,]_{eqm}$ denotes the **equilibrium concentration** of the substance in mol dm^{-3} and the value of K_c is **non-zero**.

The ratio of concentration of products to reactants at any instant throughout the reaction is known as the reaction quotient, Q.

$$Q = \frac{[\mathbf{C}]^c[\mathbf{D}]^d}{[\mathbf{A}]^a[\mathbf{B}]^b}$$

When the concentrations used in the above expression corresponds to the **equilibrium concentrations**, its value is denoted as K_c **(equilibrium constant)**.

K_c is the special value of Q when the reaction is **at equilibrium**.

The subscript “c” in K_c denotes that equilibrium constant is expressed in terms of concentrations.

Units of K_c is **(mol dm^{-3})**$^{c+d-(a+b)}$.

It was found that $\boldsymbol{K_c}$ always has the same constant value at the same particular temperature. **<u>K_c will remain constant as long as the temperature remains unchanged</u>**.

<u>Making Thinking Visible</u>

Q: Why do we need to define a K_c value? What is so helpful about knowing the K_c?

A: The K_c is defined by taking the concentrations of the products raised to the power that are the same as the stoichiometric coefficients in the chemical equation divided by the concentrations of the reactants raised to the power that are the same as the stoichiometric coefficients in the chemical equation. By having such a ratio value, it allows us to know relatively whether we get more products than reactants when certain conditions are being changed. So, a **<u>large K_c means we have more products than reactants</u>** which is a good measurement of the so-called **<u>extent of reaction</u>** (basically it reflects how much reactants has reacted only lah).

Q: Then what is the different between Q (reaction quotient) and K_c? Why do they both have the same expression?

A: Well, the Q gives the instantaneous ratio of the concentrations of the products over concentrations of reactants at a specific point of time. By having the same expression as the K_c, it can tell us “how far away” the system is with respect to the state of equilibrium. For example, if $Q > K_c$, you have more products at this instant as compared to when it is at the state of equilibrium. Thus, when equilibrium is reached, $Q = K_c$.

Q: Why is K_c only dependent on temperature?

A: Assuming the reversible reaction is an elementary reaction (meaning the reaction cannot be broken down into a few mechanistic steps, refer to Chemical Kinetics), you will see that the K_c is actually the ratio of the rate constants, k. And in Chemical Kinetics we learnt that rate constant is affected by temperature (refer to Arrhenius rate constant in Chemical Kinetics), hence, this explain the temperature dependency of K_c. In fact, take note that **<u>all equilibrium constants that you are going to learn are temperature dependent ONLY!</u>**

2.1.1 Homogeneous vs. Heterogeneous Equilibrium

- A **homogeneous equilibrium** involves substances that are **<u>all</u> in the same phase**. This include aqueous solution in which water is the solvent.
- A **heterogeneous equilibrium** involves substances that are **in different phases**.

Phase: Any uniform part of a system which is different from the rest of the system and separated from it by a distinct boundary. E.g. solid, liquid, gas and aqueous are different phases.

How many phases are there for a glass of oil floating on water?

LO (d) 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]

Example 2A

Give the K_c expression and its corresponding units for the following reversible reactions.

(a) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} \qquad \text{unit of } K_c = \frac{(\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3})^2(\text{mol dm}^{-3})} = \text{mol}^{-1}\ \text{dm}^3$$

Example 2A (continued)

Give the K_c expression and its corresponding units for the following reversible reactions.

(b) $2CrO_4^{2-}(aq) + H_2O(l) \rightleftharpoons Cr_2O_7^{2-}(aq) + 2OH^-(aq)$

$$K_c = \frac{[Cr_2O_7^{2-}][OH^-]^2}{[CrO_4^{2-}]^2} \qquad \text{unit of } K_c = \frac{(\text{mol dm}^{-3})(\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3})^2} = \text{mol dm}^{-3}$$

(c) $CH_3CO_2H(aq) + CH_3CH_2OH(aq) \rightleftharpoons CH_3CO_2CH_2CH_3(aq) + H_2O(l)$

$$K_c = \frac{[CH_3CO_2CH_2CH_3]}{[CH_3CO_2H][CH_3CH_2OH]} \qquad \text{unit of } K_c = \frac{(\text{mol dm}^{-3})}{(\text{mol dm}^{-3})^2} = \text{mol}^{-1}\ \text{dm}^3$$

Why is [$H_2O(l)$] omitted from the K_c expression for (b) and (c)?

For an equilibrium in **aqueous medium**, water is the solvent and has a much higher concentration than the other species present in the aqueous (diluted) solution. [$H_2O(l)$] remains relatively constant because the amount of H_2O reacted (or formed) is relatively insignificant.

What is the concentration of water?

Density of water = $\frac{1\ \text{g}}{1\ \text{cm}^3} = \frac{\frac{1\ \text{g}}{18.0\ \text{g mol}^{-1}}}{1\ \text{cm}^3} = \frac{0.05555\ mol}{1\ \text{cm}^3} = \frac{0.05555}{1}$ x 1000 mol dm^{-3} = 55.6 mol dm^{-3}

So, in a 1.0 mol dm^{-3} NaOH(aq), there are 1.0 mol of NaOH and 55.6 mol of H_2O molecules in 1 dm^3 solution. Do you see that the amount of water molecules is more significant than the dissolved solute in an aqueous solution???

(d) $CH_3CO_2H(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3CO_2CH_2CH_3(l) + H_2O(l)$

(Assume all reagents and products are miscible with each other.)

$$K_c = \frac{[CH_3CO_2CH_2CH_3][H_2O]}{[CH_3CO_2H][CH_3CH_2OH]} \qquad \text{unit of } K_c = \frac{(\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3})^2} = \text{no units}$$

Why is [$H_2O(l)$] NOT omitted from the K_c expression for (d)?

As water is NOT a solvent and all the species in the system are miscible, the [H_2O] needs to be included in the K_c expression as the volume of each of the species when mixed together will affect each other's concentration as the total volume is the sum of each individual volume.

(d) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$$K_c = [CO_2] \qquad \text{unit of } K_c = \text{mol dm}^{-3}$$

For heterogeneous equilibria:

- ***K*$_c$ expression** does **NOT** include the **concentration of solids and liquids.**
- **Why are concentrations of solids omitted in the *K*$_c$ expression?**
  The concentration of a solid is a constant.

<u>Derivation</u>: Since $[\text{solid}] = \dfrac{\text{amount}}{\text{volume}}$ and $\text{amount} = \dfrac{\text{mass}}{\text{molar mass}}$

Therefore, $[\text{solid}] = \dfrac{\text{mass}}{\text{volume} \times \text{molar mass}} = \dfrac{\text{density}}{\text{molar mass}} = \text{constant}$

Although the concentration of these species (solid or water [if aqueous medium]) are not included in the equilibrium expression, they do participate in the reaction and must be present in order for an equilibrium to be established.

LO (e) calculate the values of equilibrium constants in terms of concentrations or partial pressures from appropriate data

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

2.1.2 Calculation of *K*$_c$ from Concentrations

Example 2B

In a vessel, the initial concentrations of H_2(g), I_2(g) and HI (g) are 0.75, 0.83 and 0.11 mol dm^{-3} respectively. Concentration of H_2(g) is 0.15 mol dm^{-3} when equilibrium is established at 731 K.

Calculate *K*$_c$ for the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$. **[49.7]**

Solution

	H_2(g)	+	I_2(g)	$\rightleftharpoons$	2HI(g)
Initial conc / mol dm^{-3}	0.75$_{(S1)}$		0.83$_{(S1)}$		0.11$_{(S1)}$
Change in conc / mol dm^{-3}	–0.60$_{(S2)}$		–0.60$_{(S3)}$		+2(0.60)$_{(S3)}$
Eqm conc / mol dm^{-3}	0.15$_{(S1)}$		0.23$_{(S4)}$		1.31$_{(S4)}$

Tip: Create an ICE table to help you find the **<u>equilibrium</u> concentrations** of all species.

Tip: Check that you have applied the correct reacting stoichiometric ratio for change in concentration of each species.

$$K_c = \frac{[HI]^2}{[I_2][H_2]} = \frac{1.31^2}{0.23 \times 0.15} = 49.7 \text{ (no units)}$$

(Note: S1 means Step 1, S2 means Step 2… and the sequence is unique to this question)

Example 2C

2.00 mol of ethanoic acid and 2.00 mol ethanol are mixed at 350 K. 67 % of the reactants are converted into ethyl ethanoate and water.
Calculate K_c for the reaction at 350 K. **[4.12]**

Solution

	$CH_3CO_2H(l)$	+	$C_2H_5OH(l)$	$\rightleftharpoons$	$CH_3CO_2C_2H_5(l)$	+	$H_2O(l)$
Initial amount / mol	$2.00_{(S1)}$		$2.00_{(S1)}$		$0_{(S1)}$		$0_{(S1)}$
Change in amount / mol	-0.67×2.00 $= -1.34_{(S2)}$		-0.67×2.00 $= -1.34_{(S2)}$		$+1.34_{(S3)}$		$+1.34_{(S3)}$
Eqm amount / mol	$0.66_{(S4)}$		$0.66_{(S4)}$		$1.34_{(S4)}$		$1.34_{(S4)}$
Eqm conc / mol dm^{-3}	$\frac{0.66}{V}$ (S5)		$\frac{0.66}{V}$ (S5)		$\frac{1.34}{V}$ (S5)		$\frac{1.34}{V}$ (S5)

where V is the volume of the reaction vessel in dm^3.

$$K_c = \frac{[CH_3CO_2C_2H_5]}{[CH_3CO_2H][C_2H_5OH]} = \frac{\left(\frac{1.34}{V}\right)\left(\frac{1.34}{V}\right)}{\left(\frac{0.66}{V}\right)\left(\frac{0.66}{V}\right)} = 4.12 \text{ (no units)}$$

(Note: S1 means Step 1, S2 means Step 2… and the sequence is unique to this question)

2.1.3 Calculation of Concentrations from K_c

Example 2D

K_c for the reaction **A**(aq) $\rightleftharpoons$ **C**(aq) is 0.50 at 75 ºC. A solution of **A** with initial concentration of 15.0 mol dm^{-3} is allowed to reach equilibrium at 75 ºC.

