VICTORIA JUNIOR COLLEGE CHEMISTRY DEPARTMENT Dr WU Jiang (wu.jiang@vjc.sg)



REACTION KINETICS

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Completed by	T2W6	T2W7	T2'	W8	T2W9
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- 3 Experimental methods of finding reaction rates
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Reference Texts

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- 1. Chemistry for Advanced Level by Peter Cahn / Hughes
- 2. Advanced A Level Chemistry by Ramsden
- 3. Chemistry in Context by Hill & Holman

Learning outcomes (9729 H2 Chemistry)

Candidates should be able to:

- (a) explain and use the terms: rate of reaction; rate equation; order of reaction; rate constant; half-life of a reaction; rate-determining step; activation energy; catalysis
- (b) construct and use rate equations of the form rate = k[A]^m[B]ⁿ (limited to simple cases of single-step reactions and of multi-step processes with a rate-determining step, for which m and n are 0, 1 or 2), including:
 - (i) deducing the order of a reaction by the initial rates method
 - (ii) justifying, for zero- and first-order reactions, the order of reaction from concentration-time graphs
 - (iii) verifying that a suggested reaction mechanism is consistent with the observed kinetics
 - (iv) predicting the order that would result from a given reaction mechanism
 - (v) calculating an initial rate using concentration data [integrated forms of rate equations are not required]
- (c) (i) show understanding that the half-life of a first-order reaction is independent of concentration
- (ii) use the half-life of a first-order reaction in calculations
- (d) calculate a rate constant using the initial rates method
- (e) devise a suitable experimental technique for studying the rate of a reaction, from given information
- (f) explain qualitatively, in terms of collisions, the effect of concentration changes on the rate of a reaction
- (g) show understanding, including reference to the Boltzmann distribution, of what is meant by the term activation energy
- (h) explain qualitatively, in terms both of the Boltzmann distribution and of collision frequency, the effect of temperature change on a rate constant (and hence, on the rate) of a reaction
- (i) (i) explain that, in the presence of a catalyst, a reaction has a different mechanism, i.e. one of lower activation energy, giving a larger rate constant
 - (ii) interpret this catalytic effect on a rate constant in terms of the Boltzmann distribution
- (j) outline the different modes of action of homogeneous and heterogeneous catalysis, including:
 - (i) the Haber process
 - (ii) the catalytic removal of oxides of nitrogen in the exhaust gases from car engines
 - (iii) the catalytic role of atmospheric oxides of nitrogen in the oxidation of atmospheric sulfur dioxide
 - (iv) catalytic role of Fe²⁺ in the I⁻/S₂O₈²⁻ reaction
- (k) describe enzymes as biological catalysts which may have specific activity
- (I) explain the relationship between substrate concentration and the rate of an enzyme-catalysed reaction in biochemical systems

Learning outcomes (8873 H1 Chemistry)

Candidates should be able to:

- (a) explain and use the terms: rate of reaction; rate equation; order of reaction; rate constant; half-life of a reaction; activation energy; catalysis;
- (b) construct and use rate equations of the form rate = k[A]^m[B]ⁿ (limited to simple cases of single-step reactions, for which m and n are 0, 1 or 2), including:
 - (i) deducing the order of a reaction by the initial rates method;
 - (ii) justifying, for zero- and first-order reactions, the order of reaction from concentration-time graphs;
 - (iii) calculating an initial rate using concentration data; [integrated forms of rate equations are not required]
- (c) show understanding that the half–life of a first–order reaction is independent of concentration;
- (d) explain qualitatively, in terms of collisions, the effect of concentration changes on the rate of a reaction;
- (e) show understanding, including reference to the Boltzmann distribution, of what is meant by the term activation energy;
- (f) explain qualitatively, in terms both of the Boltzmann distribution and of collision frequency, the effect of temperature change on a rate constant (and, hence, on the rate) of a reaction;
- (g) (i) explain that, in the presence of a catalyst, a reaction follows a different pathway, i.e. one of lower activation energy, giving a larger rate constant;
 - (ii) interpret this catalytic effect in terms of the Boltzmann distribution;
- (h) Outline the mode of action of heterogeneous catalysis, as exemplified by the catalytic removal of oxides of nitrogen in the exhaust gases from car engines.
- (i) describe enzymes as biological catalysts which may have specific activity.

