Rate of reaction

The rate at which a reaction proceeds.

Following the rate of reaction with measurable quantities

Quantities that may be measured to indicate progress of a reaction

Quantity	Special Requirements
Pressure	Gas must be formed/ consumed, and a closed container must be used.
Volume of gas formed	Gas must be formed
Mass of a mixture	Some products should escape from the reaction mixture to produce a change in mass
Colour intensity	There must only be one coloured species in the reaction solution
Titrimetric analysis	Reaction progress should be able to be found by titration. Quenching (putting the reaction mixture into ice water) should be done before each trial to quickly stop the reaction.

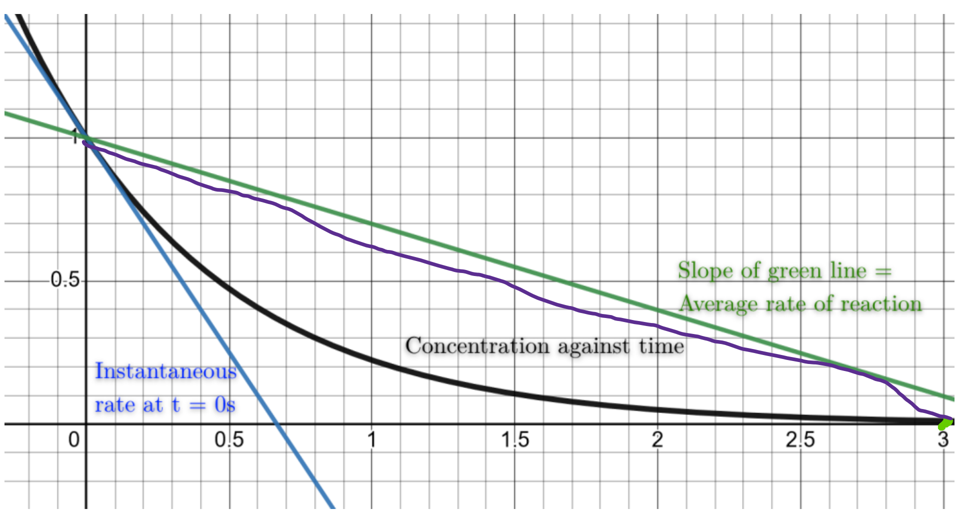
Fundamentally, rate is how fast a quantity changes **with respect to (wrt) time**

$$\text{Rate} = \frac{\Delta l}{\Delta t}, \text{where } l \text{ is quantity to be measured.}$$

As Δt *tends* to 0, we can get the *instantaneous rate of change*

$$\text{Instantaneous rate} = \lim_{\Delta t \to 0} \frac{\Delta l}{\Delta t} = \frac{dl}{dt}$$

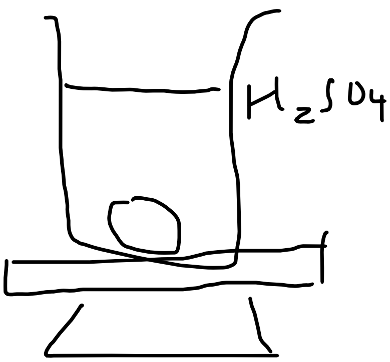
On a graph, the instantaneous rate of change of a (function) reaction can be represented by the gradient of the tangent line to the graph at that instant. [Fun demo graph]

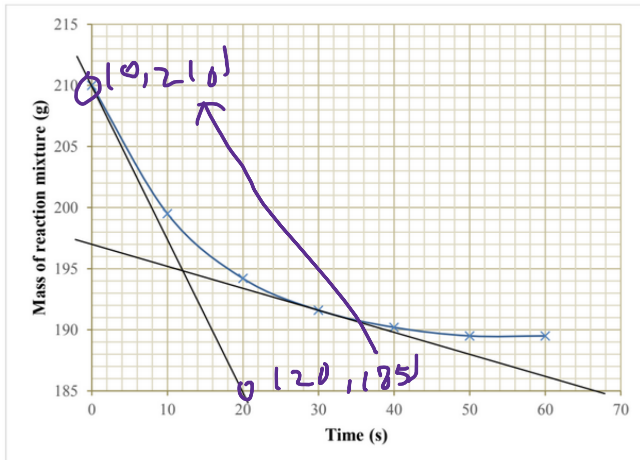


Without further to do, let's get into some examples.