(a) Calculate the concentrations of **A** and **C** at equilibrium. **[5.00 mol dm^{-3}, 10.0 mol dm^{-3}]**

(b) Calculate the degree of dissociation. **[0.333]**

Degree of dissociation, α = fraction of A dissociated or reacted

$$= \frac{\text{Amount of A reacted}}{\text{Initial amount of A}} \text{ or } \frac{\text{Concentration of A reacted}}{\text{Initial concentration of A}}$$

Solution

(a) Let x be the concentration of **A** reacted.

	A(aq)	$\rightleftharpoons$	**C**(aq)
Initial conc / mol dm^{-3}	$15.0_{(S1)}$		$0_{(S1)}$
Change in conc / mol dm^{-3}	$-x_{(S2)}$		$+x_{(S3)}$
Eqm conc / mol dm^{-3}	$(15.0-x)_{(S4)}$		$x_{(S4)}$

(Note: S1 means Step 1, S2 means Step 2… and the sequence is unique to this question)

$$K_c = \frac{[\mathbf{C}]}{[\mathbf{A}]}$$

$$0.50 = \frac{x}{15.0 - x}$$

$$x = 0.50(15.0 - x)$$

$$x = 5$$

$[\mathbf{C}]_{eqm}$ = **5.00 mol dm^{-3}** $[\mathbf{A}]_{eqm}$ = 15.0 – 5.00 = **10.0 mol dm^{-3}**

(b) Degree of dissociation $= \frac{5.00}{15.0} = \mathbf{0.333}$ (no units)

Example 2E [N94/P3/Q2]

For the reaction $CH_3CO_2H(l) + C_2H_5OH(l) \rightleftharpoons CH_3CO_2C_2H_5(l) + H_2O(l)$, the value of the equilibrium constant, K_c, is 4.0.

(a) Write an expression for the equilibrium constant, K_c', of the reverse reaction, *i.e.* the hydrolysis of ethyl ethanoate, stating its numerical value. [2]

(b) In an experiment, 2 mol of ethyl ethanoate and 2 mol of water are mixed. Calculate the amount of each substance present when equilibrium is reached.

(i) $CH_3CO_2H(l)$ **(ii)** $C_2H_5OH(l)$ **(iii)** $CH_3CO_2C_2H_5(l)$ **(iv)** $H_2O(l)$ [4]

[(a) 0.250; (b)(i) 0.667 mol; (ii) 0.667 mol; (iii) 1.33 mol; (iv) 1.33 mol]

Solution

(a) $CH_3CO_2C_2H_5(l) + H_2O(l) \rightleftharpoons CH_3CO_2H(l) + C_2H_5OH(l)$

$$K_c' = \frac{[CH_3CO_2H][C_2H_5OH]}{[CH_3CO_2C_2H_5][H_2O]} = \frac{1}{K_c} = \frac{1}{4.0} = \mathbf{0.250}$$

(b) Let x be the amount of $CH_3CO_2C_2H_5$ reacted

	$CH_3CO_2C_2H_5(l)$	+	$H_2O(l)$	$\rightleftharpoons$	$CH_3CO_2H(l)$	+	$C_2H_5OH(l)$
Initial amount / mol	$2_{(S1)}$		$2_{(S1)}$		$0_{(S1)}$		$0_{(S1)}$
Change in amount / mol	$-x_{(S2)}$		$-x_{(S2)}$		$+x_{(S2)}$		$+x_{(S2)}$
Eqm amount / mol	$2 - x_{(S3)}$		$2 - x_{(S3)}$		$x_{(S3)}$		$x_{(S3)}$
Eqm conc / mol dm^{-3}	$\frac{2-x}{V}$ (S4)		$\frac{2-x}{V}$ (S4)		$\frac{x}{V}$ (S4)		$\frac{x}{V}$ (S4)

where V is the volume of the reaction vessel.

(Note: S1 means Step 1, S2 means Step 2… and the sequence is unique to this question)

$$K_c' = \frac{[CH_3CO_2H][C_2H_5OH]}{[CH_3CO_2C_2H_5][H_2O]} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{2-x}{V}\right)\left(\frac{2-x}{V}\right)}$$

$$\frac{1}{4.0} = \left(\frac{x}{2-x}\right)^2$$

$$\frac{x}{2-x} = \pm\frac{1}{2}$$

$$x = \frac{2}{3} \text{ or } -2\text{(rejected)}$$

(i) Amount of CH_3COOH at eqm = **0.667 mol**

(ii) Amount of C_2H_5OH at eqm = **0.667 mol**

(iii) Amount of $CH_3CO_2C_2H_5$ at eqm = **1.33 mol**

(iv) Amount of H_2O at eqm = **1.33 mol**

Self Check 2A

Solutions of **A** and **B** are mixed. The initial concentrations of **A** and **B** in the mixture are 3.00 mol dm^{-3} and 7.00 mol dm^{-3} respectively. When equilibrium is established, [**B**(aq)] = 5.00 mol dm^{-3}.

Calculate K_c for the reaction **A**(aq) + 2**B**(aq) $\rightleftharpoons$ 4**C**(aq). **[5.12 mol dm^{-3}]**

Self Check 2B

Consider the reaction: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

1.00 mol of SO_3 is placed in a 2 dm^3 vessel initially. When equilibrium is reached at a particular temperature, the vessel is found to contain 0.54 mol of SO_2.

Calculate K_c. **[5.38 mol^{-1} dm^3]**

Self Check 2C

K_c for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 54 at 700 K. When an equimolar mixture of hydrogen and iodine is allowed to reach equilibrium at this temperature, the equilibrium concentration of HI is 0.85 mol dm^{-3}.

Calculate the equilibrium concentration of H_2 and I_2. **[0.116 mol dm^{-3}]**

Important concepts to remember:

(i) I need to know how to write the K_c expression in terms of concentration for a given reversible reaction.
(ii) I need to know how to determine the units for a K_c expression.
(iii) I need to know that if water is a solvent or there are other non-miscible solid or liquid in the reversible equation, these should not be included in the K_c expression.
(iv) I need to know how to calculate K_c from given information OR calculate the concentration of reactant or product from given K_c.

2.2 Equilibrium Constant, K_p (For GASEOUS systems only)

When dealing with reversible reactions involving gases

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

the equilibrium constant of the system can also be expressed in terms of partial pressures of the gases as follows:

$$K_p = \frac{p_C^c \times p_D^d}{p_A^a \times p_B^b}$$

where p_x is the partial pressure of gas x at equilibrium.

Units of K_p (depending on the units of pressure):
(atm)$^{c+d-a-b}$ or **(Pa)$^{c+d-a-b}$** or **(Nm^{-2})$^{c+d-a-b}$**

Note for H1 Chemistry students:

Knowledge, understanding, and application of K_p is **not required** for students reading H1 Chemistry.

Recall that the partial pressure of gas **A** in a mixture of gases is the pressure that gas **A** would exert if it is present in the container by itself.

$$p_A = \chi_A \times p_T$$
$$= \frac{n_A}{n_T} \times p_T$$

where
$n_T = n_A + n_B + n_C + n_D$
n_A = amount of gas **A**
$p_T = p_A + p_B + p_C + p_D$

Example 2F

Give the K_p expression and its corresponding units for the following reversible reactions. Use atm as the unit for pressure.

(a) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$$K_p = \frac{p_{SO_3}^2}{p_{SO_2}^2 \times p_{O_2}} \qquad \text{units} = \frac{(\text{atm})^2}{(\text{atm})^2(\text{atm})} = \text{atm}^{-1}$$

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

$$K_p = \frac{p_{NH_3}^2}{p_{N_2} \times p_{H_2}^3} \qquad \text{units} = \frac{(\text{atm})^2}{(\text{atm})(\text{atm})^3} = \text{atm}^{-2}$$

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

$$K_p = \frac{p_{H_2}^4}{p_{H_2O}^4} \qquad \text{units} = \frac{(\text{atm})^4}{(\text{atm})^4} = \text{no units}$$

K_p expression **does not** include solids and liquids because solids and liquids contribute ***little or no pressure to the system.***

2.2.1 Calculation of K_p from Partial Pressures

Example 2G

Consider the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

3.00 mol of SO_2, 3.60 mol of O_2 and 4.80 mol of SO_3 were heated initially in a vessel and allowed to reach equilibrium at 1.40 atm. The equilibrium amount of SO_2 is 2.60 mol.
Calculate **(a)** the partial pressures of SO_2, O_2 and SO_3 at equilibrium, **(b)** K_p for the reaction.

[(a) 0.325 atm; 0.425 atm; 0.650 atm (b) 9.41 atm^{-1}]

	$2SO_2(g)$	+	$O_2(g)$	⇌	$2SO_3(g)$
Initial amount / mol	3.00(S1)		3.60(S1)		4.80(S1)
Change in amount /mol	–0.40(S2)		$-\frac{0.40}{2}$ (S3)		+0.40(S3)
Eqm amount / mol	2.60(S1)		3.40(S4)		5.20(S4)

(Note: S1 means Step 1, S2 means Step 2… and the sequence is unique to this question)

Total amount of gases at eqm = **2.60 + 3.40 + 5.20 = 11.2 mol**

(a)

$$p_{SO_2} = \frac{2.60}{11.2} \times 1.40 = 0.325 \text{ atm}$$

$$p_{O_2} = \frac{3.40}{11.2} \times 1.40 = 0.425 \text{ atm}$$

$$p_{SO_3} = \frac{5.20}{11.2} \times 1.40 = 0.650 \text{ atm}$$

(b)

$$K_p = \frac{p_{SO_3}^2}{p_{SO_2}^2 \times p_{O_2}} = \frac{0.650^2}{0.325^2 \times 0.425} = \mathbf{9.41\,atm^{-1}}$$

2.2.2 Calculation of Partial Pressures from K_p

Example 2H

Consider $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $K_p = 0.725$ atm at 323 K

A sample of $N_2O_4(g)$ is heated and equilibrium is established at 323 K. The partial pressure of N_2O_4 at equilibrium is 0.500 atm.

