2022 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, $\Delta G^{\ominus}$. [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

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1 INTRODUCTION

1.1 Reversible Reaction

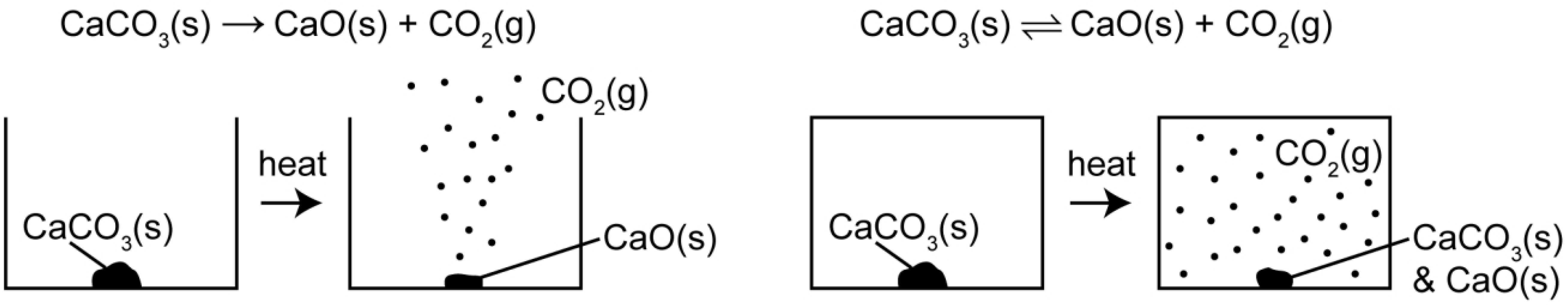
Notation: A reversible reaction is denoted by using the $\rightleftharpoons$ sign in the equation.

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: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
   - At any time (*except t = 0*), 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 = +ve/–ve
   - **A** & **B** are referred to as ***reactants*** and **C** & **D** as ***products***.
   - $\mathbf{A + B \rightarrow C + D}$ 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.

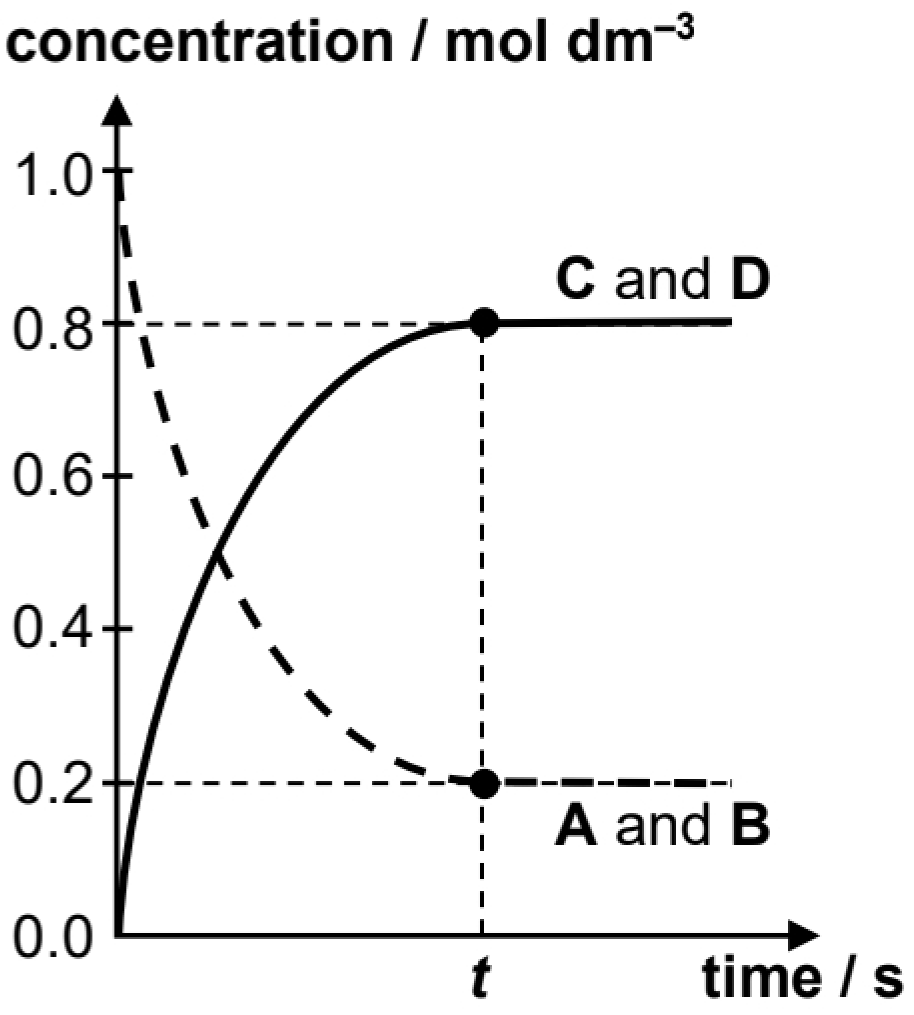
1.2 Dynamic Equilibrium

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.

<table>
<tr><th></th><th>forward reaction</th><th>backward reaction</th></tr>
<tr><td>at the beginning of the reaction
(time = 0)</td><td>• [A] and [B] are high, rate of forward reaction is high</td><td>• C and D are not present, rate of backward reaction is zero</td></tr>
<tr><td>as reaction proceeds,
(time = 0 to <i>t</i>)</td><td>• [A] and [B] decrease, hence rate of forward reaction decreases</td><td>• [C] and [D] increase, hence rate of backward reaction increases</td></tr>
<tr><td>after a period of time
(time = <i>t</i>)</td><td colspan="2">• 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.</td></tr>
</table>



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

For an elementary reversible reaction, this would hence imply:

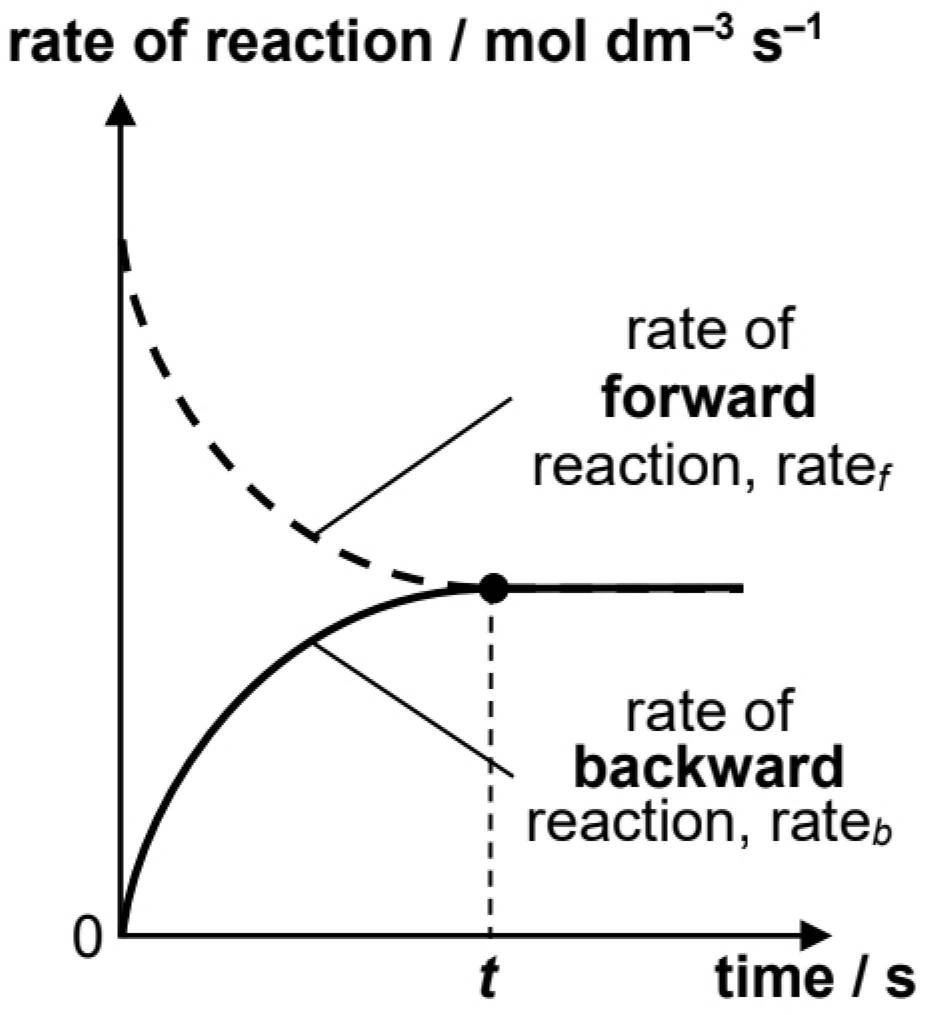
$$k_f[\mathbf{A}][\mathbf{B}] = k_b[\mathbf{C}][\mathbf{D}]$$

By re-arrangement,

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

$$= \textbf{constant}$$

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 **concentrations of reactants and products are constant**, ***rate of the forward reaction equals to the rate of backward reaction and is non-zero***.

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***.

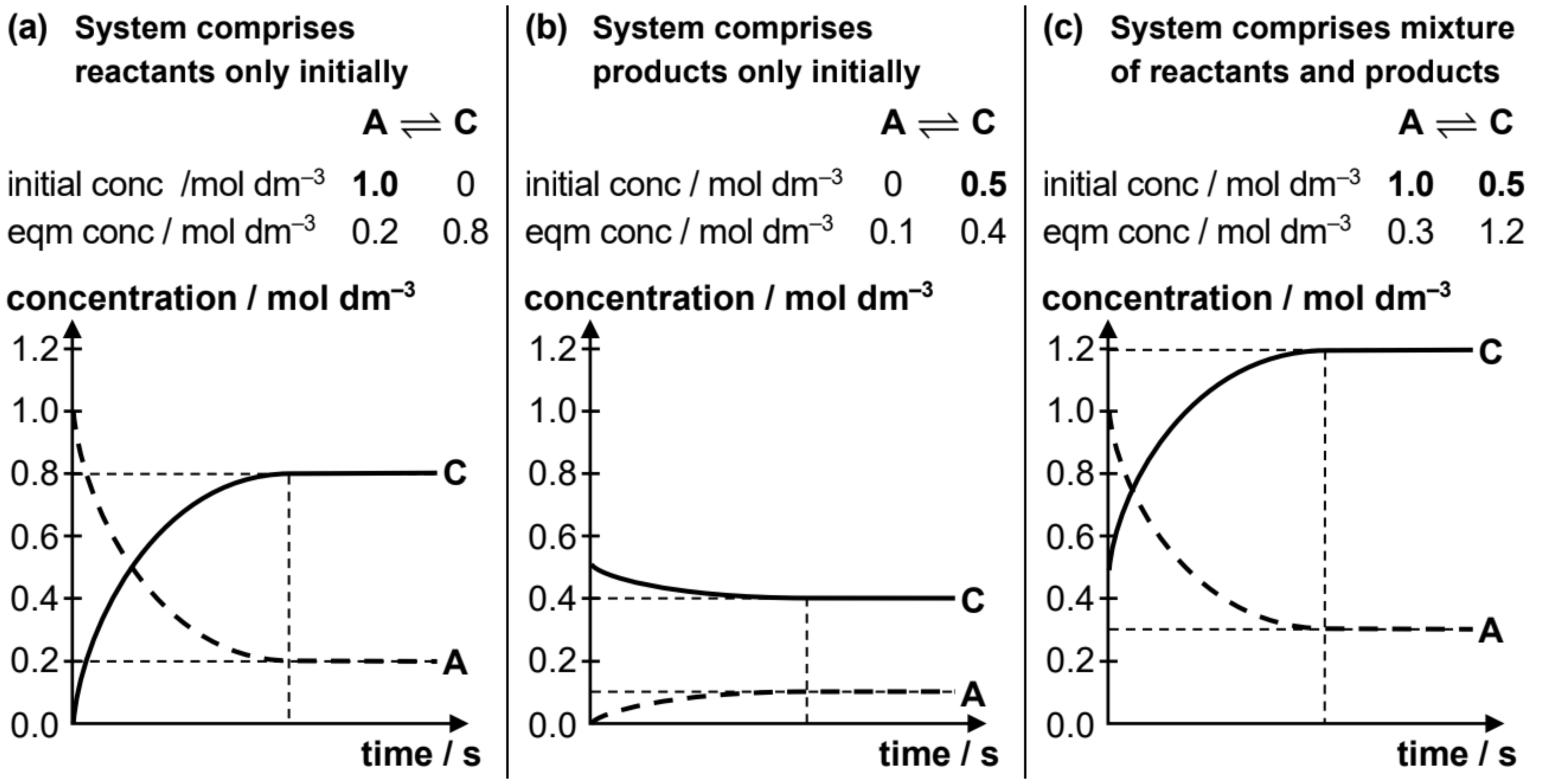
3. ***Equilibrium can only be achieved in a closed system,*** where there is no loss or gain of substances to and from the surroundings.

