RAFFLES INSTITUTION
Year 5 H2 CHEMISTRY 2022
Lecture Notes 7 – Chemical Equilibria

A **Content**

Chemical Equilibria: reversible reactions; dynamic equilibrium

(i) factors affecting chemical equilibria
(ii) equilibrium constants
(iii) the Haber process

B **Learning Outcomes**

Candidates 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

C **Lecture Outline**

1. Reversible Reactions
2. Dynamic Equilbrium
3. The Equilibrium Law & Equilibrium Constants
4. Homogeneous and Heterogeneous Equilbria
5. Calculations involving Equilibrium Constants
6. Standard Gibbs Free Energy and Position of Equilbrium
7. Le Chatelier's Principle and Position of Equilibrium
8. Industrial Process: The Haber Process
9. Appendix

PREAMBLE

The concepts covered in Kinetics and Thermodynamics form the basis of Chemical Equilibrium. We have studied the *feasibility* of a reaction in Thermodynamics (using ΔG) and *how fast* a reaction can proceed in Kinetics, now we will look at ***how far*** (extent) a reaction can proceed in this topic. Not all reactions go to completion; there are many reactions that are reversible and hence would not achieve completion. The following questions will help to guide us in the understanding of reversible systems:

1. What are the characteristics of a reversible reaction?
2. How can we describe a system at equilibrium?
3. What happens when a system at equilibrium is disturbed?
4. Why would systems tend towards a state of equilibrium?
5. What are the factors to consider for optimal yield in a reversible reaction?
6. How can we measure the extent of a reaction in an equilibrium?

1 REVERSIBLE REACTIONS

Candidates should be able to explain, in terms of rates of the forward and reverse reactions, what is meant by a reversible reaction and dynamic equilibrium.

- Reversible reactions are reactions that proceed in **both the forward and backward directions.**
- These reactions are denoted by a **double–headed arrow** ($\rightleftharpoons$).
- Reversible reactions are **not complete**; instead, a **state of dynamic equilibrium** will be attained.
- A **mixture of both reactants and products** is obtained when a system reaches equilibrium.

Examples:

Esterification: $CH_3CH_2COOH(l) + CH_3OH(l) \rightleftharpoons CH_3CH_2COOCH_3(l) + H_2O(l)$

Restoration of ozone: $3O_2(g) \rightleftharpoons 2O_3(g)$

2 DYNAMIC EQUILIBRIUM

Dynamic equilibrium refers to a **state in a reversible system** in which the **rates of the forward and backward reactions are continuing at the same rate,** resulting in **no net change in the macroscopic properties** (e.g. concentrations, partial pressure) of the reactants and products.

- Equilibrium can only be achieved in a **closed system**, one which does not allow matter to enter or leave but allows free transfer of energy.
- Equilibrium can be attained **from either direction**, starting with reactants or with products, provided the appropriate amounts are used.
- The same equilibrium state can be attained starting from any amount of reactants and products, provided the **temperature remains constant**.
- The time taken, t_{eqm}, for the system to reach equilibrium is dependent on the forward and backward reaction rates.
- Once equilibrium is reached, the system will remain in this state until the system is disturbed. *(Refer to Section 7)*

Consider the elementary reversible reaction:

$$A + B \underset{\text{backward reaction}}{\overset{\text{forward reaction}}{\rightleftharpoons}} C + D$$

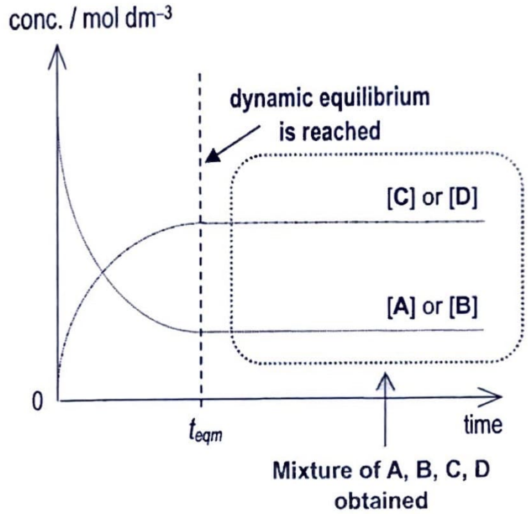
(i) At time = 0,

- **A** and **B** are mixed and the forward reaction proceeds (i.e. from left to right) to form **C** and **D**.

$$\mathbf{A + B \longrightarrow C + D}$$

rate of forward rxn: **rate$_f$ = k_f [A][B]**

- no **C** and **D** are present
rate of backward rxn: **rate$_b$ = k_b [C][D] = 0**



(ii) As the reaction proceeds,

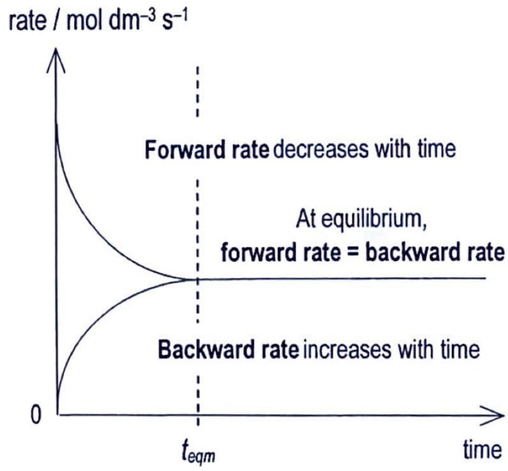
- [**A**] and [**B**] decrease ⇒ **forward rate decreases**

- Since **C** and **D** are being formed, backward reaction commences (i.e. from right to left) to form **A** and **B**.

$$\mathbf{A + B \longleftarrow C + D}$$

rate of backward reaction: **rate$_b$ = k_b [C][D]**

- As [**C**] and [**D**] increases ⇒ **backward rate increases**



(iii) At t_{eqm}, a state of **dynamic equilibrium** is attained where

forward rate = backward rate ≠ 0

- Forward and backward reactions are both still occurring.
- The rate of **A** and **B** reacting to form **C** and **D** is **equal** to the rate of **C** and **D** reacting to form **A** and **B**.
- $[A]_{eqm}$, $[B]_{eqm}$, $[C]_{eqm}$ and $[D]_{eqm}$ become **constant**.
- However, the reaction is **not complete** (i.e. not 100% conversion) and a **mixture of both reactants** (**A** & **B**) **and products** (**C** & **D**) are present at equilibrium.

Candidates should be able to deduce expressions for equilibrium constants in terms of concentration, K_c, and partial pressure, K_p. [Treatment of the relationship between K_p and K_c is NOT required.]

3.1 Reaction Quotient, Equilibrium Constant and Position of Equilibrium

Consider the reversible reaction:

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

- At **any given time,** the **reaction quotient, Q_c**, is given by the ratio of the **concentrations** of the reactants and products raised to their stoichiometric ratios:

Reaction quotient, $Q_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$ where [A], [B], [C] and [D] are the concentration in mol dm^{-3} at any given time

- As the reaction proceeds towards equilibrium, Q_c changes as the concentrations of reactants and products change continually until equilibrium is reached.

- When dynamic equilibrium is attained at a **given temperature**,
  ⇒ [A], [B], [C] and [D] remain constant
  ⇒ $Q_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$ becomes a **constant** and this is known as the **equilibrium constant, K_c**.

At equilibrium: $Q = K$ (at the given temperature)

equilibrium constant, $K_c = \dfrac{[C]^c_{eqm}[D]^d_{eqm}}{[A]^a_{eqm}[B]^b_{eqm}}$ units of K_c = (mol dm^{-3})$^{(c+d)-(a+b)}$

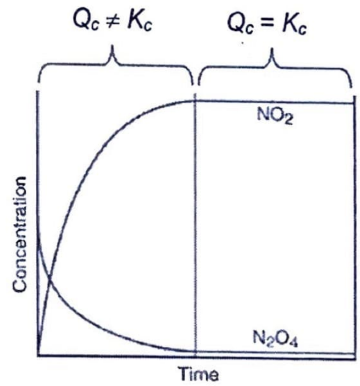
where $[X]_{eqm}$ is the concentration of **X** in mol dm^{-3} at **equilibrium**

This empirical (experimentally found) mathematical relationship which relates the concentration of the species in an equilibrium mixture is known as the **Equilibrium Law.**

Consider the reversible breakdown of N_2O_4 to NO_2:

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\quad Q_c = \dfrac{[NO_2]^2}{[N_2O_4]}$

colourless brown



- The concentration of $[NO_2]$ and $[N_2O_4]$ change smoothly and continually during the reaction so does the value of Q_c.
- Once the system reaches equilibrium (i.e. no net change in the colour of the mixture, the brown intensity stays constant), the concentrations remain constant and $Q_c = K_c$.

- The relative composition (e.g. concentration) of the products and reactants present in a reaction mixture at equilibrium is known as the **position of equilibrium**.

Exercise 1

Write the K_c expressions for the following reversible reactions and give its units.

	Equation	K_c	Units for K_c
(a)	$2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$	$K_c = \frac{[H_2][Br_2]}{[HBr]^2}$	no units
(b)	$Cu(NH_3)_4^{2+}(aq) \rightleftharpoons Cu^{2+}(aq) + 4NH_3(aq)$	$K_c = \frac{[NH_3]^4[Cu^{2+}]}{[Cu(NH_3)_4^{2+}]}$	$mol^4\ dm^{-12}$

3.2 Equilibrium Constant, K_p, for gaseous system

It is easier to measure pressure of a gas than its concentration, so for gaseous system, the reaction quotient and equilibrium constant are often expressed in terms of partial pressures instead of concentrations.

Consider the reversible **gaseous** system:

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

Equilibrium constant, K_p = $\frac{p_C^{\ c}\, p_D^{\ d}}{p_A^{\ a}\, p_B^{\ b}}$ units of K_p = Pa $^{(c+d)-(a+b)}$ or atm $^{(c+d)-(a+b)}$

where p_Z is the partial pressure of gas **Z** (in Pa, kPa or atm) at **equilibrium**

Hence, for the equilibrium system: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

We can write either $K_c = \frac{[HI]^2}{[H_2][I_2]}$ in terms of concentrations or $K_p = \frac{p_{HI}^2}{p_{H_2}p_{I_2}}$ in terms of partial pressures.

Exercise 2

Write the K_p expressions for the following reversible reactions and give its units in Pa.

