SciFun

Chemical Kinetics – 1

Mario González-Jiménez
(mario.gonzalezjimenez@glasgow.ac.uk)

What is chemical kinetics?

$$\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{C}$$

$$x\mathrm{A} + y\mathrm{B} \longrightarrow z\mathrm{C}, z?$$

$$2\mathrm{Na} + \mathrm{Cl}_2 \longrightarrow 2\mathrm{NaCl}$$

Chemical kinetics is the area of chemistry that deals with ~~what happens~~ ~~"in the middle"~~

1- Reaction mechanisms – the intermediate steps a reaction goes through.
2- Reaction rates – the speed at which a reaction occurs and how factors such as concentration, temperature, or catalysts affect that speed.

"It's the not the Destination, It's the journey" - Ralph Waldo Emerson (1803 – 1882)

A brief reminder: components of a reaction

Catalytic decomposition of hydrogen peroxide by manganese dioxide

Catalyst

$$2\,H_2O_2\,(aq) \xrightarrow{\Delta,\ MnO_2} 2\,H_2O\,(l) + O_2(g)$$

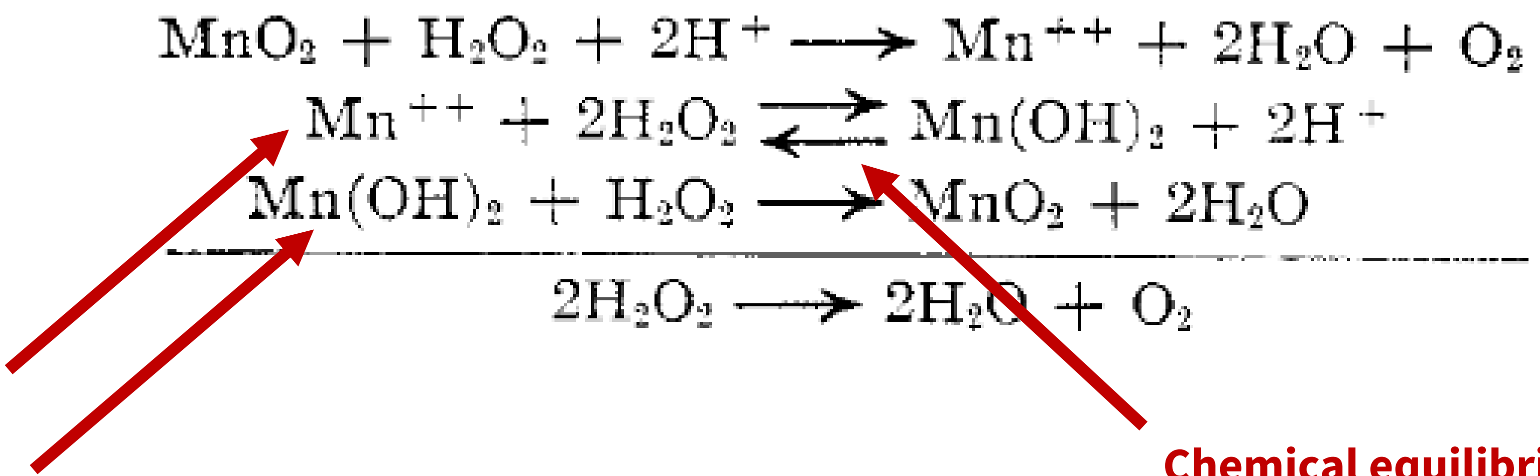
Reactive — Product — Product

Stoichiometric coefficient: The number that indicates how many moles of a species take part in a chemical reaction.
Reaction environment: The physical and chemical conditions under which a reaction takes place (e.g. temperature, solvent, pressure).
Catalyst: A substance that increases the reaction rate without being consumed in the process.

A brief reminder: components of a reaction

Catalytic decomposition of hydrogen peroxide by manganese dioxide

“The reaction mechanism”



Reaction intermediates

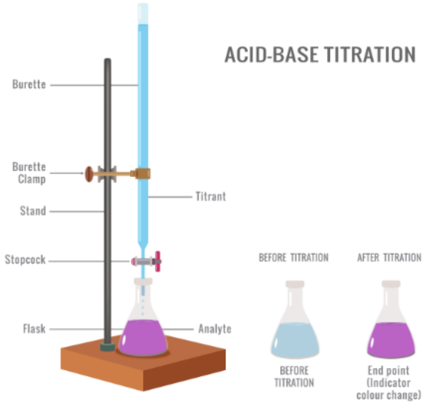
Chemical equilibrium

https://doi.org/10.1021/ja01196a003

Reaction mechanism: The sequence of elementary steps that connect reactants and products.
Reaction intermediates: Molecules or chemical species that form temporarily during the reaction and disappear before the final products are formed.
Chemical equilibrium: State in which the forward and reverse reactions occur at the same rate, so the concentrations of reactants and products remain constant over time.

The study of how fast chemical reactions happen

Acid-base titration



Near-instantaneous
(diffusion-controlled)