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**

Checkpoint for Section 1

At the end of this section, you should know that:

1. A reversible reaction is a reaction where reagents react to form products that can react again to re-form the reagents.
2. The sign of the ΔH value stated for any reversible reaction applies to the forward reaction.
3. Equilibria can only be set up in closed systems.
4. The concentrations of all reagents and products remain constant at equilibrium.
5. The rates of the forward and backward reactions are equal and non-zero (*i.e.* reactions exist in dynamic equilibrium)
6. Equilibria can be set up from either direction.

2 EQUILIBRIUM CONSTANTS, K_c and K_p

Consider the following general reversible reaction:

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

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)**.

Hence, $K_c = Q$ when the reaction is **at equilibrium**.

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

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)**.

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

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

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

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

It was found that K_c always has the same constant value at the same particular temperature. **K_c will remain constant as long as the temperature remains unchanged**. (See Section 4)

2.1.1 Homogeneous vs. Heterogeneous Equilibrium

- A **homogeneous equilibrium** involves substances that are **all in the same phase**.
- 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.

For homogeneous equilibria:

- K_c **expression** includes the **concentration of reactants and products** in the reaction mixture (which can be a homogeneous liquid or gaseous).
- $\left[\text{substance}\right]=\dfrac{\text{amount of substance}}{\text{total volume of reaction mixture}}$ **(*Worked Example 2A part (a) and (b)*)**
- Reactions in **aqueous medium** are considered homogeneous as the substances are dissolved in H_2O, and **[$H_2O(l)$] is omitted from the K_c expression** even if it is involved in the reaction, since H_2O is the solvent and [$H_2O(l)$] is a constant (refer to the derivation below). **(*Worked Example 2A part (c)*)**

For heterogeneous equilibria:

- K_c **expression** does **NOT** include the **concentration of pure solids and liquids.**
- **Why are concentrations of solids and liquids omitted in the K_c expression for heterogeneous equilibrium? (*Worked Example 2A part (d)*)**

  The concentration of a pure solid or a pure liquid is a constant.

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

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

  Although the concentration of these species (solid or liquid) 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.

Example 2A

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

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

(b) $CH_3CO_2H(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3CO_2CH_2CH_3(l) + H_2O(l)$
(Assume all reagents and products are miscible with each other.)

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

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

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}					
Change in conc / mol dm^{-3}					
Eqm concentration / mol dm^{-3}					

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

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

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							
Change in amount / mol							
Eqm amount / mol							
Eqm concentration / mol dm^{-3}							

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

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 °C. A solution of **A** with initial concentration of 15.0 mol dm^{-3} is allowed to reach equilibrium at 75 °C.

(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

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

Solution

(a)

	A(aq)	$\rightleftharpoons$	**C**(aq)
Initial conc / mol dm^{-3}			
Change in conc / mol dm^{-3}			
Eqm conc / mol dm^{-3}			

where x is the concentration of **A** reacted

$[\mathbf{C}]_{eqm}$ =

$[\mathbf{A}]_{eqm}$ =

(b)

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) $K_c' =$

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

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

Initial amount / mol

Change in amount / mol

Eqm amount / mol

Eqm conc / mol dm^{-3}

where V is the volume of the reaction vessel.

(i) Amount of CH_3COOH at eqm =

(ii) Amount of C_2H_5OH at eqm =

(iii) Amount of $CH_3CO_2C_2H_5$ at eqm =

(iv) Amount of H_2O at eqm =

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}]**

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:

$$K_p = \frac{p_{\mathbf{C}}^c \times p_{\mathbf{D}}^d}{p_{\mathbf{A}}^a \times p_{\mathbf{B}}^b}$$

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 was present in the container by itself.

$$p_{\mathbf{A}} = \chi_{\mathbf{A}} \times p_T = \frac{n_{\mathbf{A}}}{n_T} \times p_T$$

where
$n_T = n_{\mathbf{A}} + n_{\mathbf{B}} + n_{\mathbf{C}} + n_{\mathbf{D}}$
$n_{\mathbf{A}}$ = amount of gas **A**
$p_T = p_{\mathbf{A}} + p_{\mathbf{B}} + p_{\mathbf{C}} + p_{\mathbf{D}}$

Example 2F

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

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

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

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

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}]

	$2SO_2(g)$	+	$O_2(g)$	$\rightleftharpoons$	$2SO_3(g)$
Initial amount / mol					
Change in amount /mol					
Eqm amount / mol					

(a) $p_{SO_2} =$

$p_{O_2} =$

$p_{SO_3} =$

(b) $K_p =$

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			
Change in partial pressure / atm			
Eqm partial pressure / atm			

(a) $K_p =$

(b) Final pressure =

(c) Initial pressure of N_2O_4 =

(d) % of N_2O_4 dissociated =

Self Check 2D

Consider $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$

At 375 °C and 1.01×10^5 Nm^{-2}, a sample of $SO_2Cl_2(g)$ was found to be 84 % dissociated.

Calculate **(a)** the initial pressure of SO_2Cl_2, **(b)** K_p for the above reaction under these conditions.

[(a) 5.49×10^4 N m^{-2} (b) 2.42×10^5 N m^{-2}]

2.3 Interpreting and Working with Equilibrium Constants

1. The value of equilibrium constant K_c or K_p is **<u>not affected</u>** 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 $\boldsymbol{K_c}$ or $\boldsymbol{K_p}$ for a reversible reaction **<u>only depends</u>** on **TEMPERATURE**!

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

The value of equilibrium constant provides a <u>measure of the **position of equilibrium**</u> (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	$\boldsymbol{K_c}$ **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 $= \dfrac{1}{K_c} = \boldsymbol{K_c^{-1}}$.

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

$K_c' =$

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

$K_c'' =$

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 (Reason 1). When equilibrium is established at a fixed temperature, the reaction mixture is then rapidly cooled (Reason 2), followed by titrating a fixed volume of the mixture rapidly (Reason 3) with standard NaOH(aq) to determine the concentration of CH_3COOH in the equilibrium mixture.

Reason 1: ....

....

Reason 2:..

....

Reason 3:..

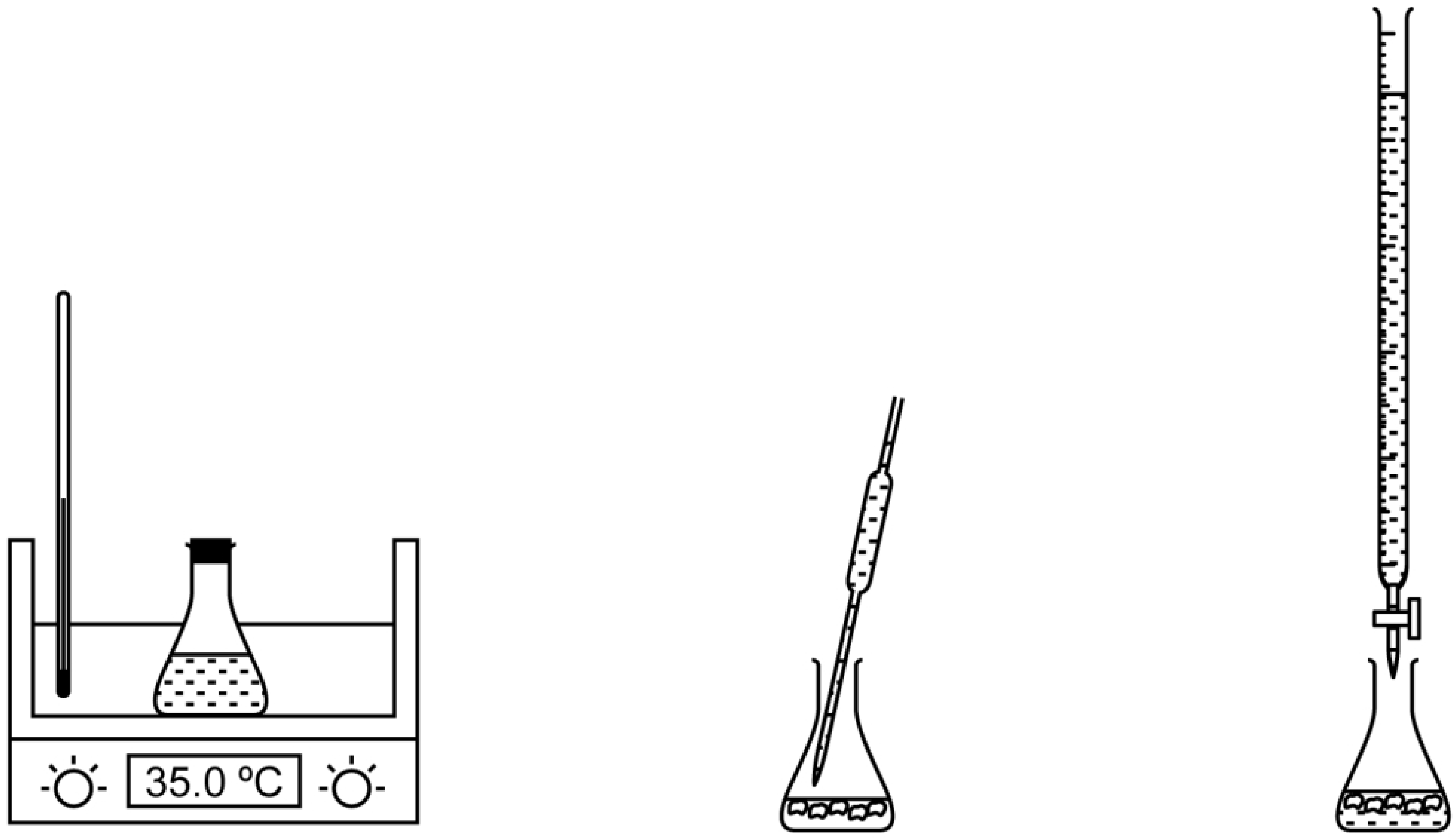
....