Example 1: Mass of mixture

1. A sample of sodium hydrogencarbonate was added to excess dilute sulphuric acid. The mass of the reaction mixture was measured, and the results were presented in the following graph.





a. Explain why the mass of the reaction mixture decreases with time (1 mark)

$$2NaHCO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O + 2CO_2$$

$CO_{2(g)}$ is formed **and escapes the reaction mixture as it is a gas.** So the mass of the mixture will decrease.

b. Calculate, with the information from the above graph:

i. Average rate of reaction from t = 0 to t = 50s

$$\text{Rate} = \left|\frac{189.5 - 210}{50}\right| = 0.41 \text{ gs}^{-1}$$

ii. Instantaneous rate at the 30th second (t = 30s)

$$\text{Rate} = \left|\frac{191.5 - 197}{30}\right| = 0.183 \text{ gs}^{-1}$$

iii. Initial rate of the reaction – Instantaneous rate of reaction at t = 0s

(Find the slope of the tangent line to the curve at t=0s)

$$Rate = \left|\frac{185 - 210}{20}\right| = 1.25g\ s^{-1}$$

c. Is the rate of reaction higher initially or at the 30th second?

Higher initially, the slope of the tangent line to the curve at t=0s is steeper than that at t=30s

d. Calculate the mass of $NaHCO_{3(s)}$ used.

$$2NaHCO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O + 2CO_2$$

Change in mass = 20.5g → 20.5g CO_2 formed (0.465 mol)

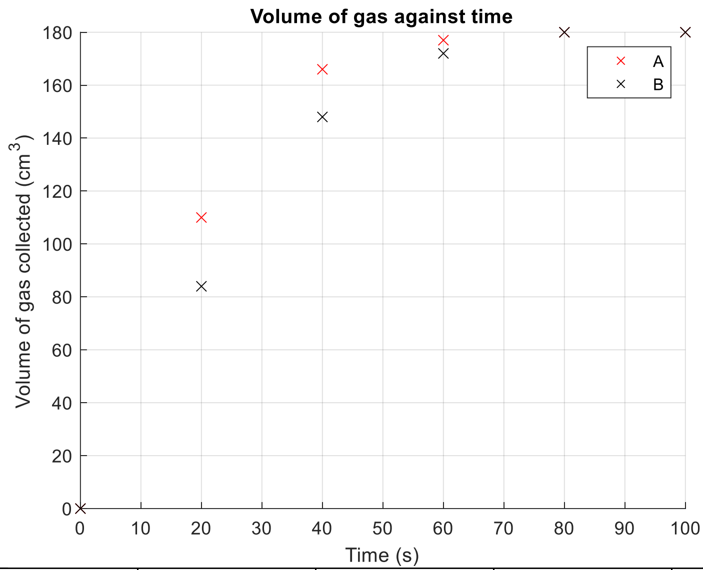
Mol of $NaHCO_3$: Mol of CO_2 = 1:1 → Mol of $NaHCO_3$ = 0.465 mol

Mass of $NaHCO_3$ = 0.465 (23+1+12+16*3) = 39.1g

Example 2: Volume of gas given off

Two conical flasks A and B contained equal volumes of dilute hydrochloric acid with different concentrations. Equal masses of limestone chips of similar sizes and shapes were added to the two flasks. The volumes of gas given off were measured at regular intervals and were recorded in the following tables.

thanks MATLAB



Time(s)	0	20	40	60	80	100
Flask **A** (cm^3)	0	110	166	177	180	180
Flask **B** (cm^3)	0	84	148	172	180	180

2. With reference to the graph, answer the following questions:
   a. Determine the average reaction rates in flasks A and flask B over the entire reaction from t = 0 s to t = 100s.

$$\text{Rate}_{\text{AB}} = \frac{180 - 0}{100} = 1.8 \text{ cm}^3 \text{ s}^{-1}$$

   b. Explain which flask contains a higher concentration of hydrochloric acid.

