# Rates, Equilibrium and Redox

Physical and chemical changes, collision theory and the rate of reaction, practical methods and graphs, reversible reactions and equilibrium including the Haber and Contact processes, and oxidation, reduction and oxidation numbers.

## 6.1 Physical and chemical changes

| | Physical change | Chemical change |
|---|---|---|
| **new substance made?** | no | **yes** |
| **can it be reversed easily?** | usually yes | usually difficult |
| **energy change** | small | usually a larger energy change (heat, light) |
| **examples** | melting, boiling, dissolving, crushing | burning, rusting, a metal reacting with acid, cooking an egg |

Signs of a chemical change: a **new substance** forms, there is a **colour change**, a **gas** is given off, a **precipitate** forms, or there is a change in **temperature** or **light**.

## 6.2 Rate of reaction

The **rate of reaction** is how fast reactants are used up or products are formed. It can be measured as the change in the amount of a reactant or product in a given time.

### Collision theory

A reaction happens only when particles **collide** with **enough energy**. The collision theory says that a reaction occurs when:

1. the particles **collide** with each other, and
2. the collision has **at least the activation energy**, $E_a$ (the collision is "successful").

The **rate** depends on the **frequency of successful collisions**.

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## Factors that change the rate

| Factor | Effect on rate | Explanation using collision theory |
|---|---|---|
| **increase the concentration** of a solution | faster | more particles in the same volume, so **more frequent collisions** |
| **increase the pressure** of a gas | faster | the particles are squashed closer together (more particles per unit volume), so more frequent collisions |
| **increase the surface area** of a solid (smaller pieces, powder) | faster | more particles of the solid are exposed, so more frequent collisions |
| **increase the temperature** | faster | the particles move **faster**, so they collide **more often**, and more of the collisions have **at least the activation energy**. The second reason matters most |
| **add a catalyst** | faster | provides an alternative pathway with a **lower activation energy**, so more collisions are successful |

**A catalyst increases the rate of a reaction by lowering the activation energy, $E_a$, and it is unchanged at the end of the reaction. Enzymes are biological catalysts.**

NOTE

For a temperature rise, do not stop at "more collisions". A good answer says that the particles have **more energy**, so a **greater proportion** of the collisions have energy **greater than or equal to the activation energy**.

TRY IT

Explain why powdered calcium carbonate reacts faster with acid than large lumps of marble.

The powder has a larger **surface area**, so more particles are exposed to the acid, and there are more frequent collisions between the acid and the calcium carbonate particles.

## Investigating the rate

A reaction that gives off a gas can be followed in two ways, for example $\mathrm{CaCO_3 + 2\,HCl \longrightarrow CaCl_2 + H_2O + CO_2}$.

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| Method | What is measured | Notes |
|---|---|---|
| **volume of gas collected** (gas syringe or an upturned measuring cylinder over water) | the volume of gas at regular times | a gas syringe is more accurate. Check the apparatus is gas-tight |
| **loss of mass** (flask on a balance) | the mass at regular times, which falls as the gas escapes | a loose plug of cotton wool lets gas out but keeps the spray in. Does not work well for a gas of low density such as hydrogen, as the mass change is very small |

Keep everything else the same (**control variables**): the same amounts, the same temperature and the same size of pieces, changing only one factor at a time.

### Interpreting rate graphs

- The **gradient** (steepness) of the curve is the **rate**. The curve is **steepest at the start**, when the reactants are at their highest concentration, and it gets **less steep** as reactants are used up.
- The curve becomes **flat** (horizontal) when the reaction has **finished** and one reactant has run out.
- A **steeper** curve means a **faster** reaction. If the same amount of the limiting reactant is used, both curves **end at the same final volume**, but the faster one gets there sooner.
- If more of the **limiting reactant** is used, the curve ends at a higher level.

To find the rate at a particular time, draw a **tangent** to the curve and find its gradient, or compare the volumes made in equal times.

## 6.3 Reversible reactions and equilibrium

Some reactions are **reversible**: they can go in both directions. This is shown by the symbol ⇌.