Oxidation of iron powder

16 h

Vinegaring of wine

days

Photochemical degradation of paint

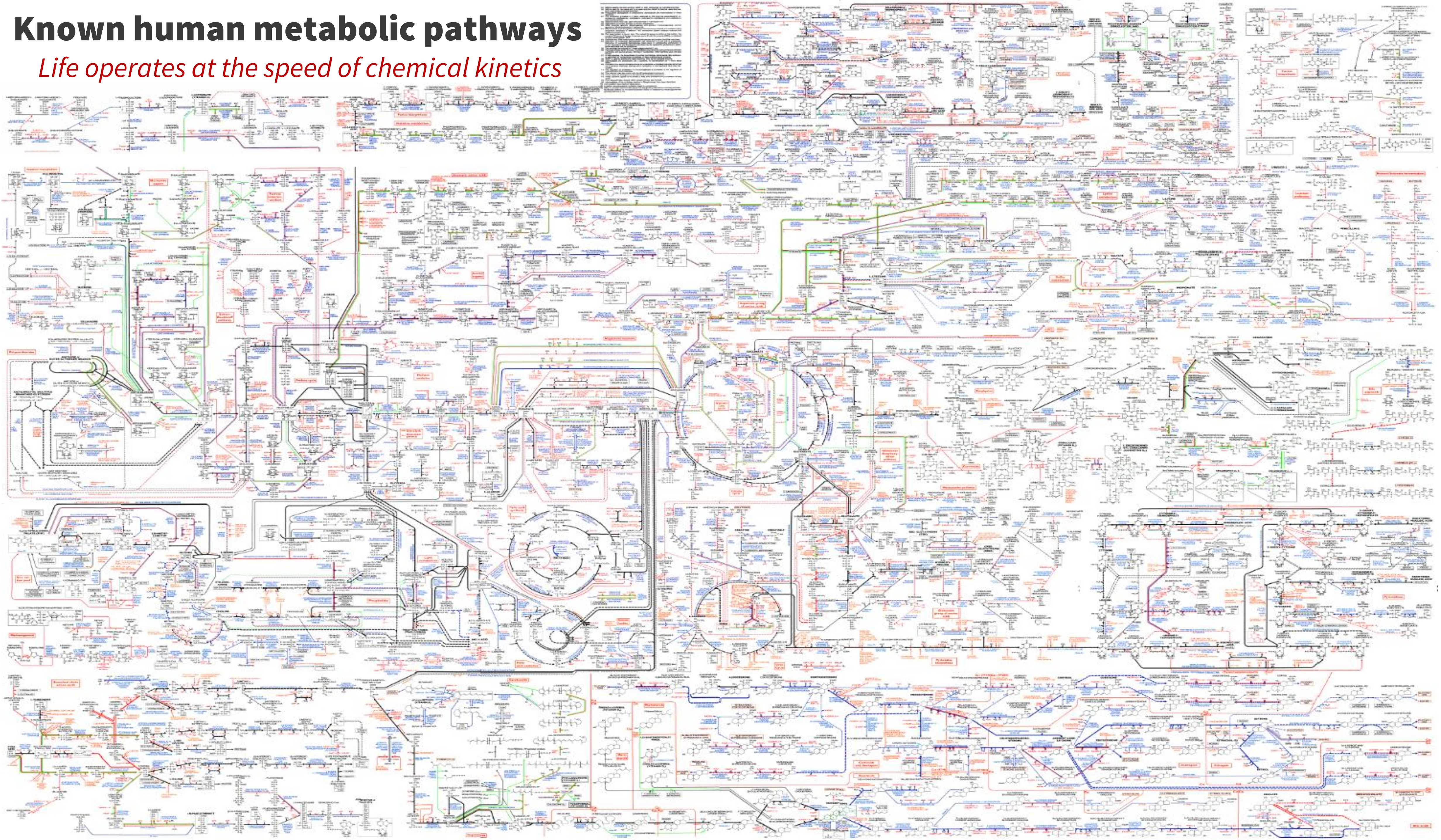
years

time


Why is important?

Known human metabolic pathways

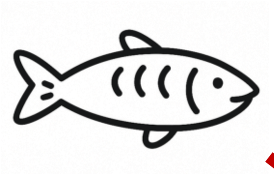
Life operates at the speed of chemical kinetics



