Chemical Equilibrium
Module 1.2

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CHEMICAL EQUILIBRIUM

Definitions	
Positive catalyst	A substance that increases the speed of a chemical reaction without undergoing a permanent change itself.
Le Chatelier's principle	When the equilibrium is disturbed in a closed system, the system sets a new equilibrium in motion through the reaction that works against the disturbance, for example.

Basic definitions and terms

Definition: *Open System* Where there is an interplay between the system and the environment, which means that reactants/ products can escape from the system.

- The container and the reaction mixture are considered as a system.
- A familiar example of an open system is a container without a lid.
- Example: When a pot boils without a lid, the water will evaporate and the evaporation process will continue until all the water has evaporated.
- The following reaction has taken place: $H_2O(\ell) \rightarrow H_2O(g)$.
- It is not a reversible reaction.

Closed system

Definition: *Closed system*
Where there is no interplay between the system and the environment which means that no reactants/ products can escape from the system.

- If there is a lid placed on the container or if the reactants are in solution in the open container, no gas can escape and it is then considered as a closed system.
- If you boil water in a closed system, the water level will initially decrease. Liquid particles evaporate and converted into gas particles.
- After more damp particles are formed the condensation process will begin and some of the gas particles returns to liquid phase.
- The speed of condensation increases until the speed of condensation is equaled to the speed of evaporation.
- As soon as this happens the amount of liquid will stay constant and it seems as though the evaporation has stopped.
- In this case there is an ***equilibrium phase*** because evaporation and condensation takes place at the same speed: $H_2O(\ell) \leftrightarrow H_2O(g)$.
- It is therefore an irreversible reaction.
- In closed systems a **dynamic equilibrium** takes place. On a *macroscopic* level it seems as if the reaction has stopped (T, p, V, color, c), but the reaction continues on a *microscopic* level.

Definition: *Dynamic Equilibrium*
Pace of the forward reaction = pace of the backward reaction and both reactions happen simultaneously and the concentrations of the reactants and products stay constant.

- *Backward and forward reactions happen* ***simultaneously****.*
- ***Speed*** *of the* ***forward*** *reaction =* ***Speed*** *of the* ***backward*** *reaction.*
- *[****Reagents****] and [****Products****] remain* ***constant****. ([...] means concentration of)*

Irreversible reaction
Reagents react to form products and products react to form the original reagents.

A familiar irreversible reaction is the one between ammoniac and hydrochloric acid fumes to form a white powder- ammoniochloride:

$NH_3(g) + HCl(g) \rightarrow NH_4C\ell(s)$ ΔH = neg.

- Reactants: $NH_3(g)$ and $HC\ell$ (g)
- Products: $NH_4C\ell$ (s)
- Exothermic – releases energy.

If ammoniochloride is heated, more ammoniac and hydrochloric acid fumes are formed.

$NH_4C\ell(s) \rightarrow NH_3(g) + HC\ell(g)$ ΔH = pos.

- Opposite of above reaction
- Reactants: $NH_4C\ell(s)$
- Products: $NH_3(g)$ and $HC\ell(g)$
- Endothermic – takes in energy.

If ammoniochloride is placed in a closed container then both of the abovementioned reactions will take place- therefore an irreversible reaction. If the temperature is kept constant, a dynamic equilibrium will be set up.

$NH_4C\ell(s) \rightleftharpoons NH_3(g) + HC\ell(g)$ ΔH = pos.

- Forward reaction- left to right (reagents → products).
- Backward reaction – right to left (products → reagents).
- ΔH in equilibrium reaction always refers to the forward reaction.
- If ΔH is positive for the forward reaction, it will be negative in the backward reaction.