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1 Introduction

Industrially, chemists want to know the rate of a reaction as they want the most economical process of making a product. This would not only save time but makes it profitable as well.

Archaeologists can estimate the age of fossils of prehistoric remains by a process known as radioactive decay. This involves measuring the concentration of a decaying radioactive isotope ¹⁴C in the object under study.

Reaction kinetics is the study of the rates of chemical reactions, which include the factors that affect them and the mechanisms by which the reactions occur.

2 Concept of Reaction Rate

The rate of reaction can be defined as the **change** in the **concentration** of a particular reactant or product **per unit time**. Mathematically, it can be calculated as:

Rate of reaction =

The rate can show how fast a product is formed or how fast a reactant is used up in a given time. It has the unit of **mol dm⁻³ s⁻¹**. (sometimes, **mol dm⁻³ min⁻¹** may be used.)

For a hypothetical reaction, $aA + bB \rightarrow cC + dD$

rate =
$$-\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

Worked Example 1

For reaction, $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$, the concentration-time graph is given below.



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Making Thinking Visible			man da se for an aller
1. How do we get the concentration-time gr	aph?	a reactant or formation of a	product from the
Is the rate of consum of reaction?	ption of a reactant or fo	rmation of a product always th	e same as the rate
Why is it necessary reaction?	to divide by the stoich	niometric coefficient when calc	culating the rate of
 Why is there a negati of a reactant? 	ve sign when determini	ng the rate of reaction based o	n the concentration

Exercise 1: (with reference to the graph on page 3)

- 1. Without drawing a tangent, suggest the rate of formation of O_2 at 100 s.
- 2. Determine from the graph the rate of reaction at t = 150 s.

Instantaneous rate v.s. Average rate

In the earlier discussion, we have used the instantaneous rate to represent the rate of reaction.

The **instantaneous rate** is the rate at **a particular time**, i.e. the rate **at a particular instant** during the reaction.

That is why the tangent is plotted at the particular time before the gradient is plotted.

The **average rate** of a reaction during **a specified time interval** is the change in concentration of a reactant or a product over that **time interval**.



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Concept of Initial Rate

Initial rate is the _____

It is the rate at the start of a reaction, when an **infinitely small amount** of the reactant has been used up. In the figure, the gradient of the tangent to the curve at t = 0 gives the initial rate.



Initial rate =
$$\frac{0.0023}{50}$$
 = 4.60 x 10⁻⁵ mol dm⁻³ s⁻¹

Theoretically, the initial rate refers to the instantaneous rate at time t = 0. However, in practice, the initial rate can be approximated by the average rate provided that,

- 1. The time interval is small enough and
- 2. The time interval starts from t = 0.

Assumptions: when a small amount of reactant is used (or when a small amount of product is formed), the initial portion of the graph is almost linear.

3 Experimental Methods of Measuring Reaction Rates

To measure the rate of a reaction, it is necessary to measure the way in which **concentration of reactants or products** changes with time at **a fixed temperature**.

Any <u>property proportional to the concentration of product or reactant</u> can be measured e.g. pressure (for gases), colors, pH etc. The method used will therefore depend on the reaction under consideration.

3.1 <u>Titrimetric Analysis</u>

This is very suitable for reactions in solutions such as that between iodine and propanone catalysed by acid.

 $\begin{array}{rrrr} \mathsf{H}^{+} \\ \mathsf{CH}_3\mathsf{COCH}_3 & + & \mathrm{I}_2 & \rightarrow & \mathsf{CH}_3\mathsf{COCH}_2\mathrm{I} & + & \mathsf{H}^{+} & + & \mathrm{I}^{-} \end{array}$

Method:

- A small portion of the reaction mixture is removed and analysed at a fixed time interval.
- The removed portion is added to some reagent to '**quench**' i.e. stop the reaction. This prevents further changes in concentration before analysis is carried out.

Reaction Kinetics

 Making Thinking Visible

 1. Why is quenching necessary?

 2. How is quenching done?

Worked Example 2:

In the reaction between I_2 and CH_3COCH_3 , portions of the reaction mixture can be pipetted into NaHCO₃ solutions. This quenches the reaction by neutralising the acid present.

The quenched mixture can then be analysed by titrating the <u>unreacted iodine</u> against a standard solution of sodium thiosulfate, $Na_2S_2O_3$.



