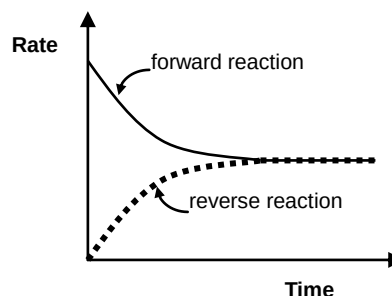


Chemical Equilibrium

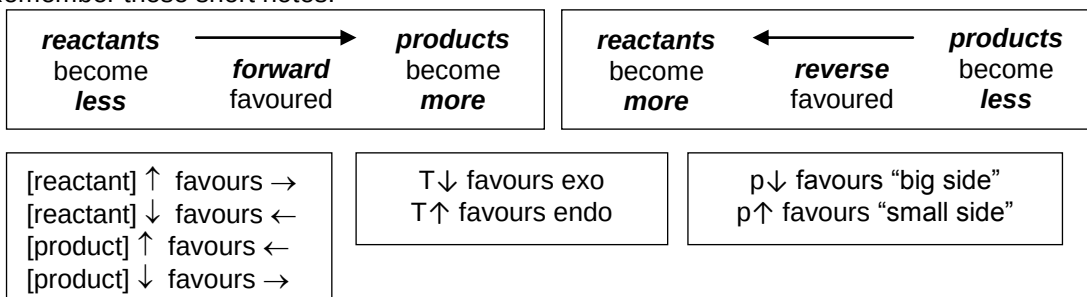
DISTURBANCE OF THE EQUILIBRIUM

- An **open** system continuously interacts with its environment, while a **closed** system is isolated from its surroundings.
- A reaction is **reversible** when products can be converted back to reactants.
- **Dynamic equilibrium** = Two opposing chemical reactions take place at the same rate.
- To create a **dynamic equilibrium**, the
 1. reaction has to be reversible;
 2. system has to be closed.
- **Chemical equilibrium**: It is a dynamic equilibrium when the rate of the forward reaction equals the rate of the reverse reaction.
- **Homogenous equilibrium**: An equilibrium in which all the substances in the system are in the same phase. E.g. all the substances are gases.
- The rates of the forward and the reverse reactions can be represented on a graph:

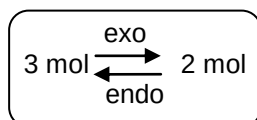


- When one reaction is **favoured** with regards to the other, it means that that reaction takes place at a higher rate, $\therefore$ faster.
 - E.g. when a reversible reaction starts, the forward reaction is ALWAYS favoured initially (has higher rate);
 - at equilibrium the rate of the forward and the reverse reactions are equal, $\therefore$ none is favoured.
- **Le Chatelier's principle**: When the equilibrium in a closed system is disturbed, the system will re-instate a new equilibrium by favouring the reaction that will oppose the disturbance.
- **FACTORS THAT INFLUENCE EQUILIBRIUM:**
 1. Change in **concentration**.
 - Concentration is decreased: The reaction that increases that concentration is favoured.
 - Concentration is increased: The reaction that decreases that concentration is favoured.
 2. Change in **temperature**.
 - Decrease in temperature favours the exothermic reaction $\therefore$ the reaction with $\Delta H < 0$.
 - Increase in temperature favours the endothermic reaction $\therefore$ the reaction with $\Delta H > 0$.
 3. Change in **pressure** (gases only).
 - Increase in pressure favours the reaction that renders the least particles.
 - Decrease in pressure favours the reaction that renders the most particles.
- Addition of a **catalyst**:
 - It does not influence the equilibrium – the equilibrium is not disturbed.
 - The rates of both the forward and the reverse reaction are increased, equally.
 - In a reaction where equilibrium is not yet reached, equilibrium is reached quicker when a catalyst is added. (See graphs on p.6.)