Consider the following reaction:

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

- In a closed system the change in reaction speed depends on the concentrations of the reacting substances.
- When H_2 and I_2 initially react, the speed of the forward reaction is high.
- Just as the concentration of the reagents decreases, the speed of the forward reaction also decreases.
- Just as he concentration of the products increases, the speed of the backward reaction also increases until a state is reached where the speed of the forward and backward reactions are equal- *dynamic equilibrium*.
- **The [ ] of all the substances stay constant** and it may seem as if the reaction has stopped.
- ***The opposite reactions in a closed system both proceed at the same speed – i.e. a dynamic equilibrium exists.***

FACTORS THAT INFLUENCE THE POSITION OF EQUILIBRIUM

- The position of equilibrium refers to the amount of products and reagents at equilibrium.
- Factors that affect equilibrium:
  - **concentration**
  - **pressure**
  - **temperature**.
- If the abovementioned factors change, the speed of the forward and backward reactions change.
- This has an influence on the amount of reagents and products.
- We then say that the position of equilibrium has *moved/shifted...*
- The effect of the change of any of these factors at the position of equilibrium can be determined with the help of ***Le Chatelier's principle***.

- **Indirect disturbances**
  - Volume increases → pressure decreases
  - Catalyst: no disturbance, speed backward and forward is equally increased.
  - H^+ and OH^-.
  - The inactive gas: no disturbance.
  - H_2SO_4 (gek) dehydration means
  - Precipitate eg. AgCl, AgBr, Agl $BaSO_4$, $BaCO_3$.

Remember that chemical equilibrium/balance is a dynamic process that consists of 2 opposing reactions that happen at the same speed in different directions. If one of the factors cause a disturbance, the reaction that leads to the recovery of the equilibrium's speed will increase until balance is set up again.

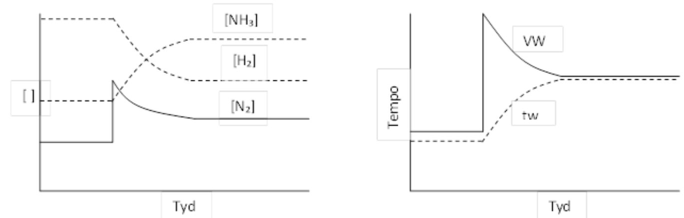
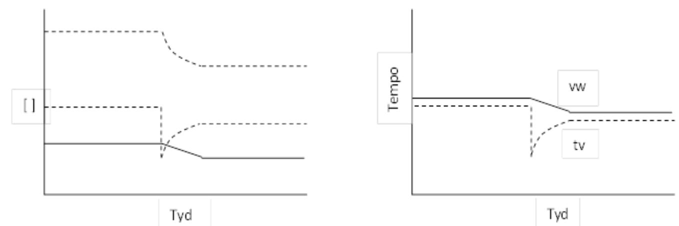
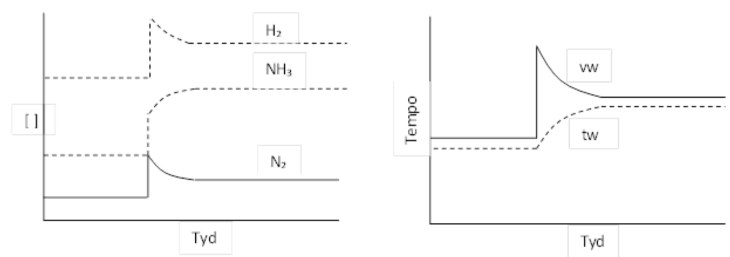
If you have to answer an exam question where you have to use Le Chatelier's principle to explain the disturbance in the position of equilibrium, always mention the following:

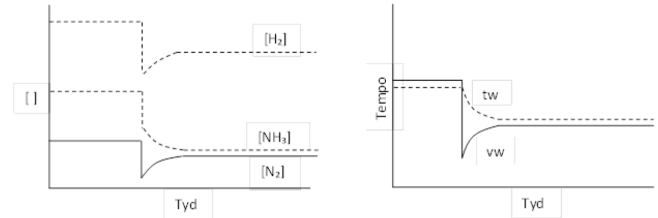
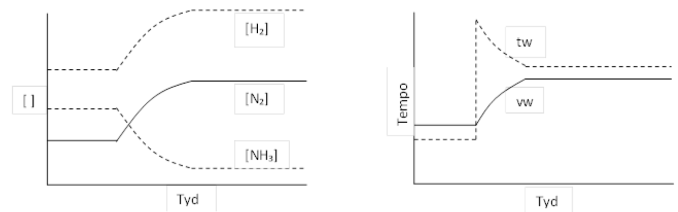
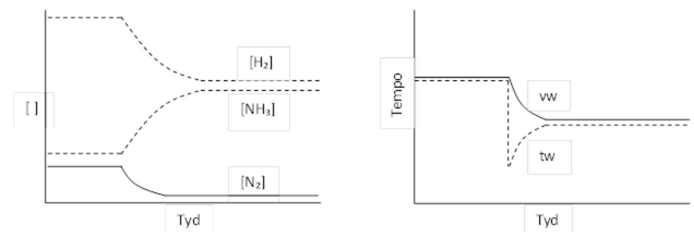
Identify the disturbance

- Mention that the system will work against the change as predicted by Le Chatelier's principle.

- Decide whether the backward/forward reaction is benefitting, i.e. whether the backward/forward reaction will happen faster.
- Discuss the result if this reaction will benefit. It includes the following:
    - Why you are benefitting backward/forward
    - Color changes.
    - Change in concentration etc. depending on the observation that has to be explained.

Effect on chemical equilibrium

Disturbance	Effect on equilibrium	Effect of K_C - value
Concentration	↑ Benefits **away from the increased** [ ] Benefits reaction that uses up extra  Konsentrasieverandering: Verhoog die konsentrasie stikstof	None
	↓ benefits **to the decreased** [ ] Benefits the reaction that can produce more  Konsentrasieverandering: Verlaag die konsentrasie van ammoniak	None
Pressure (only applicable to gas)	↑ p, lowers V – benefits the side with the **least amount of mole** – works against the increase of pressure  Drukverandering: Verhoog die druk	None

	↓ p, raises V – benefits the side with the **largest amount of mole**– works against the decrease of pressure  Drukverandering: Verlaag die druk	None
Temperature (forward exothermic)	↑ benefits **endothermic** reaction – uses up E – backwards. [R] ↑  Temperatuurverandering: Verhoog die temperatuur	Decreases [P] < [R]
	↓ benefits **exothermic** reaction – Releases E – forward. [P] ↓  Temperatuurverandering: verlaag die temperatuur	Increases [P] > [R]
Temperature (forward endothermic)	↑ benefits **endothermic** reaction – Uses up E – forward. [P] ↑	Increases [P] > [R]
	↓ benefits **exothermic** reaction – releases E – backwards [R] ↑	Decreases [P] < [R]
Catalyst	No effect. Equilibrium is reached faster.	None

Application

Consider the following balance that is set up if cobalt chloride is solved on ethanol:

$COC\ell_4^{2-} + 6H_2O \rightleftharpoons CO(H_2O)_6^{2+} + 4C\ell^-$ $\Delta H < 0$
Blue Pink

1. Water is added to the equilibrium mixture. Explain what will happen.

- $[H_2O]$ increases and will therefore disturb the balance.
- According to Le Chatelier the system will work against the disturbance with ℓ. The forward reaction will be benefitted and will accelerate until a new balance is set up.
- $[COC\ell_4^{2-}]$ and $[H_2O]$ decreases
- $[CO(H_2O)_6^{2+}]$ and $[C\ell^-]$ increases.
- The color of the solution becomes pink.

2. Concentrated $HC\ell$ is added to the equilibrium mixture. Explain what will happen.

- If $HC\ell$ is added, the $[C\ell^-]$ rises. We call it the *common ionic effect (adding of a substance that contains the same ions as is inside the solution)*
- According to Le Chatelier the system will work against the disturbance by benefitting the reaction that uses up the $C\ell^-$ ions.
- The backward reaction will be benefitted and will therefore accelerate until a new equilibrium is reached.
- $[COC\ell_4^{2-}]$ and $[H_2O]$ increases.
- $[CO(H_2O)_6^{2+}]$ and $[C\ell^-]$ decreases
- The color of the solution becomes blue.