Resource in moodle: High resolution map

Nitrosocompounds

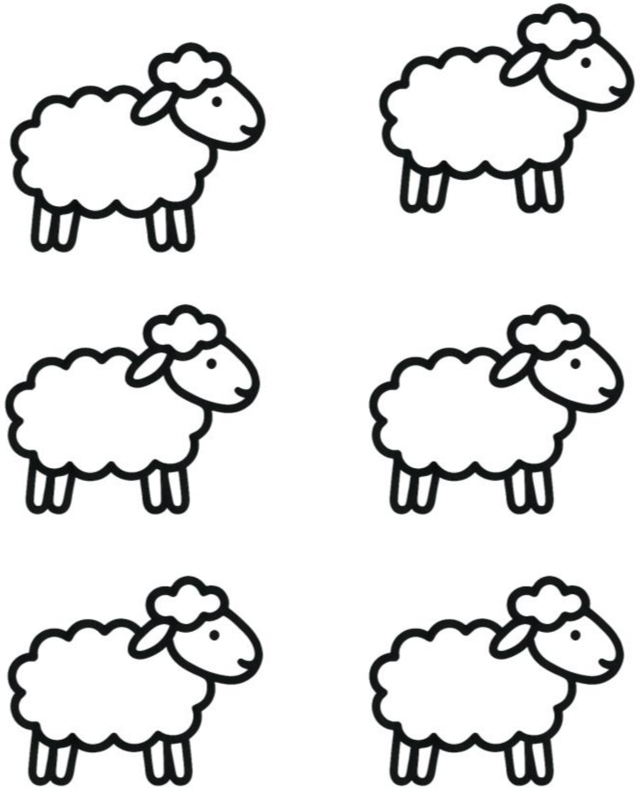
Norway, 1964



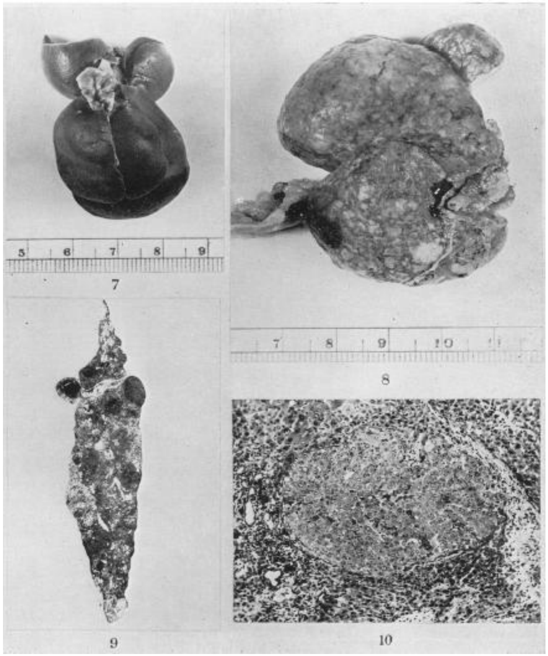
Herring

$NaNO_2$

Preservative



Hungry sheep

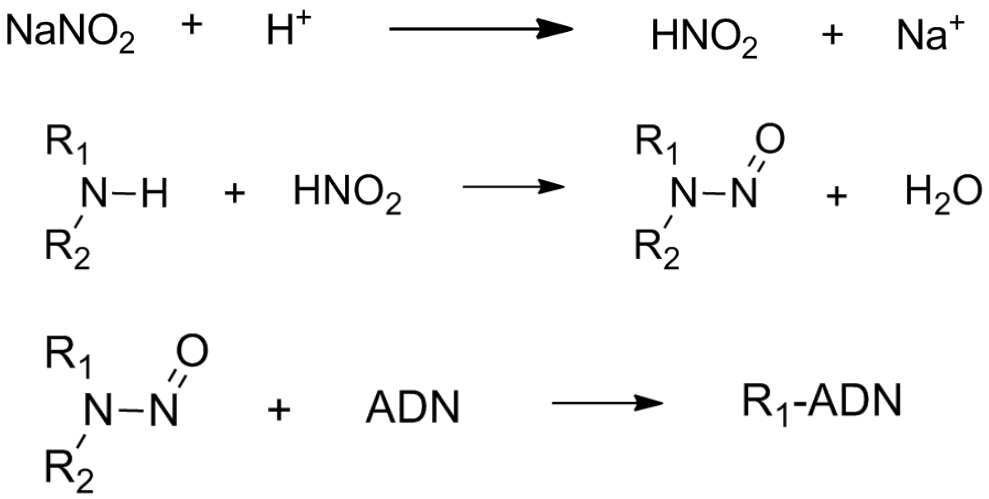


Hepatic cancer

https://doi.org/10.1186/bf03547224

Nitrosocompounds

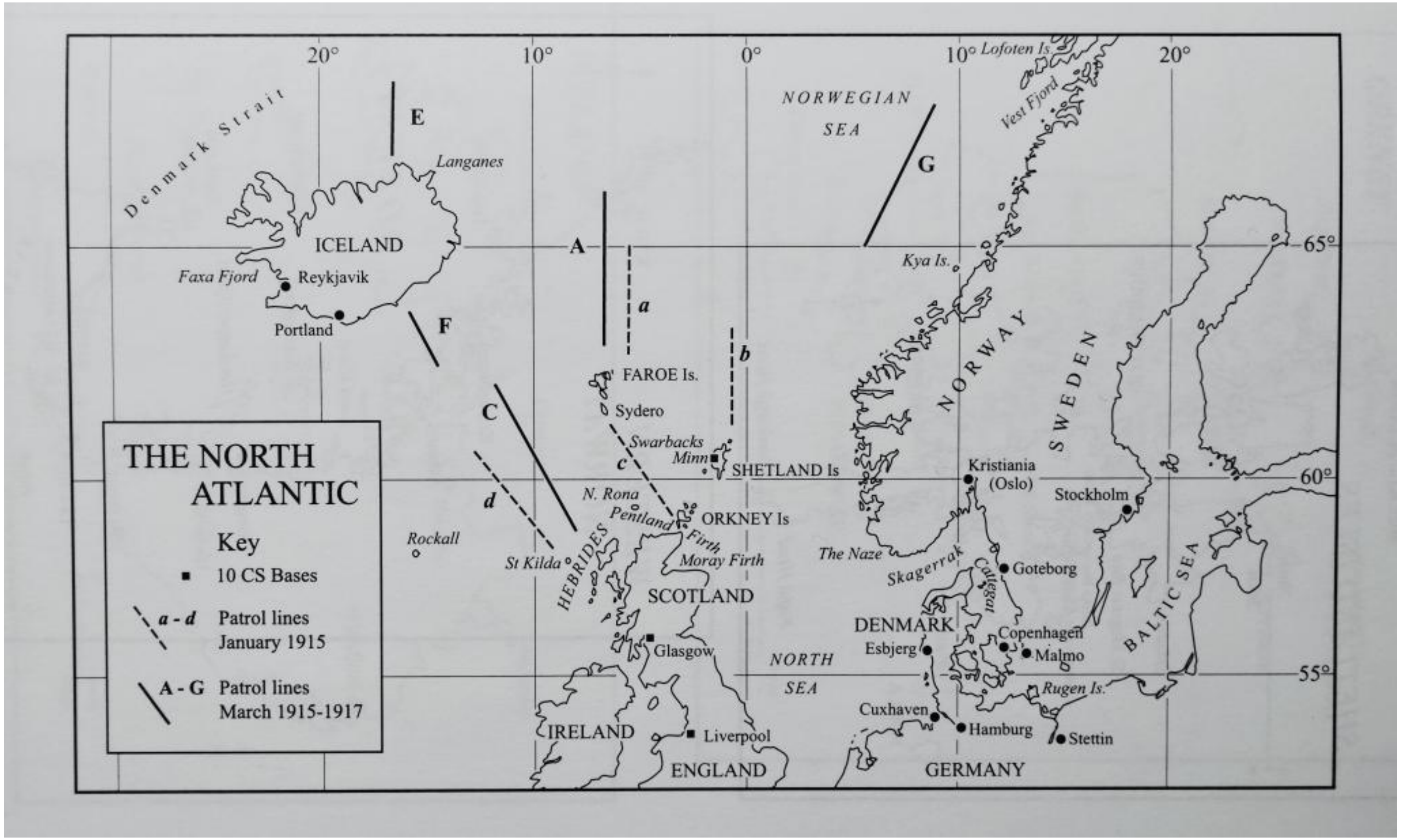
NaNO2 – Sodium nitrite (E250)



Is this reaction sufficiently rapid to generate a significant amount of nitrosocompounds within the duration of digestion?