Calculate the **(a)** partial pressure of NO_2 at equilibrium,
(b) final pressure,
(c) initial pressure of N_2O_4,
(d) percentage of $N_2O_4(g)$ dissociated.

Solution

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
Initial partial pressure / atm	$0.500 + \frac{1}{2}p_{NO_2}$ (S4)		0 (S1)
Change in partial pressure / atm	$-\frac{1}{2}p_{NO_2}$ (S3)		$+p_{NO_2}$ (S3)
Eqm partial pressure / atm	0.500 (S1)		p_{NO_2} (S2)

(Note: S1 means Step 1, S2 means Step 2…, and the sequence is unique to this question)

(a)
$$K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}}$$
$$0.725 = \frac{p^2_{NO_2}}{0.500}$$
$$p_{NO_2} = \mathbf{0.602\ atm}$$

(b) Final pressure $= p_{NO_2} + p_{N_2O_4}$
$= 0.602 + 0.500$
$= \mathbf{1.10\ atm}$

(c) Initial pressure of N_2O_4 = **0.500 + ½(0.602)** = **0.801 atm**

(d) % of N_2O_4 dissociated $= \frac{\frac{1}{2}(0.602)}{0.801} \times 100\%$
$= \mathbf{37.6\%}$

2.3 Interpreting and Working with Equilibrium Constants

1. The value of equilibrium constant K_c or K_p is **not affected** by concentration or partial pressure of reactants and products, pressure of the system, the presence of catalysts, and does not depend on reaction mechanism.

The **value** of K_c or K_p for a reversible reaction **only depends** on **TEMPERATURE**!

2. What information can be obtained from the equilibrium constants?

The value of equilibrium constant provides a measure of the **position of equilibrium** (the ***extent*** of the reactions at equilibrium).

$$A(g) + B(g) \rightleftharpoons C(g) + D(g) \qquad K_c = \frac{[C][D]}{[A][B]} \text{ and } K_p = \frac{p_C p_D}{p_A p_B}$$

The value of equilibrium constant tells us the ***extent*** of the forward reaction at equilibrium.

K_c or $K_p \gg 1$	forward reaction proceeds almost to completion
K_c or $K_p \ll 1$	forward reaction hardly proceeds.

For example,

reaction	**K_c at 298 K**	**position of equilibrium**
$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$	10^{33} (very large value)	lies to the far right
$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$	10^{-31} (very small value)	lies to the far left

3. The equilibrium constant will vary in accordance to the way the chemical equation for a reaction is defined.

Let the equilibrium constant for a reaction be $\boldsymbol{K_c}$.

- If the equation of that reaction is multiplied by ***n***, new equilibrium constant $= \boldsymbol{K_c^n}$.
- If the equation of that reaction is reversed, new equilibrium constant $= \dfrac{1}{K_c} = \boldsymbol{K_c^{-1}}$.

Making Thinking Visible

Q: What do you mean by the position of equilibrium?

A: Position of equilibrium refers to a particular state of equilibrium, i.e. when equilibrium is reached, the concentrations of the reactants and products that are present at this state of equilibrium. Basically, position of equilibrium reflects the composition of this state of equilibrium.

Example 2I

For the reaction $2A_2(g) + B_2(g) \rightleftharpoons 2A_2B(g)$, K_c = 100 mol^{-1} dm^3. Under the same conditions, calculate the equilibrium constant K_c for

(i) $4A_2(g) + 2B_2(g) \rightleftharpoons 4A_2B(g)$

$$K_c' = \frac{[A_2B]^4}{[A_2]^4[B_2]^2} = \left(\frac{[A_2B]^2}{[A_2]^2[B_2]}\right)^2 = K_c^2 = 100^2\ (\text{mol}^{-1}\ \text{dm}^3)^2 = \mathbf{10000\ mol^{-2}\ dm^6}$$

(ii) $A_2B(g) \rightleftharpoons A_2(g) + \tfrac{1}{2}B_2(g)$

$$K_c'' = \frac{[A_2][B_2]^{\frac{1}{2}}}{[A_2B]} = \left(\frac{[A_2]^2[B_2]}{[A_2B]^2}\right)^{\frac{1}{2}} = \left(\frac{1}{K_c}\right)^{\frac{1}{2}} = \left(\frac{1}{100}\right)^{\frac{1}{2}} (\text{mol dm}^{-3})^{\frac{1}{2}} = \mathbf{0.1\ mol^{\frac{1}{2}}\ dm^{-\frac{3}{2}}}$$

4. However, equilibrium constants **do not** give any information on:
    - rates of forward and backward reactions
    - time required for the reaction to reach equilibrium.

These two sets of data can only be obtained experimentally.

5. Equilibrium constants can only be determined ***experimentally***.

Experimental determination of K_c [N83/P1/Q3(part)]

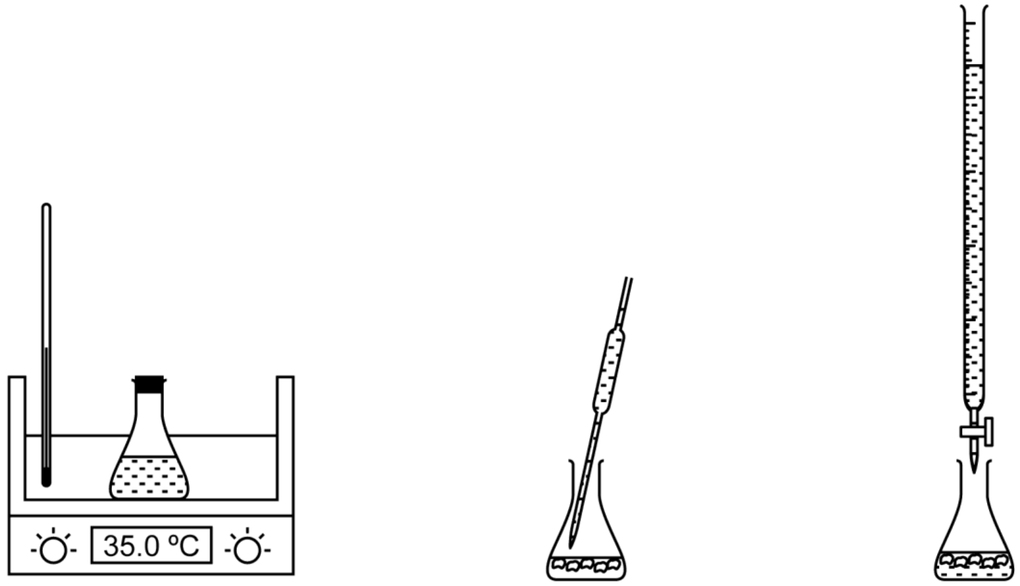
Describe, with essential experimental details, how you would determine the equilibrium constant, K_c, for the following reaction:

$$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOCH_2CH_3(l) + H_2O(l)$$

Mix a known amount of CH_3COOH and CH_3CH_2OH in a conical flask. Allow the solution to stand for some time to establish equilibrium (why?). When equilibrium is established at a fixed temperature, the reaction mixture is then rapidly cooled (why?), followed by titrating a fixed volume of the mixture rapidly (why?) with standard NaOH(aq) to determine the concentration of CH_3COOH in the equilibrium mixture. The concentrations of other species in the equilibrium mixture are then calculated and hence, K_c can be calculated.

$$K_c = \frac{[CH_3COOCH_2CH_3]_{eqm}[H_2O]_{eqm}}{[CH_3COOH]_{eqm}[CH_3CH_2OH]_{eqm}}$$

The above procedure is repeated at the same temperature by using different initial amounts of CH_3COOH and CH_3CH_2OH so that an average value of K_c at that particular temperature can be obtained.



mixture allowed to **equilibrate** in a **thermostatically-controlled water bath** (temperature is controlled)

a 10 cm^3 sample of the mixture is run into a flask containing ice and water

CH_3COOH in the reaction mixture is titrated quickly with an alkali, *e.g.* NaOH

Fig. 3 Method for determining the equilibrium constant of the reaction between ethanol and ethanoic acid.

Important concepts to remember:

(i) I need to know that ALL equilibrium constants are temperature dependent.

(ii) I need to know that larger the equilibrium constant, the greater the extent of the reaction i.e. position of equilibrium lies towards the product side.

(iii) I need to know that equilibrium constant DOES NOT indicate the kinetics of the reaction, i.e. it doesn't tell us how fast the reaction is.

(iv) I need to know how plan an experiment to determine the equilibrium constant.

LO (g) show understanding that the position of equilibrium is dependent on the standard Gibbs free energy change of reaction, ΔG. [Quantitative treatment is **not** required]

3 Gibbs Free Energy and Equilibrium Constant

3.1 $\Delta G^\ominus$ and State of Dynamic Equilibrium

Whether a reaction is spontaneous or not depends on the value of ΔG at that particular composition.

Note for H1 Chemistry students:

Understanding and application of the relationship between ΔG and K is **not required** for students reading H1 Chemistry.

- If **$\Delta G^\ominus < 0$**, the reaction proceeds in the direction of **forward reaction** which is **spontaneous**; the forward reaction occurs at a faster rate than the backward reaction (when equilibrium has yet to reach).
- If **$\Delta G^\ominus > 0$**, the reaction proceeds in the direction of **backward reaction** which is **spontaneous**; the backward reaction occurs at a faster rate than the forward reaction (when equilibrium has yet to reach).
- If **$\Delta G = 0$**, the system is in **dynamic equilibrium**; rate of forward reaction is equal to rate of backward reaction (at equilibrium).

Hence, the **condition for a system in a state of dynamic equilibrium at a particular constant temperature and pressure is $\Delta G = 0$** (i.e. **G is at its minimum**).

3.2 $\Delta G^\ominus$ and Equilibrium Constant

ΔG represents the change in Gibbs free energy of a reaction at any composition of the reaction mixture at a particular constant temperature (which may not be under standard conditions).