	Equation	K_p	Units for K_p
(a)	$4PF_5(g) \rightleftharpoons P_4(g) + 10F_2(g)$	$K_p = \frac{[P_4][F_2]^{10}}{[PF_5]^4}$	Pa^7
(b)	$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	$K_p = \frac{P_{SO_3}^2}{P_{SO_2}^2 + P_{O_2}}$	Pa^{-1}

3.3 Relating rate constants and equilibrium constants

Consider the reversible reaction:

$$aA + bB \underset{k_b}{\overset{k_f}{\rightleftharpoons}} cC + dD$$

Assuming that the reactions involved are elementary reactions,

rate of forward reaction, $rate_f = k_f [A]^a[B]^b$, and
rate of backward reaction, $rate_b = k_b [C]^c[D]^d$

At dynamic equilibrium, $rate_f = rate_b$

$$k_f [A]^a[B]^b = k_b [C]^c[D]^d$$

Rearranging $$\frac{k_f}{k_b} = \frac{[C]^c[D]^d}{[A]^a[B]^b} = K_c$$ at a given temperature

3.4 Variations in the forms of *K*

3.4.1 Form of *K* for a forward and a backward reaction

The equilibrium constant of the backward reaction is the reciprocal of the equilibrium constant of the forward reaction and vice versa.

$$K_{forward} = \frac{1}{K_{backward}} \quad ; \quad K_{backward} = \frac{1}{K_{forward}}$$

Exercise 3

The oxidation of sulfur dioxide to sulfur trioxide is a key step in acid rain formation and sulfuric acid production. The numerical value of K_c for the reaction at 1000 K is given below:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad K_c = 261$$

Calculate the K_c for the backward reaction at the same temperature.

Answer:

$$K_{c(forward)} = \frac{[SO_3(g)]^2}{[SO_2(g)]^2[O_2(g)]} \quad \text{and} \quad K_{c(backward)} = \frac{[SO_2(g)]^2[O_2(g)]}{[SO_3(g)]^2} = \frac{1}{K_{c(forward)}}$$

Therefore $K_{c(backward)} = \frac{1}{261} = 3.83 \times 10^{-3}$ mol dm^{-3} (3sf)

3.4.2 Form of K for an overall reaction

If an overall reaction is the sum of two or more reactions, the overall equilibrium constant is the product of the equilibrium constants for the steps:

$$K_{overall} = K_1 \times K_2 \times \cdots$$

Exercise 4

Nitrogen and oxygen react to form nitrogen dioxide, a toxic pollutant that contributes to photochemical smog. The reaction sequence, together with the numerical values of the K_c for each step of the reaction, is as shown below:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad K_{c1} = 4.3 \times 10^{-25}$$

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) \qquad K_{c2} = 6.4 \times 10^{9}$$

Given that the reactions occur at the same temperature, calculate the K_c for the overall reaction:

$$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$$

Answer:

$$K_c = \frac{[NO_2(g)]^2}{[N_2(g)][O_2(g)]^2} = \frac{[NO(g)]^2}{[N_2(g)][O_2(g)]} \times \frac{[NO_2(g)]^2}{[NO(g)]^2[O_2(g)]}$$

Therefore, $K_c = (4.3 \times 10^{-25}) \times (6.4 \times 10^{9}) =$ **2.75×10^{-15} mol^{-1} dm^3**

3.4.3 Form of K for a Reaction with Coefficients Multiplied by a Common Factor, n

When the stoichiometric coefficients of a balanced equation are multiplied by a factor, n, then K is raised to the power of the same factor, n.

$$\text{New } K = K^n$$

Exercise 5

The numerical value of the K_c for the ammonia formation reaction at 1000 K is given below:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad K_c = 2.4 \times 10^{-3}$$

If we change the coefficients of the equation, which we will call the reference (ref) equation, what are the numerical values of K_c for the following balanced equations?

a) $\frac{1}{3}N_2(g) + H_2(g) \rightleftharpoons \frac{2}{3}NH_3(g)$ **Answer:** $K_c = K_{c(ref)}^{\frac{1}{3}} = (2.4 \times 10^{-3})^{\frac{1}{3}} = 0.134$ (3sf)

b) $NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$ **Answer:** $K_c = K_{c(ref)}^{-\frac{1}{2}} = (2.4 \times 10^{-3})^{-\frac{1}{2}} = 20.4$ (3sf)

3.5 Factors affecting Equilibrium Constants

Candidates should be able to deduce whether changes in concentration, pressure or temperature or the presence of a catalyst affect the value of the equilibrium constant for a reaction.

As derived in section 3.3, K_c (or K_p) can be regarded as the ratio of the forward rate constant, k_f, over the backward rate constant, k_b, for an elementary reaction:

$$K_c \text{ (or } K_p) = \frac{k_f}{k_b} \text{ , where } k = Ae^{-Ea/RT} \text{ (Arrhenius equation)}$$

Since the rate constants, k_f and k_b, are independent of concentration (or partial pressure) but dependent on temperature, K_c (or K_p) is a **constant at a specific temperature** and it **varies with temperature.**

The value of equilibrium constant K_c (or K_p) is **NOT** affected by:

- changes in the concentrations of reactants and products (e.g. addition / removal of a reactant or product)
- changes in total pressure of reaction system / partial pressures of reactants and products,
- presence / absence of catalyst.

IMPORTANT NOTE:

Equilibrium constant, K_c (or K_p), is only affected by **temperature** changes.

(Refer to Section 7.4)

3.6 Significance of Equilibrium Constants

- Equilibrium constant, K, is a measure of the extent of reaction.
- The value K_c (or K_p) gives an indication of *how far* a reaction proceeds towards the product side at a given temperature.

Reactions	Value of K at 1000 K	Remarks
$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$	1×10^{-30}	Small value of K indicates that the reaction yields little products when equilibrium is reached. In other words, the reaction favours the reactants over products at equilibrium. **If K is very small, the position of equilibrium** lies very much to the _left_. We can say that there is "_'no reaction_" or forward reaction does not proceed to any appreciate extent.

Reactions	Value of *K* at 1000 K	Remarks
$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$	2.2×10^{22}	Large value of *K* indicates that very little reactants remain when equilibrium is reached. In other words, the reaction favours the products over reactants at equilibrium. **If *K* is <u>very large</u>, the position of equilibrium** lies very much to the _right_. We can say that the reaction "_goes into completion_" or the forward reaction is "almost complete".
$2BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$	5	Intermediate value of *K* indicates that significant amounts of reactants and products are present at equilibrium.

In summary,

- The expression of K_c (or K_p) must be accompanied by the chemical equation of interest as it is sensitive to the stoichiometric coefficients of the reaction. The units of K_c and K_p vary depending on the stoichiometric coefficents and should always be stated (unless otherwise stated).
- K_c (or K_p) is only affected by changes in temperature.
- K_c (or K_p) is unaffected by changes in the concentrations/partial pressures of either reactants or products. The position of equilibrium shifts such that the equilibrium concentrations (or partial pressures) gives the same numerical value for K_c (or K_p) at a given temperature.
- The magnitude of K_c (or K_p) <u>does not</u> give any information on the rates of forward and backward reactions.

4 HOMOGENEOUS AND HETEROGENEOUS EQUILIBRIA

4.1 Homogeneous Equilibrium

Homogeneous equilibrium refers to an equilibrium system in which all the substances involved are in the **same phase**.

Examples	Equilibrium Constant
$4PF_5(g) \rightleftharpoons P_4(g) + 10F_2(g)$	$K_c = \frac{[P_4(g)][F_2(g)]^{10}}{[PF_5(g)]^4}$ $K_p = \frac{p_{P_4}\, p^{10}_{F_2}}{p^4_{PF_5}}$
$C_2H_5OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$	$K_c = \frac{[CH_3COOC_2H_5(l)][H_2O(l)]}{[C_2H_5OH(l)][CH_3COOH(l)]}$
$Cu(NH_3)_4^{2+}(aq) \rightleftharpoons Cu^{2+}(aq) + 4NH_3(aq)$	$K_c = \frac{[Cu^{2+}(aq)][NH_3(aq)]^4}{[Cu(NH_3)_4^{2+}(aq)]}$

4.2 Heterogeneous Equilibrium

Heterogeneous equilibrium refers to an equilibrium system involving substances that are **not in the same phase**.

Examples:

- Sublimation: $I_2(s) \rightleftharpoons I_2(g)$
- Dissolution: $AgCl(s) + aq \rightleftharpoons Ag^+(aq) + Cl^-(aq)$
- Decomposition of calcium carbonate: $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

Consider the K_c expression for the decomposition of calcium carbonate:

$$K_c = \frac{[CaO(s)][CO_2(g)]}{[CaCO_3(s)]} \quad \text{----- } \mathbf{(1)}$$

- Solids have **fixed density** and hence, **fixed concentration**, i.e. same number of particles per unit volume. Adding more solid will not increase its concentration.

$$\text{conc (in mol dm}^{-3}) = \frac{n}{V} = \frac{m/M}{V} = \frac{m}{V} \times \frac{1}{M} = \frac{density}{M} = \text{constant}$$

- Therefore, the concentrations of pure solids, i.e. $[CaO(s)]$ and $[CaCO_3(s)]$ are **constant**. Hence, the above expression **(1)** can be rearranged mathematically to give

$$[CO_2(g)] = K_c \times \frac{[CaCO_3(s)]}{[CaO(s)]} = K'_c$$

- K'_c is taken to be the equilibrium constant for the decomposition of calcium carbonate and is dependent only on $[CO_2(g)]$.

  ⇒ The equilibrium expression can be simply written as $\boxed{K_c = [CO_2(g)]}$

Consider the K_p expression for the decomposition of calcium carbonate:

$$K_p = \frac{p_{CaO}\,p_{CO_2}}{p_{CaCO_3}} \quad \text{----- } \mathbf{(2)}$$

- At a given temperature, the **vapour pressure of a solid is a constant**.
  ⇒ p_{CaO} and p_{CaCO_3} can be taken as constant
- Hence, the above expression **(2)** can be rearranged mathematically to give

$$p_{CO_2} = K_p \times \frac{p_{CaCO_3}}{p_{CaO}} = K'_p$$

- K'_p is taken to be the equilibrium constant for the decomposition of calcium carbonate and is dependent only on p_{CO_2}.

  ⇒ The equilibrium expression can be simply written as $\boxed{K_p = p_{CO_2}}$

In summary,

K_c (and K_p) expression of heterogeneous equilibrium **exclude**:

- the concentration (or partial pressure) of pure solids and pure liquids because they are constant at a given temperature.
- the concentration of water when it is present in large amount (as a solvent) in an aqueous solution. In such instance, $[H_2O]$ is approximately constant.

Note: $[H_2O]$ = density / molar mass = 1000 / 18.0 = 55.6 mol dm^{-3}

Example: Write the K_c expression for the dissociation of NH_3 in water:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$K_c = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Note: $[H_2O]$ is **excluded** from the K_c expression because the reaction takes place in **aqueous** medium where water is present is large amount and hence, $[H_2O]$ is approximately constant.

Exercise 6

Write the K_c and K_p expressions for the following heterogeneous equilibrium systems.