A has a higher concentration of hydrochloric acid, because the slope of the tangent to A at t=0s is steeper than that of B, indicating that A has a higher initial rate of reaction, which is achieved by having a higher concentration of HCl.

   c. Explain whether calcium carbonate is the limiting reactant in both flasks.

Yes, the two flasks contain different amount of mol of HCl, yet they form the same amount of CO_2 in the end.

   d. State how you can calculate the instantaneous rate in flask A at the 20th second.

Calculate the slope of the tangent (line) to the curve of flask A at t=20s.

Example 3: [MC] Colorimetry

3. That question

28. **[2021-Q26]**
Refer to the following experiment on the study of the rate of reaction between $HCO_2H(aq)$ and $Br_2(aq)$ at a certain temperature. It is given that the rate depends on both the concentrations of $HCO_2H(aq)$ and $Br_2(aq)$:

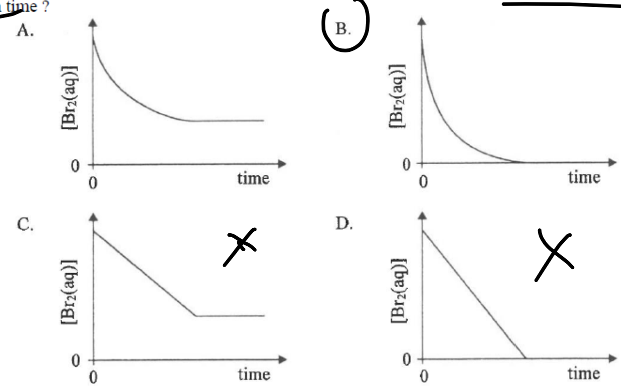
$$HCO_2H(aq) + Br_2(aq) \rightarrow 2HBr(aq) + CO_2(g)$$

$2{,}5 \cdot 10^{-4}$

5.0 cm^3 of 0.05 M $HCO_2H(aq)$ are separately added to four conical flasks each containing $Br_2(aq)$ prepared by mixing different volumes of 0.05 M $Br_2(aq)$ and water as shown in the table below :

Conical flask	Volume of 0.05 M $Br_2(aq)$ / cm^3	Volume of water / cm^3
A	1.0	4.0
B	2.0 $1 \cdot 10^{-4}$	3.0
C	3.0	2.0
D	4.0	1.0

Which of the following graphs best represents the variation of $[Br_2(aq)]$ in the reaction mixture of conical flask **B** with time ?



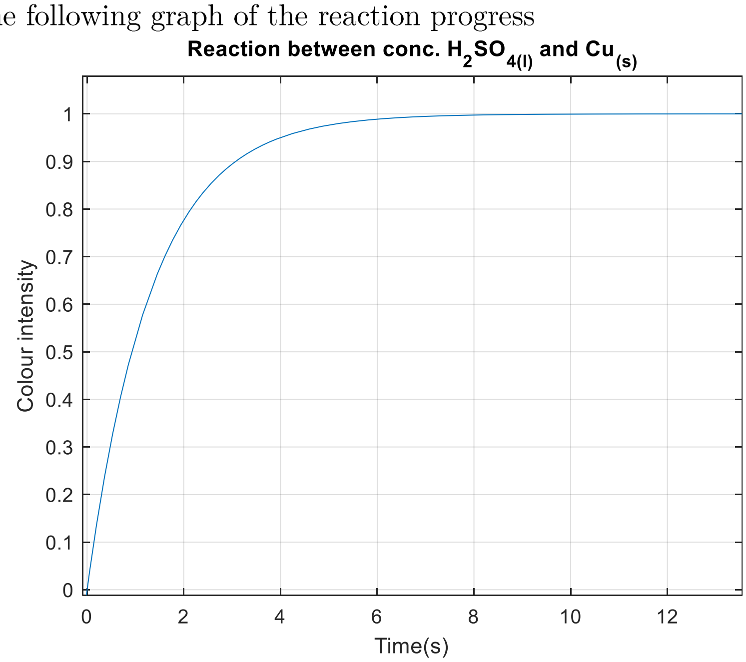
Example 4: Colorimetry (again)

4. Consider the following reaction between conc. $H_2SO_{4(l)}$ and $Cu_{(s)}$

   a. Write the equation for the reaction, state the colour change in the solution

$$2H^+ + H_2SO_4 + Cu \rightarrow SO_2 + 2H_2O + Cu^{2+}$$

   b. Consider the following graph of the reaction progress



i. Here colour intensity is measured, why is this a suitable way to track the progress of the reaction?