....

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.

<u>Checkpoint for Section 2</u>

At the end of this section, you should know that:

1. K_c is the ratio of the concentrations of products to reactants at equilibrium.
2. For gaseous systems, K_p is used instead of K_c.
3. K_c and K_p only vary when temperature of the system is varied.
4. A homogeneous equilibrium is one where all reactants and products are in the same phase.
5. A heterogeneous equilibrium is one where reactants and/or products are in different phases.
6. K_c expressions do not include solids and liquids.
7. Varying concentrations of reagents and/or products and addition of a catalyst will change the concentrations of reagents and products but will not change the value of K_c and K_p.
8. The magnitude of K_c and K_p provide an indication of the extent of the forward and backward reactions at equilibrium.
9. K_c and K_p do not provide any information about the rates of the forward and backward reactions and the time required to achieve equilibrium.

3 Gibbs Free Energy and Equilibrium Constant

Note for H1 Chemistry students:

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

3.1 ΔG and State of Dynamic Equilibrium

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

- If **$\Delta G < 0$**, the reaction proceeds in the direction of **forward reaction** which is **spontaneous**; the forward reaction occurs at a faster rate than the backward reaction (not at equilibrium).
- If **$\Delta G > 0$**, the reaction proceeds in the direction of **backward reaction** which is **spontaneous**; the backward reaction occurs at a faster rate than the forward reaction (not at equilibrium).
- 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, $\Delta G^{\ominus}$, (see Annex A1, pg 34) as follows:

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

where Q is the reaction quotient (see page 6).

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:

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

Thus, 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.

Checkpoint for Section 3

At the end of this section, you should know that:

1. If $\Delta G < 0$, the forward reaction is spontaneous. If $\Delta G > 0$, then the backward reaction is spontaneous.
2. When $\Delta G = 0$, the system is in dynamic equilibrium.
3. Since $\Delta G^{\ominus} = -RT \ln K$, when $\Delta G^{\ominus} \ll 0$, it implies that $K \gg 1$ and the equilibrium position lies to the far right (almost reaches completion). When $\Delta G^{\ominus} \gg 0$, it implies that $K \ll 1$ and the equilibrium position lies to the far left (hardly proceeds).

4 FACTORS AFFECTING CHEMICAL EQUILIBRIA

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 ***equilibrium POSITION*** 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 $\mathbf{A} \rightleftharpoons \mathbf{C}$ 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 equilibrium position 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 equilibrium position 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. $\therefore$ System is at equilibrium once again.

Example 4A

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

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

(a) Addition of ammonia

When ammonia is added, the ________________________ shifts to the __________ to __________________ of the ammonia that was added.

(b) Removal of nitrogen

When nitrogen is removed, the ________________________ shifts to the __________ to __________________ of the nitrogen that was removed.

(c) Increase partial pressure of hydrogen

When partial pressure of hydrogen is increased, the _______________________ shifts to the __________ to __________________ of the hydrogen _____________.

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

$$\therefore \uparrow \text{ in } p_{H_2} \Rightarrow \text{addition of } H_2$$

Example 4B

State the changes in equilibrium position and predict the observation when $FeCl_3$(aq) is added to the following system in equilibrium.

$$\underset{\text{pale yellow}}{Fe^{3+}(aq)} + SCN^{-}(aq) \rightleftharpoons \underset{\text{blood-red}}{[Fe(SCN)]^{2+}}$$

When $FeCl_3$ is added, the concentration of Fe^{3+}(aq) _____________. The equilibrium position will shift to the ___________ to remove _____________ of the Fe^{3+}(aq) added. This causes ___________ of the $[Fe(SCN)]^{2+}$ to be formed and thus a ____________________________ colouration will be observed.

Summary: Consider **A** $\rightleftharpoons$ **C**,

(a) ***Effect of changes in concentration (or partial pressure) on equilibrium position:***

removal of **A** would shift the equilibrium position to the ___________.

addition of **A** would shift the equilibrium position to the ___________.

addition of **C** would shift the equilibrium position to the ___________.

removal of **C** would shift the equilibrium position to the ___________.

(b) ***Effect of changes in concentration (or partial pressure) on K_c / K_p value:***
No effect (K_c and K_p are only affected by temperature).

(c) ***Effect of changes in concentration (or partial pressure) on the rate at which equilibrium is established:***
With an increase in concentration (of reactants or products), equilibrium will be established at a higher rate because frequency of effective collisions between the molecules/species is higher.

2. Note that:
   - If a large excess of one reactant is used, the equilibrium position 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 equilibrium position is continuously shifted to the right.

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

Example 4C

The system **A** $\rightleftharpoons$ **B** is in equilibrium at 75 °C 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 °C.

Let the change in [A] be x mol dm^{-3}

	A	$\rightleftharpoons$	**B**
new “initial” conc. / mol dm^{-3}			
new eqm conc. / mol dm^{-3}			

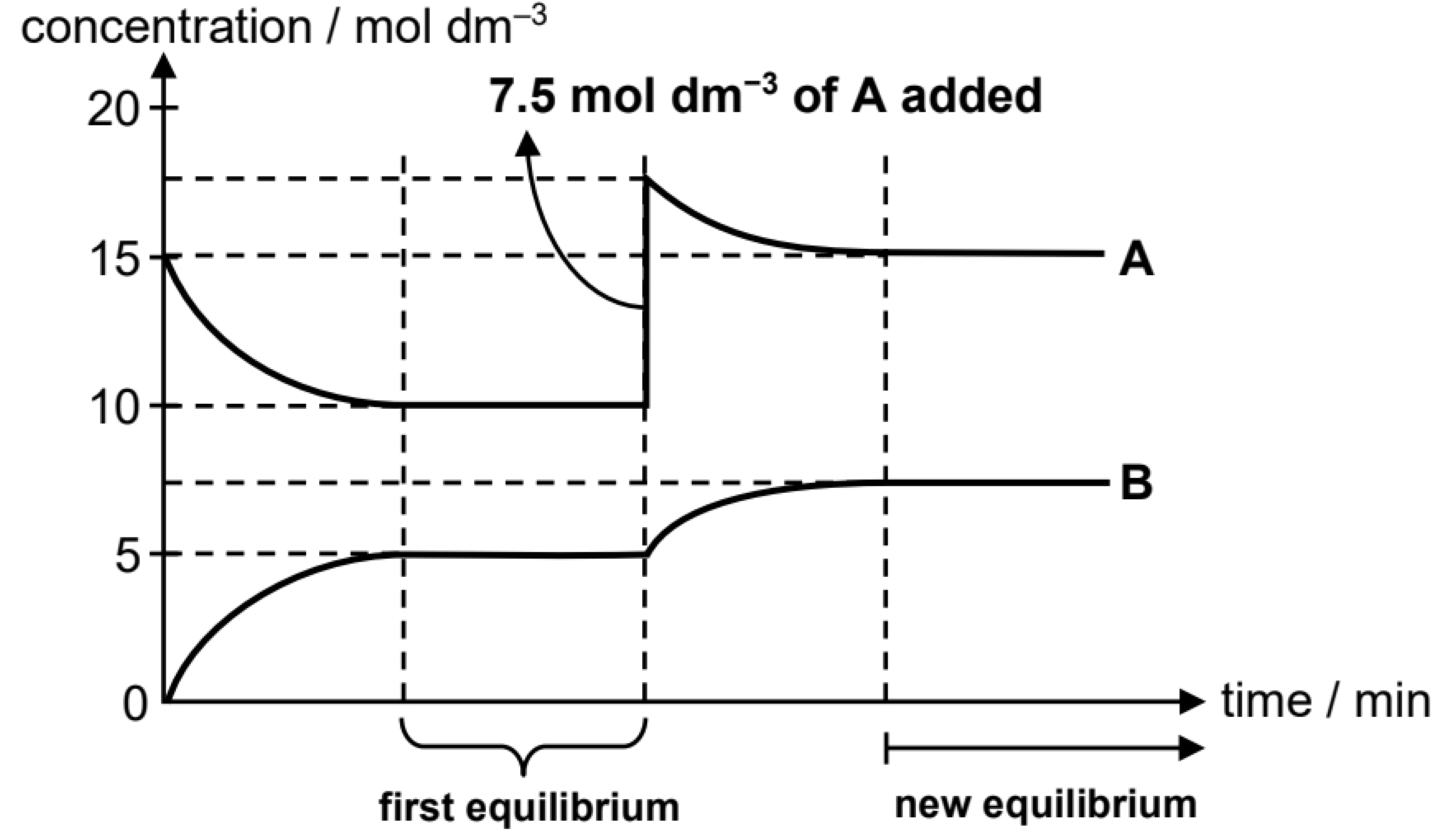
System is no longer at equilibrium; system responds to remove some of the **A** added *i.e.* forward reaction occurs.
⇒ ① equilibrium shifts to the right.
② when equilibrium is re-established, conc. of **A** is between 10 and 17.5 mol dm^{-3}.