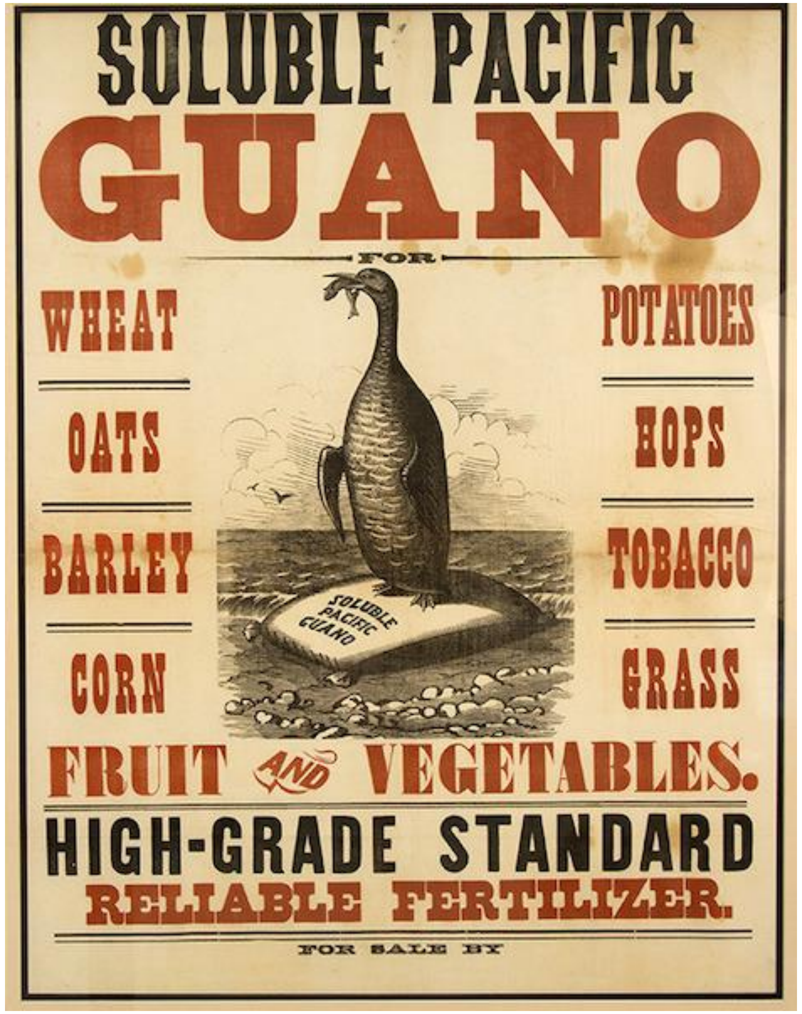
https://doi.org/10.1021/ja010348+

The Naval Blockade of Germany in WWI



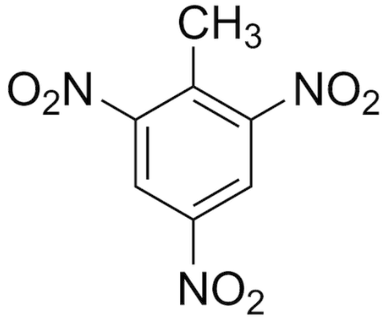
The Naval Blockade of Germany in WWI

Guano (Bird poo) mining

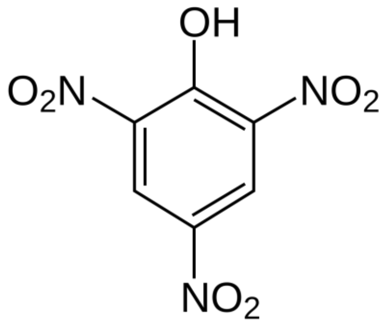


Germany relied on nitrate supplies to fertilize its agricultural land and thereby sustain food production for its population.

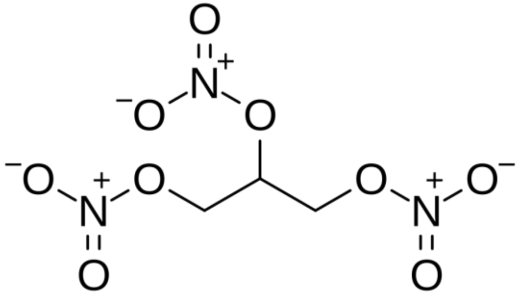
Most common explosives of WWI



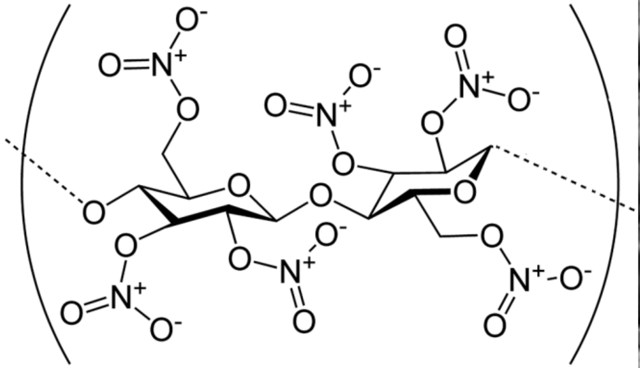
Trinitrotoluene



Picric acid



Nitroglycerin (dynamite)



Nitrocellulose

The Haber-Bosch Process

Fritz Haber (1868 –1934)

$$3\ H_2 + N_2 \nrightarrow 2\ NH_3$$

This reaction does not proceed because the molecules lack sufficient energy to break the N≡N triple bond

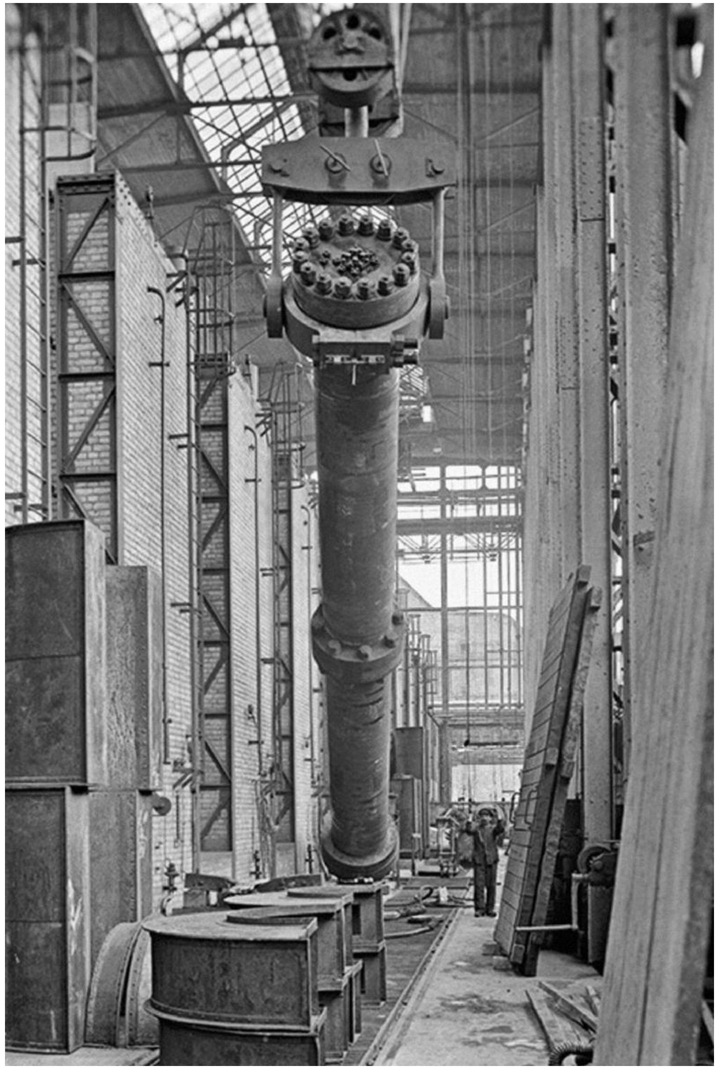
$$3\ H_2 + N_2 \xrightarrow{500\ °C,\ Fe} 2\ NH_3$$