Cu^{2+} ions are the only colour species with a blue colour.

ii. If the absorbance is measured instead of colour intensity, what should be the colour of the colour filter of the absorbance meter such that a similar graph to above is produced?

Orange

iii. It is given that the initial mass of $Cu_{(s)}$ is 8.90g, calculate the average rate of reaction in g s^{-1}. Assume conc. H_2SO_4 to be in excess.

$$\overline{\text{Rate}} = \frac{\Delta \text{m}}{\Delta \text{t}} = \frac{8.90}{8} = 1.11\ \text{gs}^{-1}$$

iv. Give another method to track the progress of the reaction

Measure the volume of $SO_{2(g)}$ formed during the reaction.

Factors affecting rate of reaction

Concentration of reactant(s)	Higher concentration → Higher rate of reaction
Temperature	Higher temperature → Higher rate of reaction
Surface area	Higher surface area to volume ratio → Higher rate of reaction
Catalyst	Positive Catalyst → Higher rate of reaction Negative Catalyst (inhibitor) → Lower rate of reaction # Almost ALL catalysts you see in chemistry DSE are positive catalyst

How to answer questions!

Formula to answering rate questions:

[Factor] + **higher/lower frequency of effective collisions + rate of reaction increases/decreases.**

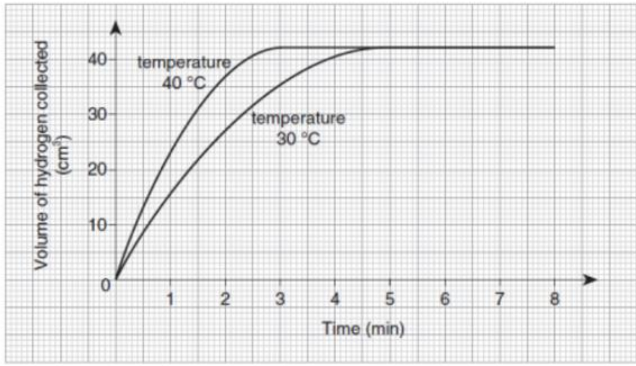
Concentration & Surface area: Particles have larger change to collide with each other

Temperature: Reactant particles possesses more kinetic energy

Catalyst: Provides alternative reaction pathway with lower activation energy (Industrial Chemistry)

Example 5: Magnesium

5. When magnesium reacts with hydrochloric acid, it produces hydrogen. Two experiments were carried out at different temperatures to study the reaction. The hydrogen gas evolved was measured at regular time intervals in each experiment. The graph shows the experimental results.

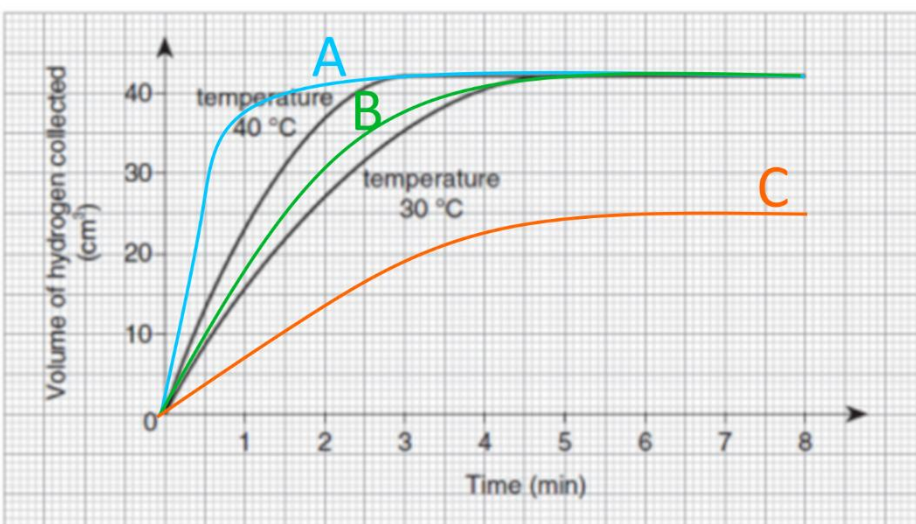


a. State the relationship between the reaction rate and temperature. Explain your answer at molecular level.