### Hydrated and anhydrous compounds

Heating a hydrated compound drives off the water of crystallisation. Adding water to the anhydrous compound reverses the change.

| | Hydrated | Anhydrous |
|---|---|---|
| **copper(II) sulfate** | blue crystals, $CuSO_4 \cdot 5\,H_2O$ | white powder, $CuSO_4$ |
| **cobalt(II) chloride** | pink, $CoCl_2 \cdot 6\,H_2O$ | blue, $CoCl_2$ |

$$CuSO_4 \cdot 5\,H_2O\,(s) \rightleftharpoons CuSO_4\,(s) + 5\,H_2O\,(l)$$

Note Academy

The forward reaction (**heating**) is endothermic and the reverse reaction (**adding water**) is exothermic: the anhydrous solid becomes hot as it turns blue again.

## Dynamic equilibrium

> **A reversible reaction in a closed system (nothing can enter or escape) reaches equilibrium when (a) the rate of the forward reaction equals the rate of the reverse reaction, and (b) the concentrations of reactants and products are no longer changing.**

At equilibrium both reactions are still happening, so it is **dynamic**. The amounts of reactants and products stay constant, though they need not be equal.

## Changing the position of equilibrium

The **position of equilibrium** says how much reactant and product there is at equilibrium. If a condition is changed, the system **opposes the change**.

| Change | Effect on the position of equilibrium |
|---|---|
| **raise the temperature** | moves in the direction of the **endothermic** reaction (which takes in heat) |
| **lower the temperature** | moves in the direction of the **exothermic** reaction (which gives out heat) |
| **raise the pressure** (gases) | moves to the side with **fewer moles of gas** |
| **lower the pressure** | moves to the side with **more moles of gas** |
| **increase the concentration** of a reactant | moves to the **right**, to use up the extra reactant |
| **remove a product** | moves to the **right**, to make more product |
| **add a catalyst** | **no effect** on the position. It speeds up both directions equally, so equilibrium is reached **sooner** |

**TRY IT**

The reaction $\mathrm{N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)}$ is endothermic in the forward direction. What happens to the position of equilibrium if the pressure is increased, and if the temperature is increased?

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There is **1** mole of gas on the left and **2** moles on the right. Increasing the pressure moves the equilibrium to the side with **fewer** moles, the **left**, so less $NO_2$. Increasing the temperature favours the **endothermic** (forward) reaction, so it moves to the **right** and more $NO_2$ forms.

## The Haber process

The Haber process makes **ammonia**, used for fertilisers.

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \qquad \text{(forward reaction exothermic)}$$

- **Nitrogen** comes from the **air** and **hydrogen** from **methane** (natural gas).
- **Conditions:** $450\,°C$, $20\,000\ kPa$ $(200\ atm)$ and an **iron** catalyst.
- The mixture is cooled so that **ammonia liquefies** and is removed. The **unreacted nitrogen and hydrogen are recycled**.

| Condition | Why this value |
| --- | --- |
| **high pressure** ( $200\ atm$) | there are $4$ moles of gas on the left and $2$ on the right, so a high pressure moves the equilibrium to the right and gives a **higher yield**, and it also speeds up the reaction. A higher pressure would need stronger, more expensive equipment and be more dangerous |
| $450\,°C$ **(a compromise)** | the forward reaction is **exothermic**, so a **low** temperature gives a **higher yield**, but then the rate is **too slow**. $450\,°C$ gives a reasonable yield at an acceptable rate |
| **iron catalyst** | **speeds up** the reaction so it reaches equilibrium faster, at a lower temperature than would be needed otherwise. It does not change the yield |

## The Contact process

The Contact process makes **sulfur trioxide**, which is used to make **sulfuric acid**.

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g) \qquad \text{(forward reaction exothermic)}$$

- **Sulfur dioxide** comes from **burning sulfur** or **roasting sulfide ores**, and **oxygen** from the **air**.
- **Conditions:** $450\,°C$, $200\ kPa$ $(2\ atm)$ and a **vanadium(V) oxide**, $V_2O_5$, catalyst.