	Equation	K_c	K_p
(a)	$I_2(s) \rightleftharpoons I_2(g)$	$K_c = [I_2(g)]$	$K_p = p_{I_2}$
(b)	$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$	$K_c = [Ag^+][Cl^-]$	Not applicable
(c)	$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$	$K_c = \frac{[H_2(g)]^4}{[H_2O(g)]^4}$	$K_p = \frac{P_{H_2(g)}^4}{P_{H_2O(g)}^4}$
(d)	$PCl_3(l) + Cl_2(g) \rightleftharpoons PCl_5(s)$	$K_c = \frac{1}{[Cl_2(g)]}$	$K_p = \frac{1}{P_{Cl_2(g)}}$

- ☑ Candidates should be able to calculate the values of equilibrium constants in terms of concentrations or partial pressures from appropriate data.
- ☑ Candidates should be able to calculate the quantities present at equilibrium, given appropriate data (such calculations will not require the solving of quadratic equations).

Calculations that seek to solve for K_c (or K_p) values require the following information:

- the balanced chemical equation,
- the K_c (or K_p) expression, and
- equilibrium concentrations (or partial pressures) of all species

5.1 Calculation of K_c from concentrations

Worked Example 1

When 2 mol of HI is allowed to dissociate in a 2.0 dm^3 vessel at 440 °C, only 1.7 mol of the HI is left at equilibrium. Calculate the equilibrium constant, K_c, at this temperature.

Solution:

❶ Construct an "I.C.E" table with the balanced chemical equation, and the **I**nitial, **C**hange in and **E**quilibrium amount or concentration of the species involved. Fill in all known values into the table.

	2HI(g)	⇌	H_2(g)	+	I_2(g)
Initial amt / mol	2		0		0
Change in amt / mol	-0.3		+0.15		+0.15
Equilibrium amt / mol	1.7		0.15		0.15

❷ Write the K_c expression and hence, calculate K_c.

$$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{\left(\frac{0.15}{2.0}\right)\left(\frac{0.15}{2.0}\right)}{\left(\frac{1.7}{2.0}\right)^2} = 7.79 \times 10^{-3} \text{ (3sf)}$$

K_c in this instance has no units

in terms of concentration, not amount!

5.2 Calculations of concentrations from K_c

Worked Example 2

1.00 mol each of methanol and ethanoic acid react together according to the equation:

$$CH_3OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOCH_3(l) + H_2O(l)$$

The equilibrium mixture contains 0.20 mol each of methyl ethanoate and water at room temperature.

(i) Calculate K_c for the reaction at room temperature.

(ii) 2 mol of methanol and 2 mol of ethanoic acid were mixed together at the same temperature. Calculate the amount of methyl ethanoate produced at equilibrium. Hence, calculate the percentage yield of methyl ethanoate under these conditions.

Solution:

(i) ❶ Let V dm³ be the volume of the mixture [Assumption: volume change is negligible].
❷ Construct "I.C.E" table and fill in all known values

	$CH_3OH(l)$	+	$CH_3COOH(l)$	$\rightleftharpoons$	$CH_3COOCH_3(l)$	+	$H_2O(l)$
Initial conc / mol dm^{-3}	$\frac{1.00}{V}$		$\frac{1.00}{V}$		0		0
Change in conc / mol dm^{-3}	$-\frac{0.20}{V}$		$-\frac{0.20}{V}$		$+\frac{0.20}{V}$		$+\frac{0.20}{V}$
Equilibrium conc / mol dm^{-3}	$\frac{0.80}{V}$		$\frac{0.80}{V}$		$\frac{0.20}{V}$		$\frac{0.20}{V}$

❸ Write the K_c expression and calculate K_c.

$$K_c = \frac{[CH_3COOCH_3(l)][H_2O(l)]}{[CH_3OH(l)][CH_3COOH(l)]} = \frac{\left(\frac{0.20}{V}\right)\left(\frac{0.20}{V}\right)}{\left(\frac{0.80}{V}\right)\left(\frac{0.80}{V}\right)} = 0.0625$$

Note: Here, the reaction does not take place in the aqueous medium, i.e. water is not a solvent and it does not exist in large amount. Therefore, the concentration of water varies as it is being produced and hence [H_2O] should be included in the K_c expression.

(ii) ❶ Let x mol be the amount of methyl ethanoate produced at equilibrium and V dm³ be the volume of the mixture [Assumption: volume change is negligible].
❷ Construct "I.C.E" table and fill in all known values.
❸ Write the K_c expression and calculate x. Hence, determine the percentage yield of methyl ethanoate.

	$CH_3OH(l)$	+	$CH_3COOH(l)$	$\rightleftharpoons$	$CH_3COOCH_3(l)$	+	$H_2O(l)$
Initial conc / mol dm^{-3}	$\frac{2.00}{V}$		$\frac{2.00}{V}$		0		0
Change in conc / mol dm^{-3}	$-\frac{x}{V}$		$-\frac{x}{V}$		$+\frac{x}{V}$		$+\frac{x}{V}$
Equilibrium conc / mol dm^{-3}	$\frac{2.00-x}{V}$		$\frac{2.00-x}{V}$		$\frac{x}{V}$		$\frac{x}{V}$

$$K_c = \frac{[CH_3COOCH_3(l)][H_2O(l)]}{[CH_3OH(l)][CH_3COOH(l)]} = \frac{(\frac{x}{V})(\frac{x}{V})}{(\frac{2.00-x}{V})(\frac{2.00-x}{V})} = \frac{(\frac{x}{V})^2}{(\frac{2.00-x}{V})^2} = \underline{0.0625}$$

Solving the quadratic equation,

$$\frac{x}{(2.00-x)} = \sqrt{0.0625} = 0.25 \quad \text{(reject } -0.25\text{)}$$

$x = \underline{0.400}$

The value of K_c remains at 0.0625 because temperature is unchanged.

Equilibrium amount of methyl ethanoate = **0.400 mol**

$$\text{Percentage yield} = \frac{0.400}{2.00} \times 100\,\% = \underline{\mathbf{20.0\%}}$$

5.3 Calculations of K_p from Partial Pressures

Worked Example 3

The gaseous equilibrium mixture in a flask at temperature T was found to consist of 0.50 mol of SO_2, 0.12 mol of O_2 and 5.0 mol of SO_3. The pressure of the flask was 800 kPa.

(i) Calculate the partial pressures of the three gases in the flask.
(ii) Calculate the K_p for the mixture in the flask at the given temperature.

Solution:
[Note: Since the equilibrium quantities of all species are given in the question, there is no need to construct the ICE table.]

(i)

$$p_{SO_2} = \frac{0.50}{0.50 + 0.12 + 5.0} \times 800\text{ kPa} = \mathbf{71.2\ kPa}$$

$$p_{O_2} = \frac{0.12}{0.50 + 0.12 + 5.0} \times 800\text{ kPa} = \mathbf{17.1\ kPa}$$

$$p_{SO_3} = \frac{5.0}{0.50 + 0.12 + 5.0} \times 800\text{ kPa} = \mathbf{712\ kPa}$$

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

$$K_p = \frac{p^2_{SO_3}}{p^2_{SO_2}\,p_{O_2}} = \frac{(712)^2}{(71.2)^2(17.1)}\text{ kPa}^{-1} = \mathbf{5.85\ kPa^{-1}}$$

5.4 Calculations of Partial Pressures from K_p

Worked Example 4

A sample of dinitrogen tetroxide, N_2O_4, is heated and the following equilibrium is established at 323 K:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Given that the partial pressure of N_2O_4 at equilibrium is 0.50 atm and the equilibrium constant K_p for the dissociation of dinitrogen tetroxide into nitrogen dioxide at 323 K is 0.725 atm, calculate the

(i) partial pressure of NO_2 at equilibrium,

(ii) final pressure of the system.

Solution:

[Note: Since the K_p is given and the equilibrium quantity of only 1 species is unknown, there is no need to construct the ICE table.]

(i) Let x atm be the partial pressure of NO_2 at equilibrium.

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
Equilibrium partial pressure / atm	0.50		x

$$K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}} = \frac{x^2}{0.50} = 0.725 \text{ atm} \quad \Rightarrow \quad p_{NO2} = x = \underline{\mathbf{0.602\ atm}}$$

(ii) Final pressure = 0.50 + 0.602 = **1.10 atm**

5.5 Calculations involving Degree of Dissociation, α

Some gases undergo **dissociation** i.e. they break down to form smaller gaseous fragments.

Examples: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

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

At equilibrium, the equilibrium mixture would contain both the undissociated gas and the gases which it has dissociated into. The total number of gaseous molecules is therefore greater than that present before dissociation.

Degree of dissociation, α

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

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

Worked Example 5

Dinitrogen tetroxide dissociates into nitrogen dioxide on heating:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

At a total pressure of 2 atm, dinitrogen tetroxide is 35 % dissociated into nitrogen dioxide.

(i) Calculate the value of K_p under these conditions.

(ii) What will be the degree of dissociation of dinitrogen tetroxide at the same temperature but under a total pressure of 1 atm?

Solution:

(i) Method 1 – work in terms of amount

Let x be the initial amount of dinitrogen tetroxide.

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$	Total
Initial amt / mol	x		0	x
Change in amt / mol	$-0.35x$		$+0.7x$	
Equilibrium amt / mol	$0.65x$		$0.7x$	$1.35x$
Equilibrium mole fraction	$\frac{0.65}{1.35}$		$\frac{0.7}{1.35}$	
Equilibrium partial pressure / atm	0.963		1.04	

$$K_p = \frac{p_{NO_2}^2}{p_{N_2O_4}} = \frac{(1.04)^2}{(0.963)} = 1.12 \text{ atm}$$

Method 2 – work in terms of partial pressures

Let p be the initial pressure of N_2O_4. (Note: the initial pressure is not 2 atm)

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$	Total
Initial pressure / atm	p		0	p
Change in partial pressure / atm	$-0.35p$		$+0.70p$	
Equilibrium partial pressure/ atm	$0.65p$		$0.70p$	$1.35p$

Since p_T = 2 atm = $1.35p \Rightarrow p = 1.48$ atm

$$K_p = \frac{p_{NO_2}^{\ 2}}{p_{N_2O_4}} = \frac{(0.70 \times 1.48)^2}{(0.65 \times 1.48)} = 1.12 \text{ atm}$$

(ii) Let the initial pressure of N_2O_4 be y atm and the degree of dissociation of dinitrogen tetroxide be α.

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$	Total
Initial pressure / atm	y		0	y
Change in pressure /atm	$-\alpha y$		$+2\alpha y$	
Equilibrium partial pressure/ atm	$y-\alpha y$		$2\alpha y$	$y+\alpha y$

At equilibrium, the total pressure of the system is 1 atm, therefore

$$(1+\alpha)y = 1$$
$$y = \frac{1}{1+\alpha}$$

Substitute the expression of y into K_p:

$$K_p = \frac{(2\alpha y)^2}{(1-\alpha)y} = \frac{4\alpha^2 y}{(1-\alpha)} = \frac{4\alpha^2}{(1-\alpha)(1+\alpha)} = 1.12$$

The value of K_p remains at 1.12 because the temperature is unchanged.