3. Temperature rises. Explain what will happen.

- If the temperature rises the balance is disturbed.
- According to Le Chatelier the system will work against the disturbance by benefitting the reaction that will lower the temperature of the reaction.
- A rise in temperature always benefits the endothermic reactions and in this case the backward reaction will therefore benefit.
- $[COC\ell_4^{2-}]$ and $[H_2O]$ increases.
- $[CO(H_2O)_6^{2+}]$ and $[C\ell^-]$ decreases
- The color of the solution becomes blue.
- When the blue mixture is cooled down, it changes to pink (forward reaction is exothermic and low T benefits forward exothermic reaction).

REMEMBER!!!!

Increased temperature will accelerate the reaction speed of both backward and forward reactions, but the speed of the forward reaction will be faster. (T ↑ benefits endothermic).

Just the same a decrease in temperature will delay both the backward and forward reactions, but exothermic reactions will be faster than endothermic reactions, because exothermic will be benefitted with a T lowering..

4. Consider the following gas reaction at equilibrium:

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

If p ↑, then V will ↓ and particles are pressed closer together (from pV = nRT we see that p α n).
If p rises, the system will lower by lowering n – benefits least mole.
Remember that pressure affects only GAS at equilibrium.

The pressure on the system rises. Explain what will happen.

If pressure rises, the equilibrium is disturbed.

- According to Le Chatelier the system will work against the disturbance by benefitting the reaction that will lower the amount of molecules of the reaction.
- The backward reaction will thus be benefitted because it has the least amount of mole. $[N_2O_4]$ increases
- $[NO_2]$ decreases
- The solution becomes colorless (lighter)

Adding of a catalyst

A catalyst increases both the reaction speeds of the backward and forward reactions in the same way because it lowers both the activating energies of the backward and forward reactions. It has **NO effect on the equilibrium! [reactants] and [products] remain unchanged.**

In order to complete the following, we revise some grade 10 and 11 work.

Solubility Rules

- ALL nitrates (NO_3^-) are soluble in water.
- The following salts are insoluble (↓) in water:

AgCl (White precipitate) {ALL 3 OF THE FOLLOWING SALTS ARE ALSO INSOLUBLE
AgBr (cream precipitate) IN HNO_3}
AgI (yellow precipitate)

Ag_2CO_3 (white precipitate) {Soluble in HNO_3 to form $AgNO_3$ and CO_2 }

$BaSO_4$ (white precipitate) {Also insoluble in HNO_3}

$BaCO_3$ (white precipitate) {Soluble in HNO_3 to form $Ba(NO_3)_2$ and CO_2}

Remember:

1. If an acid is added to a solution, the $[H^+]$ increases. If OH^- is present in the solution, then $[OH^-]$ will decrease because it reacts with H^+ -ions $\{H^+ + OH^- \rightarrow H_2O\}$.
2. If a base is added to a solution, the $[OH^-]$ increases. If there are H^+ -ions present in the solution, then the $[H^+]$ will decrease, because it reacts with OH^- -ions $\{H^+ + OH^- \rightarrow H_2O\}$.

Factors that influence the following:

Yield/Return	Speed
Temperature	Nature of the substances
Concentration	Temperature
Pressure/Volume	Concentration (l) Pressure (g)
	Surface area (s)
	Catalyst

EQUILIBRIUM CONSTANTS

- To determine the effectivity of industrial chemical processes, it is necessary to know how many of the reactants are converted to products.
- The equilibrium constants are therefore an indication of how effectively the reaction has taken place.
- The higher the value of the equilibrium constants, the more effective the process.

The equilibrium constant is a number that indicates to what extent the reagents change into products by the time that equilibrium is reached.