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| Condition | Why this value |
|---|---|
| **low pressure** ($2\ \text{atm}$) | the equilibrium already gives a **very high yield** at this pressure, so a high pressure would **add expense and danger** for very little extra product |
| $450\ ^\circ\text{C}$ | the forward reaction is exothermic, so a lower temperature would raise the yield but make the reaction too slow. A compromise |
| **vanadium(V) oxide** | speeds up the reaction |

# 6.4 Redox

**A redox reaction is one in which reduction and oxidation happen at the same time.**

| | Oxidation | Reduction |
|---|---|---|
| in terms of **oxygen** | **gain** of oxygen | **loss** of oxygen |
| in terms of **electrons** | **loss** of electrons | **gain** of electrons |
| in terms of **oxidation number** | **increase** in oxidation number | **decrease** in oxidation number |

Remember **OIL RIG**: Oxidation Is Loss, Reduction Is Gain (of electrons).

## Oxidation numbers

The **oxidation number** shows the charge an atom has, or would have, if the compound were made of ions.

- The oxidation number of an **uncombined element** is $0$ (for example $\text{Mg}$, $\text{O}_2$, $\text{Cl}_2$).
- For a **monatomic ion**, it is the **charge on the ion** ($\text{Na}^+$ is $+1$, $\text{Cl}^-$ is $-1$).
- The **sum** of the oxidation numbers in a **compound** is $0$.
- The sum of the oxidation numbers in an **ion** is equal to the **charge on the ion**.
- Common values: hydrogen is $+1$ and oxygen is $-2$ in most compounds.

A **Roman numeral** in a name gives the oxidation number: iron(II) is $\text{Fe}^{2+}$ with oxidation number $+2$, and iron(III) is $+3$. In manganate(VII), manganese is $+7$.

TRY IT

Find the oxidation number of (a) sulfur in $\text{SO}_2$, (b) chromium in $\text{Cr}_2\text{O}_7^{2-}$ (c) nitrogen in $\text{NO}_3^-$.

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(a) Oxygen is $-2$, so $x + 2(-2) = 0$ and $x = +4$. (b) $2x + 7(-2) = -2$, so $2x = +12$ and $x = +6$. (c) $x + 3(-2) = -1$, so $x = +5$.

## Identifying redox

> **TRY IT**
>
> In the reaction $\mathrm{CuO + Mg \longrightarrow Cu + MgO}$ say which substance is oxidised and which is reduced, and identify the oxidising agent and the reducing agent.

Copper(II) oxide **loses oxygen**, so it is **reduced** (copper goes from $+2$ to $0$). Magnesium **gains oxygen**, so it is **oxidised** (from $0$ to $+2$). The **oxidising agent** is copper(II) oxide, and the **reducing agent** is magnesium.

**An oxidising agent is a substance that oxidises another substance and is itself reduced. A reducing agent is a substance that reduces another substance and is itself oxidised.**

Reactions of ions can be redox reactions too. In $\mathrm{Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu}$, zinc **loses** two electrons (oxidised, so it is the reducing agent), and $\mathrm{Cu^{2+}}$ **gains** two electrons (reduced, so it is the oxidising agent). In $\mathrm{Cl_2 + 2\,Br^- \longrightarrow 2\,Cl^- + Br_2}$, chlorine is the oxidising agent and bromide ions are oxidised.

> **NOTE**
>
> If a reaction has **no** change in oxidation number, it is not a redox reaction. Neutralisation and precipitation are not redox reactions.

## Colour changes that show a redox reaction

| Reagent | Colour change | What it shows |
|---|---|---|
| **acidified aqueous potassium manganate(VII)**, $\mathrm{KMnO_4}$ (an oxidising agent) | **purple → colourless** | it has been **reduced** by a reducing agent |
| **aqueous potassium iodide**, $\mathrm{KI}$ (a reducing agent) | **colourless → brown** | iodide ions have been **oxidised** to iodine by an oxidising agent: $\mathrm{2\,I^- \longrightarrow I_2 + 2\,e^-}$ |

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