Solving for α, $\alpha = \pm 0.468$

Since $\alpha > 0$, $\alpha =$ **0.468**

Thus, the degree of dissociation of dinitrogen tetroxide at a total pressure of 1 atm is **0.468**, i.e. it is **46.8 % dissociated**.

Note: You can also work out **(ii)** in terms of amount. Try it out yourself by letting z be the initial amount of N_2O_4.

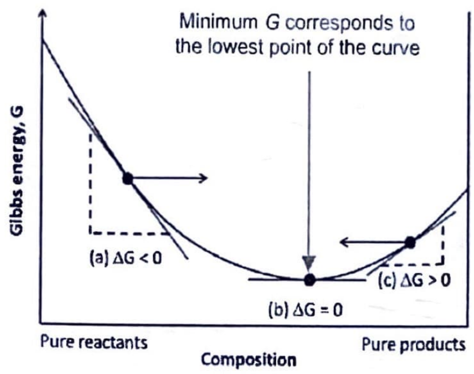
6 STANDARD GIBBS FREE ENERGY AND POSITION OF EQUILIBRIUM

Candidates should be able to 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]

Consider the reversible system:

$$\textbf{A} \rightleftharpoons \textbf{B}$$

- In a reversible system under constant temperature and pressure, the reaction mixture tends to adjust its composition until its Gibbs free energy, *G*, is at a **minimum**.



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

- Recalling the concepts in Energetics 2, the mixing of **A** and **B** results in increase of entropy, *S*, and hence a decrease in Gibbs free energy, *G*. This is why the value of *G* when equilibrium is reached is lower than that of pure **A** and pure **B** alone.

- The *change* in Gibbs free energy, ΔG, of a reaction is the derivative of Gibbs free energy, *G*, with respect to the composition of the reaction mixture. On the curve above, ΔG is the instantaneous gradient at any point along the curve.

- The condition of equilibrium, where *G* is at minimum, is **$\Delta G = 0$** under constant T and P.

- The value of ΔG can be used to predict if a reaction is spontaneous at that particular composition:

  - If $\Delta G < 0$, forward reaction tending towards the equilibrium is spontaneous; rate of forward reaction is faster than the backward reaction.
  - If $\Delta G > 0$, backward reaction tending towards the equilibrium is spontaneous; rate of backward reaction is faster than the forward reaction.
  - At $\Delta G = 0$, the system is at dynamic equilibrium where the forward rate is equal to the backward rate.

- In Energetics 2, the concept of using standard Gibbs free energy change, $\Delta G^{\ominus}$, to predict the spontaneity of a reaction was introduced.

  The relationship between the Gibbs free energy of reaction at any moment in time, ΔG, and the standard Gibbs free energy change, $\Delta G^{\ominus}$, is described by the following equation:

  $$\Delta G = \Delta G^{\ominus} + RT \ln Q$$ [Note: Not necessary to memorise this formula!]

  where *R* is the ideal gas constant 8.31 J mol^{-1} K^{-1}, *T* is the temperature in K, and *Q* is the reaction quotient at that moment in time.

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

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

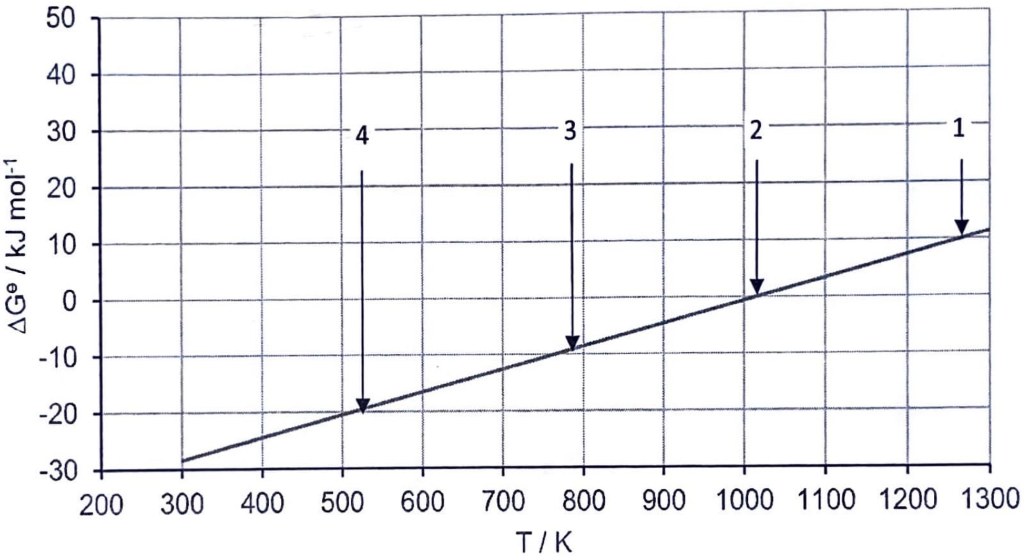
Cross reference with section 3.6

- In reactions where $\Delta G^\ominus < 0$, $K > 1$. This means that the position of equilibrium lies more to the **right** side, favouring products over reactants. In cases where $K >> 1$, we can say the reaction goes to "completion".
- In reactions where $\Delta G^\ominus > 0$, $K < 1$. This means that the position of equilibrium lies more to the **left** side, favouring reactants over products. In cases where $K << 1$, we can say that there is "no reaction".

Exercise 7 [N2017/1/14]

The graph shows how $\Delta G^\ominus$ changes with temperature for the reaction shown.

$$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$$



Equimolar amounts of H_2O and CO were introduced into a sealed container and allowed to reach equilibrium.

At which points will the concentration of H_2 be **greater** than the concentration of H_2O at equilibrium?

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

Solution:

For $[H_2]$ to be greater than $[H_2O]$,

- this means that there are more products over reactants at equilibrium,
- the position of equilibrium lies to the right, implying that $K > 1$.

Using the relationship $\Delta G^\ominus = -RT \ln K$, this means that $\Delta G^\ominus < 0$.

Answer: D

Candidates should be able to 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.

- When a system at equilibrium is disturbed by subjecting it to a change, the system will react in a manner to re-establish the equilibrium.

- These changes include:
  - Changes in concentration
  - Changes in pressure (or volume)
  - Changes in temperature
  - Addition of catalyst

Approach 1 – Le Chatelier's Principle

- The Le Chatelier's principle gives a useful 'rule of thumb' to predict the direction in which equilibrium position will shift when an equilibrium system is disturbed.

Le Chatelier's Principle states that ...

When a system at equilibrium is subjected to a change, the system will react to **counteract the change** imposed so as to **re–establish the equilibrium.**

Approach 2 – Analysis of forward and backward reaction rates using collision theory

- When the conditions change such that the system is no longer in equilibrium, the rates of forward and backward reactions are **no longer equal**.

- Consider the elementary reversible system:

$$aA + bB \underset{k_b}{\overset{k_f}{\rightleftharpoons}} cC + dD$$

  - If more reactant **A** (or **B**) is introduced to the system at equilibrium under constant V and T,

    ⇒ [**A**] (or [**B**]) increases

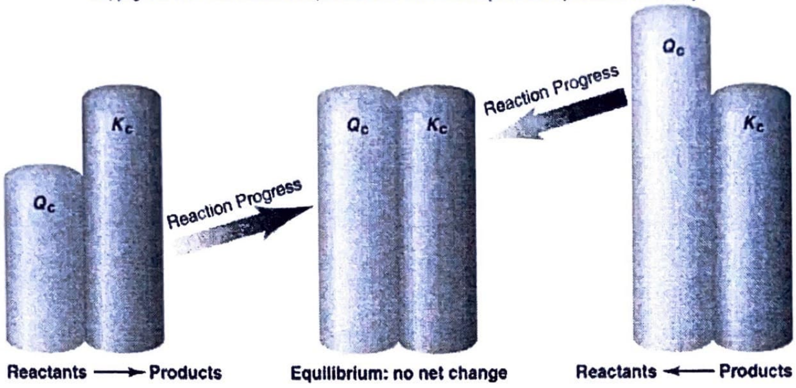
    ⇒ Frequency of effective collisions between reactants increases

    ⇒ Rate of forward reaction increases
  - The rate of forward reaction will be greater than the rate of backward reaction until equilibrium is re-established.

- In conclusion, increasing the concentration of reactants will favour the forward reaction while increasing the concentration of products will favour the backward reaction.

Approach 3 – Comparing reaction quotient Q to equilibrium constant K

- A more quantitative approach to predict the effect on the position of equilibrium when a change is imposed is to compare the value of Q and K.



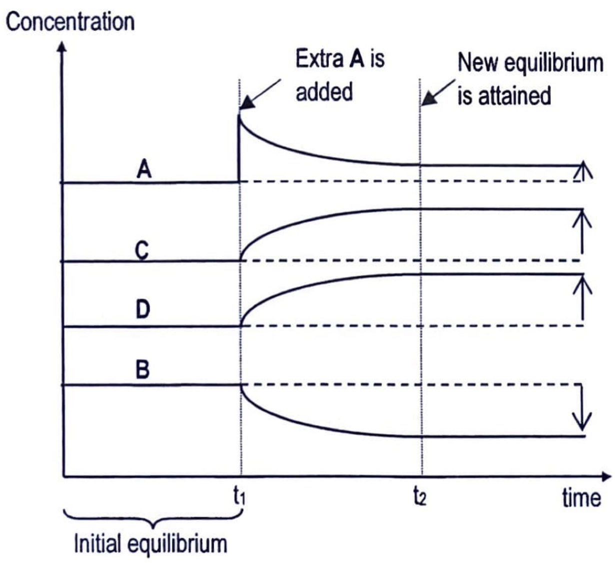
$Q_c < K_c$	$Q_c = K_c$	$Q_c > K_c$
Forward reaction favoured	System is at **equilibrium**	**Backward** reaction favoured

7.1 Effect of concentration changes

Consider the reversible reaction at equilibrium: a**A** + b**B** $\rightleftharpoons$ c**C** + d**D**

❖ When extra **A** (reactant) is **added** at constant V and T ⇒ **[A] increases**

- By Le Chatelier's Principle, equilibrium position will shift _right_ to partially offset the increase in **[A]** by removing **A** until a new equilibrium is reached.
- The new equilibrium mixture will contain **more A, C and D** but **less B**.