At the new eqm,

K_c =

[**A**]$_{\text{new eqm}}$ =

[**B**]$_{\text{new eqm}}$ =



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

4.3 Effect of Pressure (or Volume) Changes

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

1. Changes in pressure affect **only** reactions involving **gases**.

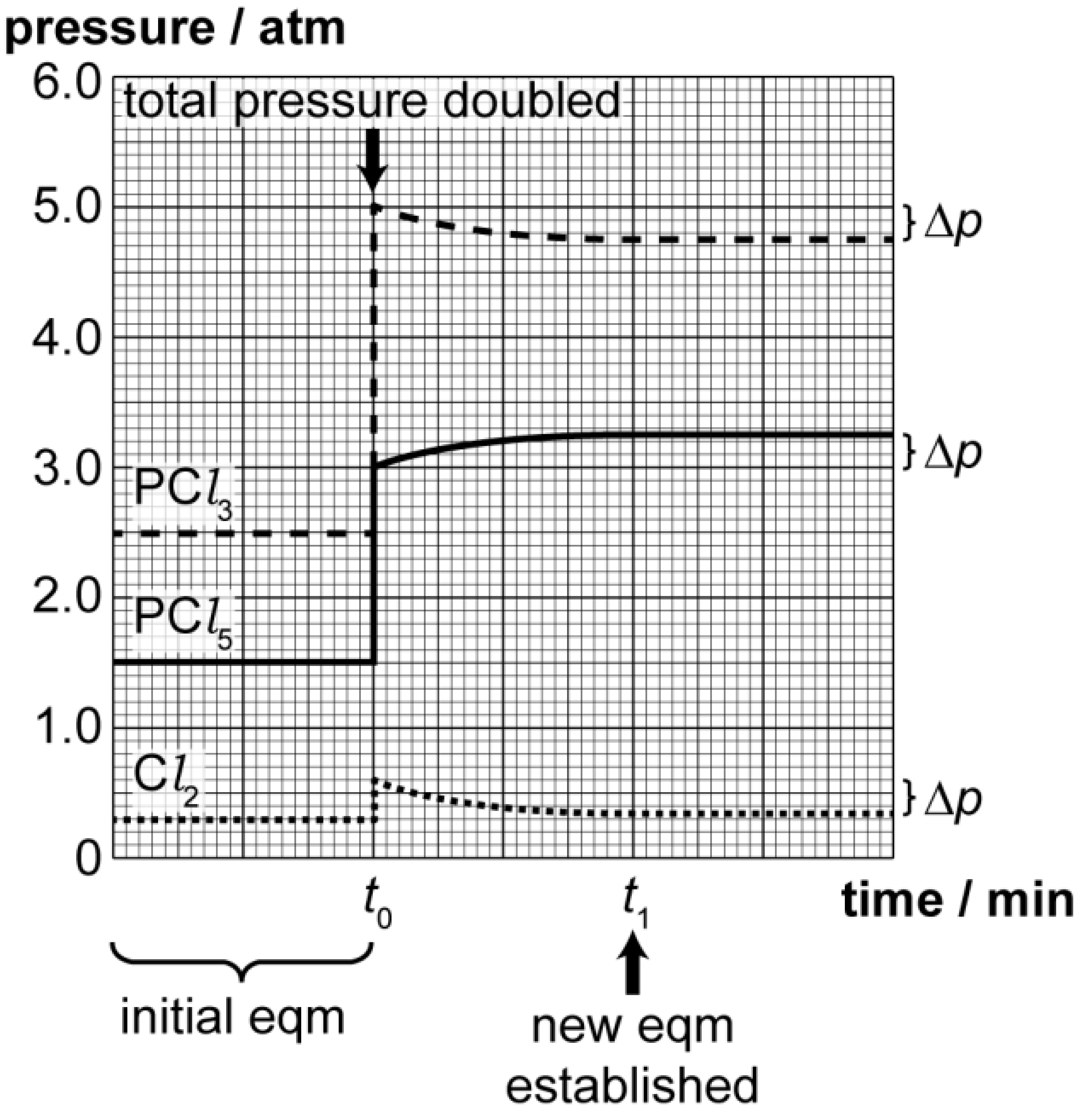
2. According to Le Chatelier’s principle, if the **total pressure** of a gaseous mixture is **increased** (by decreasing the volume), the system will respond to ***reduce*** the pressure by reducing the <u>number of **GASEOUS** molecules</u>. Thus, the equilibrium position is shifted towards the direction that results in a ***decrease in number of gaseous molecules***.

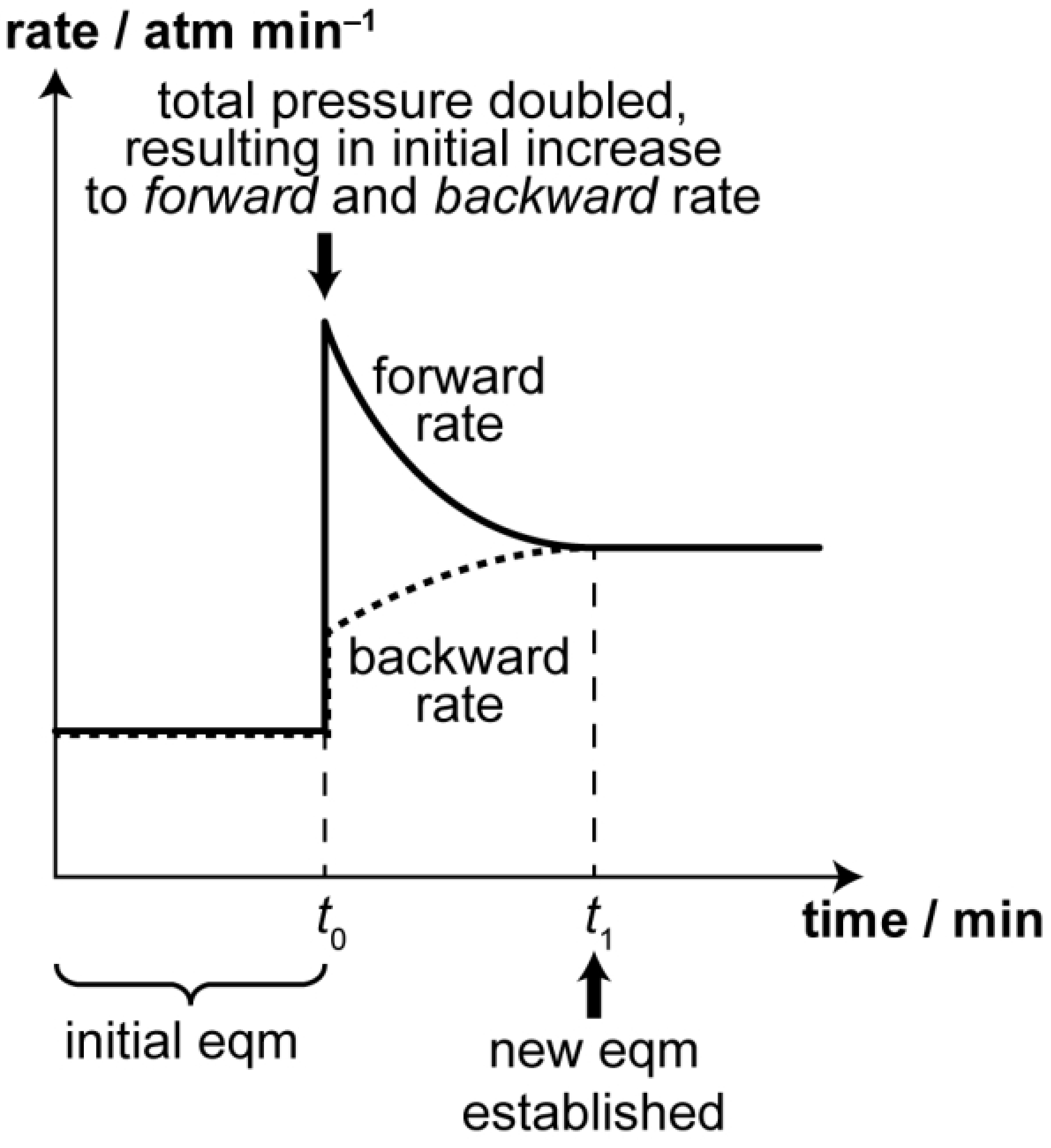
E.g. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

- When pressure is increased, the position of equilibrium shifts to the _________ so as to ____________ the pressure by ____________________ the number of gas molecules.
- When pressure is decreased, the position of equilibrium shifts to the ________ so as to ____________ the pressure by ____________________ the number of gas molecules.

E.g. Changes to pressure and rate when <u>total pressure increases</u> 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 4D

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

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

Pressure increase, equilibrium position shifts to the ____________, to ____________ the number of gas molecules.

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

Pressure has **no effect** on the equilibrium position if the amount of gaseous reactants is ***equal*** to the amount of gaseous products.

Pressure increases, equilibrium position __________________________.

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

Pressure decreases, equilibrium position __________________________.

Summary:

(a) ***Effect of changes in pressure on equilibrium position*:**
- When ***pressure* increases**, equilibrium position shifts towards the direction that decreases the number of gaseous molecules, so as to reduce the pressure.
- When ***pressure* decreases**, equilibrium position shifts towards the direction to increases the number of gaseous molecules, so as to increase the pressure.

(b) ***Effect of changes in pressure on K_c or K_p value:***
No effect (K_c and K_p are only affected by temperature).

(c) ***Effect of changes in pressure on rate at which equilibrium is established*:**
A gaseous system at higher pressures usually reaches equilibrium more quickly than at lower pressures because reaction rate increase as the molecules are forced closer together. This causes the frequency of effective collisions between gas molecules to be higher at higher pressures.

3. What happens if we add some inert gas to the equilibrium **A**(g) + **B**(g) $\rightleftharpoons$ **C**(g)?

Scenario 1: Noble gas is added at constant pressure…
- Total volume increases
- Partial pressure of *each* gas decreases

WHY?

Let the total pressure of the system be p.

At the initial equilibrium, $p_{X,\text{ initial}} = \chi_{X,\text{ initial}} \times p = \dfrac{n_X}{n_A + n_B + n_C} \times p$

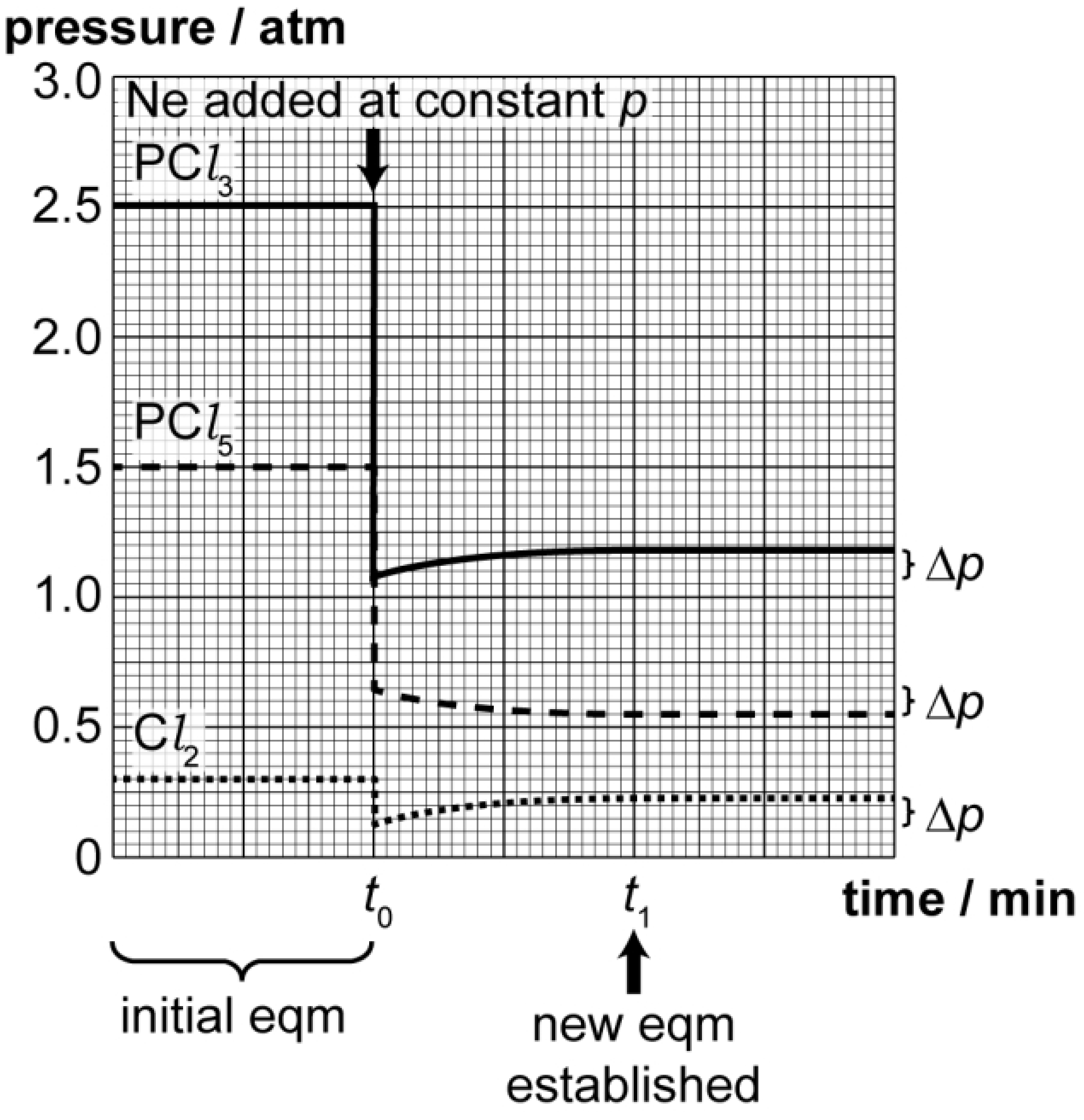
After n_{noble} mol of noble gas has been added,

