



Reactants \rightleftharpoons Products

Reversible Reactions, Chemical Equilibrium, Ammonia - its synthesis and uses

1. Reversible Reactions

- A reversible reaction is a chemical in which the products can be converted back to reactants under suitable conditions.
- A reversible reaction is shown by the sign \rightleftharpoons a half-arrow to the right (forward reaction) and a half-arrow to the left (backward reaction).
- Most reactions are not reversible and have the usual complete arrow \longrightarrow only pointing to the right.

Three examples of reversible reactions are given below:

(a) The thermal decomposition of ammonium chloride.

- On heating strongly, the white solid ammonium chloride, decomposes into a mixture of two colourless gases ammonia and hydrogen chloride.
- On cooling the reaction is reversed and solid ammonium chloride reforms.
 - This is an example of **sublimation** but involving both physical and chemical changes.
 - **Ammonium chloride** + heat \rightleftharpoons **ammonia** + **hydrogen chloride**
 - **NH₄Cl_(s)** \rightleftharpoons **NH_{3(g)}** + **HCl_(g)**
- **Note:**
 - Reversing the reaction conditions reverses the direction of chemical change, typical of a reversible reaction.
 - Thermal decomposition means using 'heat' to 'break down' a molecule into smaller ones.
 - The decomposition is endothermic (heat absorbed or heat taken in) and the formation of ammonium chloride is exothermic (heat released or heat given out).
 - This means if the direction of chemical change is reversed, the energy change is also reversed.

(b) The thermal decomposition of hydrated copper(II) sulphate.

- On heating the blue solid, hydrated copper(II) sulphate, steam is given off and the white solid of anhydrous copper(II) sulphate is formed.
- When the white solid is cooled and water added, blue hydrated copper(II) sulphate is reformed.

blue hydrated copper(II) sulphate + heat \rightleftharpoons white anhydrous copper(II) sulphate + water



Note:

- The **5H₂O** in the formula of hydrated copper(II) sulphate is called the **water of crystallisation** and forms part of the crystal structure when copper(II) sulphate solution is evaporated and crystals form.
- This crystal structure is broken down on heating and the water is given off.
- The thermal decomposition is endothermic as heat is absorbed to drive off the water.
- The reverse reaction is exothermic ie on adding water to white anhydrous copper(II) sulphate the mixture heats up as the blue crystals reform.
- The reverse reaction is used as a simple chemical test for water ie white anhydrous copper(II) sulphate turns blue.

2. Reversible reactions and Equilibrium.

Reversible reactions and equilibrium

A reversible reaction is one in which the **products** of a reaction can react back to produce the original reactants. The reaction can go both ways:

| | | |
|---|----------------------|---|
| $\text{H}_2(\text{g}) + \text{I}_2(\text{g})$ | \rightleftharpoons | $2\text{HI}(\text{g})$ |
| hydrogen combines with iodine in the forward reaction | \rightleftharpoons | hydrogen iodide molecules react to form hydrogen and iodine in the reverse reaction |

If the reaction is carried out in a closed container, a point is reached where the concentration of products and reactants does not change. We say that an **equilibrium** (balance) has been reached.

The amounts of reactants and products present at equilibrium depend on the temperature, pressure and concentration of reactants at the start.

If we remove the products from an equilibrium reaction more reactants are converted to products.

For an **exothermic** equilibrium reaction, the amount of product **decreases** as the temperature increases. For an **endothermic** equilibrium reaction, the amount of product **increases** as the temperature increases.

| Equation | | | Effect of increasing pressure |
|---|----------------------|---|---|
| $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$ 4 molecules | \rightleftharpoons | $2\text{NH}_3(\text{g})$ 2 molecules | More ammonia is formed. Increasing the pressure pushes the reaction in the direction of fewer molecules. |
| $\text{N}_2\text{O}_4(\text{g})$ 1 molecule | \rightleftharpoons | $2\text{NO}_2(\text{g})$ 2 molecules | More $\text{N}_2\text{O}_4(\text{g})$ is formed. Increasing the pressure pushes the reaction in the direction of fewer molecules. |
| $\text{H}_2(\text{g}) + \text{I}_2(\text{g})$ 2 molecules | \rightleftharpoons | $2\text{HI}(\text{g})$ 2 molecules | No effect, because there are the same number of molecules on each side of the equation. |

- When a reversible reaction occurs in a **closed system** an **equilibrium is formed**, in which the original **reactants and products formed coexist**.
- In an equilibrium there is a state of balance between the concentrations of the reactants and products.
- At equilibrium the rate at which the reactants change into products is exactly equal to the rate at which the products change back to the original reactants.
- The result is that the concentrations of the reactants and products remain the same BUT the reactions don't stop!
- However the relative amounts of the reactants and products depend on the reaction conditions eg the temperature and pressure.
- For industrial processes, it is important to maximise the concentration of the desired products and minimise the 'leftover' reactants. A set of rules can be used to predict the best reaction conditions to give the highest possible yield of product.

Rule 1a: If the forward reaction forming the product is **endothermic**, **raising the temperature** favours its formation **increasing the yield** of product (lowering the temperature decreases the yield).

Rule 1b: If the forward reaction forming the product is exothermic, decreasing the temperature favours its formation (increasing temperature decreases the yield).