- Remember these short notes:



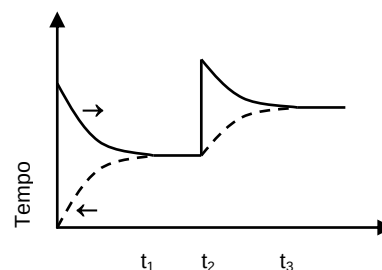
- E.g. suppose the reaction $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$, with $\Delta H < 0$, reaches equilibrium.



- With $[\text{SO}_2] \uparrow$, $\rightarrow$ is favoured; $\therefore [\text{O}_2] \downarrow$ and $[\text{SO}_3] \uparrow$.
- With $[\text{SO}_2] \downarrow$, $\leftarrow$ is favoured; $\therefore [\text{O}_2] \uparrow$ and $[\text{SO}_3] \downarrow$.
- With T $\downarrow$, $\rightarrow$ is favoured; $\therefore [\text{SO}_2] \downarrow$, $[\text{O}_2] \downarrow$ and $[\text{SO}_3] \uparrow$.
- With T $\uparrow$, $\leftarrow$ is favoured; $\therefore [\text{SO}_2] \uparrow$, $[\text{O}_2] \uparrow$ and $[\text{SO}_3] \downarrow$.
- With p $\downarrow$, $\leftarrow$ is favoured; $\therefore [\text{SO}_2] \uparrow$, $[\text{O}_2] \uparrow$ and $[\text{SO}_3] \downarrow$.
- With p $\uparrow$, $\rightarrow$ is favoured; $\therefore [\text{SO}_2] \downarrow$, $[\text{O}_2] \downarrow$ and $[\text{SO}_3] \uparrow$.

- Consider as an example the rate time graph of a system:

- At t_1 equilibrium is reached for the first time.
- At t_2 equilibrium is disturbed.
- At t_3 the new equilibrium is reached.
- After the disturbance the rate of both reactions (forward and reverse) have increased.
- After the disturbance the rate of the forward reaction is favoured.



- The effect of **change in volume**:

- A change in pressure can be created by a change in volume of the reactor (because $p \propto \frac{1}{V}$):
 - Volume increases $\rightarrow$ pressure is decreased.
 - Volume decreases $\rightarrow$ pressure is increased.
- Remember: A change in volume also changes the concentration (because $c = \frac{n}{V}$):
 - Volume increases $\rightarrow$ concentration is decreased.
 - Volume decreases $\rightarrow$ concentration is increased.
- Therefore: if a volume change takes place, the concentration of ALL changes.

- With regards to **pressure changes**:

- The equilibrium in reactions where the mole quantities of the reactants and the products are equal are not disturbed by pressure changes.
 - e.g. In $\text{A}_2 + \text{B}_2 \rightleftharpoons 2\text{AB}$ a pressure change will not influence the equilibrium; only temperature and concentration changes (2 mole volumes left and 2 mol volumes right).
- Only gases are influenced by pressure changes.
 - e.g. In $\text{A}(\text{g}) + \text{B}(\text{s}) \rightleftharpoons \text{C}(\text{g})$ a pressure change will not influence the equilibrium; only temperature and concentration changes (1 mole volume left and 1 mol volume right).
- The equilibrium is not disturbed when an inactive gas (e.g. helium) is pumped into the system.

- Use the following **arguments** in your explanation of Le Chatelier's principle:

- Increase in temperature:**

- According to Le Chatelier's principle
- if the temperature of the system is *increased*,
- a reaction will take place that tends to oppose the change.
- The system will therefore *decrease* the temperature.
- A reaction that uses/takes up energy will be favoured,
- therefore the endothermic reaction.
- The (forward/reverse) reaction will be favoured and
- the equilibrium position shifts to the (right/left).
- The [] of will therefore increase/decrease.