- At the time t_1, **[A]** increases.

$$Q_C = \frac{[C]^c[D]^d}{[A]^a[B]^b} < K_C$$

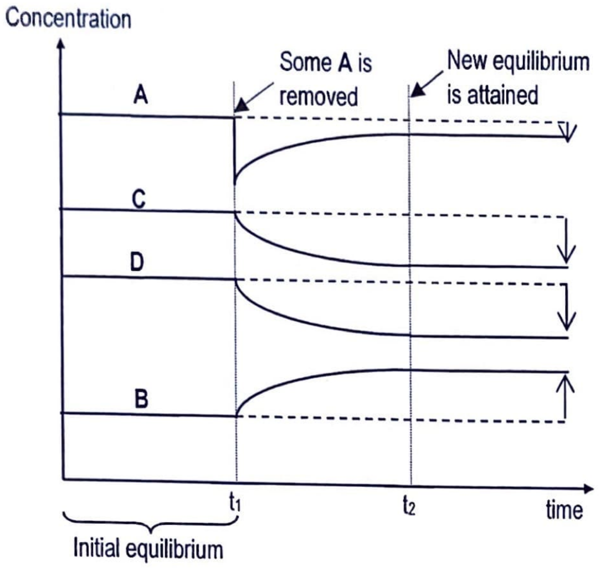
The system is no longer at equilibrium.

- To re-establish equilibrium, **[A]** and **[B]** would decrease while **[C]** and **[D]** would increase until $Q_C = K_C$
- New equilibrium is reached at time t_2.

Note: New equilibrium **[A]** is still higher than the initial equilibrium **[A]** as the change is only partially offset.

- When some **A** (reactant) is **removed** at constant V and T ⇒ **[A] decreases**

  - By Le Chatelier's Principle, equilibrium position will shift **left** to partially offset the decrease in **[A]** by producing more A until a new equilibrium is reached.
  - The new equilibrium mixture will contain **less A, C** and **D** but **more B.**



- At the time t_1, **[A]** decreases.

$$Q_C = \frac{[C]^c[D]^d}{[A]^a[B]^b} > K_C$$

The system is no longer at equilibrium.

- To re-establish equilibrium, **[A]** and **[B]** would increase while **[C]** and **[D]** would decrease until $Q_C = K_C$
- New equilibrium is reached at time t_2.

Note: New equilibrium **[A]** is still lower than the initial equilibrium **[A]** as the change is only partially offset.

Tips: In using Le Chatelier's Principle to answer question, the answer contains three parts: "where", "why" and "how".

By Le Chatelier's Principle, equilibrium position will shift left to partially offset the decrease in [A] by producing more A until a new equilibrium is reached.

where — why — how

Exercise 8

Summarise the effect of change in concentration of the components of the system

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

by indicating the direction of shift in the position of equilibrium when the concentrations of the components are changed as stated:

Change in Concentration	Shift in Equilibrium Position
↑ [A] (or [B])	right
↓ [A] (or [B])	left
↑ [C] (or [D])	left
↓ [C] (or [D])	right

Worked Example 6

State the differences in observations that are expected when the following system at equilibrium is subjected to the changes stated:

$$\underset{\text{yellow}}{2CrO_4^{2-}(aq)} + 2H^+(aq) \rightleftharpoons \underset{\text{orange}}{Cr_2O_7^{2-}(aq)} + H_2O(l)$$

Changes	Observations	Explanation
Decreasing pH	The solution becomes more orange.	pH decreases ⇒ $[H^+]$ increases. The increase in $[H^+]$ causes the equilibrium position to shift right, forming more orange $Cr_2O_7^{2-}(aq)$.
Adding NaOH(s) to the above resulting mixture	The solution turns from orange to yellow.	Solid NaOH dissolves to give $OH^-(aq)$. $OH^-(aq)$ reacts with $H^+(aq)$ to form water. The decrease in $[H^+]$ causes the equilibrium position to shift left, forming more yellow $CrO_4^{2-}(aq)$.

Worked Example 7

The K_c for the reaction **B**(aq) ⇌ **C**(aq) is 0.50 at 80 °C.

(i) A solution of **B**, initial concentration 0.0150 mol dm^{-3}, is allowed to reach equilibrium at 80 °C. Calculate the equilibrium concentrations of **B** and **C**.

(ii) If the concentration of **B** in the equilibrium mixture in **(i)** is increased by 0.0075 mol dm^{-3} at time = t_1, what will be the concentrations of **B** and **C** when equilibrium is established again at 80 °C at time = t_2?

(iii) Sketch the concentration–time graph for the reaction **B**(aq) ⇌ **C**(aq), from time = 0 to time = t_2.

Solution:

(i) Let x be the equilibrium concentration of **C**.

	B(aq)	⇌	C(aq)
Initial conc / mol dm^{-3}	0.0150		0
Change in conc / mol dm^{-3}	–x		+x
Eqm conc / mol dm^{-3}	0.0150 – x		x

$$K_c = \frac{[C]}{[B]} = \frac{x}{0.0150 - x} = 0.50 \Rightarrow x = [C] = \underline{\mathbf{5.00 \times 10^{-3}\ mol\ dm^{-3}}}$$

$[B] = 0.0150 - (5.00 \times 10^{-3}) = \underline{\mathbf{0.0100\ mol\ dm^{-3}}}$

(ii) Let y be the change in concentration of **C**.

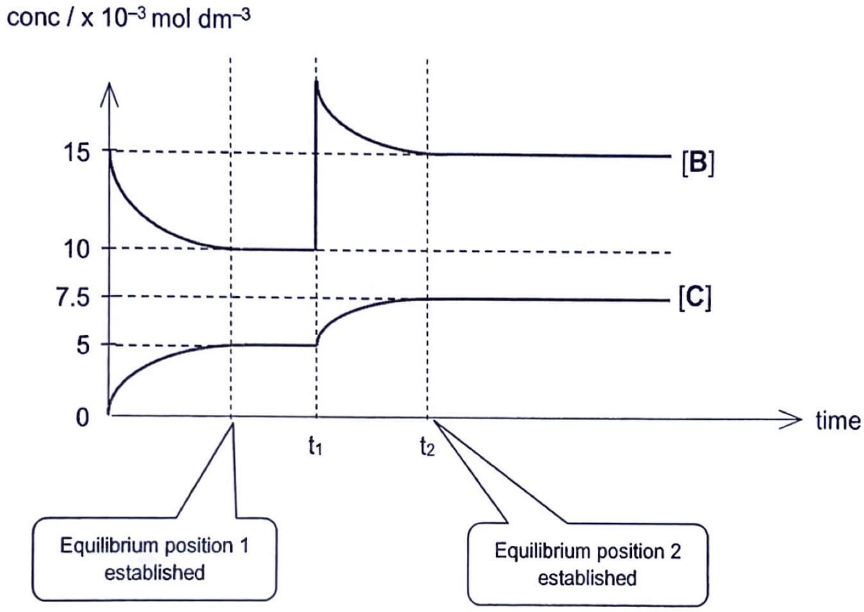
	B(aq)	⇌	C(aq)
Initial conc / mol dm^{-3}	0.0100 + 0.0075		0.00500
Change in conc / mol dm^{-3}	−y		+y
New eqm conc / mol dm^{-3}	0.0175 − y		0.00500 + y

$$K_c = \frac{[C]}{[B]} = \frac{0.0050 + y}{0.0175 - y} = 0.50 \Rightarrow y = 0.0025 \text{ mol dm}^{-3}$$

$[B]_{new\ eqm}$ = 0.0175 – 0.0025 = **0.0150 mol dm^{-3}**

$[C]_{new\ eqm}$ = 0.0050 + 0.0025 = **0.0075 mol dm^{-3}**

(iii)



Note: Notice that while the equilibrium positions have changed (i.e. the relative concentrations of **B** and **C** are different) but the value of *K* is unchanged. This is because *K* is only dependent on temperature and in this example, the temperature remains constant at 80°C.

7.2 Effect of pressure changes

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

7.2.1 Changes in Partial Pressure of Substances

- The **partial pressure** of a particular gaseous component (e.g. gas A) in an equilibrium may be
  - increased by adding gas A
  - decreased by removing gas A

- The effect of changing partial pressure of any of the gaseous components, at constant temperature, is similar to that of changing concentration.

For gas A, $p_A V = n_A RT \Rightarrow p_A = \frac{n_A}{V} RT = [A] \times RT$

Hence, $\boxed{p_A \propto [A]}$

Exercise 9

Summarise the effect of change in partial pressure on the composition of the gaseous system

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

by indicating the direction of shift in the position of equilibrium if partial pressures of the components are changed as stated:

Change in partial pressure	Shift in Equilibrium Position
$\uparrow p_A$ (or p_B)	right
$\downarrow p_A$ (or p_B)	left
$\uparrow p_C$ (or p_D)	left
$\downarrow p_C$ (or p_D)	right

7.2.2 Changes in Total Pressure of System

- **Total pressure** of the system could be
  - increased by compression (i.e. decreasing volume)
  - decreased by expansion (i.e. increasing volume)

- When the partial pressures of the gaseous reactants and products (and hence the total pressure of the system) are changed due to changes in volume, the equilibrium system will be disturbed.

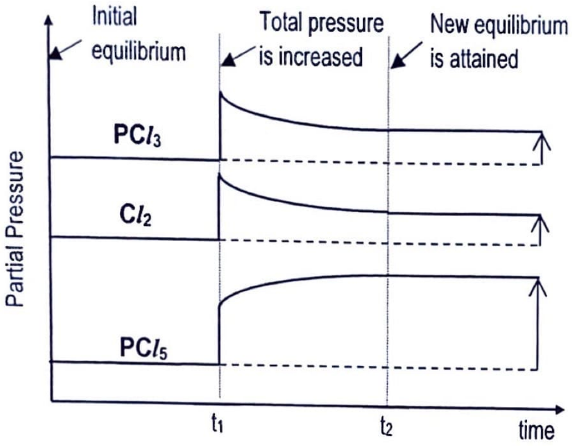
- The effect of changing total pressure of a gaseous system depends on the **stoichiometry** of the reaction, i.e. whether more, less, or equal number of gaseous particles are produced after a reaction.

0 **When number of gas particles on each side of equation is <u>different</u>**

Example: $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$

❖ When the total pressure of the equilibrium mixture is **increased**:

- By Le Chatelier's Principle, the system will try to counteract the increase in total pressure by favouring the reaction that decreases the total pressure.
- Hence, the forward reaction is favoured as it produces fewer gas particles.
- The position of equilibrium shifts to the right.



Note: New equilibrium partial pressures of PCl_3, Cl_2 and PCl_5 are still higher than their initial equilibrium partial pressures as the change is only partially offset.