This reaction proceeds in seconds

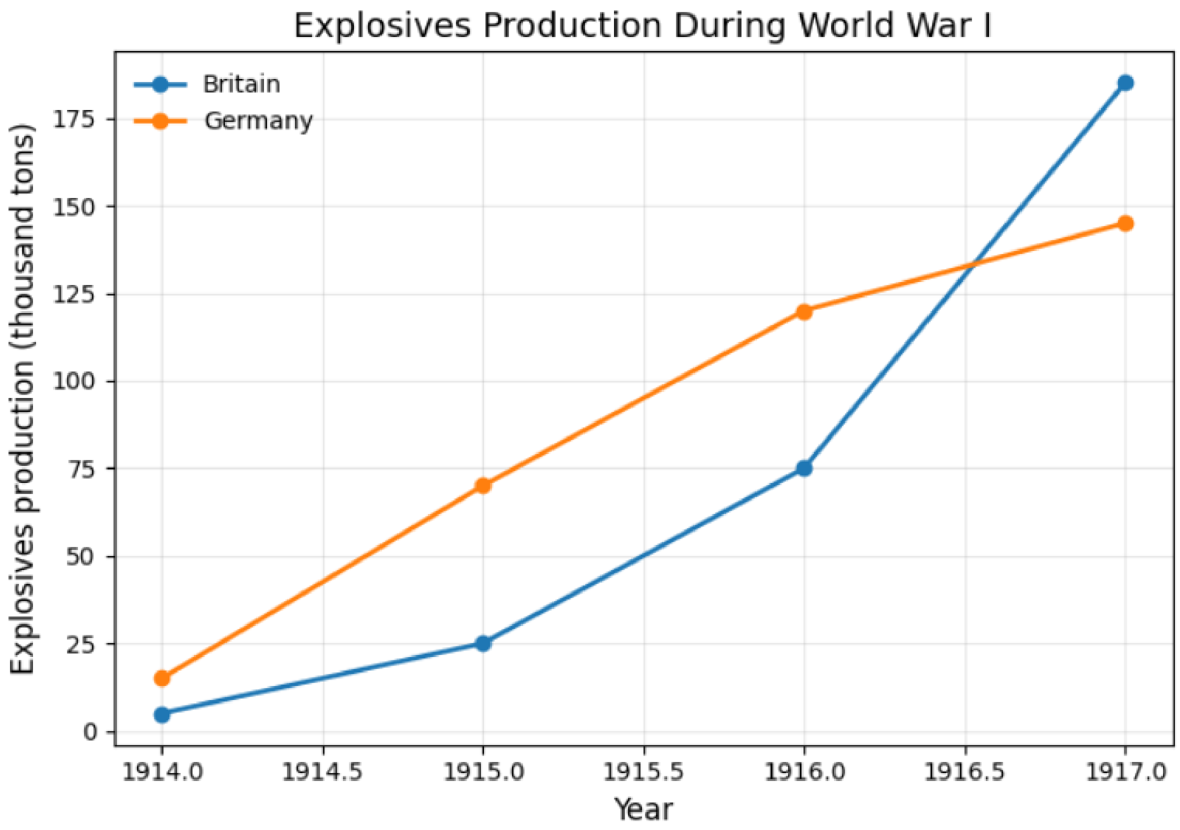
Carl Bosch (1874-1940)

🍎 **Resource in moodle:** Fritz Haber, the chemist of life and dead

The Haber-Bosch Process

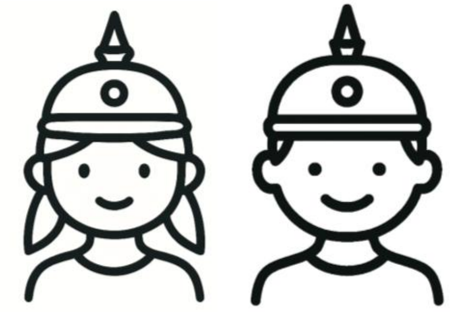


First Haber-Bosch reactor (1913)



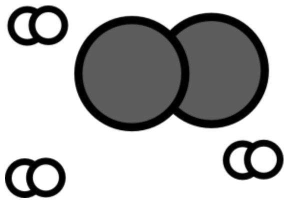
Definition of reaction rate

Imagine you are a German general…



$$3\,H_2 + N_2 \longrightarrow 2\,NH_3$$

…when will my ammonia be ready?



$$v = \frac{x_f - x_i}{t_f - t_i} = \frac{\Delta x}{\Delta t}$$

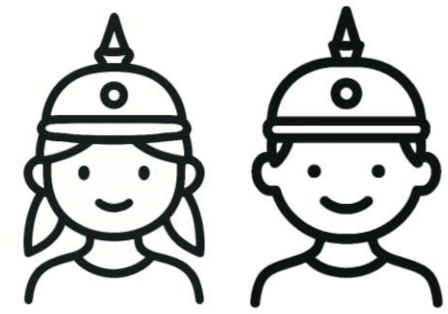
speed

$$r = \frac{(m_{NH_3})_f - (m_{NH_3})_i}{t_f - t_i} = \frac{\Delta m_{NH_3}}{\Delta t}$$

Chemical reactions occur through collisions between individual atoms, ions, or molecules. Reaction rates therefore depend on the number of reacting particles present.

Definition of reaction rate

Imagine you are a German general…

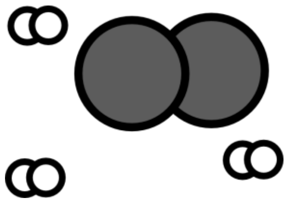


$$v = \frac{x_f - x_i}{t_f - t_i} = \frac{\Delta x}{\Delta t}$$

speed

$$3\ H_2 + N_2 \longrightarrow 2\ NH_3$$

…when will my ammonia be ready?