ΔG is also related to the change in *standard* Gibbs free energy $(\Delta G^\ominus)$ as follows:

$$\Delta G = \Delta G^\ominus + \mathrm{RT} \ln Q$$

where Q is the reaction quotient.

When a system is at a state of equilibrium at a particular constant temperature, $Q = K$ and $\Delta G = 0$ where K is the equilibrium constant. Hence $\Delta G^\ominus$ is related to equilibrium constant of a reaction as:

$$\Delta G^\ominus = -\,\mathrm{RT} \ln K = -2.303\,\mathrm{RT} \lg K$$

So the sign and value of $\Delta G^\ominus$ provides information on the position of equilibrium:

$\Delta G^\ominus \ll 0$	$K \gg 1$	position of equilibrium lies to **far right** (reaction goes almost to completion)
$\Delta G^\ominus \gg 0$	$K \ll 1$	position of equilibrium lies to **far left** (reaction hardly proceeds)

Take note that the **sign of $\Delta G^\ominus$** only provides information about whether a reaction is spontaneous or not under **standard** conditions.

Important concepts to remember:

(i) I need to know the following:

$K > 1$, $\Delta G^{e} < 0$ $\Rightarrow$ position of equilibrium lies to the right, forward reaction is spontaneous

$K < 1$, $\Delta G^{e} > 0$ $\Rightarrow$ position of equilibrium lies to the left, forward reaction is non-spontaneous.

4 FACTORS AFFECTING CHEMICAL EQUILIBRIA

LO (b) 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

(c) deduce whether changes in concentration, pressure or temperature or the presence of a catalyst affect the value of the equilibrium constant for a reaction

4.1 Le Chatelier's Principle

1. Factors that affect chemical equilibria:
   - Concentration
   - Pressure
   - Temperature
   - Catalyst

2. Changes of the above factors may result in
   - shifting of the ***POSITION of equilibrium*** to the left or right,
     - *i.e.* change in the equilibrium concentrations of substances;
   - change in K_c or K_p ***(only for changes in temperature)***;
   - change in the ***rate*** at which equilibrium is established.

How to predict?
Apply
Le Chatelier's principle

Le Chatelier's principle states that if a ***system in equilibrium*** is subjected to a ***change*** which ***disturbs the equilibrium***, the system responds in such a way to ***counteract*** the **effect of the change** imposed, in order to **re-establish the equilibrium** of the system.

4.2 Effect of Concentration (or Partial Pressure) Changes

1. Consider the system **A(g)** $\rightleftharpoons$ **C(g)** in equilibrium.

   According to Le Chatelier's principle,

   - If the concentration (or partial pressure) of **A** is increased, the system will respond to remove some (*not all!*) of **A** added. It does this by reacting some **A** to form more **C** *i.e.* the forward reaction is favoured.
     - *The position of equilibrium shifts to the right*, forming a new equilibrium mixture.

   - On the other hand, if the concentration (or partial pressure) of **A** is decreased, the system will respond to form more **A**. It does this by reacting some **C** to form more **A** *i.e.* the backward reaction is favoured.
     - *The position of equilibrium shifts to the left*, forming a new equilibrium mixture.

Why is this so?:

At a constant temperature, K_c is a constant and $K_c = \frac{[\mathbf{C}]}{[\mathbf{A}]}$.

Supposing denominator [**A**] is increased, the fraction $\frac{[\mathbf{C}]}{[\mathbf{A}]}$ decreases at that instant. The system is no longer at equilibrium. To re-establish equilibrium, [**A**] would need to decrease (react away some **A**) while [**C**] would increase (more **C** is formed) until the fraction $\frac{[\mathbf{C}]}{[\mathbf{A}]}$ becomes equal to K_c again. ∴System is at equilibrium once again.

Example 4A

State and explain the effect of the following changes on the position of equilibrium of

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

(a) Addition of ammonia

When ammonia is added, the **position of equilibrium** shifts to the **left** to **remove some** of the ammonia that was added.

(b) Removal of nitrogen

When nitrogen is removed, the **position of equilibrium** shifts to the **left** to **form some** of the nitrogen that was removed.

(c) Increase partial pressure of hydrogen

When partial pressure of hydrogen is increased, the **position of equilibrium** shifts to the **right** to **remove some** of the hydrogen **added**.

$p_{H_2} = \frac{n_{H_2}RT}{V}$ (V & T constant)

∴ ↑ in p_{H_2} ⇒ addition of H_2

2. Note that:
   - If a large excess of one reactant is used, the position of equilibrium can be made to shift towards the right-hand-side.
   - If the product in the equilibrium mixture is continuously removed, the forward reaction can go to *completion* because the position of equilibrium is continuously shifted to the right.

3. The concentration of reactants and products in the ***new equilibrium*** can be calculated:

Example 4B

The system **A** $\rightleftharpoons$ **B** is in equilibrium at 75 ºC with 10 mol dm^{-3} of **A** and 5 mol dm^{-3} of **B**. If the concentration of **A** in the equilibrium mixture is increased by 7.5 mol dm^{-3}, what will be the concentration of **A** and **B** when equilibrium is established again at the same temperature?
Given K_c = 0.50 at 75 ºC.

	A	$\rightleftharpoons$	**B**
new "initial" conc. / mol dm^{-3}	10 **+ 7.5** = **17.5** (S1)		5(S1)
Change / mol dm^{-3}	**– x**		**+ x**
new eqm conc. / mol dm^{-3}	**17.5 – x**		**5 + x**

System is no longer at equilibrium; system responds to remove some of the **A** added *i.e.* forward reaction occurs.
⇒ ① equilibrium shifts to the right.
② when equilibrium is re-established, conc. of **A** is between 10 and 17.5 mol dm^{-3}.

At the new eqm,

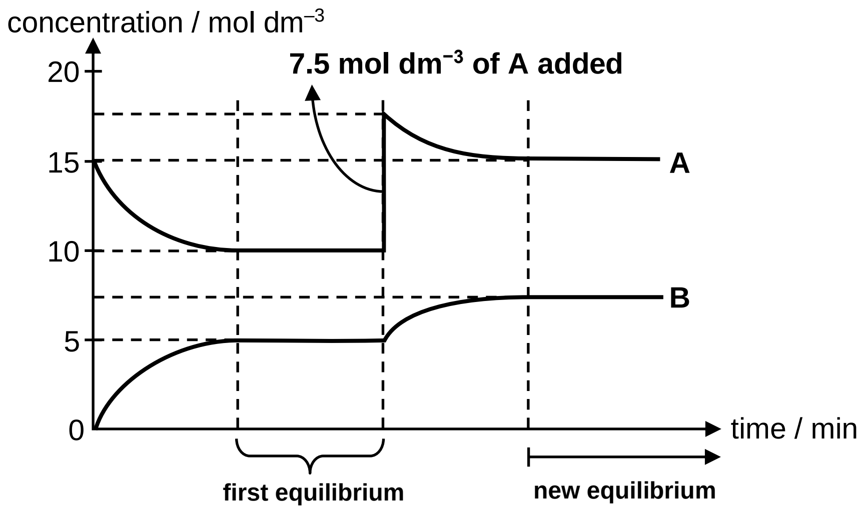
$$K_c = \frac{[\mathbf{B}]}{[\mathbf{A}]}$$

$$0.50 = \frac{5 + x}{17.5 - x}$$

$$5 + x = 0.50(17.5 - x)$$

$$x = 2.5$$

$[\mathbf{A}]_{\text{new eqm}}$ = 17.5 – 2.5 = **15.0 mol dm^{-3}**
$[\mathbf{B}]_{\text{new eqm}}$ = 5 + 2.5 = **7.5 mol dm^{-3}**



Note:
When eqm is re-established, the conc. of **A** and **B** in the new eqm will be different from those in the first eqm.

The ratio $\frac{[\mathbf{B}(\text{aq})]}{[\mathbf{A}(\text{aq})]}$ is **always 0.50**, since K_c is a constant at constant temperature.

Important concepts to remember:

(i) ***I need to know the definition of Le Chatelier's Principle and use it to explain the position of equilibrium when a system at equilibrium is subjected to a change.***
(ii) ***I need to know that a change made to a system at equilibrium CANNOT be totally removed.***
(iii) ***I need to know that change of concentration (partial pressure) DOES NOT affect the equilibrium constant.***
(iv) ***I need to know that if the change is an increase in concentration, then at the new equilibrium, both the forward rate and backward rate will be greater than before the change is made.***

4.3 Effect of Pressure (or Volume) Changes (Pressure is total pressure)

$$\text{pressure} \propto \frac{1}{\text{volume}}$$

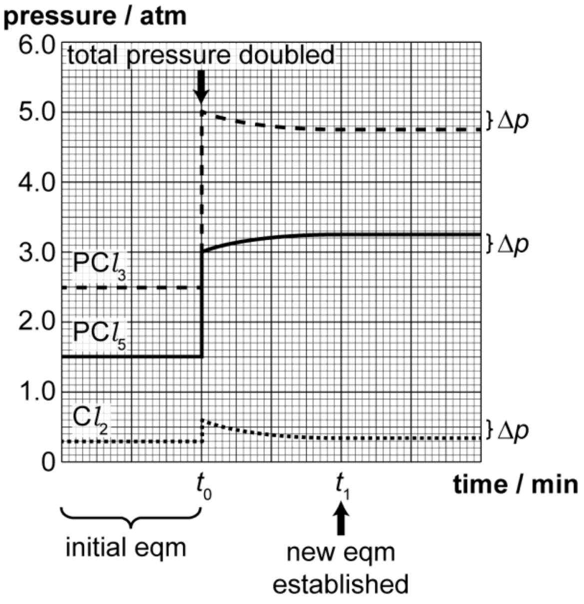
1. Changes in pressure affect **only** reactions involving **gases**.
2. According to Le Chatelier's principle, if the **total pressure** of a gaseous mixture is **increased** (by decreasing the volume), the system will respond to ***reduce*** the pressure by reducing the number of **GASEOUS** molecules. Thus the position of equilibrium is shifted towards the direction that results in a ***decrease in number of gaseous molecules***.