Consider the following reaction at equilibrium:

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

- As the reaction takes place, reactants are converted to products to a point where the speed of the forward reaction = the speed of the backward reaction.
- At this point a dynamic equilibrium is reached and the concentrations of the reactants and products remain **constant**.
- The ratio of product to reactant is called the **equilibrium constant (K_C)**.
- For the abovementioned reaction the expression for K_C is as follows: $K_C = \frac{[HI]^2}{[H_2][I_2]}$
- Everything right of the = is known as the **law of chemical balance**.
- Every reaction has a specific K_C-value at a specific temperature.
- Thus only the **temperature change** can influence the value of the equilibrium constant.
- **K_C > 1.** Means that the product is high at equilibrium. Therefore, a **high yield. ECONOMIC.**
- **K_C < 1**. Means that the product is low at equilibrium. Therefore, a **low yield. UNECONOMIC.**

- Strong acids almost entirely ionizes in water, therefore the equilibrium will be far right and the equilibrium constants will be very high. With weak acids equilibrium will be far left and the constants will be very low.

Heterogenic equilibrium

A Heterogenic equilibrium is where all the reactants and the products are not in the same phase.

Considering that the concentrations of liquids and solids are ALWAYS CONSTANT, **solid (s)** and **liquid (l)** are removed from the equilibrium expression. (Therefore, only the concentrations of **gas (g)** and **ions in solution (aq)** are used to calculate equilibrium constants.

Write an equilibrium expression for the following reactions:

1. $2Hg(l) + O_2(g) \rightleftharpoons 2HgO(s)$
2. $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

Answers:

1. $$K_C = \frac{1}{[O_2]}$$

2. $$K_C = \frac{[CO][H_2]}{[H_2O]}$$

Effect of temperature on the K_C – value.

- If → endothermic, T will ↑ the K_C-value ↑.
- If → endothermic, T will ↓ the K_C-value ↓.
- If → exothermic, T will ↑ the K_C-value ↓.
- If → exothermic, T will ↓ the K_C-value ↑.

Therefore if forward reactions are benefitted, then K_C will ↑ and if the backward reaction benefits then K_C will ↓.

CALCULATIONS

Example 1

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad \Delta H < 0$

If 5 mole $H_2(g)$, 4mole $I_2(g)$ and 2 mole HI(g) at equilibrium is in a 2dm^3 container, calculate K_C.

Solution

$[H_2]$ = n/V = 4/2 = 2,5 mol.dm^{-3}
$[I_2]$ = n/V = 10/2 = 2 mol.dm^{-3}
[HI] = n/V = 3/2 = 1 mol.dm^{-3}

$$K_c = \frac{[HI]^2}{[H][I]} = \frac{1}{2{,}5\ x\ 2} = \frac{1}{5} = 0.2$$

What does this value mean?

- Equilibrium is far left.
- [Reactants] are higher than [products].
- To raise the value of K_C- the forward reaction must benefit. T must therefore be lowered.

Example 2

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

3mole $N_2(g)$ is added to 6 mole $H_2(g)$ in an empty 2dm^3 container. At equilibrium there is 2 mole H_2 left in the container. Calculate K_C at equilibrium.

	Reactants		Product	Type of reaction
Chemical substances	$N_2(g)$	$H_2(g)$	$2NH_3(g)$	The H_2 has decreased – therefore the reaction is forward. • ΔH <0 • Spontaneous • Forward reaction
Amount of molecules in a balanced comparison	1	3	2	
Amount of mole at the START of reaction **(MOL)**	3	6	0 **(Indien daar geen geggewens is oor die hoeveelheid nie is dit 0 mol)**	
Amount of mole Used/Formed during the reaction **(MOL)**	***-1*** ***(stap 1)***	-(3 x 1) = **-3** **(stap 2)**	(-2 x 1) = +**2** **(stap 3)**	
Amount of mole at the END of the reaction **(MOL)**	3-1=2	6-3=3	0+2=2	
VOLUME OF THE CONTAINER where the reaction takes place (**dm^{-3}**)	2	2	2	
CONCENTRATION of substances **(mol·dm^{-3})**	$C = \frac{n}{v} = \frac{2}{2} = 1$	$C = \frac{n}{v} = \frac{3}{2} = 1{,}5$	$C = \frac{n}{v} = \frac{2}{2} = 1$	

- To calculate the amount of mole used/formed you have to use the balanced comparison/equation to get the correct ratios!!!
- Ratio N_2:$3H_2$ – i.e. there is 3 x more N_2 used than H_2. 3 x 1 = 3.
- Ratio $2NH_3$:N_2 – i.e. there is 2 x more NH_3 formed than N_2 used. 2 x 1 = 2.