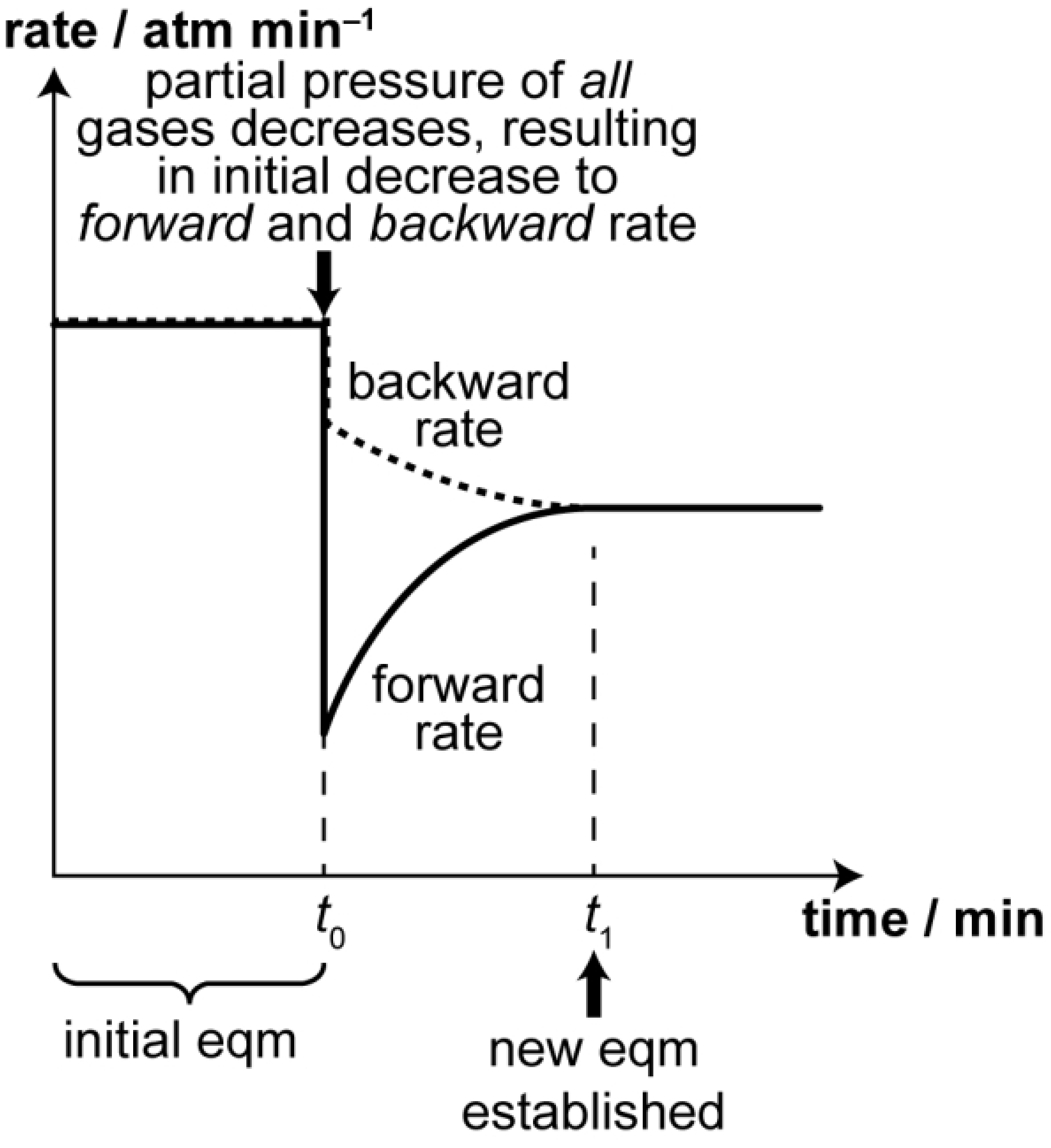
$$p_{X,\text{ after addition}} = \frac{n_X}{n_A + n_B + n_C + \boxed{n_{\text{noble}}}} \times p < \frac{n_X}{n_A + n_B + n_C} \times p = p_{X,\text{ initial}}$$

- Number of gas particles per unit volume decreases
- Hence, position of equilibrium will shift to increase total number of gaseous particles
- Since there are two molecules of gas on the left-hand side of the equation and one on the right, backward reaction is favoured
- Position of equilibrium shifts to the side with more gaseous particles, *i.e.* left side
- **C** decomposes to form more **A** and **B** until a new equilibrium is reached

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





Scenario 2: Noble gas is added at constant volume…

- Total pressure increases, but partial pressure of each gas remains the same

WHY?

Let the volume of the system be V.

At the initial equilibrium, let the initial pressure be p_i.

$$p_iV = (n_A + n_B + n_C)RT \Rightarrow p_i = \frac{(n_A + n_B + n_C)RT}{V}$$

$$p_{X,\text{ initial}} = \chi_{X,\text{ initial}} \times p_i = \frac{n_X}{n_A + n_B + n_C} \times \frac{(n_A + n_B + n_C)RT}{V} = \frac{n_XRT}{V}$$

After n_{noble} mol of noble gas has been added, let the pressure be p_g.

$$p_gV = \left(n_A + n_B + n_C + \boxed{n_{\text{noble}}}\right)RT \Rightarrow p_g = \frac{\left(n_A + n_B + n_C + \boxed{n_{\text{noble}}}\right)RT}{V}$$

$$p_{X,\text{ after addition}} = \frac{n_X}{n_A + n_B + n_C + \boxed{n_{\text{noble}}}} \times p_g = \frac{n_X}{n_A + n_B + n_C + \boxed{n_{\text{noble}}}} \times \frac{\left(n_A + n_B + n_C + \boxed{n_{\text{noble}}}\right)RT}{V}$$

$$= \frac{n_XRT}{V} = p_{X,\text{ initial}}$$

- Since partial pressure of each gas remains the same, position of equilibrium will not change.

4.4 Effect of Temperature Changes

1. According to Le Chatelier's principle, if the temperature of an equilibrium mixture ***increases***, the system will adjust itself to ***decrease*** the temperature by ***using up (absorbing)* some of the heat energy in the reaction**, hence shifting the equilibrium towards the ***endothermic*** direction.

   E.g. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\Delta H = -94.9\ \text{kJ mol}^{-1}$

   - When temperature increases, equilibrium position shifts to the __________ to favour the _______________ reaction so as to __________ some heat, resulting in _________ products at equilibrium.
   - When temperature decreases, equilibrium position shifts to the __________ to favour the _______________ reaction so as to __________ some heat, resulting in _________ products at equilibrium.

Example 4E

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

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

colourless dark brown

change	equilibrium position	observation
increase in temperature	shifts to the ____________ (endothermic reaction favoured)	
decrease in temperature	shifts to the ____________ (exothermic reaction favoured)	

2. ***K_c* and *K_p* are only affected by changes in temperature**.

   The explanation involves the equation: $\ln K = -\dfrac{\Delta H}{RT} + \text{constant}$

   [this is **NOT required**; refer Annex A2 pg 34]

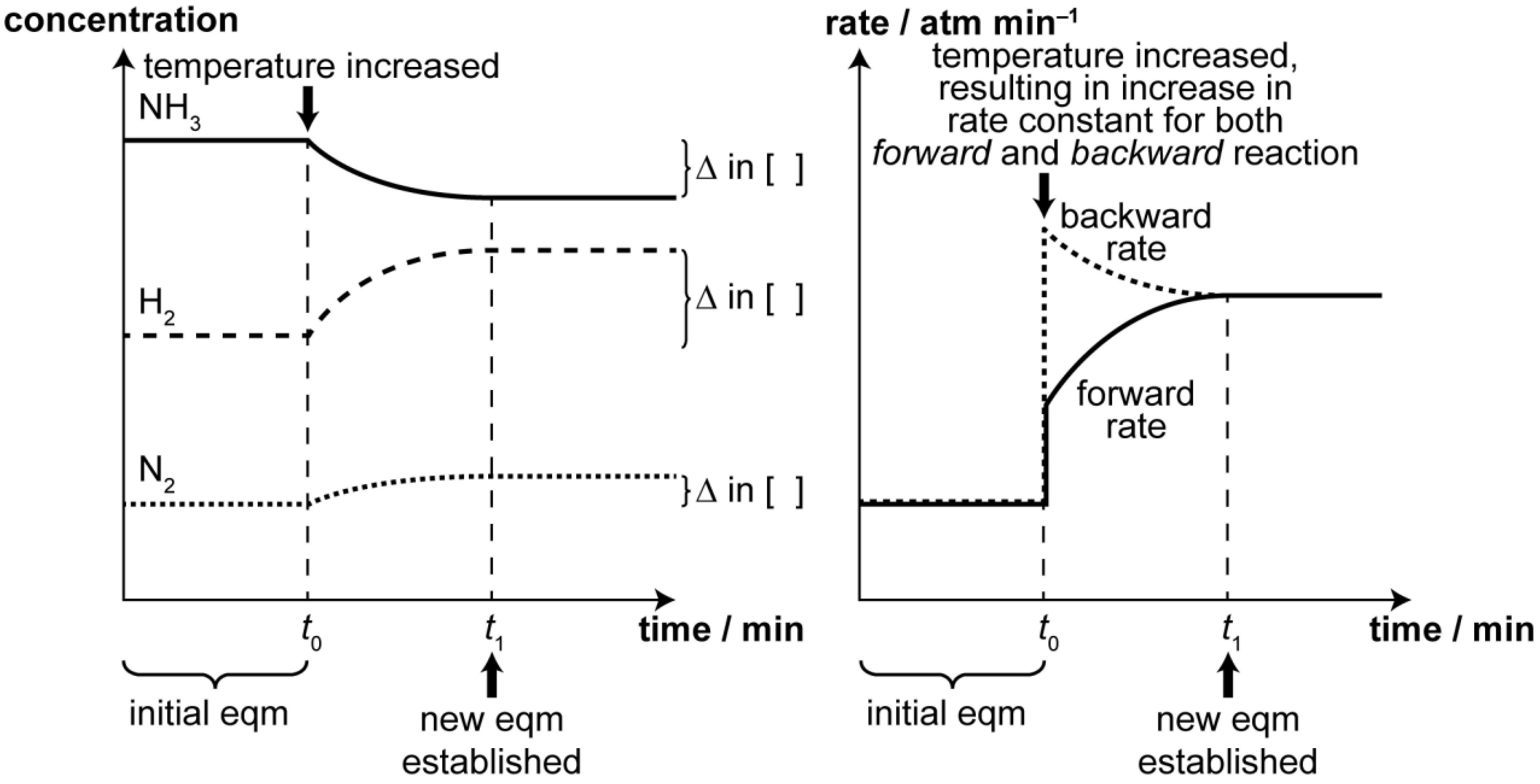
   Consider the equilibrium $a\mathbf{A} + b\mathbf{B} \rightleftharpoons c\mathbf{C} + d\mathbf{D}$

   Given, $K_c = \dfrac{[\mathbf{C}]^c_{\text{eqm}}[\mathbf{D}]^d_{\text{eqm}}}{[\mathbf{A}]^a_{\text{eqm}}[\mathbf{B}]^b_{\text{eqm}}}$ 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 equilibrium position shifts to the __________ to favour the endothermic reaction so as to ____________ some heat, resulting in ____________ products at equilibrium, hence K_c (or K_p) ___________________.