At higher temperatures, the average molecular kinetic energy increases ($E = 3/2\ k_BT$). They move faster and have a higher chance of colliding with other molecules. This increases the **frequency of effective collision**, thus the rate of reaction increases at higher temperatures.

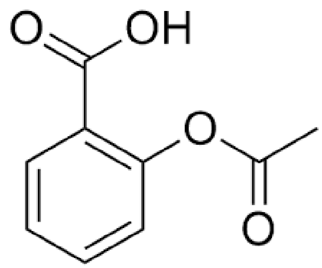
b. Sketch, in the below diagram, the curves A, B and C to show the variations of the volume of hydrogen according to the following conditions at 40^{o}C. Label the curves using the letters below.

A	**B**	**C**
Magnesium metal is cut into smaller pieces but total mass is still the same	Molarity of HCl decreases but HCl is still in excess	Molarity of HCl decreases and HCl becomes the limiting reactant



Example 6: Aspirin

6. Aspirin is a fever-reducing drug. Experiments were carried out to determine the rate of reaction between aspirin and water in body fluid. The structure of aspirin is shown below:



a. The following table shows the data collected for the *hydrolysis* of aspirin at pH 7.0 and 37 ^{o}C. Calculate the average rate of reaction (in M h^{-1}) in the first 50 hours.

Time (hour)	0	10	20	30	40	50
Concentration of product (M)	0	0.20	0.40	0.59	0.77	0.94

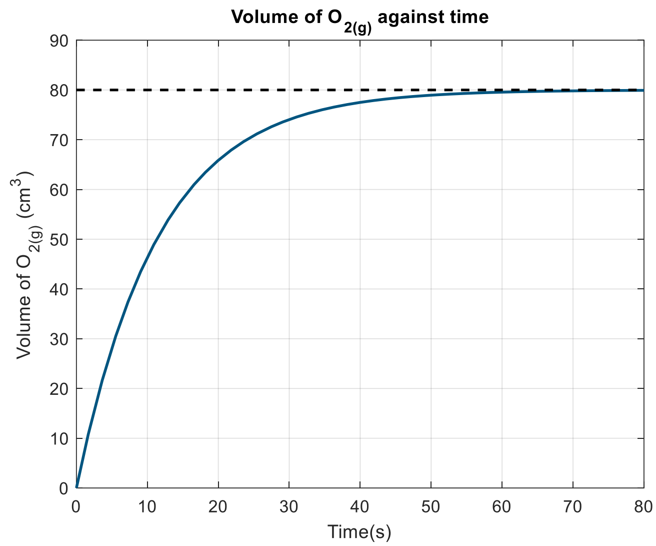
$$\text{Rate} = \frac{0.94}{50} = 0.0188\ \text{M h}^{-1}$$

b. Would the reaction rate calculated in (a) be underestimated or overestimated in the actual hydrolysis of aspirin in stomach? Explain your answer.

There is HCl in our stomach, so the pH of our stomach is much lower than 7.0. Therefore, the [H^+] concentration is much higher. As H^+ acts as a acid catalyst for hydrolysis, the rate of reaction of hydrolysis of aspirin will be higher inside our stomachs → This is an underestimation.

