

CHEMICAL EQUILIBRIUM

Dynamic

Equilibrium

- not all reactions proceed to completion
- some end up with a **mixture of reactants and products**
- this is because **some reactions are reversible**; products can revert back to reactants

As the rate of reaction is dependant on the concentration of reactants...

- the **forward reaction starts off fast** but slows as the reactants get less concentrated
- initially, there is no backward reaction but, as products form, it will get faster
- provided the temperature remains constant there will come a time when the **backward and forward reactions are equal and opposite** ; the reaction has reached equilibrium

- a reversible chemical reaction is a **dynamic** process
- everything may appear stationary but the reactions are moving both ways
- the **position of equilibrium can be varied** by changing certain conditions

Trying to get up a “down” escalator gives an excellent idea of a non-chemical situation involving **dynamic equilibrium**.

Q.1 Write out equations for the reactions between ...

- *nitrogen and hydrogen*

- *sulphur dioxide and oxygen*

- *ethanol and ethanoic acid*

What symbol, in the equations, shows the reactions are reversible ?

Summary

When a chemical equilibrium is established ...

- both the reactants and the products are present at all times
- the equilibrium can be approached from either side
- the reaction is dynamic - it is moving forwards and backwards
- concentrations of reactants and products remain constant

FACTORS AFFECTING THE POSITION OF EQUILIBRIUM

Le Chatelier's Principle

Definition "When a change is applied to a system in dynamic equilibrium, the system reacts in such a way as to oppose the effect of the change."

Everyday example A rose bush grows with increased vigour after it has been pruned.

Chemistry example If you do something to a reaction that is in a state of equilibrium, the equilibrium position will change to oppose what you have just done

Concentration

- Equilibrium constants are unaffected by changing conc. at constant temperature
- To maintain the constant the composition of the equilibrium mixture changes

example Look at the equilibrium in question Q.4. If the concentration of C is increased, the position of equilibrium will move to the LHS to oppose the change. This ensures that the value of the equilibrium constant remains the same.

Q.2 In the reaction $A + 2B \rightleftharpoons C + D$ predict where the equilibrium will move when ... a) more B is added b) some A is removed c) some D is removed.

Pressure

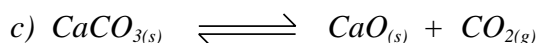
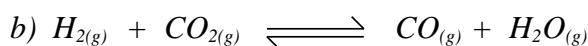
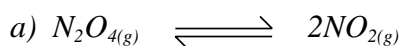
- consider the number of **gaseous molecules only**
- the more particles you have in a given volume, the greater the pressure they exert
- If you apply a greater pressure they will become more crowded
- a **move to the side with fewer gaseous molecules** will cause less stress

Summary

<i>Pressure Change</i>	<i>Effect on Equilibrium</i>
INCREASE	moves to side with FEWER GASEOUS MOLECULES
DECREASE	moves to side with MORE GASEOUS MOLECULES

No change will occur when **equal numbers** of gaseous molecules appear on both sides

Q.3 Predict the effect on the equilibrium position of an increase in pressure.



Temperature Temperature is the only thing that can **change the value of the equilibrium constant**.

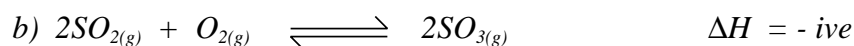
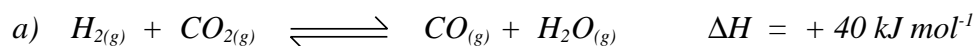
Altering the temperature affects the rate of both backward and forward reactions but to different extents. The equilibrium thus moves producing a new equilibrium constant.

The direction of movement depends on the sign of the enthalpy change.

Summary of the effect of temperature on the position of equilibrium

<i>Type of reaction</i>	ΔH	<i>Increase T</i>	<i>Decrease T</i>
EXOTHERMIC	–	moves to LEFT	moves to RIGHT
ENDOTHERMIC	+	moves to RIGHT	moves to LEFT