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

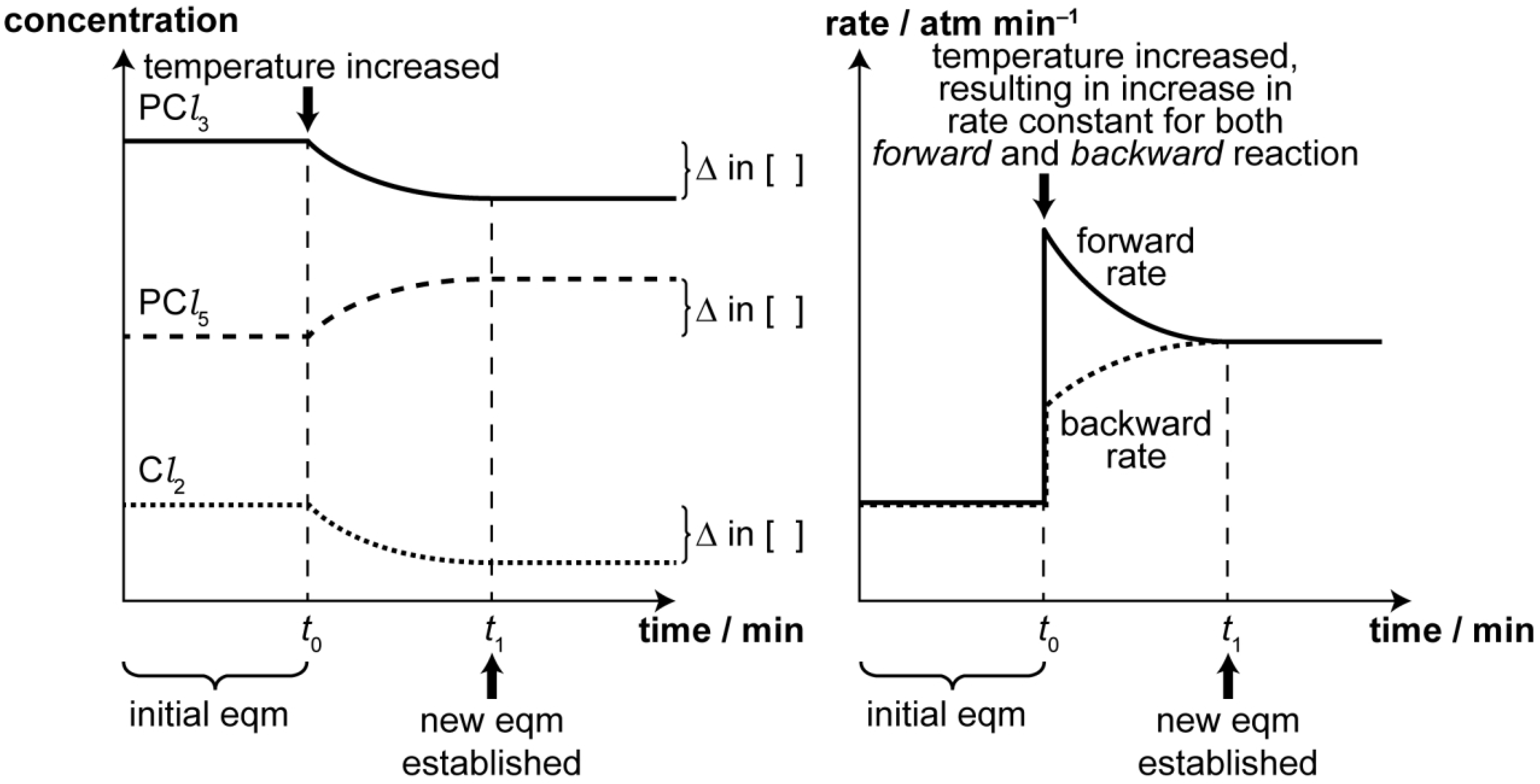


- As temperature *decreases*, the equilibrium position shifts to the __________ to favour the exothermic reaction so as to ____________ some heat, resulting in ____________ products at equilibrium, hence K_c (or K_p) ___________________.

(b) If Δ*H* is positive (***endothermic***):

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

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



- As temperature *decreases*, the equilibrium position shifts to the __________ to favour the exothermic reaction so as to ___________ some heat, resulting in ___________ products at equilibrium, hence K_c (or K_p) __________________.

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

Summary:

(a) *Effect of changes in temperature on equilibrium position*:

- When temperature increases, the equilibrium position shifts to favour the endothermic reaction to *use up some heat* so as to reduce the temperature.
- When *temperature decreases*, the equilibrium position shifts to favour the exothermic reaction to *produce some heat* so as to increase the temperature.

(b) *Effect of changes in temperature on K_c / K_p:*

- When the equilibrium position shifts to the right, K_c and K_p increases.
- When the equilibrium position shifts to the left, K_c and K_p decreases.
- For reaction with $\Delta H = 0$, equilibrium position is NOT affected. Thus for such reactions, temperature change has no effect on K_c / K_p.

(c) *Effect of changes in temperature on rate at which eqm is established*:

A gaseous system at higher temperature reaches eqm more quickly. Reaction rate increases as the molecules have higher kinetic energy and frequency of effective collisions between gas molecules is higher at higher temperatures.

Example 4F

reaction	**ΔH / kJ mol^{-1}**	**temperature**	**equilibrium position**	**value of K_c or K_p**
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	–92	increases	shifts to the **left**	**decreases**
$2CHClF_2(g) \rightleftharpoons C_2F_4(g) + 2HCl(g)$	+128	increases	shifts to the __________	
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	–197	decreases	shifts to the __________	
$Br_2(g) \rightleftharpoons 2Br(g)$	+193	decreases	shifts to the __________	

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.

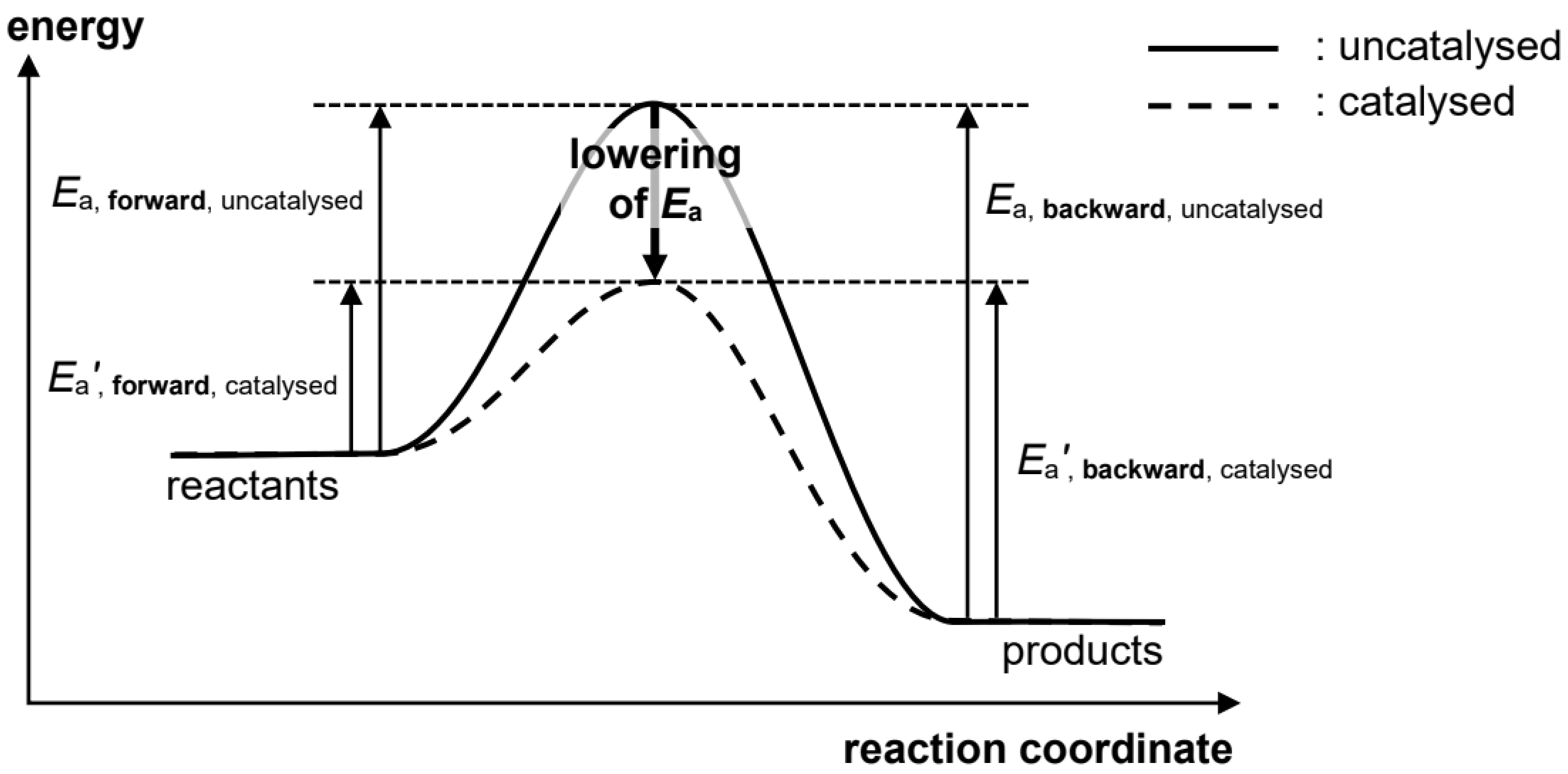


Fig. 4 Catalyst lowers the activation energy of both forward reaction and backward reaction by the same extent

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).