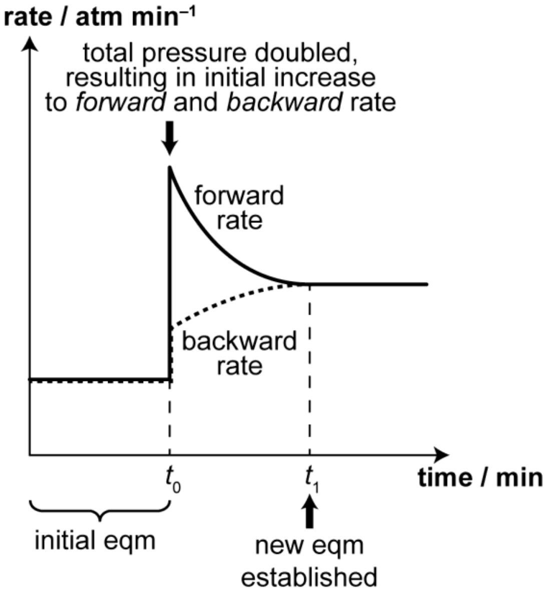
E.g. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

- When pressure is increased, the position of equilibrium shifts to the **right** so as to **decrease** the pressure by **decreasing** the number of gas molecules.
- When pressure is decreased, the position of equilibrium shifts to the **left** so as to **increase** the pressure by **increasing** the number of gas molecules.

E.g. Changes to pressure and rate when total pressure increases in $PCl_3 + Cl_2 \rightleftharpoons PCl_5$ (for instance, total pressure doubles when the volume of vessel is halved)

	PCl_3	+	Cl_2	$\rightleftharpoons$	PCl_5
initial eqm partial pressure / atm	2.500		0.300		1.500
partial pressure **when V is halved** / atm	5.000		0.600		3.000
new eqm partial pressure / atm	4.743		0.343		3.257





Example 4C

State the changes in the following position of equilibrium when the pressure changes.

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

Pressure increase, position of equilibrium shifts to the **right**, to **decrease** the number of gas molecules.

(b) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Pressure increases, position of equilibrium **remains unchanged**.

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

Pressure decreases, position of equilibrium **remains unchanged**.

3. What happens if we add some inert gas to the equilibrium system??

Scenario 1: Noble gas is added at constant pressure…

- From $pV = nRT$, when n increase (due to inert gas), in order for p to be the same, V has to increase!
- When V increase, concentrations of **A**, **B** and **C** all decrease.
- According to Le Chatelier's principle, the system will respond to ***increase*** the concentration by increasing the number of **GASEOUS** molecules. Thus the position of equilibrium is shifted towards the direction that results in an ***increase in number of gaseous molecules***.

For **A**(g) + **B**(g) $\rightleftharpoons$ **C**(g): Position of equilibrium shifts left.

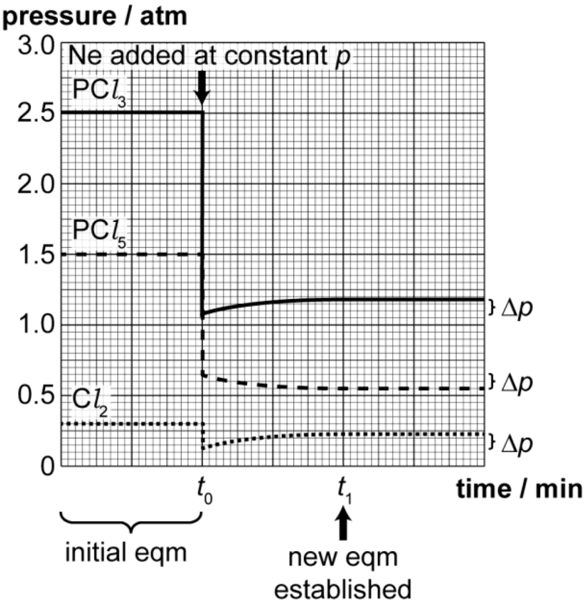
For **A**(g) $\rightleftharpoons$ **C**(g): No shift in position of equilibrium.

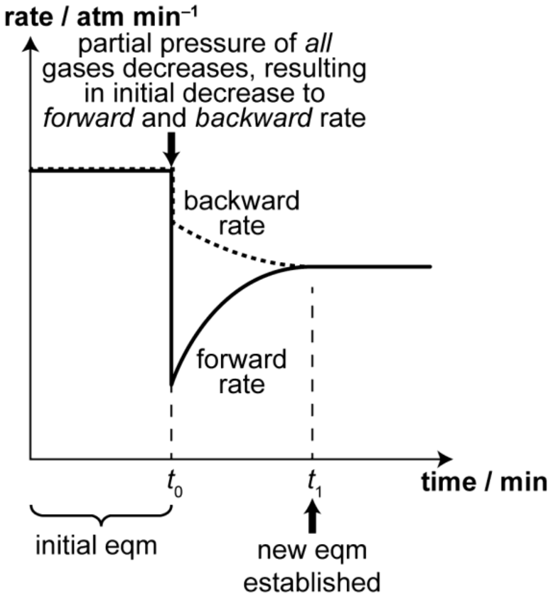
Scenario 2: Noble gas is added at constant volume…

- From $pV = nRT$, when n increase (due to inert gas), in order for V to be the same, p has to increase!
- When V is the same, concentrations of **A**, **B** and **C** DO NOT change.
- According to Le Chatelier's principle, the system will not respond! Thus the position of equilibrium remains unchange.

E.g. Changes to pressure and rate when Ne gas is added to $PCl_3 + Cl_2 \rightleftharpoons PCl_5$ at constant pressure

	PCl_3	+	Cl_2	$\rightleftharpoons$	PCl_5
initial eqm partial pressure / atm	2.500		0.300		1.500
partial pressure **after adding Ne** / atm	1.075		0.129		0.645
new eqm partial pressure / atm	1.177		0.231		0.543





Important concepts to remember:

(i) I need to know that change of pressure (or volume) has no effect on the position of equilibrium for a reversible reaction that have equal number of moles of gas particles on both sides of the equation.

(ii) I need to know that change of pressure (or volume) DOES NOT affect the equilibrium constant.

(iv) I need to know that if the change is an increase in pressure, then at the new equilibrium, both the forward rate and backward rate will be greater than before the change is made.

4.4 Effect of Temperature Changes

1. According to Le Chatelier's principle, if the temperature of an equilibrium mixture ***increases***, the system will respond to ***decrease*** the temperature by ***absorbing* some of the heat**, hence shifting the position of equilibrium towards the ***endothermic*** direction.

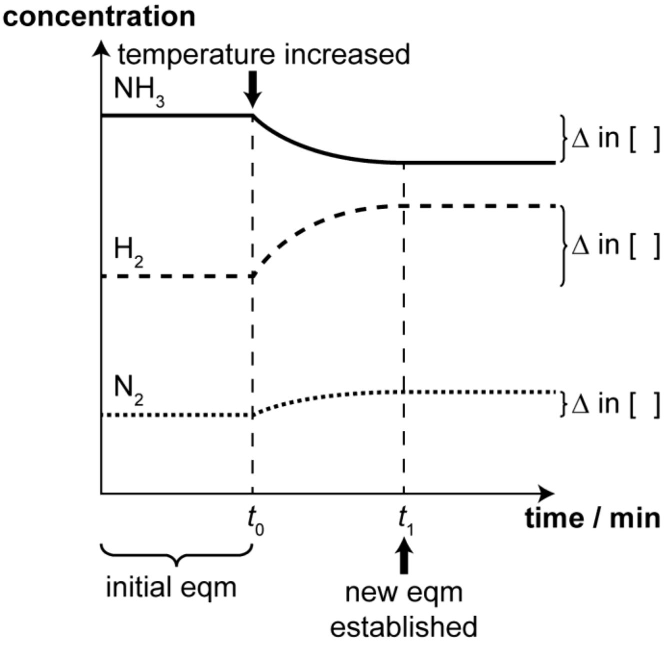
2. **K_c and K_p are only affected by changes in temperature.**
Consider the equilibrium $a\mathbf{A}(g) + b\mathbf{B}(g) \rightleftharpoons c\mathbf{C}(g) + d\mathbf{D}(g)$

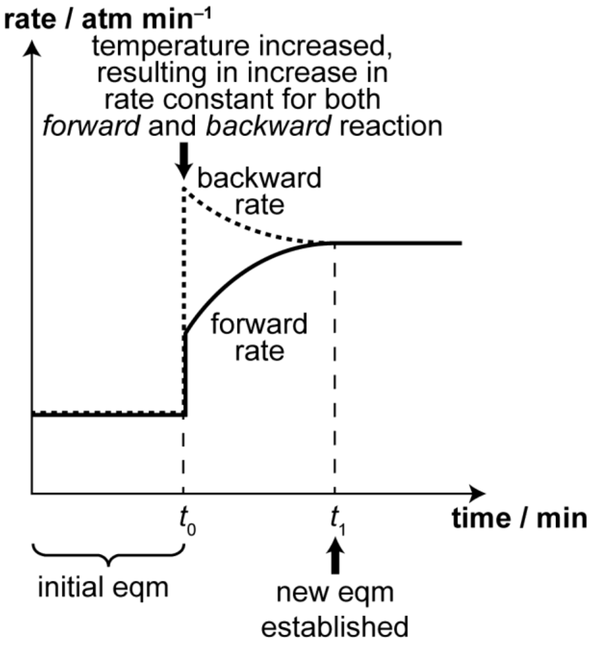
Given, $K_c = \dfrac{[\mathbf{C}]^c_{eqm}[\mathbf{D}]^d_{eqm}}{[\mathbf{A}]^a_{eqm}[\mathbf{B}]^b_{eqm}}$ and $K_p = \dfrac{p^c_{\mathbf{C}} \times p^d_{\mathbf{D}}}{p^a_{\mathbf{A}} \times p^b_{\mathbf{B}}}$

(a) If ΔH is negative (***exothermic***):

- As temperature *increases*, the position of equilibrium shifts to the **left** to favour the endothermic reaction so as to **absorb** some heat, resulting in **less** products at equilibrium, hence K_c (or K_p) **decreases**.