Choose now the reaction with $\Delta H > 0$

◦ **Decrease in temperature:**

- * According to Le Chatelier's principle
- * if the temperature of the system is *decreased*,
- * a reaction will take place that tends to oppose the change.
- * The system will therefore *increase* the temperature.
- * A reaction that liberates energy will be favoured,
- * therefore the exothermic reaction.
- * The (forward/reverse) reaction will be favoured and
- * the equilibrium position shifts to the (right/left).
- * The [] of will therefore increase/decrease.

Choose now the reaction with $\Delta H < 0$

◦ **Increase in pressure:**

- * According to Le Chatelier's principle
- * if the pressure of the system is *increased*,
- * a reaction will take place that tends to oppose the change.
- * The system will therefore *decrease* the pressure.
- * A reaction that forms the lowest number of gas molecules will be favoured.
- * The (forward/reverse) reaction will be favoured and
- * the equilibrium position shifts to the (right/left).
- * The [] of will therefore increase/decrease.

Choose now the "small" side

◦ **Decrease in pressure:**

- * According to Le Chatelier's principle
- * if the pressure of the system is *decreased*,
- * a reaction will take place that tends to oppose the change.
- * The system will therefore *increase* the pressure.
- * A reaction that forms the highest number of gas molecules will be favoured.
- * The (forward/reverse) reaction will be favoured and
- * the equilibrium position shifts to the (right/left).
- * The [] of will therefore increase/decrease

Choose now the "big" side

◦ **Increase in [] of reactant:**

- * According to Le Chatelier's principle
- * if the concentration of a reactant is *increased*,
- * a reaction will take place that tends to oppose the change.
- * The system will therefore *decrease* the concentration.
- * The reaction that uses the reactant will be favoured.
- * The forward reaction will be favoured and
- * the equilibrium position shifts to the right.
- * The [] of will therefore increase/decrease.

◦ **Decrease in [] of reactant:**

- * According to Le Chatelier's principle
- * if the concentration of a reactant is *decreased*,
- * a reaction will take place that tends to oppose the change.
- * The system will therefore *increase* the concentration.
- * The reaction that forms the reactant will be favoured.
- * The reverse reaction will be favoured and
- * the equilibrium position shifts to the left.
- * The [] of will therefore increase/decrease.

◦ **Increase in [] of product:**

- * According to Le Chatelier's principle
- * if the concentration of a product of the system is *increased*,
- * a reaction will take place that tends to oppose the change.
- * The system will therefore *decrease* the concentration.
- * The reaction that uses the product will be favoured.
- * The reverse reaction will be favoured and
- * the equilibrium position shifts to the left.
- * The [] of will therefore increase/decrease.

- **Decrease in [] of product:**
 - * According to Le Chatelier's principle
 - * if the concentration of a product of the system is *decreased*,
 - * a reaction will take place that tends to oppose the change.
 - * The system will therefore *increased* the concentration.
 - * The reaction that forms the product will be favoured.
 - * The forward reaction will be favoured and
 - * the equilibrium position shifts to the right.
 - * The [] of will therefore increase/decrease.

EQUILIBRIUM CONSTANT (K_c)

- The equilibrium constant (K_c) is an indication of how effective a reaction is.
 - A high K_c means that a great percentage of the reactants was changed into product $\therefore$ it is an effective reaction.
 - A low K_c means that a small percentage of the reactants was changed into product $\therefore$ it is an ineffective reaction.

- For the reaction $aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$ the expression for the equilibrium constant (K_c) is:

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

- **Only gases** (g) and **solutions** (aq) are present in the K_c expression.
- **No solids** (s) or **pure liquids** (l) substances are present in the K_c expression.
- The K_c value does not have a unit.
- The value of K_c only changes when the **temperature** changes!
 - If the temperature change favours the **forward** reaction $\rightarrow K_c$ **increases**.
 - If the temperature change favours the **reverse** reaction $\rightarrow K_c$ **decreases**.
- Because K_c is calculated in terms of concentration, the concentration of all the species in the system at equilibrium have to be calculated:

$$c = \frac{n}{V}$$

or, if masses are given,

$$c = \frac{m}{MV}$$

because

$$n = \frac{m}{M}$$

- Draw the following table in the calculation of K_c :

	aA(g)	+	bB(g)	$\rightleftharpoons$	cC(g)	+	dD(g)
n (start)							
n (react)							
n (equilibrium)							
$c = \frac{n}{V}$							

Now calculate K_c :

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

The **reactants** always become **less** towards equilibrium. **Subtraction** is done in these columns.