Example 7: Hydrogen peroxide

7. Manganese(IV) oxide is a catalyst of decomposition of Hydrogen peroxide (H_2O_2) into oxygen and water. The setup contains H_2O_2 in presence of Manganese(IV) oxide at room temperature. In the experiment, the volume of oxygen evolved with time is recorded and the results are shown on the following graph.



a. Write down the chemical equation for the decomposition of $H_2O_{2(aq)}$

b. Why is the graph flat after t = 70s?

c. How will the rate of reaction be affected if $H_2O_{2(aq)}$ was placed into the freezer prior to the experiment? Explain your answer.

d. An smaller volume of $H_2O_{2(aq)}$ but at a higher concentration is used instead, sketch the resulting graph of volume of gas collected against time, assuming that the amount of mol of H_2O_2 in the new solution is less than the original solution. Explain the shape of the graph.

e. Suggest a method to increase the rate of reaction by improving the catalytic effectiveness of the Manganese(IV) oxide catalyst.

Molar volume of gases

According to more physics, the volume of gases is the same regardless of the type/compound of the gas molecules. It is determined experimentally that one mole of gas will occupy 24 dm^3 at room temperature and pressure (rtp, i.e. 298K & 1atm). In other words, *molar volume* **FOR ALL GASES** = 24 dm^3

$$\mathrm{V} = 24 \cdot n$$

Where: V = Volume occupied by gas AT RTP

n = Number of moles of gas molecules

Example:

Volume occupied by 1 mol of $SO_{2(g)}$

$$V = 24 \cdot 1 = 24 \text{ dm}^3$$

Number of mole of $CO_{2(g)}$ in 1.2 dm^3 at rtp.

$$n = \frac{1.2}{24} = 0.05 \text{ mol}$$

Continuation, mass of $CO_{2(g)}$ in 1.2 dm^3 at rtp:

$$m = \ 12 + 16 \cdot 2 \ \ \cdot n$$

$$m = 44 \cdot 0.05 = 2.2\text{g}$$

There is also concentration of gas, given by:

$$[gas] = \frac{n}{V}$$

At rtp, where all gases have the same molar volume.

$$[gas] = \frac{1}{24} = 0.0417 \text{ mol dm}^{-3}$$

It is important to remember that such calculations only hold at rtp (298K & 1atm). For all other pressures the molar volumes are different. However, all gas molecules still behave the same (to a certain extent). If you are interested in how different temperatures and pressure affect gases for chemistry, you may look at the *ideal gas law* as follows:

$$PV = nRT$$

Where: P = Pressure (Pa); V = Volume (m^3); n = number of mole (mol);

Universal gas constant: R = 8.31 (J mol^{-1} K^{-1}); T = Temperature (K)

This law will be useful for understanding certain concepts of the next topic (chemical equilibrium), though it will not be assessed in actual chemistry exams.

Example 8: Sodium azide (Partly adapted from DSE 2013 Q11)

8. The operation of automobile airbags depends on the rapid decomposition of sodium azide, NaN_3, to its elements. A balanced equation for this decomposition is shown below:

$$2\ NaN_{3(s)} \rightarrow 2\ Na_{(s)} + 3\ N2_{(g)}$$

a. If an airbag has a volume of 6.50×10^4 **cm³**, calculate the number of moles of nitrogen gas required to fill it at room temperature and pressure.

b. Calculate the mass of sodium azide needed to provide such volume of nitrogen. (Relative atomic mass of N = 14.0 , Na = 23.0)

c. If the decomposition is complete in 38×10^{-3} s, calculate the average rate of formation of nitrogen in dm^3s^{-1}.

In fact, airbags also contain $KNO_{3(s)}$, which can further react with $Na_{(s)}$ as follows:

$$10Na_{(s)} + 2KNO3_{(s)} \rightarrow K_2O_{(s)} + 5Na_2O_{(s)} + N_{2(g)}$$

d. Explain why $NaN_{3(s)}$ and $KNO_{3(s)}$ are used in the form of fine powder.

e. Considering both reactions, calculate the theoretical volume of $N_{2(g)}$ formed at rtp when the bag is inflated. Given that there are 100g of $NaN_{3(s)}$ and 200g of $KNO_{3(s)}$ inside an airbag. (Formula masses: NaN3 = 65.0, KNO3 = 101.1; Molar volume of gas at room temperature and pressure = 24 dm3)

f. The main function of NaN3(s) is to produce N2(g) for inflating the airbags. Suggest why it is necessary to include KNO3(s) in the airbags.