E.g. Changes to concentration and rate when temperature increases for an exothermic reaction: $3H_2 + N_2 \rightleftharpoons 2NH_3$



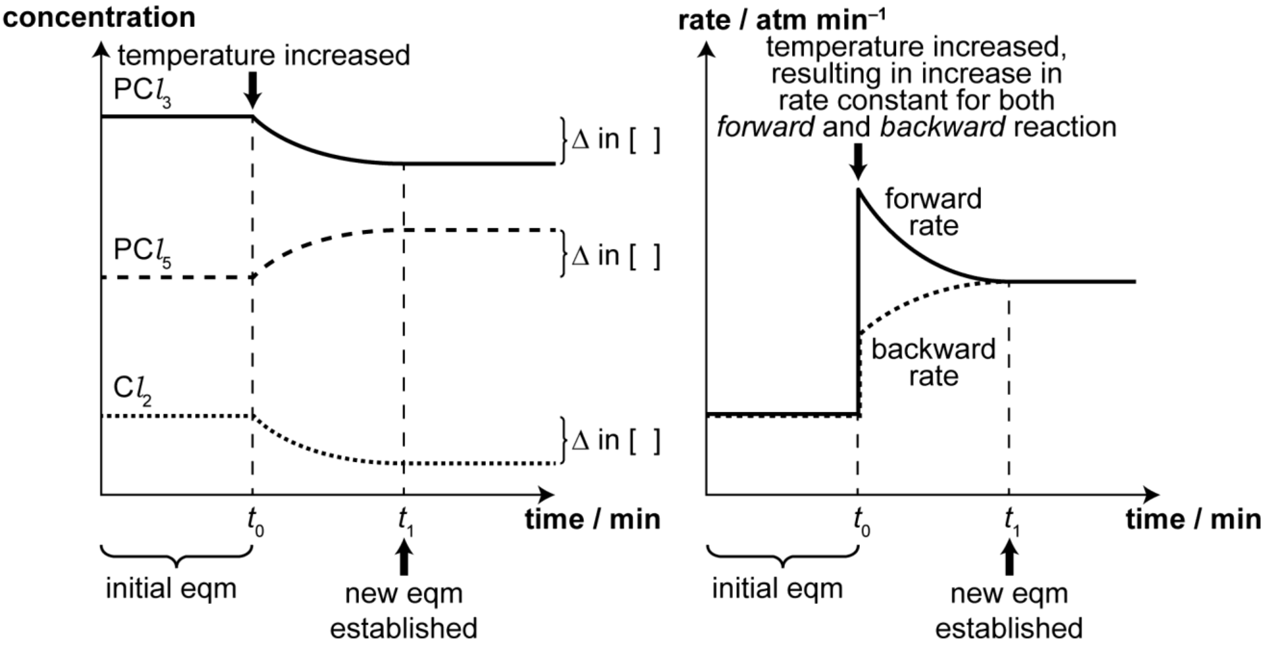


- As temperature *decreases*, the position of equilibrium shifts to the **right** to favour the exothermic reaction so as to **produce** some heat, resulting in **more** products at equilibrium, hence K_c (or K_p) **increases**.

(b) If ΔH is positive (***endothermic***):

- As temperature *increases*, the position of equilibrium shifts to the **right** to favour the endothermic reaction so as to **absorb** some heat, resulting in **more** products at equilibrium, hence K_c (or K_p) **increases**.

E.g. Changes to concentration and rate when temperature increases for an endothermic reaction: $PCl_3 + Cl_2 \rightleftharpoons PCl_5$



As temperature *decreases*, the position of equilibrium shifts to the **left** to favour the endothermic reaction so as to **produce** some heat, resulting in **less** products at equilibrium, hence K_c (or K_p) **decreases**.

Example 4D

State the change in the position of the equilibrium and predict the observation when temperature changes.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H = +57.2 \text{ kJ mol}^{-1}$$

colourless dark brown

change	position of equilibrium	observation	K_c
increase in temperature	shifts to the **right** (endothermic reaction favoured)	**turns darker brown**	**increase**
decrease in temperature	shifts to the **left** (exothermic reaction favoured)	**turns lighter brown**	**decrease**

(c) For reaction with $\Delta H = 0$, changes in temperature have no effect on the value of K_c or K_p since the position of equilibrium is unchanged.

Important concepts to remember:

(i) I need to know that increase in temperature favours the endothermic reaction as heat is being absorbed while decrease in temperature favours the exothermic reaction.

(ii) I need to know that K_c for an exothermic reaction decreases with temperature increase. Vice versa for an endothermic reaction.

(iv) I need to know that increase in temperature increase BOTH the forward and backward reactions. Vice versa for a decrease in temperature.

4.5 Effect of Addition of Catalyst

A catalyst is a substance which **increases** the **rate of a reaction** by providing an *alternative reaction pathway with a lower activation energy*, without itself undergoing any permanent chemical change. Thus, catalysts generally do not appear in the overall chemical equation as reactants or products.

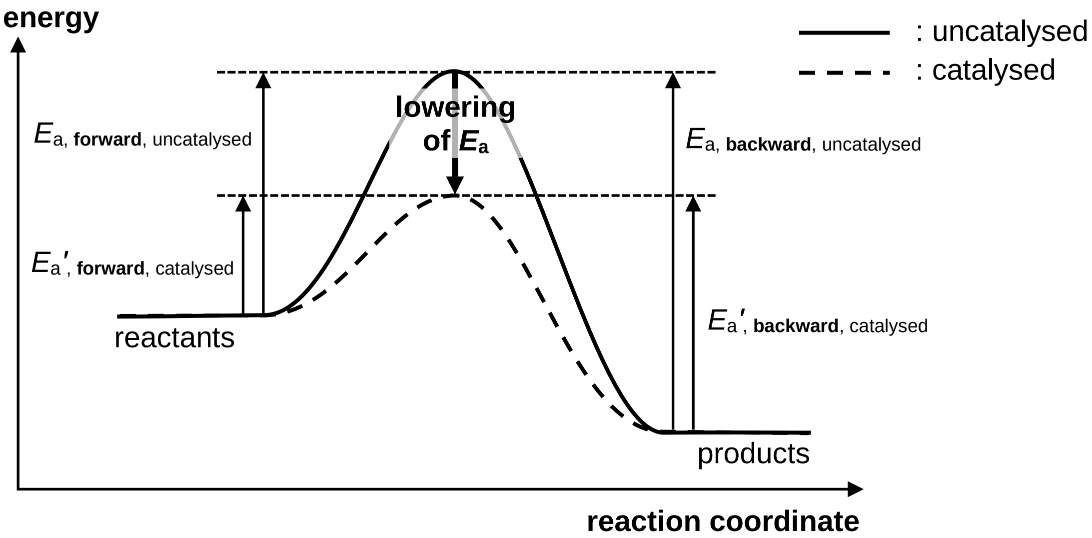


Fig. 4 Catalyst lowers the activation energy of both forward reaction and backward reaction by the same extent

As shown in Fig. 4, catalyst lowers the activation energy of the forward and backward reactions **by the same extent**. This means the rate constant of the forward and backward reactions will be increased **by the same extent** (recall Arrhenius equation, $k = Ae^{-\frac{E_a}{RT}}$).

Since rate is directly proportional to rate constant, presence of **catalyst increases the rates of both the forward and backward reactions by the same extent**. This implies that the presence of catalyst **does not affect the position of equilibrium** and the system merely reaches equilibrium **faster** (see Fig. 5).

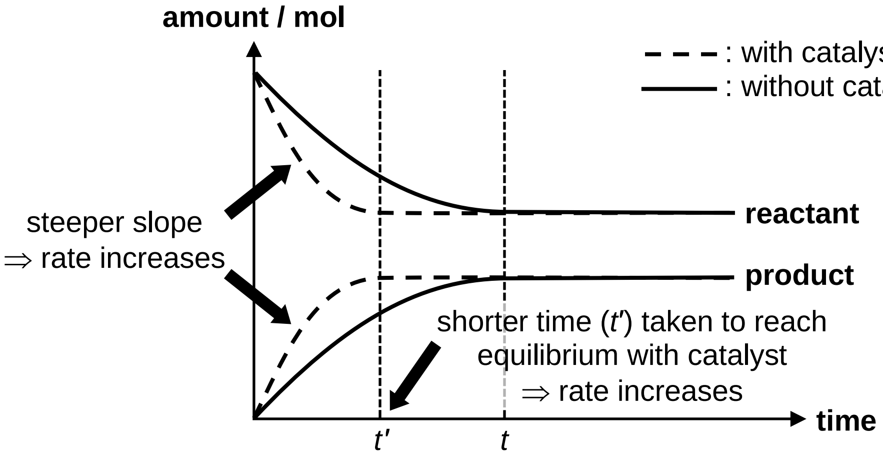


Fig. 5 Effect of catalyst on rate and position of equilibrium

To conclude, the presence or absence of catalyst ***does not affect the position of equilibrium and equilibrium constant,*** K_c **or** K_p.

Important concepts to remember:

(i) ***I need to know that catalyst DOES NOT affect the*** K_c***!***
(ii) ***I need to know that catalyst increase both forward and backward rate by same extent, hence, system reach equilibrium in a shorter time.***

Self-Check 4A

The following equilibrium exists in a system containing carbon monoxide and hydrogen gases.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H < 0$$

Which of the following actions would result in an increase in the yield of methanol gas?