Q.4 Predict the effect of a temperature increase on the equilibrium position of,



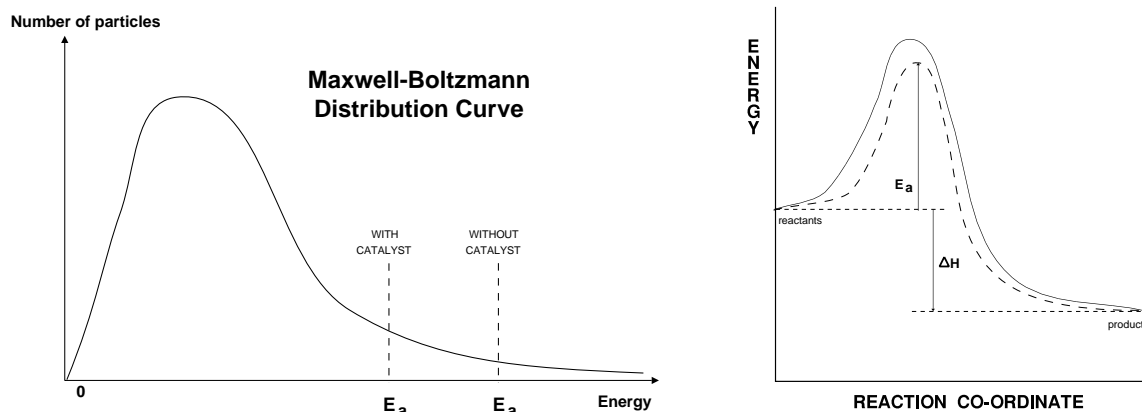
Possible problem

- an **increase in temperature** is used to **speed up** chemical reactions
- it **can have an undesired effect when the reaction is reversible and exothermic**
- you get to the **equilibrium position quicker** but with a **reduced yield** because the increased temperature moves the equilibrium to the left
- In many industrial processes a **compromise temperature** is used

*To reduce the problem one must look for a way of increasing the rate of a reaction without decreasing the yield i.e. with a **catalyst**.*

Catalysts Adding a catalyst DOES NOT AFFECT THE POSITION OF EQUILIBRIUM. However, it does increase the rate of attainment of equilibrium. This is especially important in reversible, exothermic industrial reactions such as the Haber or Contact Processes where economic factors are paramount.

Catalysts provide an alternative reaction pathway involving a lower activation energy.



INDUSTRIAL APPLICATIONS

The Haber Process



<i>Typical conditions</i>	Pressure	20000 kPa (200 atmospheres)
	Temperature	380-450°C
	Catalyst	iron

<i>Equilibrium theory favours</i>	low temperature high pressure	exothermic reaction - higher yield at lower temperature decrease in number of gaseous molecules
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<i>Kinetic theory favours</i>	high temperature high pressure catalyst	greater average energy + more frequent collisions more frequent collisions for gaseous molecules lower activation energy
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Compromise conditions Which is better? A low yield in a shorter time or a high yield over a longer period. The conditions used are a **compromise** with the catalyst enabling the rate to be kept up, even at a lower temperature.

Q.5

Find details of the Contact Process. List the essential features such as temperature, pressure and a named catalyst. Using what you have learned so far, appreciate why the conditions are chosen to satisfy economic principles

The Equilibrium Law

Simply states "If the concentrations of all the substances present at equilibrium are raised to the power of the number of moles they appear in the equation, the product of the concentrations of the products divided by the product of the concentrations of the reactants is a constant, provided the temperature remains constant" ... **WOW!**

Calculating Equilibrium Constants

Types K_c equilibrium values expressed as **concentrations in mol dm⁻³**
 K_p equilibrium values expressed as **partial pressures** - system at constant temperature

The partial pressure expression can be used for reactions involving gases

Calculating K_c for a reaction of the form $aA + bB \rightleftharpoons cC + dD$

then (at constant temperature)
$$\frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b} = \text{a constant, } (K_c)$$

[] denotes the equilibrium concentration in mol dm⁻³

K_c is known as the Equilibrium Constant

Value of K_c

- **AFFECTED** by a change of **temperature**
- **NOT AFFECTED** by a change in **concentration** of reactants or products
a change of **pressure**
adding a **catalyst**

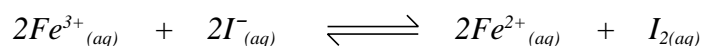
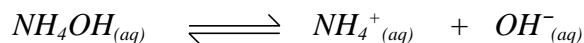
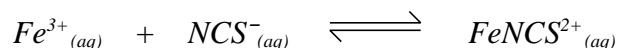
Q.6 What happens to the theoretical yield of a reaction if...

- K_c increases
- K_c decreases ?

Q.7 What happens to the value of K_c if...

- the **temperature is increased** in an **exothermic** reaction
- the **temperature is decreased** in an **exothermic** reaction
- the **temperature is increased** in an **endothermic** reaction
- the **temperature is decreased** in an **endothermic** reaction

Q.8 Write expressions for the equilibrium constant, K_c of the following reactions. Remember, equilibrium constants can have units.



Calculating value of K_c

- construct the balanced equation, including state symbols (aq), (g) etc.
- determine the number of moles of each species at equilibrium
- divide moles by the volume (in dm^3) to get the equilibrium concentrations in $mol\ dm^{-3}$ (If no volume is quoted, use a V ; it will probably cancel out)
- from the equation constructed in the first step, write out an expression for K_c .
- substitute values from third step and calculate the value of K_c with any units

Example 1 One mole of ethanoic acid reacts with one mole of ethanol at 298K. When equilibrium is reached it is found that two thirds of the acid has reacted. Calculate the value of K_c .

	$CH_3COOH_{(l)}$	+	$C_2H_5OH_{(l)}$	\rightleftharpoons	$CH_3COOC_2H_5_{(l)}$	+	$H_2O_{(l)}$
moles (initially)	1		1		0		0
moles (at equilibrium)	$1 - 2/3$		$1 - 2/3$		$2/3$		$2/3$
equilibrium concs.	$1/3 / V$		$1/3 / V$		$2/3 / V$		$2/3 / V$

$V = \text{volume } (dm^3) \text{ of the equilibrium mixture}$

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{2/3 / V \cdot 2/3 / V}{1/3 / V \cdot 1/3 / V} = 4$$

Example 2 Consider the equilibrium $P + 2Q \rightleftharpoons R + S$ (all species are aqueous)

One mole of P and one mole of Q are mixed. Once equilibrium has been achieved 0.6 moles of P are present. How many moles of Q , R and S are present at equilibrium?