Exercise 2:

Similarly, the alkaline hydrolysis of an ester can also be analysed:

 $\mathsf{HCOOCH}_3 \quad \textbf{+} \quad \mathsf{OH}^- \quad \rightarrow \quad \mathsf{HCOO}^- \ \textbf{+} \quad \mathsf{CH}_3\mathsf{OH}$

Suggest the following:

- 1. The reagent of which its concentration could be determined:
- 2. Quencher: _____
- 3. Indicator for the titration: ______
- 4. Colour change at the end-point:

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3.2 Colorimetric Analysis

This is convenient for systems in which one of the substances is colored. The intensity of color can be followed during the reaction using a photoelectric colorimeter or spectrophotometer i.e. concentration of the coloured substance can be obtained at different times.

Example: In the reaction between iodine and propanone, portions of the reaction mixture can be pipetted into a base such as <u>NaHCO₃ or NaOH</u> solutions. This quenches the reaction by <u>neutralising</u> the acid catalyst. The quenched mixture can then be analysed in a colorimeter.



3.3 Volume Measurements

Suitable for systems in which one of the substances is gaseous.

The volume of gas produced can be followed during the reaction using a graduated syringe, hence the amount of the gaseous substances can be obtained at different times.

e.g. Decomposition of hydrogen peroxide



3.4 Pressure Measurements

Suitable for gaseous reactions which involve changes in pressure.

Example: Gaseous decomposition of 2–methyl–2–iodopropane can be followed by measuring the pressure at suitable time intervals.

 $\begin{array}{cccc} e.g.1 & CH_3C(CH_3)ICH_3(g) & \rightarrow & (CH_3)_2CCH_2(g) & + & HI(g) \\ e.g.2 & H_2O_2(g) & \rightarrow & O_2(g) & + & H_2O(g) \end{array}$

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3.5 Conductometric Analysis

Many reactions in aqueous solutions involve **changes in the ions present** as the reaction proceeds. Consequently, the electrical conductivity of the solution will change during the reaction. This can be used to determine the changing concentrations of reactants and products with time.

Note: The measurements on the reacting system do not give the rate of reaction directly. It gives the concentration of a particular reactant or product, X, at a given time, t. By plotting a graph of the concentration of X against time, the reaction rate can be determined. This involves <u>finding the</u> <u>slope of the tangent to the curve at the required time.</u>

Exercises 3:

For the following reactions, put a tick under the possible physical properties that can be used to study the rate of the reaction. More than one property maybe used.

	Conc	Color	Volume
$HCOOCH_3(aq) + OH^-(aq) \rightarrow HCOO^-(aq) + CH_3OH(aq)$			
$2H_2O_2$ (l) $\rightarrow O_2$ (g) + $2H_2O$ (l)			
CH_3COCH_3 (aq) + $I_2(aq)$ + $H^+ \rightarrow CH_3COCH_2I(aq)$ +HI(aq)			
$NH_4^+(aq) + NO_2^-(aq) \rightarrow N_2(g) + 2H_2O(l)$			
$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$			

4 <u>The Rate Equation</u> 4.1 <u>The Rate Constant</u>

For a hypothetical reaction $xA + yB \rightarrow zC$

the reaction rate is found experimentally to be



- The expression is called the **rate equation** for the reaction
- *k* **= rate constant** (constant at a given temperature)
- [] = concentration of the respective reactant in mol dm⁻³
- p is not necessarily the same as x; q is not necessarily equal to y

NOTE: The rate equation can only be <u>determined experimentally</u> and <u>cannot</u> be deduced from the stoichiometry of the chemical equation.

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4.2 <u>The order of a reaction</u>

<u>Definition</u>: Order of a reaction with respect to a reactant is the **power** to which the **concentration** of that reactant is raised in the **experimentally determined** rate equation.

For the hypothetical rate equation,

Rate = k [A] ^p [B] ^q

order of reaction with respect to **A** = order of reaction with respect to **B** = overall order of the reaction =

The <u>overall order</u> of a reaction is the sum of the individual orders. It is usually **1** or **2**, but it can also be **0** or fractions. Thus reactions can be classified as <u>first or second order</u>, <u>zero order or fractional order</u>.

The order of reaction can be determined by initial rate method or graphical method. We will first illustrate the initial rate method here. Graphical method will be discussed in the next few sections.