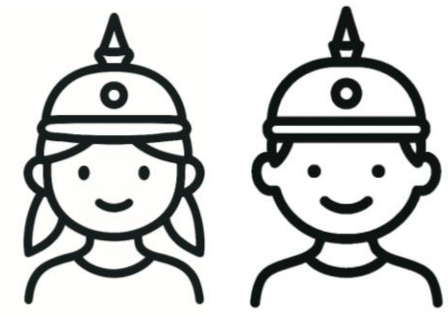


$$r = \frac{(mol_{NH_3})_f - (mol_{NH_3})_i}{t_f - t_i} = \frac{\Delta mol_{NH_3}}{\Delta t}$$

Much better! However, this is not independent of the system size…

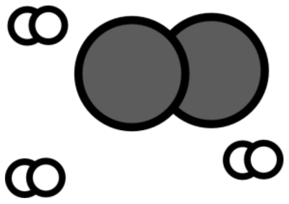
Definition of reaction rate

Imagine you are a German general…



$$3\ H_2 + N_2 \longrightarrow 2\ NH_3$$

…when will my ammonia be ready?



$$v = \frac{x_f - x_i}{t_f - t_i} = \frac{\Delta x}{\Delta t}$$

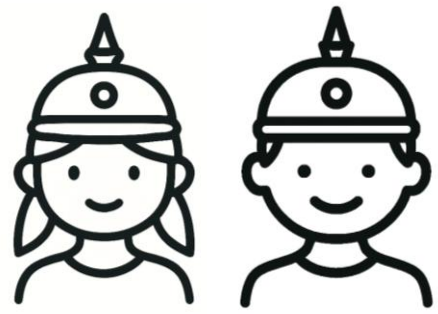
speed

$$r = \frac{[NH_3]_f - [NH_3]_i}{t_f - t_i} = \frac{\Delta [NH_3]}{\Delta t}$$

Almost there!

Definition of reaction rate

Imagine you are a German general…

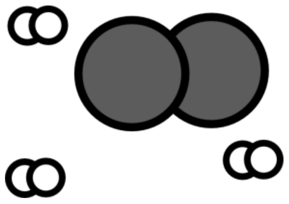


$$v = \frac{x_f - x_i}{t_f - t_i} = \frac{\Delta x}{\Delta t}$$

speed

$$3\,H_2 + N_2 \longrightarrow 2\,NH_3$$

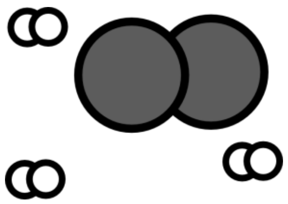
…when will my ammonia be ready?



$$r = \frac{1}{2}\frac{[NH_3]_f - [NH_3]_i}{t_f - t_i} = \frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$$

Perfection!

Definition of reaction rate



$$3\,H_2 + N_2 \longrightarrow 2\,NH_3$$

$$r = \frac{1}{2}\frac{\Delta[NH_3]}{\Delta t} = -\frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = -\frac{\Delta[N_2]}{\Delta t}$$

$$r = \frac{1}{\xi_P}\frac{\Delta[\text{Product}]}{\Delta t} = -\frac{1}{\xi_R}\frac{\Delta[\text{Reactant}]}{\Delta t}$$

Units: $\frac{1}{\xi_P(dimensionless)}\frac{\Delta[\text{Product}]\ (mol \cdot L^{-1})}{\Delta t\ (s)} = r(mol \cdot L^{-1} \cdot s^{-1}) = r(M \cdot s^{-1})$

Exercises

At a certain time in a reaction, it is observed that:

Substance **X** is disappearing at a rate of 3.0×10^{-2} M/s

Substance **Y** is disappearing at a rate of 6.0×10^{-2} M/s

Substance **Z** is appearing at a rate of 9.0×10^{-2} M/s

Which of the following could be the stoichiometry for the reaction being studied?

a) $X + Y \rightarrow Z$

b) $X + 2Y \rightarrow 3Z$

c) $2X + Y \rightarrow 3Z$

d) $3X + 6Y \rightarrow 9Z$

Exercises

Consider the following reaction:

$$2\ NO(g)\ +\ O_2(g)\ \rightarrow\ 2\ NO_2(g)$$

At a particular moment, the rate of disappearance of O_2 is measured to be 2.5×10^{-3} M/s.

a) What is the rate of disappearance of NO at this moment?
b) What is the rate of appearance of NO_2?
c) What is the overall rate of reaction?

Overall rate of reaction: The reaction rate that is independent of which reactant or product is being monitored.

Exercises

For the reaction:

$$4\ NH_3(g)\ +\ 5\ O_2(g)\ \longrightarrow\ 4\ NO(g)\ +\ 6\ H_2O(g)$$

At a certain instant, ammonia is being consumed at a rate of 0.24 M/s.

a) At what rate is oxygen being consumed?

b) At what rate is water being formed?

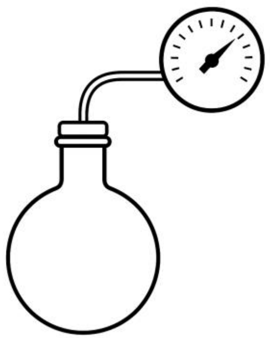
c) What is the overall rate of reaction?

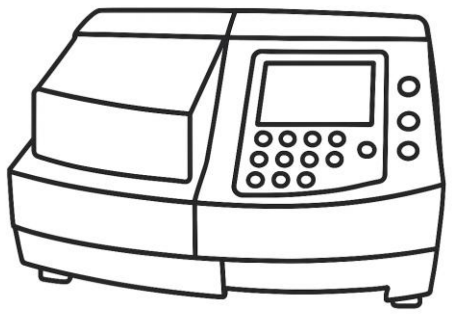
How to follow a chemical reaction

Short answer: *However you can…*

If it changes colour → measure the UV/Vis spectrum
If it forms or breaks a new type of bond → measure the IR spectrum
If it forms or consumes an acidic compound → measure the pH
If it releases a gas → measure the pressure
If it forms or removes ions → measure the conductivity
If you don't really know → measure by HPLC (just separate everything and see what shows up!)