- At the time t_1, when total pressure increases (partial pressures of all gases increase), the increase in the denominator is greater than the increase in the numerator, resulting in

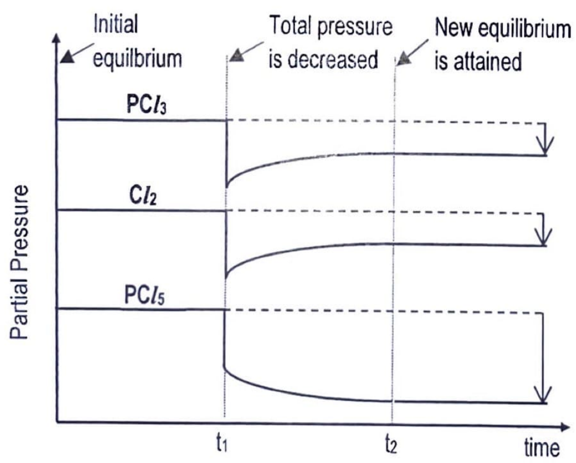
$$Q_p = \frac{p_{PCl5}}{p_{PCl3} \times p_{Cl2}} < K_p$$

The system is no longer at equilibrium.

- To re-establish equilibrium, partial pressures of PCl_3 and Cl_2 would decrease while partial pressure of PCl_5 would increase until $Q_p = K_p$

❖ When the total pressure of the equilibrium mixture is **decreased**:

- By Le Chatelier's Principle, the system will try to counteract the decrease in total pressure by favouring the reaction that increases the total pressure.
- Hence, the backward reaction is favoured as it produces more gas particles.
- The position of equilibrium shifts to the left.



Note: New equilibrium partial pressures of PCl_3, Cl_2 and PCl_5 are still lower than their initial equilibrium partial pressures as the change is only partially offset.

- At the time t_1, when total pressure decreases (partial pressures of all gases decrease), the decrease in the denominator is greater than the decrease in the numerator, resulting in

$$Q_p = \frac{p_{PCl5}}{p_{PCl3} \times p_{Cl2}} > K_p$$

The system is no longer at equilibrium.

- To re-establish equilibrium, partial pressures of PCl_3 and Cl_2 would increase while partial pressure of PCl_5 would decrease until $Q_p = K_p$

❷ **When number of gas particles on each side of equation is <u>equal</u>**

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

- Since the number of gaseous particles on both sides of the system is equal, the change in total pressure does not favour the forward or the backward reaction.
- Position of equilibrium shifts neither to the left nor to the right.
  ⇒ **System remains at equilibrium** with no change to the composition of the equilibrium mixture.

Approaching this quantitatively,

$$Q_p = \frac{p_{HI}^{\ 2}}{p_{H2} \times p_{I2}} = K_p$$

The increase (or decrease) of the numerator is the same as the increase (or decrease) of the denominator since the power of the terms are the same. Hence, ***Q* is still equals to *K*** and **there is no shift in the equilibrium position.**

SUMMARY

For a system with **different** number of gaseous reactants and products:
- When the total pressure of the system is increased (decreased), the equilibrium position will shift in the direction that leads to a decrease (increase) in the number of gas particles.

For system with **equal** number of gaseous reactants and products:
- Change in total pressure of the system does not affect the equilibrium position.

Exercise 10

For the following reactions, state whether an increase or decrease in total pressure would favour the forward reaction.

Reaction	Change in p_T that favours forward rxn
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	increase P_T
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$	decrease P_T
$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$	not affected by P_T

7.3 Effect of volume changes

For **gaseous** systems, the effect of **increasing (decreasing) volume** under constant temperature conditions is similar to that of **decreasing (increasing) total pressure** (Boyle's Law - assuming ideal gas behaviour).

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

- When volume of reaction system is **increased** under constant T:
  - Total pressure ___ decreases ___ (since the gas particles are now further apart).
  - According to Le Chatelier's Principle, the system counteracts this by favouring the ___ backwards ___ reaction which produces _ more ___ gas particles.
  - Hence, the position of equilibrium shifts to the left.

  Impact on the rate of reactions:

  - When V increases, partial pressures of all gases decrease, since $p \propto$ conc, conc decreases, rate of ___ both ___ forward and backward reactions ___ decreases ___.
  - The reaction takes a __ longer ___ time to reach equilibrium.

- When volume of reaction system is **decreased** under constant T:
  - Total pressure increases (since the gas particles are now closer together).
  - According to Le Chatelier's Principle, the system counteracts this by favouring the forward reaction which produces less gas particles.
  - Hence, the position of equilibrium shifts to the right.

  Impact on the rate of reactions:

  - When V decreases, partial pressures of all gases increase, since $p \propto$ conc, conc increases, rate of both forward and backward reactions increase.
  - The reaction takes a shorter time to reach equilibrium.

Exercise 11

Summarise the effect of volume change on the composition of the following gaseous systems by indicating the direction of the shift in position of equilibrium if volume is changed as stated:

Change in volume	Increase	Decrease
Impact on total pressure	↓	↑
Reaction favoured	_ more _ gaseous molecules	_ less _ gaseous molecules
Rate of reaction	Forward and backward rate _ decrease _	Forward and backward rate _ increase _

Change in volume	Increase	Decrease
	Shift in eqm position	
$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$	right	left
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	not affected	not affected
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	left	right

Note: Refer to Appendix for a discussion on the effect on the equilibrium position due to addition of inert gas.

7.4 Effect of temperature changes

Consider a system at equilibrium with an **ENDOTHERMIC** forward reaction:

$$aA + bB \rightleftharpoons cC + dD \qquad \Delta H > 0$$

❖ When the temperature is **increased**:

- According to Le Chatelier's Principle, the system will try to counteract the increase in temperature by favouring the ___ forward endothermic ___ reaction in order to ___ absorb ___ heat.
- Equilibrium position shifts ___ right ___ favouring formation of more products.
- New equilibrium mixture contains more **C** and **D** and less **A** and **B**.

Impact on equilibrium constant:

- Since [C] and [D] increase, and [A] and [B] decrease,

$$\text{new } K_c = \frac{[C]\uparrow[D]\uparrow}{[A]\downarrow[B]\downarrow} > \text{old } K_c \Rightarrow \mathbf{K_c \text{ increases}}$$

❖ When the temperature is **decreased**:

- According to Le Chatelier's Principle, the system will try to counteract the decrease in temperature by favouring the backward exothermic reaction that releases heat.
- Equilibrium position shifts left favouring formation of more reactants.
- New equilibrium mixture contains more **A** and **B** and less **C** and **D**.

Impact on equilibrium constant:

- Since [A] and [B] increase, and [C] and [D] decrease,

$$\text{new } K_c = \frac{[C]\downarrow[D]\downarrow}{[A]\uparrow[B]\uparrow} < \text{old } K_c \Rightarrow \mathbf{K_c \text{ decreases}}$$

Similarly, for a system at equilibrium with an **EXOTHERMIC** forward reaction:

$$aA + bB \rightleftharpoons cC + dD \qquad \Delta H < 0$$

- <u>When the temperature is **increased**</u>:
  - According to Le Chatelier's Principle, the system will try to counteract the increase in temperature by favouring the __backwards endothermic__ reaction that <u>absorbs</u> heat.
  - Equilibrium position shifts <u>left</u> favouring formation of more reactants.
  - New equilibrium mixture contains <u>more **A** and **B**</u> and <u>less **C** and **D**</u>.

Impact on equilibrium constant:

- Since [A] and [B] increase, and [C] and [D] decrease,

$$new\ K_c = \frac{[C]\downarrow [D]\downarrow}{[A]\uparrow [B]\uparrow} < \text{old } K_c \qquad \Rightarrow \qquad \underline{\mathbf{K_c \text{ decreases}}}$$

- <u>When the temperature is **decreased**</u>:
  - According to Le Chatelier's Principle, the system will try to counteract the decrease in temperature by favouring the <u>forward exothermic</u> reaction that <u>releases</u> heat.
  - Equilibrium position shifts <u>right</u> favouring formation of more products.
  - New equilibrium mixture contains <u>more **C** and **D**</u> and <u>less **A** and **B**</u>.

Impact on equilibrium constant:

- Since [C] and [D] increase, and [A] and [B] decrease,

$$new\ K_c = \frac{[C]\uparrow [D]\uparrow}{[A]\downarrow [B]\downarrow} > \text{old } K_c \qquad \Rightarrow \qquad \underline{\mathbf{K_c \text{ increases}}}$$

<u>7.4.1 Effect of Temperature on Time Taken to reach Equilibrium</u>

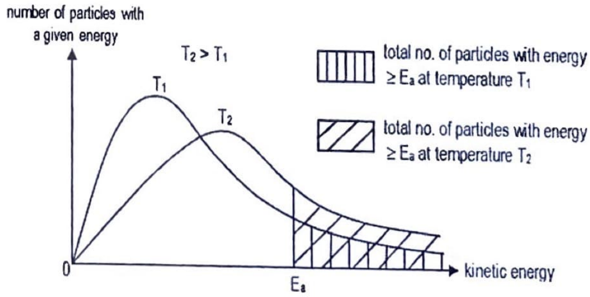
- When temperature is increased, the **rate constants**, *k*, of **both** the forward and backward reactions **increase** since

$$k = Ae^{-Ea/RT} \text{ (Arrhenius equation)}$$

  the number of particles with energy greater than or equal to the activation energy, E_a, increases.

  Hence, rates of forward and backward reactions both increase and dynamic equilibrium is reached more quickly

  ⇒ **t_{eqm} decreases**



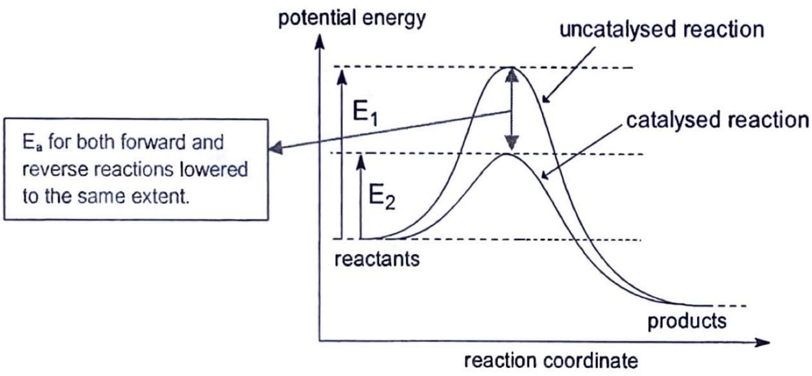
- Conversely, when temperature is decreased, **t_{eqm} increases.**

In summary,

change in temperature	equilibrium position	t_{eqm}	rate constants	forward endothermic	forward exothermic
Increase	Favours **endothermic** reaction	Decrease	k_f and k_b both increase	POE shifts right K_c increases	POE shifts left K_c decreases
Decrease	Favours **exothermic** reaction	Increase	k_f and k_b both decrease	POE shifts left K_c decreases	POE shfits right K_c increases

7.5 Effect of catalyst

- A catalyst lowers the activation energy of both the forward and backward reactions to the same extent. Hence, the rates of both the forward and backward reactions are increased to the same extent.
- As such, adding a catalyst has no effect on **equilibrium constant, *K*,** and the **composition** of an equilibrium mixture.