Rule 1 applies to any reaction BUT rule 2 applies to a reaction with one or gaseous reactants or products.

Rule 2a: **Increasing the pressure favours** the side of the equilibrium with **the least number of gaseous molecules** as shown by the balanced symbol equation.

Rule 2b: Decreasing the pressure favours the side of the equilibrium with the most number of gaseous molecules as shown by the balanced symbol equation

Rule 3a: If the concentration of a reactant (on the left) is increased, then some of it must change to the products (on the right) to maintain a balanced equilibrium position.

Rule 3b: If the concentration of a reactant (on the left) is decreased, then some of the products (on the right) must change back to reactants to maintain a balanced equilibrium position.

- eg **nitrogen + hydrogen** \rightleftharpoons **ammonia** or $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
 - if the nitrogen or hydrogen concentration was increased, some of this extra gas concentration would change to ammonia
 - if the nitrogen or hydrogen concentration was decreased, some of ammonia would change to nitrogen and ammonia
 - increasing nitrogen => decreases hydrogen and increases ammonia
 - increasing hydrogen => decreases nitrogen and increases ammonia
 - increasing ammonia => increases nitrogen and hydrogen

- decreasing ammonia => decreases nitrogen and hydrogen
- decreasing nitrogen ==> increases hydrogen and decreases ammonia
- decreasing hydrogen ==> increases nitrogen and decreases ammonia

Rule 4: A catalyst does NOT affect the position of an equilibrium, you just get there faster! A catalyst usually speeds up both the forward and reverse reaction but there is no way it can influence the final 'balanced' concentrations. However, the importance of a catalyst lies with economics eg (i) bringing about reactions with high activation energies at lower temperatures and so saving energy or (ii) saving time is saving money.

(a) The formation of calcium oxide (lime) and carbon dioxide from calcium carbonate (limestone)



The forward reaction is endothermic, 178kJ of heat energy is absorbed (taken in) for every mole of calcium oxide formed.

One mole of gas is formed in the process, so there is a net increase in the moles of gas in lime formation, since there are no gaseous reactants.

From rule 1: increasing the temperature will increase the yield of lime CaO (endothermic).

From rule 2: decreasing the pressure will favour the formation of more carbon dioxide, hence more lime (increase in gas molecules).

Lime is made commercially by heating limestone to a high temperature (eg 1000°C) in a limekiln that is well ventilated (this reduces the carbon dioxide pressure and so reduces the un-desired backward reaction).

(b) The formation of hydrogen chloride from hydrogen and chlorine



The forward reaction is exothermic, 184kJ of heat energy is given out in forming hydrogen chloride (92 kJ per mole of HCl formed).

There is no net change in the moles of gas (2 moles reactants \rightleftharpoons 2 moles of product)

From rule 1: decreasing the temperature favours the formation of hydrogen chloride HCl

From rule 2: since there is no net change in the moles of gas, pressure has no effect on the yield of hydrogen chloride!

3. The Synthesis of ammonia - The Haber Process

- **Ammonia gas is synthesised** in the chemical industry by **reacting nitrogen gas with hydrogen gas**.
- The **nitrogen is obtained from air** (80% of air is N₂).
- The **hydrogen is made by reacting methane (natural gas) and water** or from cracking hydrocarbons (both reactions are done at high temperature with a catalyst).
 - **CH₄ + H₂O ==> 3H₂ + CO**
 - eg C₈H₁₈ ==> C₈H₁₆ + H₂
- The synthesis equation for this **reversible reaction** is ...



- .. which means a **dynamic equilibrium** will form, so no chance of 100% yield!
- In forming ammonia 92kJ of heat energy is given out (ie **exothermic**, 46kJ of heat released per mole of ammonia formed).
- Four moles of 'reactant' gas form two moles of 'product' gas, so there is net decrease in gas molecules on forming ammonia.
- So applying the equilibrium rules from section 2 the **formation of ammonia** is favoured by
 - using **high pressure** because you are going from 4 to 2 gas molecules (the high pressure also speeds up the reaction because it effectively increases the concentration of the gas molecules).
 - and **low temperature** because is an exothermic reaction,
 - to try to get the **optimum conditions to get the biggest yield of ammonia**,
 - these arguments make the point that **the yield* of an equilibrium reaction depends on the conditions used**.
 - *** The word 'yield' means how much product you get compared to the theoretical maximum possible if the reaction goes 100%.**
- In industry pressures of **200 - 300 times normal atmospheric pressure are used** in line with the theory.
- Theoretically **a low temperature would give a high yield of ammonia BUT ...**
 - **Nitrogen** is very **stable molecule** and not very reactive ie **chemically inert**.
 - **To speed up the reaction** an **iron catalyst** is used as well as a **higher temperature** (eg 400-450°C).
 - The higher temperature is an economic compromise, ie it is more economic to get a low yield fast, than a high yield slowly!
 - **Note: a catalyst does NOT affect the yield of a reaction**, ie the equilibrium position BUT you do get there faster!
- On **cooling the reacted mixture the ammonia liquefies** and is removed and stored in cylinders.
- Any **unreacted nitrogen or hydrogen is recycled** back through the reactor chamber, nothing is wasted!

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