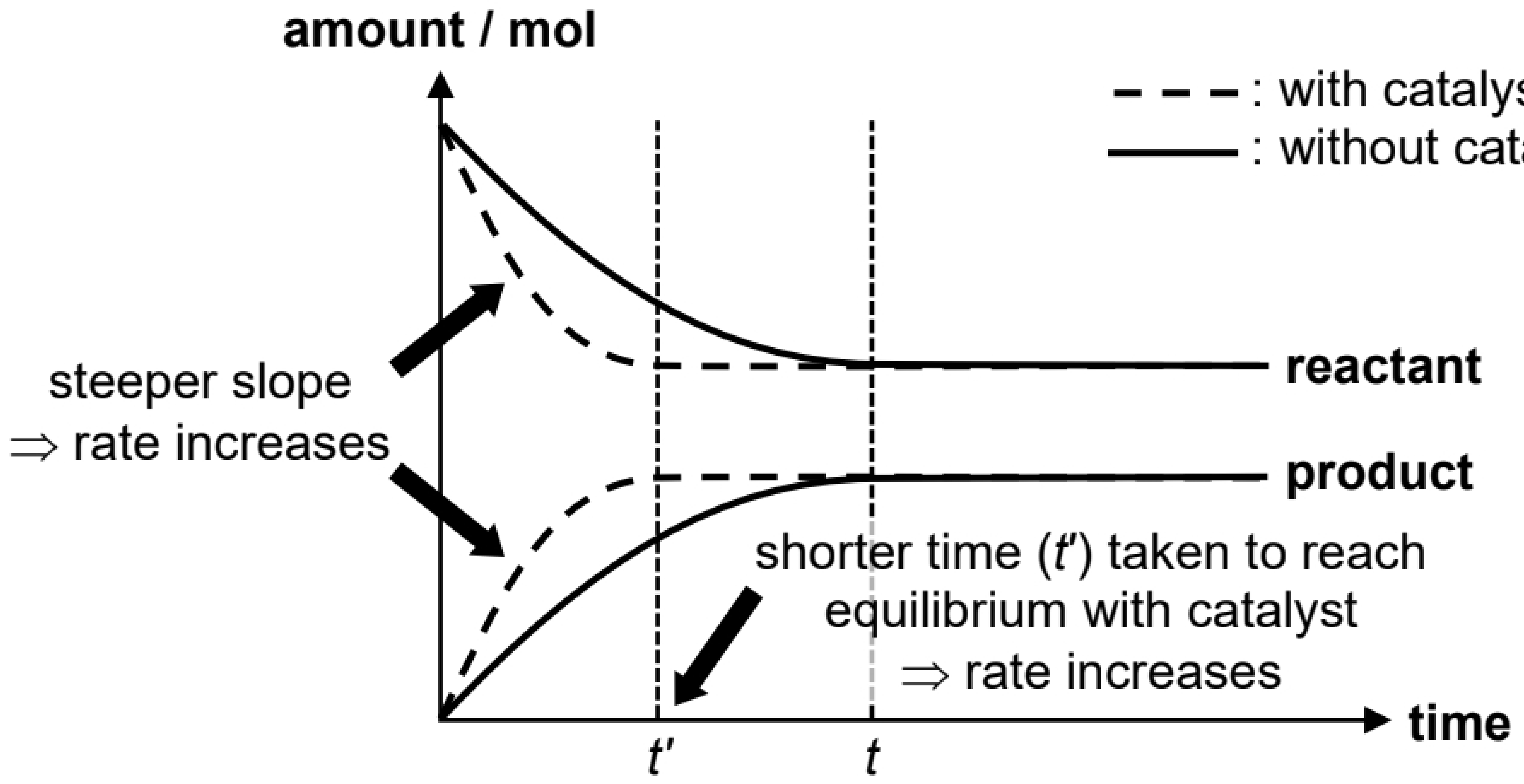


Fig. 5 Effect of catalyst on rate and position of equilibrium

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

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	**equilibrium position**	**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**

Checkpoint for Section 4

At the end of this section, you should know that:

1. Four factors affect chemical equilibria, namely concentration, pressure, temperature, and catalyst.
2. These factors may change equilibrium position, change in K_c or K_p, or the rate at which equilibrium is established.
3. When a reagent is added to a system at equilibrium, the system will respond to remove some of the reagent added. Similarly, when a portion of a reagent is removed from a system at equilibrium, the system will respond to form some of the reagent removed.
4. In a gaseous system at constant temperature, if the total pressure of a gaseous mixture is increased by decreasing the volume, the system will reduce the pressure by reducing the number of gaseous molecules. Similarly, if the total pressure of a gaseous mixture is decreased by increasing the volume, the system will increase the pressure by increasing the number of gaseous molecules.
5. When the temperature of a reaction mixture at equilibrium increases, the system will adjust itself to decrease the temperature of the system by favouring the endothermic reaction to use up some of the heat. Similarly, when the temperature of a reaction mixture at equilibrium decreases, the system will adjust itself to increase the temperature of the system by favouring the exothermic reaction to produce some of the heat.
6. Addition of a catalyst increases the rates of the forward and backward reactions by the same extent without affecting the position of the equilibrium and yield of the reaction.

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 __________ to favour the **exothermic** reaction so as to produce some heat, thereby _______________ the yield of ammonia.

However, the reaction is __________ at low temperature *due to low frequency of effective collisions between molecules*.

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 / ºC	% 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 __________ to decrease the number of gas molecules so as to decrease the pressure, thereby ___________________ the yield of ammonia.

In addition, the reaction reaches equilibrium __________ 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.

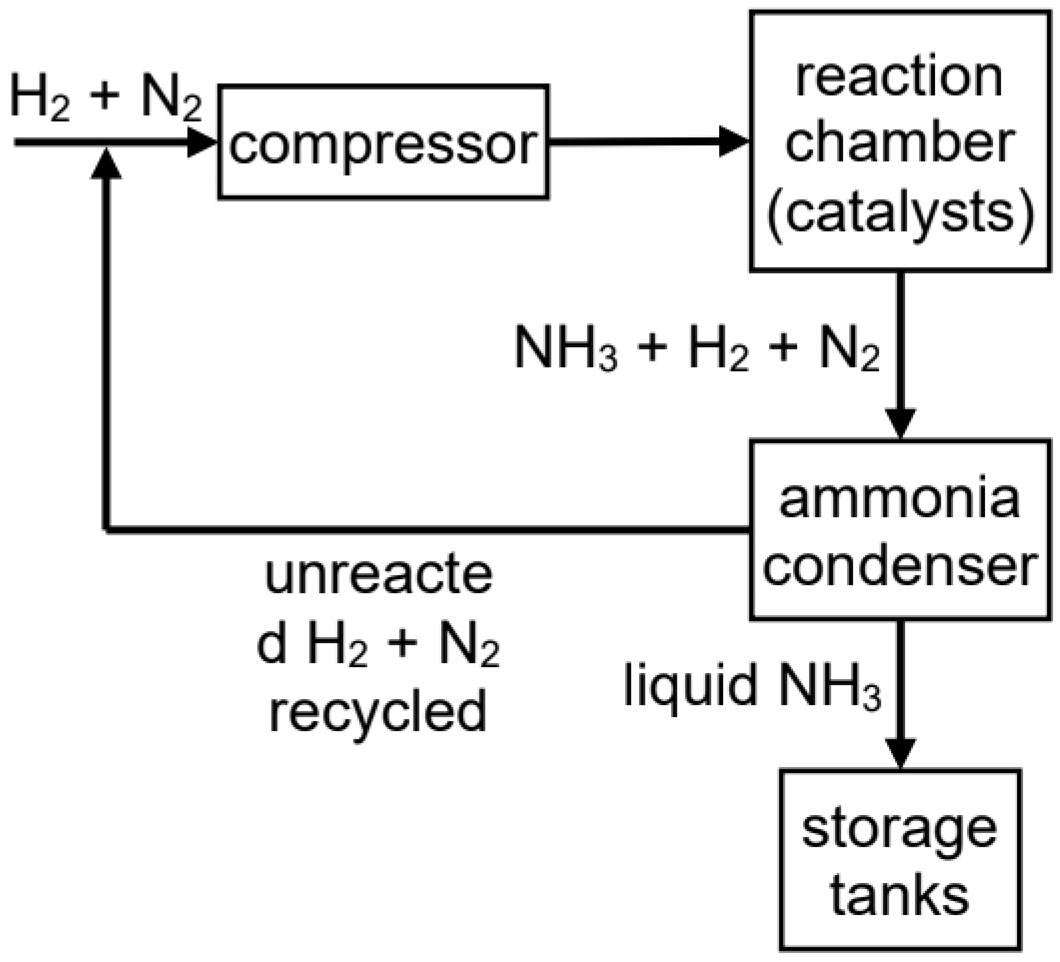
3. **Catalyst**

Finely divided iron is used as a catalyst to **ensure the equilibrium is reached** __________. 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.

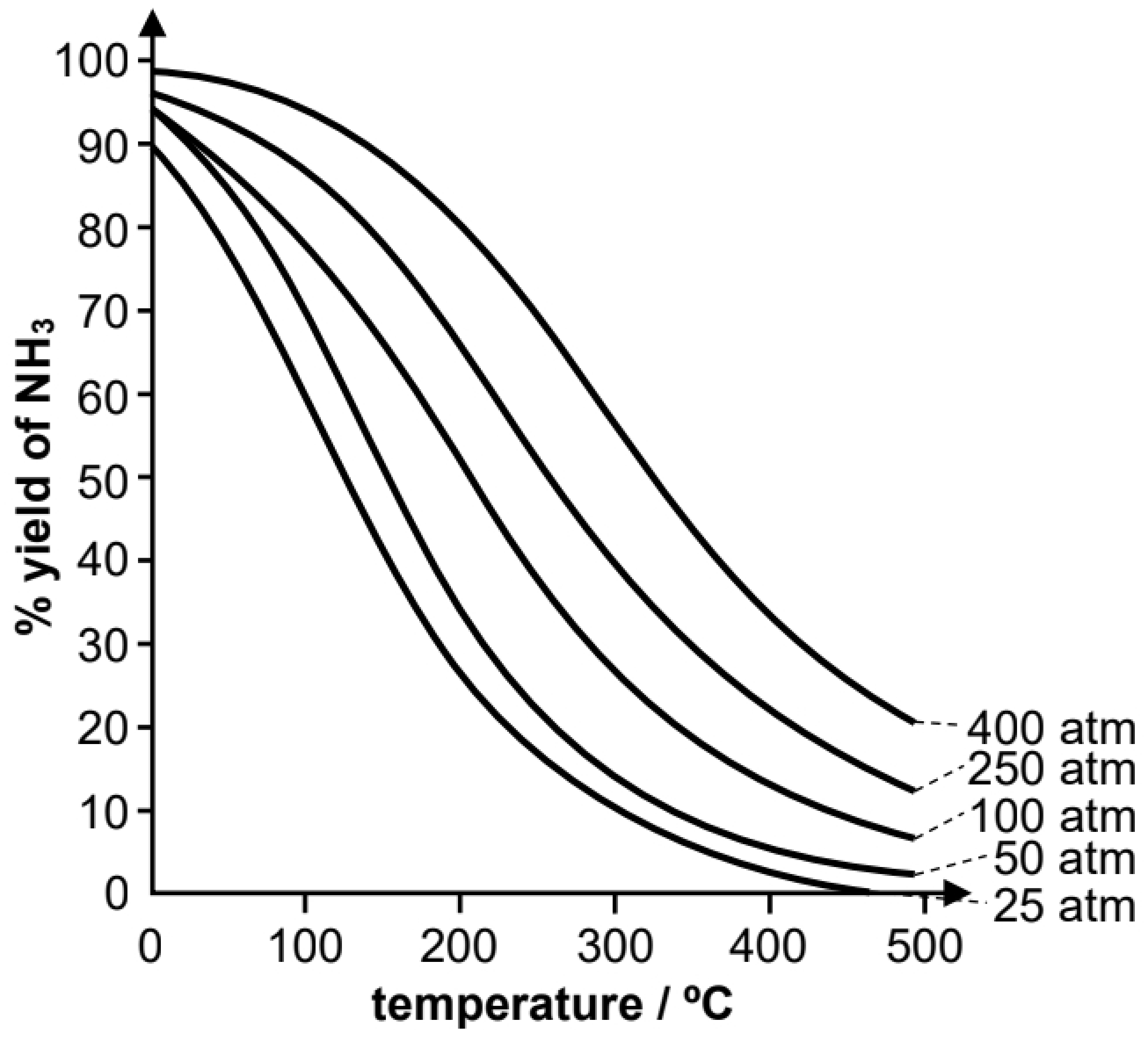
Fig. 6: Synthesis of ammonia



"Haber Process – Ammonia"