The **products** always become **more** towards equilibrium. **Addition** is done in these columns.

Hint: Use a double line between reactants and products to indicate the division between subtraction and addition.

Very important row!

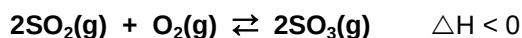
- This row is in the same ratio as the **mole ratio** of the substances A, B, C and D.
- The mole ratio is determined from the **balancing numbers** in the reaction's equation $\therefore$ a,b,c, and d.
- If one position in this row is known, the total row is completed using this ratio.

- When the table is completed in **concentration**, the table changes as follows:
 - Complete the table with concentrations instead of mole quantities. The rows are now labeled: **c(start)**, **c(react)** and **c(equilibrium)**.
 - The 4th row is deleted. The final answer of **c(equilibrium)** is substituted directly into K_c .
- Note the following: Suppose a reaction $AB \rightleftharpoons A + B$, reaches equilibrium.
 - If $\Delta H(\text{forward}) = +70 \text{ kJ} \cdot \text{mol}^{-1}$, then $\Delta H(\text{reverse}) = -70 \text{ kJ} \cdot \text{mol}^{-1}$. (One is positive, the other is negative.)
 - If $K_c(\text{forward}) = 4$, then $K_c(\text{reverse}) = \frac{1}{4}$. (One is the reciprocal of the other.)

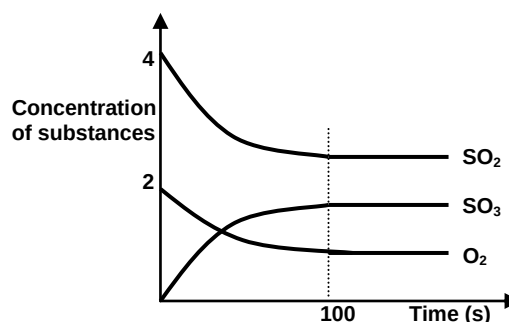
GRAPHS IN CONCENTRATION AND MOLE

- A curve is drawn for **every substance** in the system.
- The curve for every substance starts at the initial mole quantity (or concentration) of that substance on the vertical axis.
 - The quantities of the reactants decrease until the time equilibrium is reached.
 - The quantities of the products increase until the time equilibrium is reached.
- The decrease and increase in quantities is in the mole ratio.
- After equilibrium has been reached, the quantities of the substances remain constant.

- For example :** A closed container contains $4 \text{ mol-dm}^{-3} \text{ SO}_2$ and $2 \text{ mol-dm}^{-3} \text{ O}_2$. Equilibrium is reached after 100 s. The equation for the reaction is:



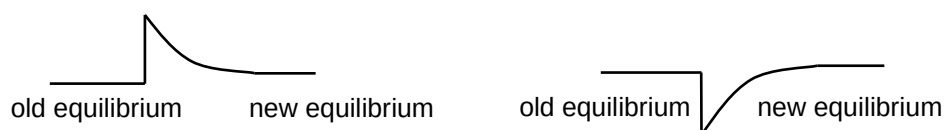
The graph shows how the concentration of each of the substances changes. Note that the decrease in SO_2 is 2x that of O_2 (the same as the mole ratio).