A adding a catalyst

B heating the system

C liquefying the product by cooling

D lowering the pressure of the system

Self-Check 4B

Circle the correct responses in the table below for the effect of varying conditions on the equilibrium

$$\mathbf{A}(g) + 2\mathbf{B}(g) \rightleftharpoons 3\mathbf{C}(g) + 4\mathbf{D}(g) \qquad \Delta H < 0$$

changes imposed on the system in equilibrium	**position of equilibrium**	**equilibrium constant**	**initial reaction rate due to change**
[**A**] and/or [**B**] increased (or partial pressure of **A** or **B** increases for gaseous systems)	shifts to the **right | left**	**no change | increases | decreases**	forward reaction: **faster | slower | same** backward reaction: **faster | slower | same**
[**C**] and/or [**D**] increased (or partial pressure of **C** or **D** increases for gaseous systems)	shifts to the **right | left**	**no change | increases | decreases**	forward reaction: **faster | slower | same** backward reaction: **faster | slower | same**
decrease in system pressure (*for gaseous systems only*)	shifts to the **right | left**	**no change | increases | decreases**	forward reaction: **faster | slower | same** backward reaction: **faster | slower | same**
increase in temperature	shifts to the **right | left**	**no change | increases | decreases**	forward reaction: **faster | slower | same** backward reaction: **faster | slower | same**
addition of a catalyst	**no change**	**no change**	forward reaction: **faster | slower | same** backward reaction: **faster | slower | same**

LO (h) 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

5 THE HABER PROCESS

Industrial Equilibrium Reactions

Many important industrial reactions are reversible reactions.

- The principles of reaction kinetics and chemical equilibria are important in the design and working conditions of industrial processes
- The speed, efficiency and economy with which products can be obtained from starting materials determine the economic and commercial competitiveness of the process.
- The aims of the chemist are to convert the reactants into products:
  - as quickly as possible : **KINETICS**
  - with as high a yield as possible : **EQUILIBRIUM**
  - as cheaply as possible
- Costs can be minimised by:
  - using the cheapest reagents (*e.g.* air and water)
  - making the reaction as rapid as possible (*e.g.* by using catalysts)
  - avoiding very high temperatures, if possible
  - avoiding very high pressures, if possible

5.1 Operating Conditions

The classic example of the practical use of the Le Chatelier's Principle is the **Haber Process**.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92.4 \text{ kJ mol}^{-1}$$

The operating conditions are typically as follows:

- Temperature: **450 ºC**
- Pressure: **250 atm**
- Catalyst: **Finely divided iron**

5.2 Explaining the Conditions

1. Temperature

When temperature decreases, the position of equilibrium will shift to the **right** to favour the **exothermic** reaction so as to produce some heat, thereby **increasing** the yield of ammonia.

However, the reaction is **slow** at low temperature *due to low frequency of effective collisions between molecules* arise from the energy needed to break the strong N≡N bond.

Therefore, a **compromise** temperature of 450 ºC (*not too high or too low*) is used to achieve reasonably high yield of ammonia at reasonably high rate.

Table 1: Effect of temperature on yield

temperature / °C	% yield of ammonia
200	88
500	15
1000	negligible

Table 2: Effect of pressure on yield

pressure / atm	% yield of ammonia
1	negligible
100	7
1000	41

2. **Pressure**

When pressure increases, the position of equilibrium will shift to the **right** to decrease the number of gas molecules so as to decrease the pressure, thereby **increasing** the yield of ammonia.

In addition, the reaction reaches equilibrium **faster** at higher pressure *(due to increase in frequency of effective collisions as the molecules are brought closer together).*

However, very high pressure will **increase both capital cost** (*in building of strong pipes and vessels*) **and operating cost** (*to produce and maintain high pressure*).

Therefore, a **compromise** pressure of 250 atm (*not too high or too low*) is used to achieve reasonably high yield at reasonably low costs.

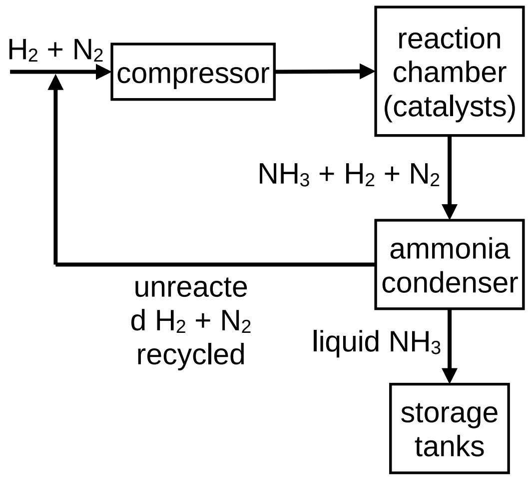
3. **Catalyst**

Finely divided iron is used as a catalyst to **ensure the equilibrium is reached** **faster**. The catalyst has **no effect on the position of equilibrium** and hence no effect on the yield of ammonia.

5.3 How to further improve the yield of ammonia?

When equilibrium is established, the gases are cooled while maintaining the pressure. The cooling causes the ammonia to condense and collected as a liquid (see Fig. 6). Since the product (NH_3) is continuously removed from the system, the position of equilibrium will keep shifting to the right to produce more ammonia until the reaction goes to completion.

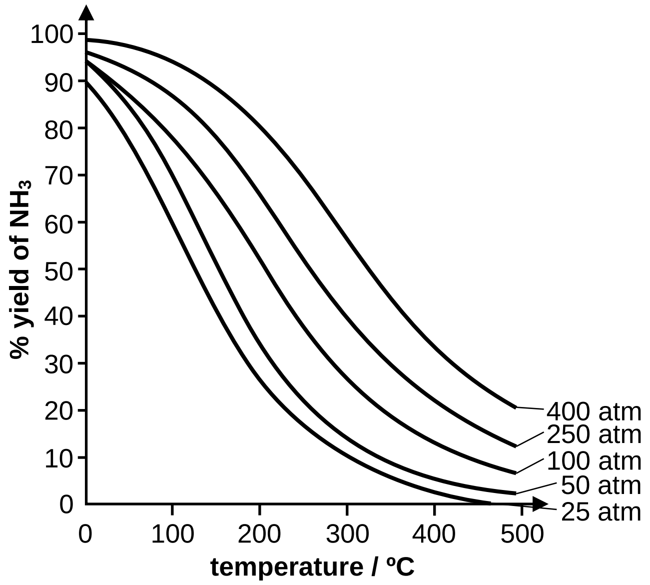
Fig. 6: Synthesis of ammonia



“Haber Process – Ammonia”

https://www.youtube.com/watch?v=Ou2U0pkCC88

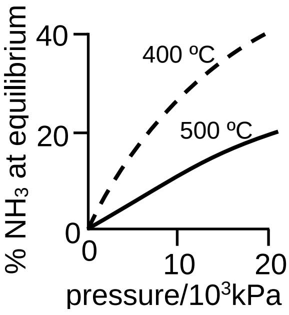
Fig. 7: Percentage yield of ammonia in the equilibrium mixture at different temperature and pressure.



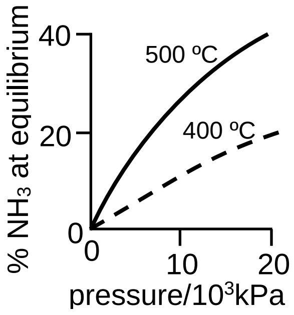
Self-Check 5A

The percentage of ammonia obtainable at equilibrium during the Haber process is plotted against the operation pressure for two temperatures, 400 ºC and 500 ºC. Which of the following correctly represents the two graphs?

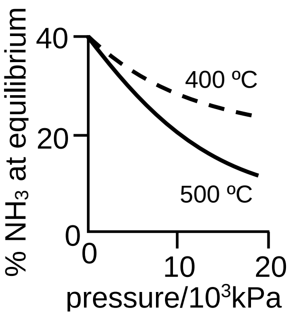
A



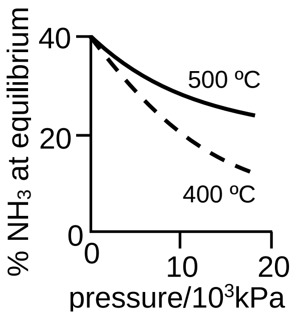
B



C



D



ANNEX A (For pleasure reading)

A1 : $\Delta G^\ominus$ and Equilibrium Constant

Determining whether a reaction goes to completion: Threshold $\Delta G^\ominus$ value

An effectively complete reaction is one that gives a yield of 99.99% products.

Hence, for a reaction R $\rightleftharpoons$ P that goes to completion at 298 K,

$$\begin{aligned}\Delta G^\ominus &= -RT\ln K = -RT\ln\frac{[\mathrm{P}]}{[\mathrm{R}]} = -RT\ln\frac{99.99}{0.01} = -8.31\times 298\times \ln 9999\\ &= -22.8\ \text{kJ mol}^{-1}\end{aligned}$$

In other words, at 298 K, any reaction with a value of $\Delta G^\ominus < -22.8$ kJ mol^{-1} will go to completion. Using the same mathematical relationship, reactions with $\Delta G^\ominus > +22.8$ kJ mol^{-1} will not occur to any noticeable extent (yield of 0.01% products). This value of $\Delta G^\ominus$ is called the threshold value.

Based on this mathematical relationship, we can deduce that the magnitude of the threshold value of $\Delta G^\ominus$ increases (*i.e.* becomes more positive or more negative) as the temperature increases. For example, for a reaction to go to completion at 750 K,

$$\begin{aligned}\Delta G^\ominus &= -RT\ln K = -RT\ln\frac{[\mathrm{P}]}{[\mathrm{R}]} = -8.31\times 750\times \ln 9999\\ &= -57.4\ \text{kJ mol}^{-1}\end{aligned}$$

A2: Effect of Temperature Changes on Equilibrium Constant

Quantitative illustration of effect of changing temperature on the position of equilibrium

In Section 4, we established the relationship between standards Gibbs energy change, $\Delta G^\ominus$ for a reaction and the equilibrium constant, *K*, $\Delta G^\ominus = -RT\ln K$. In the topic of thermodynamics, we have learnt that $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$.