	P	+	$2Q$	\rightleftharpoons	R	+	S
Initial moles	1		1		0		0
At equilibrium	0.6		0.2		0.4		0.4
	(0.4 reacted)		(2 x 0.4 reacted)		(get 1 R and 1 S for every P that reacts)		
	1 - 0.6 remain		1 - 0.8 remain				

- Explanation**
- if 0.6 moles of P remain of the original 1 mole, 0.4 moles have reacted
 - the equation states that 2 moles of Q react with every 1 mole of P
 - this means that 0.8 (2 x 0.4) moles of Q have reacted, leaving 0.2 moles
 - one mole of R and S are produced from every mole of P that reacts
 - this means 0.4 moles of R and 0.4 moles of S are present at equilibrium

Q.9 The questions refer to the equilibrium $A + B \rightleftharpoons C + D$ (all aqueous)

- (a) If the original number of moles of A and B are both 1 and 0.4 moles of A are present at equilibrium, how many moles of B , C and D are present?

What will be the value of K_c ?

- (b) At a higher temperature, the original moles of A and B were 2 and 3 respectively. If 1 mole of A is present at equilibrium, how many moles of B , C and D are present? What else does this tell you about the reaction?

Calculations involving Gases

Method

- carried out in a similar way to those involving concentrations
- one has the choice of using K_c or K_p for the equilibrium constant
- when using K_p only take into account gaseous species for the expression
- quotes the partial pressure of the gas in the equilibrium mixture
- pressure is usually quoted in Nm^{-2} or Pa - atmospheres are sometimes used
- as with K_c , the units of the constant K_p depend on the stoichiometry of the reaction

$$\text{total pressure} = \text{sum of the partial pressures}$$

$$\text{partial pressure} = \text{total pressure} \times \text{mole fraction}$$

$$\text{mole fraction} = \frac{\text{number of moles of a substance}}{\text{number of moles of all substances present}}$$

Example 1 A mixture of 16g of O_2 and 42g of N_2 , exerts a total pressure of 20000 Nm^{-2} .
What is the partial pressure of each gas ?

$$\begin{aligned} \text{moles of } \text{O}_2 &= \text{mass} / \text{molar mass} = 16\text{g} / 32\text{g} = 0.5 \text{ moles} \\ \text{moles of } \text{N}_2 &= \text{mass} / \text{molar mass} = 42\text{g} / 28\text{g} = 1.5 \text{ moles} \quad \text{total moles} = 2 \end{aligned}$$

$$\begin{aligned} \text{mole fraction of } \text{O}_2 &= 0.5 / 2 = 0.25 \\ \text{mole fraction of } \text{N}_2 &= 1.5 / 2 = 0.75 \quad \text{sum of mole fractions } (0.75 + 0.25) = 1 \end{aligned}$$

$$\begin{aligned} \text{partial pressure of } \text{O}_2 &= \text{mole fraction} \times \text{total pressure} \\ &= 0.25 \times 20000 \text{ Nm}^{-2} = \mathbf{5000 \text{ Nm}^{-2}} \end{aligned}$$

$$\begin{aligned} \text{partial pressure of } \text{N}_2 &= \text{mole fraction} \times \text{total pressure} \\ &= 0.75 \times 20000 \text{ Nm}^{-2} = \mathbf{15000 \text{ Nm}^{-2}} \end{aligned}$$

Example 2 When nitrogen (1 mole) and hydrogen (3 moles) react at constant temperature at a pressure of $8 \times 10^6 \text{ Pa}$, the equilibrium mixture was found to contain 0.7 moles of ammonia. Calculate K_p .

	$\text{N}_{2(\text{g})}$	+	$3\text{H}_{2(\text{g})}$	\rightleftharpoons	$2\text{NH}_{3(\text{g})}$	
moles (initially)	1		3		0	
moles (equilibrium)	$1 - x$		$3 - 3x$		$2x$	(x moles of N_2 reacted)
mole fractions	$(1-x)/(4-2x)$		$(3-3x)/(4-2x)$		$2x/(4-2x)$	(total moles = $4 - 2x$)
partial pressures	$P \cdot (1-x)/(4-2x)$		$P \cdot (3-3x)/(4-2x)$		$P \cdot 2x/(4-2x)$	(total pressure = P)

At equilibrium there are 0.7 moles of ammonia, so $2x = 0.7$ (therefore $x = 0.35$)
and the total pressure, $(P) = 8 \times 10^6 \text{ Pa}$.

$$\text{applying the equilibrium law} \quad K_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2}) \cdot (P_{\text{H}_2})^3} \quad \text{Pa}^{-2}$$

$$\text{Substituting in the expression gives} \quad \mathbf{ANS. \quad K_p = 1.73 \times 10^{-14} \text{ Pa}^{-2}}$$