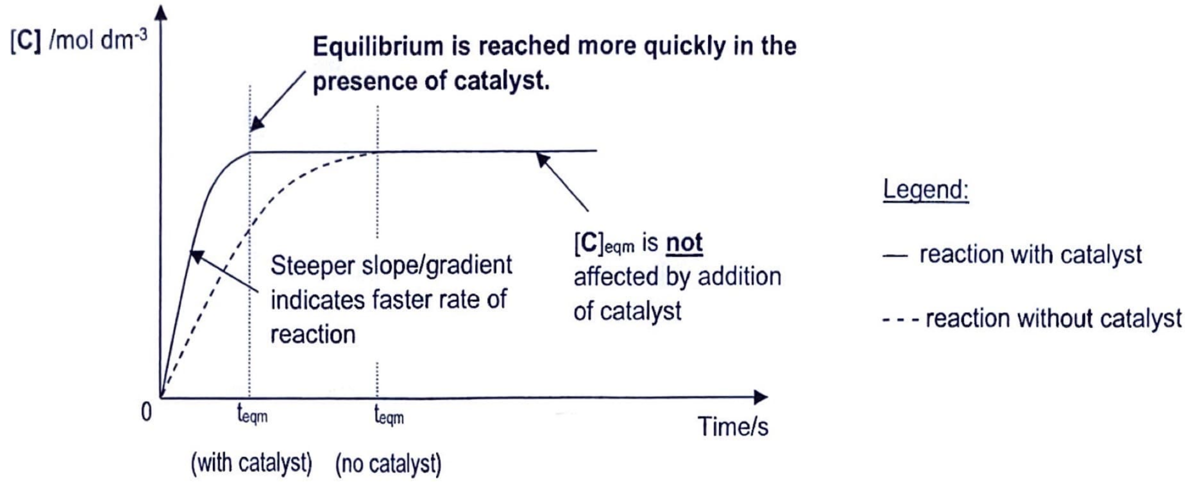
E_1 = activation energy of uncatalysed reaction
E_2 = activation energy of catalysed reaction

- Since both forward and backward rates increase, equilibrium is reached faster. However, the equilibrium position remains the same.

Consider the reversible reaction:

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

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



Exercise 12

Silver chlorate(V) reacts with chlorine in a container as follows:

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

Which of the following changes would **not** affect the equilibrium position of the above reaction?

1 Compressing the container

2 Increasing the temperature

3 Adding a suitable catalyst

4 Removing some silver chloride

A 1, 2 and 3

B 1 and 3

C 2 and 4

D 3 and 4

D

8 INDUSTRIAL PROCESS: THE HABER PROCESS

Candidates should be able to 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.

8.1 The Haber Process

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

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

Some important principles in industrial reactions are:

- The desired reaction must take place **quickly** to produce the required product in **high yield**.
  - ⇒ In the Haber process, the desired product is ammonia so conditions are adjusted to favour the forward reaction.
- The process should **minimise cost** by:
  - ⇒ using the cheapest reagents
  - ⇒ making the reaction as rapid as possible (by the use of catalysts)
  - ⇒ avoiding very high temperatures if possible
  - ⇒ avoiding very high pressures if possible

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

8.2 Conditions of Haber Process

Condition	Explanation
Temperature: **450 °C**	✧ Since the forward reaction is exothermic, a lower temperature would result in a ___higher___ yield of ammonia. ✧ However, the rate of production is ___lower___ at low temperature. ✧ On the other hand, a high temperature increases the rate of production but results in lower yield and higher production cost. ✧ Thus, a compromise is needed and a moderately high temperature of 450 °C is used to ensure a reasonable rate of production and yield.

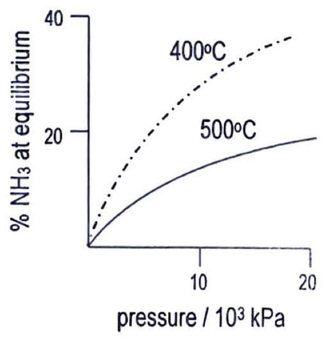
Condition	Explanation
Pressure: about **<u>200 atm</u>**	✧ The forward reaction takes place with a reduction in the number of gaseous particles. ✧ A <u>high</u> pressure will favour the desired reaction (increase yield). ✧ However, too high a pressure <u>increases cost of production</u> (more expensive and stronger pipes and equipment that could withstand the high pressure need to be used) and also <u>increases safety concerns</u>. ✧ Thus, a moderate pressure of 200 atm is used.
Catalyst: **Finely divided iron catalyst with aluminum oxide as promoter**	✧ This <u>increases the production rate</u>. **Note:** The catalyst does not affect the percentage of NH_3 in the equilibrium mixture, i.e. yield is not affected.
Continual removal of ammonia	✧ The removal of ammonia shifts the position of equilibrium to the right, thereby <u>increasing the yield</u> of ammonia. ✧ This is achieved by <u>cooling</u> the reaction mixture to –50 °C to liquefy ammonia formed (boiling point of $NH_3(l)$ is –33 °C).
Molar ratio of $N_2 : H_2$ = 1:3	✧ The molar ratio used is similar to that of the stoichiometric ratio to <u>minimise excess</u>.

<u>Exercise 13</u>

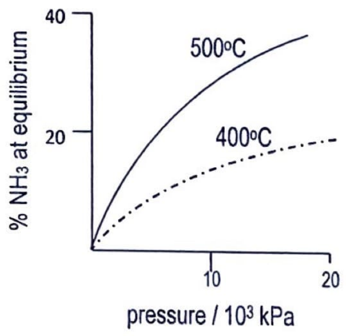
The percentage of ammonia obtainable, if equilibrium were to be established during the Haber process, is plotted against the operating pressure for two temperatures, 400 °C and 500 °C.

Which of the following correctly represents the two graphs?

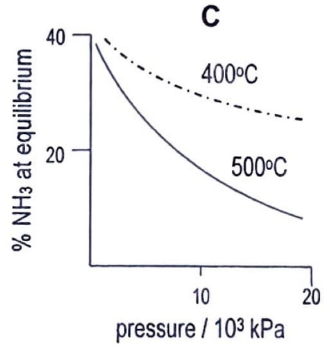
A



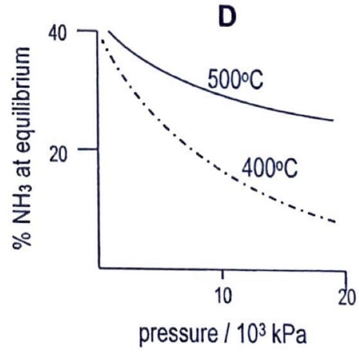
B



C



D



SUMMARY

Effect of varying conditions on the equilibrium: aA + bB ⇌ cC + dD

Change	Shift in Position of Equilibrium	Equilibrium Constant, *K*	Rate Constant k_f	Rate Constant k_b	Any other Remarks
Under constant temperature					
↑ [A] or [B] ↓ [C] or [D]	To right	No change	No change		For gaseous components, the effect of increasing / decreasing partial pressure is similar to that of increasing / decreasing concentration.
↓ [A] or [B] ↑ [C] or [D]	To left	No change	No change		
↓ P_T or ↑ V	▪ To <u>left</u> if (c+d) < (a+b) ▪ To <u>right</u> if (c+d) > (a+b) ▪ <u>No change</u> if (c+d) = (a+b)	No change	No change		Only <u>gaseous</u> system is affected.
↑ P_T or ↓ V	▪ To <u>left</u> if (c+d) > (a+b) ▪ To <u>right</u> if (c+d) < (a+b) ▪ <u>No change</u> if (c+d) = (a+b)	No change	No change		
When temperature changes					
↑T	**For endothermic forward reaction ($\Delta H > 0$)** ▪ To right	↑	↑	↑	Equilibrium is achieved in a shorter time.
	For exothermic forward reaction ($\Delta H < 0$) ▪ To left	↓	↑	↑	
↓T	**For endothermic forward reaction ($\Delta H > 0$)** ▪ To left	↓	↓	↓	Equilibrium is achieved in a longer time.
	For exothermic forward reaction ($\Delta H < 0$) ▪ To right	↑	↓	↓	
Addition of a catalyst	No change	No change	Increase by same extent		Equilibrium is achieved in a shorter time.

Addition of Inert Gas

- The total pressure or volume of a gaseous system can also be increased by the addition of an inert gas.

- The inert gas can be added to an equilibrium system at
  - constant volume, or
  - constant pressure

Example: Adding argon to the following equilibrium in a closed system

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

At constant volume:

- Total pressure of the gaseous system is increased.
- However, concentrations (or partial pressures) of the reactants and products remain unchanged. Quantitatively, *Q* is still equal to *K*.
- Hence, equilibrium position is not affected.

At constant pressure:

- Total volume of the gaseous system is increased (as the system must expand to keep its total pressure constant).
- Concentrations (or partial pressures) of the reactants and products are decreased.
- Hence, the equilibrium position will shift to the left, i.e. the side involving greater number of moles of gas.

Note:
For reactions with equal number of gaseous reactants and products, for example:

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

Addition of an inert gas at **constant pressure** (with increasing total volume) has no effect on the equilibrium system.The equilibrium position and the composition of the equilibrium mixture remains unchanged.

RAFFLES INSTITUTION
Year 5 H2 CHEMISTRY 2022
Tutorial 7 – Chemical Equilibria

Self-Check Questions

1 Two equilibria are shown below.

Reaction I: $2X_2(g) + Y_2(g) \rightleftharpoons 2X_2Y(g)$

Reaction II: $X_2Y(g) \rightleftharpoons X_2(g) + \frac{1}{2}Y_2(g)$

The numerical value of K_c for reaction I is 2. Under the same conditions, what is the numerical value of K_c for reaction II?

2 The gas-phase reaction of carbon monoxide with hydrogen forming methanol is an example of an equilibrium reaction. The reaction was investigated by mixing 2.0 mol of $H_2(g)$ with 1.0 mol of CO(g) in a 0.5 dm^3 flask and allowing equilibrium to be established.

$$2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$$

At equilibrium, x mol of H_2 had reacted with CO. What is the equilibrium concentration of CO in terms of x?

[N2014/1/13, modified]

3 At a total pressure of 1.0 atm, dinitrogen tetraoxide is 50% dissociated at a temperature of 60 °C to nitrogen dioxide.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

What is the value of the equilibrium constant, K_p, for this reaction at 60 °C?

[N2010/1/13, modified]

4 Each of the following equilibria is subjected to two changes carried out separately:

(i) the pressure is reduced at constant temperature
(ii) the temperature is increased at constant pressure

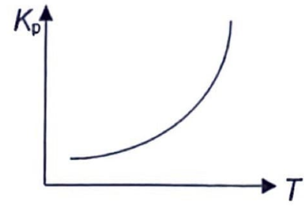
For which equilibrium will both of these changes result in an increase in the proportion of products?