- Equilibrium is now disturbed at 200 s:

PRESSURE AND TEMPERATURE CHANGE		CHANGE IN CONCENTRATION
Forward reaction is favoured: $[\text{SO}_3]$ has increased; $[\text{SO}_2]$, $[\text{O}_2]$ have decreased. Probable disturbances are: - Temperature was decreased; - or - Pressure was increased.	Reverse reaction is favoured: $[\text{SO}_3]$ has decreased; $[\text{SO}_2]$, $[\text{O}_2]$ have increased. Probable disturbances are: - Temperature was increased; - or - Pressure was decreased.	When a curve makes a <u>sudden "dip"</u>, it always indicates a change in <u>concentration</u>. In this case the $[\text{O}_2]$ was decreased at 200 s; the reverse reaction was favoured. $[\text{SO}_3]$ has decreased; $[\text{SO}_2]$, $[\text{O}_2]$ have increased.

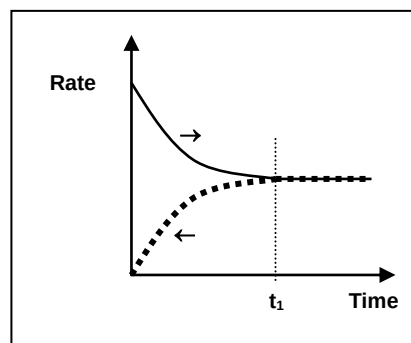
- The "dip" in concentration changes are always one of 2:



- If the disturbance is an increase in concentration, the system reacts with a decrease.
- If the disturbance is a decrease, the system reacts with an increase.

RATE GRAPHS

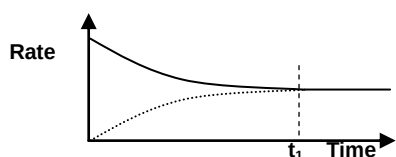
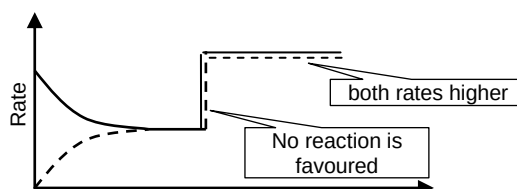
- Curves are drawn for the **forward and the reverse reactions**. The shape of the curve is identical for all equilibrium reactions.
- Equilibrium is reached at t_1 .
- The solid line represents the rate of the forward reaction:
 - Rate decreases from a maximum,
 - to a constant value at t_1 .
- The broken line represents the rate of the reverse reaction:
 - Rate increases from 0,
 - to a constant value at t_1 .
- At equilibrium the rate of the forward reaction = rate of the reverse reaction.
- There are only 4 possible rate graphs that show change in equilibrium:



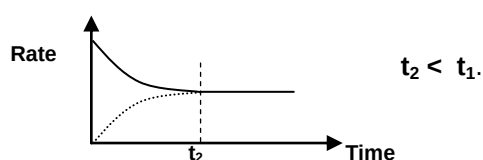
Disturbance: • Increase temperature, or • Increase concentration, or • Increase pressure*. At the new equilibrium: • the new rates are higher . * Pressure is increased by decrease in volume → at smaller volumes the concentrations are higher ($c = \frac{n}{V}$) ∴ new rates are higher.	If the forward reaction is favoured:	If the reverse reaction is favoured:

Disturbance: • Decrease temperature, or • Decrease concentration, or • Decrease pressure#. At the new equilibrium: • the new rates are lower . # Pressure is decreased by increase in volume → at greater volumes the concentrations are lower ($c = \frac{n}{V}$) ∴ new rates are lower.	If the forward reaction is favoured:	If the reverse reaction is favoured:

- Addition of a **catalyst** does not disturb the equilibrium.
 - When a system is already in equilibrium and a catalyst is added, the rates of the forward and the reverse reactions are both increased – but equally. No reaction is favoured.
 - Note the difference in the graphs if a reaction takes place without and with a catalyst.



Reaction takes place without a catalyst.



The same reaction takes place with a catalyst. Equilibrium is reached quicker.