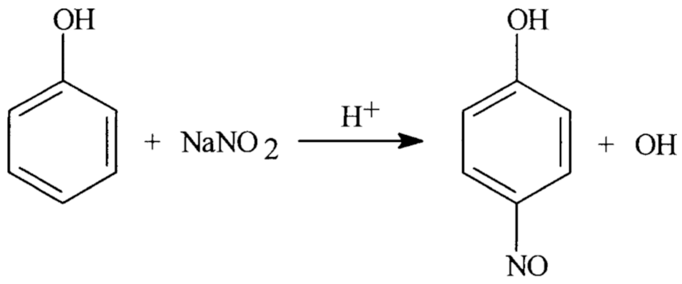
Be creative!!!


manometer

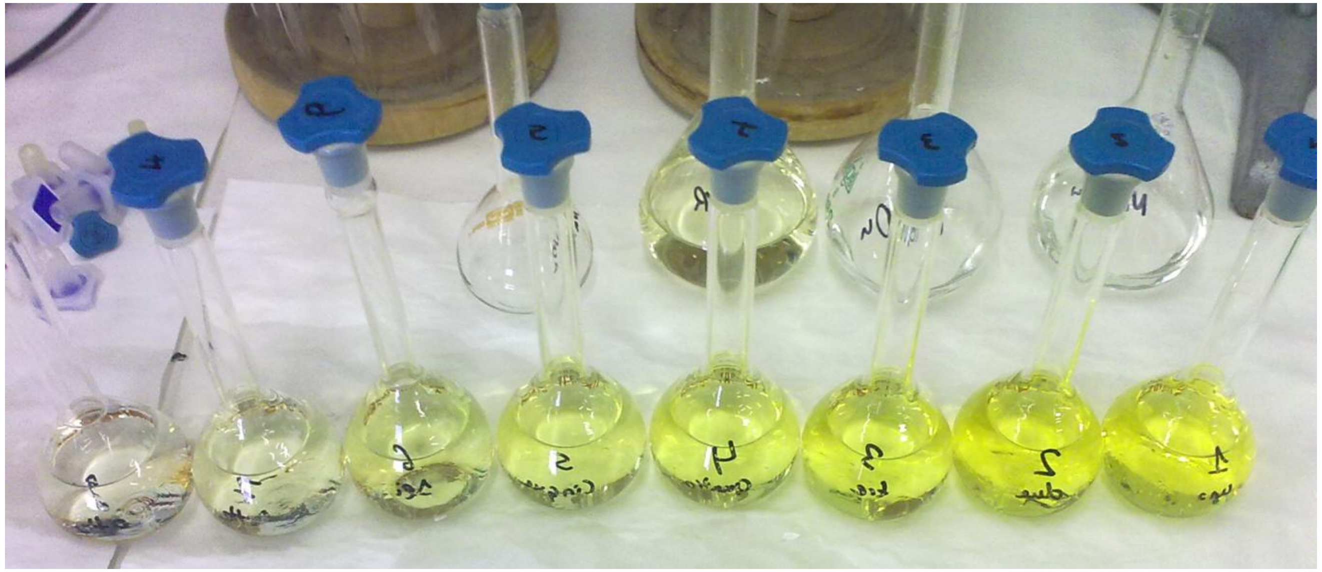

spectrometer


HPLC

Following a reaction using UV/Vis spectroscopy

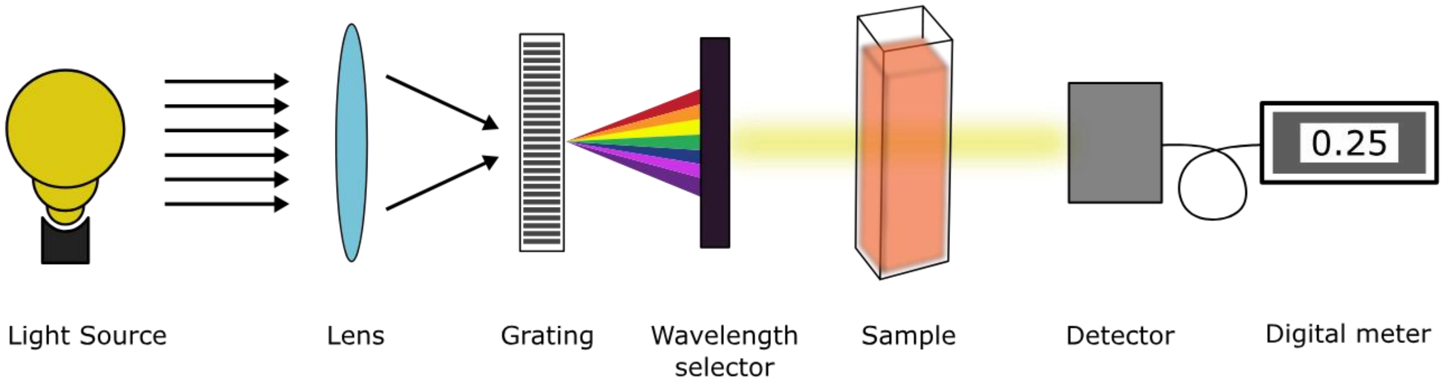


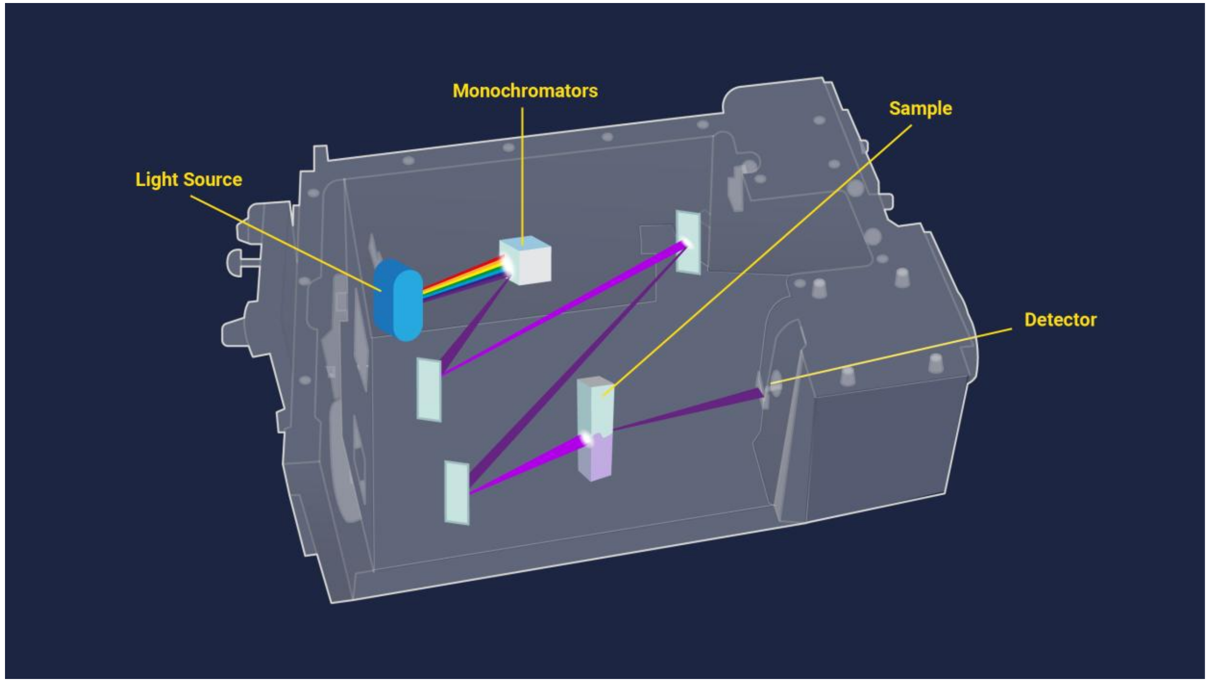
Nitrosation reaction of phenol



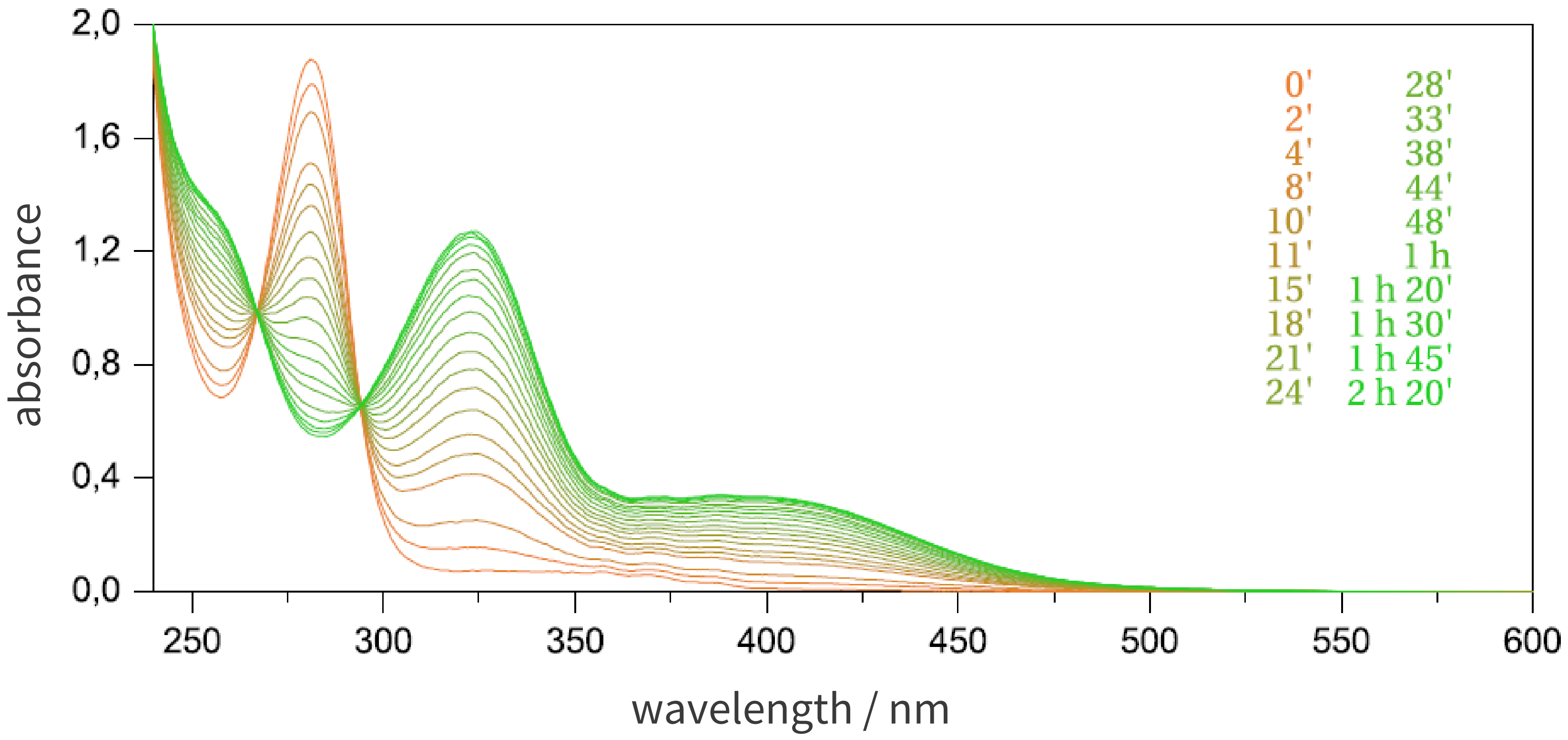
time

Following a reaction using UV/Vis spectroscopy





Following a reaction using UV/Vis spectroscopy



(Lambert-)Beer Law: The absorbance of a solution is directly proportional to the concentration of the absorbing species [s] and to the optical path length *l* through the