Equating both equations will give us

$$-RT\ln K = \Delta H^\ominus - T\Delta S^\ominus$$

$$\ln K = \frac{\Delta S^\ominus}{R} - \frac{\Delta H^\ominus}{RT}$$

Since $\Delta S^\ominus$ is independent of temperature,

$$\underbrace{\ln K = \text{constant} - \frac{\Delta H^\ominus}{RT}}_{(\textit{van't Hoff equation})}\text{, where the constant is } \frac{\Delta S^\ominus}{R}$$

For an exothermic reaction $\left(\Delta H^\ominus < 0\right)$, $-\dfrac{\Delta H^\ominus}{RT}$ is positive

- As temperature increases, $-\dfrac{\Delta H^\ominus}{RT}$ becomes less positive
- ln *K*, and hence *K* decreases

$\Rightarrow$ A larger proportion of reactants will form (*i.e.* position of equilibrium shifts to left)

A3: A graphical representation of the relationship between ΔG and K

The tendency for a reaction to reach equilibrium is driven by the Gibbs free energy as shown in Fig. 8.

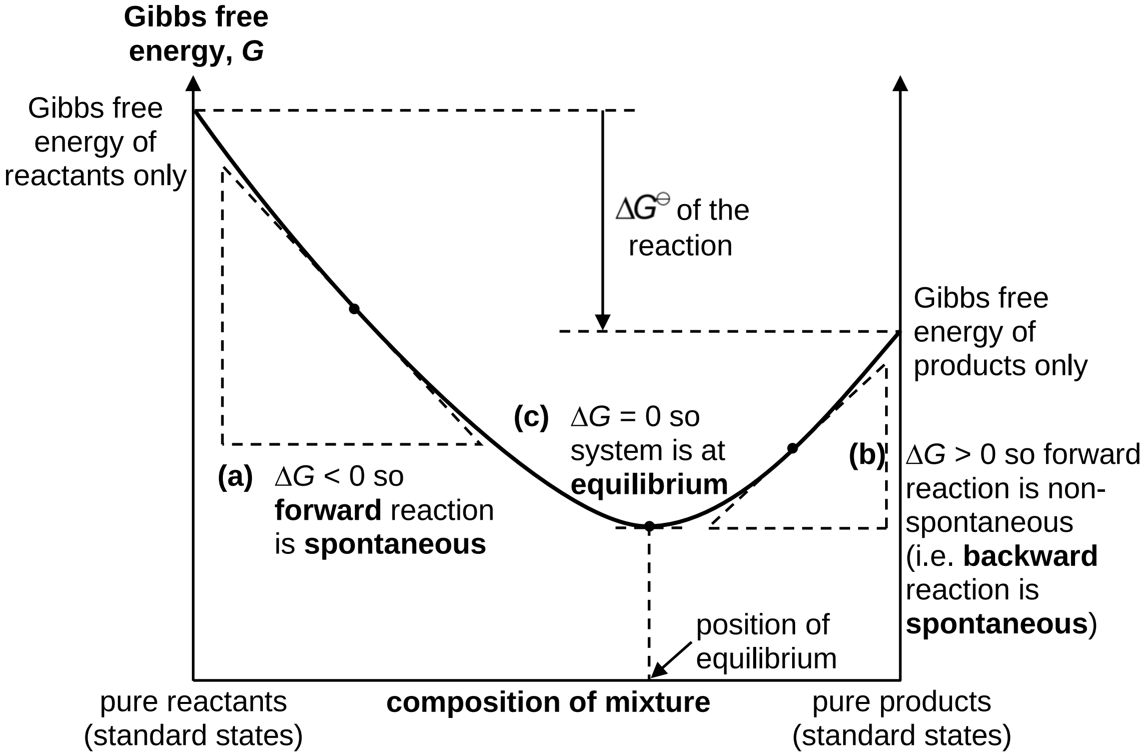


Fig. 8: Relationship between Gibbs free energy and equilibrium

The slope of the graph corresponds to Δ*G*. When substances are mixed together, the reaction will proceed in the direction where there is a decrease in Gibbs free energy (Δ*G* is negative) and hence spontaneous. They will react until **a state of equilibrium is reached where the system's Gibbs free energy is at its minimum** (i.e. **Δ*G* = 0**).

As can be seen from Fig. 8 above, Δ*G* is equal to zero at a certain ratio of products to reactants (*i.e.* composition). This explains why when a system at equilibrium is disturbed by the addition or removal of reactants or products, the position of equilibrium shifts to restore equilibrium.

ANNEX B: Suggested Answers to Self-Check Questions

Self-Check 2A

	A(aq)	+	2**B**(aq)	$\rightleftharpoons$	4**C**(aq)
initial conc / mol dm^{-3}	**3.00**		**7.00**		**0**
change in conc / mol dm^{-3}	–½**(2.00)**		**–2.00**		**+2(2.00)**
eqm conc / mol dm^{-3}	**2.00**		**5.00**		**4.00**

Tip: Check that you have applied the correct reacting stoichiometric ratio for change in concentration of each species.

$$K_c = \frac{[\mathbf{C}]^4}{[\mathbf{B}]^2[\mathbf{A}]} = \frac{4.00^4}{(5.00)^2(2.00)} = 5.12 \text{ mol dm}^{-3}$$

Self-Check 2B

	$2SO_2$(g)	+	O_2(g)	$\rightleftharpoons$	$2SO_3$(g)
initial amt / mol	0		0		1.00
change in amt / mol	+0.54		+½(0.54)		–0.54
eqm amt / mol	0.54		0.27		0.46
eqm **conc** / mol dm^{-3}	$\frac{0.54}{2} = 0.27$		$\frac{0.27}{2} = 0.135$		$\frac{0.46}{2} = 0.23$

$$K_c = \frac{[SO_3]^2}{[SO_2][O_2]} = \frac{0.23^2}{0.27^2 \times 0.135} = 5.38 \text{ mol}^{-1} \text{ dm}^3$$

Tip: Make sure concentrations are substituted into the K_c expression!

Self-Check 2C

Since initial concentration of H_2 and I_2 are equal and from the chemical equation, H_2 and I_2 react in the molar ratio of 1:1, the equilibrium concentration of H_2 and I_2 will be equal too.

	H_2(g)	+	I_2(g)	$\rightleftharpoons$	2HI(g)
eqm conc / mol dm^{-3}	x		x		0.85

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{0.85^2}{x^2} = 54 \;\Rightarrow\; x = [H_2]_{eqm} = [I_2]_{eqm} = 0.116 \text{ mol dm}^{-3}$$

Self-Check 2D

Let x be the initial partial pressure of SO_2Cl_2(g) in Nm^{-2}

	SO_2Cl_2(g)	$\rightleftharpoons$	SO_2(g)	+	Cl_2(g)
Initial partial pressure/ Nm^{-2}	x		0		0
Change in partial pressure / Nm^{-2}	$-0.84x$		$+0.84x$		$+0.84x$
Eqm partial pressure / Nm^{-2}	$x - 0.84x = 0.16x$		$0.84x$		$0.84x$

(a) total pressure at eqm, $p_{\text{total}} = 0.16x + 0.84x + 0.84x$

$$1.01 \times 10^5 = 1.84x$$

$$x = 5.49 \times 10^4$$

Initial partial pressure of SO_2Cl_2 = 5.49×10^4 Nm^{-2}

(b) $K_p = \dfrac{p_{Cl_2} \times p_{SO_2}}{p_{SO_2Cl_2}} = \dfrac{(0.84 \times 5.49 \times 10^4)(0.84 \times 5.49 \times 10^4)}{(0.16 \times 5.49 \times 10^4)} = 2.42 \times 10^5 \text{ Nm}^{-2}$

Self-Check 4A

✗ A: Adding a catalyst **will not affect the yield** of methanol gas. The presence of the catalyst will only **increase** the **rate of** both the **forward and backward reactions** to the **same extent**.

✗ B: Heating the system will cause the position of equilibrium to shift to the **left**, to favour the endothermic reaction to remove some heat. Hence yield of methanol **decreases**.

✓ C: Removing the product from the system (by liquefying the product) decreases the conc. of product. This causes the position of equilibrium to shift to the **right** to produce more methanol gas. The yield of methanol gas **increases**.

✗ D: Lowering the pressure of the system will cause the position of equilibrium to shift to the **left**, to favour the side with greater number of gaseous molecules, so as to increase the pressure. Hence yield of methanol **decreases**.

[Ans: C]

Self-Check 4B

changes imposed on the system in equilibrium	**position of equilibrium**	**equilibrium constant**	**initial reaction rate due to change**
[**A**] and/or [**B**] increased (or partial pressure of **A** or **B** increases for gaseous systems)	shifts to the **[✓ right] | left**	**[✓ no change] | increases | decreases**	forward reaction: **[✓ faster] | slower | same** backward reaction: **faster | slower | [✓ same]**
[**C**] and/or [**D**] increased (or partial pressure of **C** or **D** increases for gaseous systems)	shifts to the **right | [✓ left]**	**[✓ no change] | increases | decreases**	forward reaction: **faster | slower | [✓ same]** backward reaction: **[✓ faster] | slower | same**
decrease in system pressure (*for gaseous systems only*)	shifts to the **[✓ right] | left**	**[✓ no change] | increases | decreases**	forward reaction: **faster | [✓ slower] | same** backward reaction: **faster | [✓ slower] | same**
increase in temperature	shifts to the **right | [✓ left]**	**no change | increases | [✓ decreases]**	forward reaction: **[✓ faster] | slower | same** backward reaction: **[✓ faster] | slower | same**

addition of a catalyst	**no change**	**no change**	forward reaction: **[✓ faster] | slower | same** backward reaction: **[✓ faster] | slower | same**

Self-Check 5A

When pressure is increased at constant *T*,

⇒ **Position of equilibrium shifts to the right** to **decrease the number of gaseous molecules** to reduce the pressure. (forward reaction favoured)

⇒ % yield of NH_3 **increases**.

⇒ Increasing curve

For a Haber Process, the forward reaction is exothermic.

When temperature is increased (from 400 °C to 500 °C),

⇒ **Position of equilibrium shifts to the left** to **favour the endothermic reaction** so as to **absorb some heat** to decrease temperature. (backward reaction favoured)

⇒ % yield of NH_3 **decreases**.

⇒ 500 °C curve is **lower** than that of 400 °C.

[Ans: A]