$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{1}{1 \, x \, 1,5} = 0.67$$

- K_c is a ratio and does not have a unit.

Graph interpretation

- Usually you will get a [ ] / Time graph.
- In case there is a ***drastic*** increase/decreases (long vertical line), it means that some is added/removed.
- In case all the reactants and products show a ***small*** increase/decrease (short vertical line), it means that there has been a change in pressure.
- In case there is a ***gradual*** increase/decrease, it means that there has been a change in temperature.

Le Chatelier

3 Factors that influence equilibrium:

1- Concentration
2- Temperature
3- Pressure

Effect of using a catalyst

-No effect on equilibrium
-At beginning of process: equilibrium is set up faster
-At equilibrium: equally accelerates the reaction speeds of forward and backward reactions

Le Chatelier's principle

In case equilibrium is disturbed in a closed system, the system will try to recover balance by working against te disturbing factor.

Effect of temperature change

-If temperature rises the system will lower it by benefitting endothermic reactions.
-If temperature falls the system will raise it by benefitting exothermic reactions.

Adding reactants/concentration

-In case the concentration of 1/more of the substances increases, the system will try to decrease the concentration. The system benefits reaction that the substances use.
-In case the concentration of 1/more of the substances decrease, the system will try to increase the concentration. The system benefits reaction that these substances form.

Effect of pressure change

-If pressure rises, the reaction speed is benefitted on the side with the least amount of mole.
-If pressure falls, reaction speed is benefitted on the side with the most amount of mole.

Chemical Equilibrium

Evaporation in a closed system

-As soon as the space above water level is full of water damp, the liquid level stops dropping.
-Evaporation and condensation takes place microscopically at the same speed.
-Because the amount of damp remains constant, it means that the phase change is irreversible.

Calculation of concentration at equilibrium

1- $c = n/v$
n = amount of mole
v = volume
c = concentration
2- Draw a table

Equilibrium constants

-Kc is known as the equilibrium constant.

-$K_c = \frac{[C]^C[D]^D}{[A]^A[B]^B}$

-the concentration of (s) and (ℓ) is 1.
-The concentration of products are at the top, and reactants below them.
-Kc value > 1 → more products form than reactants,
-Kc value < 1 → more reactants needed to form a smaller amount of products.
-Only changes with temperature change
-Homogenic equilibrium: a change in the concentration of substances can occur
-Heterogenic equilibrium: concentration of these substance remain constant

Equilibrium in solutions

-Soluble equilibrium, speed at which solids dissolve is equaled to the speed at which dissolved sunbstances crystalize.
-Equilibrium → speed of the forward reaction = speed of the backward reaction
-Dynamic equilibrium → at equilibrium processes have not stopped, the forward and backward reactions stillproceed in both directions at the same speed.

Irreversible reactions and chemical equilibrium

-Some reactions only go into one direction: burning wood, food cannot be cooked again, plants use solar energy in the presence of chlorophyll to produce oxygen. The process cannot be repeated.

Measuring of reaction speed

Effect of concentration

-The speed of a chemical reaction is increased by an increase in concentration of the reactants. The reaction speed is directly even to the concentration of the reactants.

Effect of a catalyst

-Speed of a reaction increases by adding a positive catalyst.

Nature of reactants on reaction speed

-Even though the different substances like Mg, Zn and Fe deliver the same type of reaction with HCl, the reactions still take place at different speeds.

Effect of reaction surface on reaction speed

-Speed of a reaction increases the more evenly a substance is divided. The more even the solid, the bigger the reaction surfac.

Variables during the investigation

-Independent variable: changes because you control it

-Dependent variable: a variable that changes as a result of the change of the independent variable

-Controlled variables: Has to be kept constant to ensure it is a reasonable test.

Effect of temperature on the reaction speed

-The speed of a chemical reaction increases with an increase in temperature of the reactants.