solution. ε is a proportionality constant called the extinction coefficient, and it is unique for each substance and for each wavelength.

$$A = \varepsilon \cdot l \cdot [s]$$

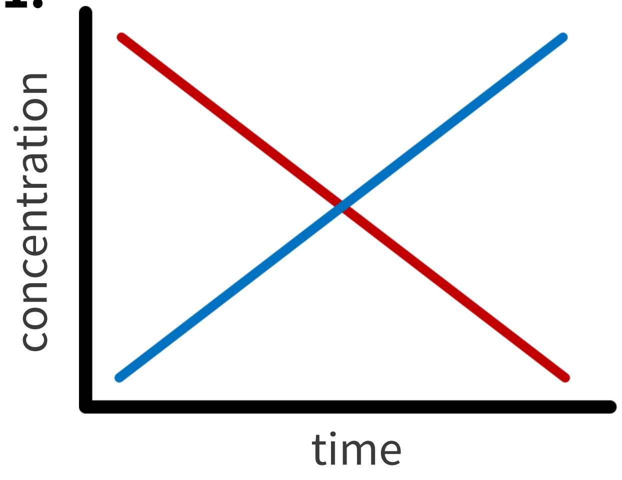
Challenge question

We have two reactants that undergo the following reaction to form a product.

$$A + B \longrightarrow C$$

Using one of the (somewhat imaginative) analytical techniques discussed earlier, we have been able to determine how the concentration of one reactant and the product evolve over time. If we plot these concentrations as a function of time, what would the graph look like?

1.



2.