A	$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	$\Delta H = +53$ kJ mol^{-1}
B	$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$	$\Delta H = -950$ kJ mol^{-1}
C	$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$	$\Delta H = +92$ kJ mol^{-1}
D	$2NO_2(g) \rightleftharpoons N_2O_4(g)$	$\Delta H = -57$ kJ mol^{-1}

5 A reversible reaction is catalysed. Which statements about the effects of the catalyst on this system are correct?

1 The catalyst alters the mechanism of the reaction.
2 The catalyst reduces the activation energy for both the forward and the backward reaction.
3 The catalyst alters the composition of the equilibrium mixture.

6 The equilibrium constant K_p for the reaction **X**(g) + **Y**(g) ⇌ **Z**(g) varies with temperature as shown in the diagram below. Which conclusions can be drawn from this information?



1 The reaction is exothermic in the forward direction.
2 The equilibrium mixture contains a greater proportion of **Z** at higher pressures.
3 The equilibrium mixture contains a greater proportion of **Z** at higher temperatures.

Practice Questions

Calculations involving K_c

7 Methanol reacts with ethanedioic acid as shown:

$$2CH_3OH(aq) + (COOH)_2(aq) \rightleftharpoons (COOCH_3)_2(aq) + 2H_2O(l)$$

20 cm^3 of 0.50 mol dm^{-3} of methanol was mixed with 30 cm^3 of 0.40 mol dm^{-3} of ethanedioic acid. After the mixture has reached equilibrium, it was found that the 10 cm^3 of the resultant mixture required 30 cm^3 of 0.10 mol dm^{-3} NaOH for neutralisation. The neutralisation reaction is given to be:

$$(COOH)_2(aq) + 2NaOH(aq) \longrightarrow (COONa)_2(aq) + 2H_2O(l)$$

(a) Calculate the concentration of methanol at equilibrium and hence the value of K_c.
(b) Explain why the titration must be done quickly.

8 **(a)** One molecule of haemoglobin, Hb, can bind up to four molecules of oxygen, according to the following equation:

$$Hb(aq) + 4O_2(aq) \rightleftharpoons Hb(O_2)_4(aq)$$

(i) Write an expression for K_c for this reaction, stating its units.
(ii) Experiments have shown that when the $[O_2] = 7.6 \times 10^{-6}$ mol dm^{-3}, the concentrations of Hb and $Hb(O_2)_4$ are equal. Use this information to calculate a value of K_c.
(iii) Use your value of K_c to calculate the $[O_2]$ necessary for 99 % of the Hb to be converted to $Hb(O_2)_4$.

(b) Myoglobin, Mb, is an oxygen-carrier protein that occurs in muscle fibres. It has a higher affinity for O_2 than does Hb, but only binds one O_2 molecule per Mb molecule.

$$Mb(aq) + O_2(aq) \rightleftharpoons MbO_2(aq) \qquad K_c = 1 \times 10^6 \text{ mol}^{-1} \text{ dm}^3$$

Calculate the percentage of MbO_2 in a Mb-MbO_2 mixture when $[O_2] = 7.6 \times 10^{-6}$ mol dm^{-3}.

[N2009/3/1(c)-(d)]

Calculations involving K_p

9 A pure sample of N_2O_4(l) is introduced into an evacuated vessel. The vessel, of constant volume, is heated to a constant temperature such that the equilibrium below is established.

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

The value of the pressure *p* is then found to be 20% greater than if only NO_2(g) were present. What is the mole fraction, *x*, of oxygen in this equilibrium mixture?

[N2008/1/7, modified]

10 0.40 dm^3 of gaseous $(HCOOH)_2$ was allowed to dissociate under constant pressure of 1 atm at 300 °C in a gas syringe according to the equation below.

$$(HCOOH)_2(g) \rightleftharpoons 2HCOOH(g)$$

When equilibrium was achieved, the total volume of the mixture increased to 0.60 dm^3.

What is the K_p for the reaction at 300 °C?

[RI2017/Y6Prelim/14, modified]

Changes to equilibrium system and K_c/K_p calculations

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

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

(a) Sketch a graph showing how the **rates** of the forward and reverse reactions change from the time the two gases are mixed to the time the reaction reaches equilibrium. Label your two lines clearly.

(b) Write an expression for K_p for this reaction, giving its units in terms of atm.

(c) A 2:1 mixture of SO_2 and O_2 was allowed to reach equilibrium at 800 K. When equilibrium was reached, the total pressure was 5.0 atm and the partial pressure of SO_3 was 4.7 atm. Use your expression in **(b)** to calculate the value for K_p.

(d) Given that the forward reaction is exothermic, explain at which temperature, 300 K or 800 K, is the equilibrium constant is larger?

(e) With reference to your answer to **(d)**, explain why the industrial process is typically carried out at about 800 K.

12 **(a)** State what is meant by the term *dynamic equilibrium*.

At high temperatures, steam and carbon undergo the following reaction.

$$H_2O(g) + C(s) \rightleftharpoons CO(g) + H_2(g)$$

(b) In a particular experiment, steam at a pressure of 2.00 atm and a temperature of 1000 K was introduced into a vessel containing an excess of powdered carbon. When equilibrium was established, the partial pressure of hydrogen was found to be 1.40 atm.

(i) Write an expression for K_p.

(ii) Calculate the partial pressures of $H_2O(g)$ and $CO(g)$ at equilibrium, and hence the total pressure at equilibrium.

(iii) Use your answer from **(b)(ii)** to calculate the value of K_p, stating its units.

(c) In another experiment, the same amount of carbon was used, but in the form of lumps rather than powder.

(i) State how this would affect the time taken to reach equilibrium. Explain your answer.

(ii) State how this would affect both the position of equilibrium and the numerical value of K_p.

13 Steam can react with carbon monoxide under appropriate conditions according to the following reversible reaction:

$$H_2O(g) + CO(g) \rightleftharpoons CO_2(g) + H_2(g) \qquad \Delta H = -40 \text{ kJ mol}^{-1}$$

(a) Calculate the amount of CO present at equilibrium if 4 mol each of CO(g) and H_2O(g) were placed in a vessel of constant volume at a temperature at which K_c is 9.0.

(b) State the amount of H_2O, CO_2 and H_2 at equilibrium.

(c) Using values in **(a)** and **(b)**, sketch a labelled graph to show how the amounts of the reactants and products change with time during the course of the reaction.

(d) Sketch 3 graphs, on the same scale, showing how the amount of CO_2 changes with time when the reaction is repeated as before except that

(i) the temperature is lowered,
(ii) the volume of the vessel is decreased and
(iii) a catalyst is added to the reaction mixture with other factors remaining constant.

Briefly explain your reasonings.

14 The following involves a reversible equilibrium process.

When brown NO_2(g) is cooled, colourless N_2O_4(g) is formed. A gas syringe is filled with NO_2(g) and the end sealed. When the gas is compressed, the brown gas fades. Warming the syringe restores the colour.

Write a chemical equation (including state symbols) to show the equilibrium, and use Le Chatelier's principle to explain the observations described.

15 An aqueous solution contains both CrO_4^{2-} and $Cr_2O_7^{2-}$ ions in equilibrium.

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

yellow orange

Which statement about this equilibrium system is **incorrect**?

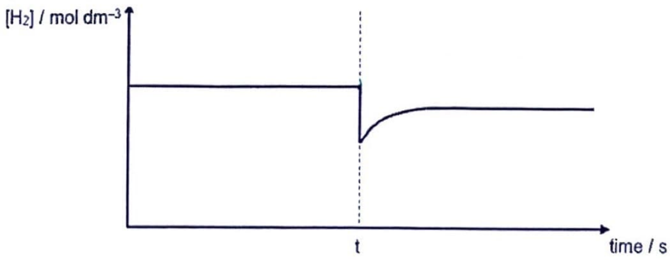
A Addition of solid $K_2Cr_2O_7$ to the solution will not change the equilibrium position.
B Addition of solid NaOH causes the colour of the solution to change from orange to yellow.
C The K_c expression is written as $\frac{[Cr_2O_7^{2-}]}{[CrO_4^{2-}]^2[H^+]^2}$.
D Diluting the solution with water causes the solution to turn more yellow.

[RI2016/Y5Promo/10, modified]

16 At 60 °C, a gas syringe contains a mixture of CS_2(g), H_2(g), CH_4(g) and H_2S(g), in equilibrium.

$$CS_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2S(g) \quad \Delta H > 0$$

The graph below shows the concentration of H_2 gas against time. The reaction mixture in the syringe is subjected to a change at time t.



Which of the following changes, when carried out separately, could have given the graph above?

1 increasing the volume of the mixture by pulling the plunger
2 lowering the temperature in the syringe from 60 °C to 50 °C
3 adding a small amount of Ar(g), while keeping the pressure and temperature in the syringe constant
(Note: refer to Appendix of lecture notes for discussion on addition of inert gas)

[RI2017/Y5Promo/11, modified]

Relationship between Gibbs free energy and equilibrium

17 Comment, with the aid of some calculations, on the following in terms of **free energy** and/or **entropy changes**.

The enthalpy change of fusion of ice (melting of ice) is +6.0 kJ mol^{-1}. At 273 K, ice and water are in equilibrium but at 298 K, ice spontaneously changes to water.

18 A mixture of nitrogen, oxygen and nitrogen monoxide are placed in a sealed container and allowed to reach equilibrium.

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ value of K_p (at 298 K) = 1×10^{-30}

(a) Use the value of K_p at 298 K to suggest the sign and magnitude for $\Delta G_f^{\ominus}$ for the formation of nitrogen monoxide from its elements at 298 K. Explain your answer.

Ammonia can be formed from its elements.

$\frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \rightleftharpoons NH_3(g)$ $\Delta G_f^{\ominus} = -16.6$ kJ mol^{-1}

(a) Suggest whether the ratio of [products]/[reactants] at equilibrium for the formation of ammonia at 298 K will be less than, equal to or greater than 1. Give a reason for your answer.

[N2018/2/2 modified]

19 In non-polar solvents, ethanoic acid, CH_3CO_2H, can form a dimer containing two hydrogen bonds.

$2CH_3CO_2H \rightleftharpoons (CH_3CO_2H)_2$ $K_c = 1.51 \times 10^2$ mol^{-1} dm^3 at 298 K
monomer dimer

(a) A solution of 0.100 mol dm^{-3} CH_3CO_2H is allowed to reach equilibrium in a non-polar solvent at 298 K. The equilibrium concentration of the dimer is 0.0417 mol dm^{-3}. Calculate the ratio $[(CH_3CO_2H)_2]/[CH_3CO_2H]$ at equilibrium.

(b) Suggest how the $\Delta G^{\ominus}$ for this equilibrium in an aqueous solution would differ from the $\Delta G^{\ominus}$ in a non-polar solvent. Explain your answer.

[N2020/3/4(d)]