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

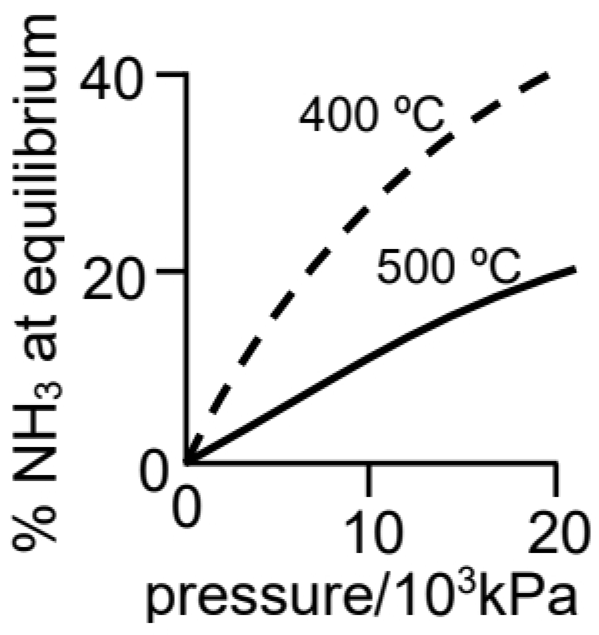
Fig. 7: Percentage yield of ammonia in the equilibrium mixture at different temperature and pressure.



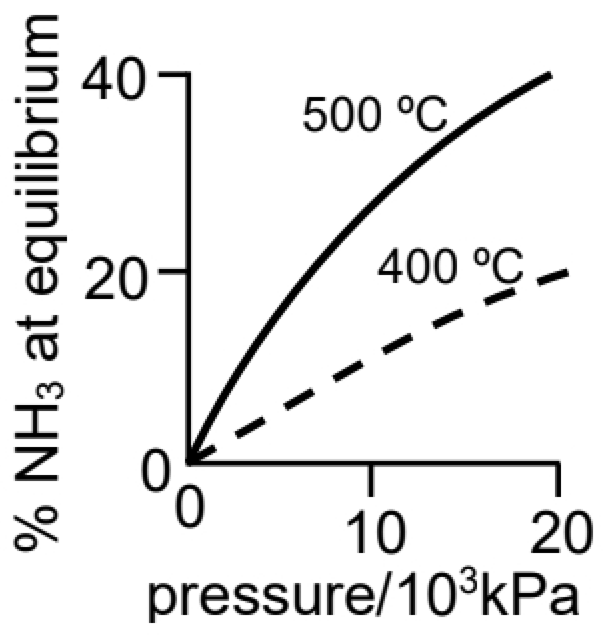
Self-Check 5A

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?

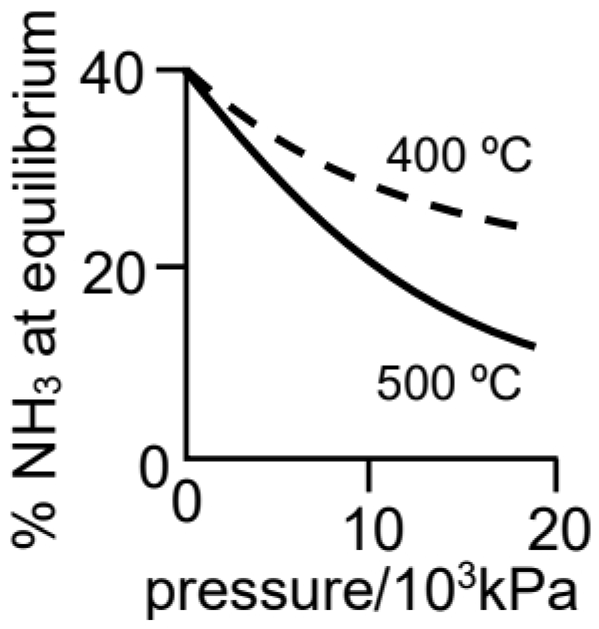
A



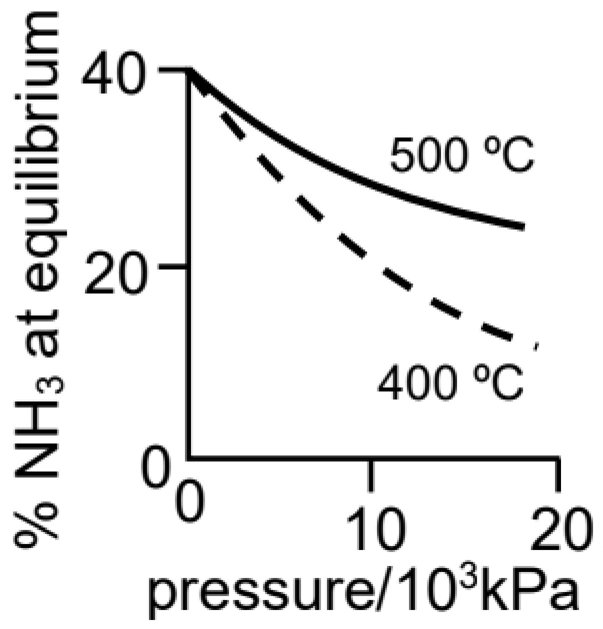
B



C



D



ANNEX A

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,

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

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,

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

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
- In 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 ∆G and K

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

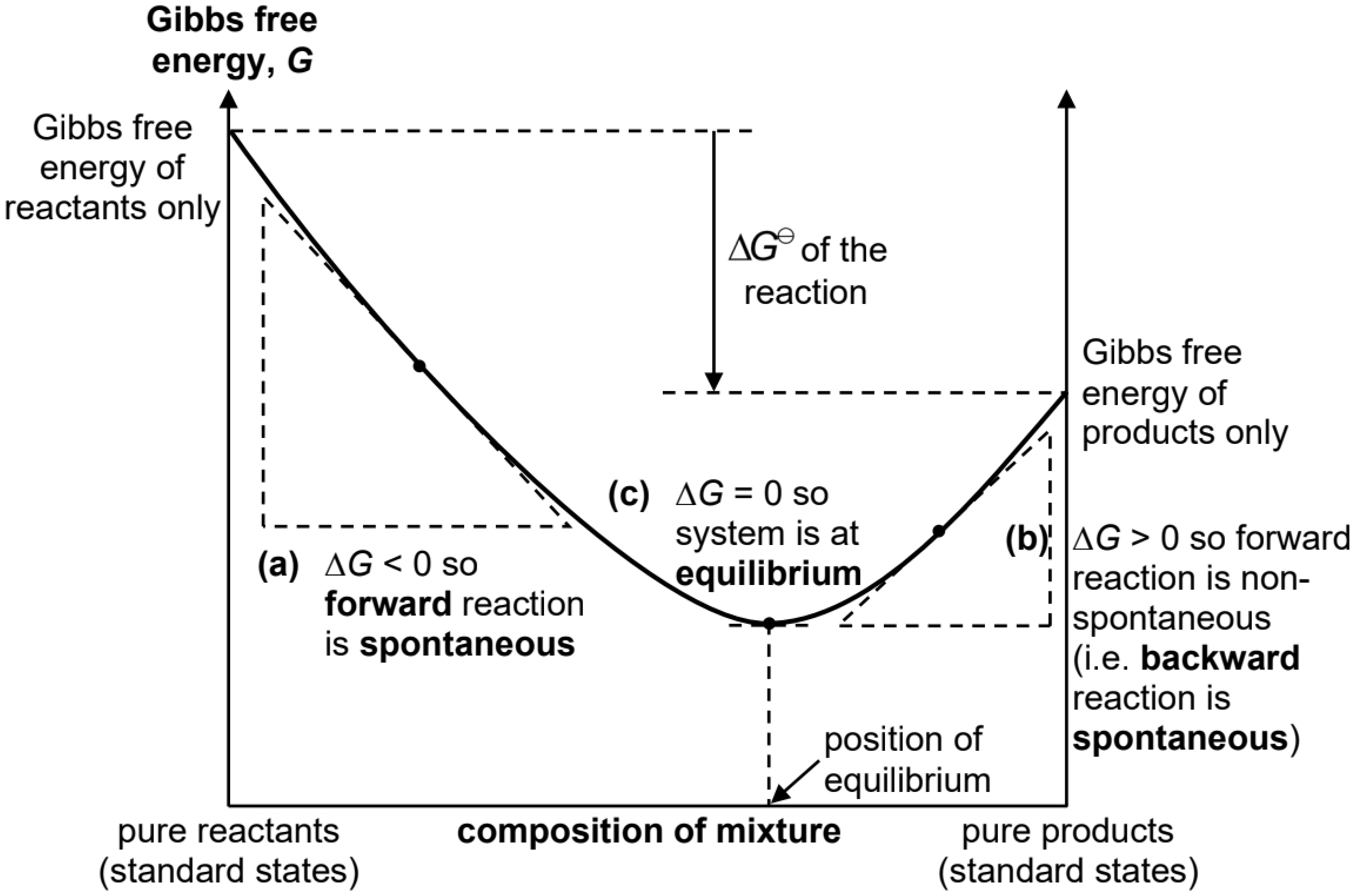


Fig. 8: Relationship between Gibbs free energy and equilibrium

The slope of the graph corresponds to ΔG. When substances are mixed together, the reaction will proceed in the direction where there is a decrease in Gibbs free energy (ΔG 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. $\mathbf{\Delta G = 0}$).

As can be seen from Fig. 8 above, ΔG 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

	$\mathbf{A}(aq)$	+	$2\mathbf{B}(aq)$	$\rightleftharpoons$	$4\mathbf{C}(aq)$
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}	$x - 0.84x = 0.16x$		$0.84x$		$0.84x$

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

(a) $$1.01 \times 10^5 = 1.84x$$

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

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

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

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** at the **same extent**.
- ✗ B: Heating the system will cause the equilibrium position 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 concentration of the product. This causes the equilibrium position to shift to the **right** to produce more methanol gas. The cooling of the system will further shift the equilibrium position to the right as the exothermic reaction will be favoured to produce some heat. The yield of methanol gas **increases**.
- ✗ D: Lowering the pressure of the system will cause the equilibrium position 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	**equilibrium position**	**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 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 ºC to 500 ºC),

⇒ **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 ºC curve is **lower** than that of 400 ºC.

[Ans: A]