Worked Example 3: (Initial Rate Method)

The reaction kinetics of the following reaction was studied, and the results are as shown:

$BrO_{3}^{-}(aq) + 5 Br^{-}(aq) + 6H^{+}(aq) \rightarrow 3 Br_{2}(aq) + 3 H_{2}O(l)$

Mixturoo	Initial concentra	Initial rate/mal dm ³ a ⁻¹		
wixtures	[BrO ₃ -]	[Br⁻]	[H⁺]	
Ι	0.10	0.10	0.10	0.010
Π	0.20	0.10	0.10	0.020
III	0.10	0.30	0.10	0.030
IV	0.10	0.10	0.20	0.040

Find the order of reaction with respect to (a) BrO_3^- (b) Br^- and (c) H^+

Let rate equation be Rate = k[BrO ₃ -] ^a [Br-] ^b (Approach I: By inspection:)	[H ⁺] ^c (Approach II: by calculation:)
The rate equation is Rate =	
The reaction is order with resp	ect to BrO_{3}^{-} ;
order with respe	ect to Br-;
order with respe	ect to H ⁺
Overall, it is a order reaction	

Note: The order of a reaction with respect to the reactants **DO NOT** necessarily correlate to the stoichiometry of the equation.

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4.2.1 Zero Order Reaction		Why are the unit	s for k <u>mol dm⁻³ s⁻¹?</u>
For the reaction A	\rightarrow B + C , if it is a zero	order,	
The rate equation is r ate in the rate of	ate = k [A] ⁰ = k <u>mol dm⁻³ s⁻¹</u>		
The reaction is zero c reaction is independer	order with respect to A nt of the concentration	, i.e. the of A.	

A zero order reaction can be recognised from the various plots,



4.2.2 First Order Reaction

For the reaction $\mathbf{A} \rightarrow \mathbf{B} + \mathbf{C}$, if it is a first order,

The rate equation is Rate = k [A] ¹ unit for k: s⁻¹ (or min⁻¹)

The rate is directly proportional to concentration of reactant A, slope of curve should decrease as [reactant] decreases. A first order reaction can be recognised from the following plots:

Why are the units for k s⁻¹?



Half – life

Definition:

The half-life of a reaction, $t_{1/2}$, is the time taken for the concentration of a reactant to fall to half its initial value.

It gives an indication of the rate of any change, particularly in radioactivity. The way in which the half-life for a reaction varies with concentration depends on the order of the reaction.

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How do you determine the half-life from a concentration-time graph?

For a reaction,

 $A \rightarrow \text{products}$

Half-Life	change in [A]
first t _{1/2}	from [A] , to [A] , /2
second t _{1/2}	from [A] _o /2 to [A] _o /4
third t _{1/2}	from [A] _o /4 to [A] _o /8

where $[A]_0$ is the concentration of A at time zero.

If this reaction is a first order reaction, all the three $t_{1/2}$ should be the same. This is also how we can determine if a reaction is a first order reaction.

Graphically, the $t_{\frac{1}{2}}$ can be determined from the following plots:



Making Thinking Visible

- 1. Can we still determine the half-life when the concentration of A at a particular instance is not [A]_o/2 or [A]_o/4, maybe [A]_o/3?
- 2. Can we determine a half-life for a second-order reaction?
- 3. How do I know if a reaction is a first order reaction from a concentration-time graph?

All overall first order reactions have a **constant half-life**, which is **In2/k**.

If the reaction, $A \rightarrow products$ is a first order reaction, Rate = k [A]

If you are interested, you can prove the relationship between k and $t_{1/2}$ mathematically by substitute *rate* with -d[A]/dt to form a differential equation.

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The half-life can also be determined from the **[product]-time graph**. First, let's look at the relationship between the [reactant] and [product].

Consider the following reaction.

	Α	\rightarrow	Р	+	Q
initially	а		0		
after one t _{1/2}	$\frac{1}{2}a$		$\frac{1}{2}a$		
after two t1/2	$\frac{1}{4}a$		$\frac{3}{4}a$		
end of reaction	0		a=[P] _{ma}	ax	



Making Thinking Visible

- 1. How do you determine the 3rd half-life from the above graph?
- 2. Can I determine the half-life from any points on the graph, say 0.4[P]_{max}?
- 3. Why should [P]_{max} be determined first?

Exercise 4

Decomposition of H_2O_2 to H_2O and O_2 follows first–order kinetics.

A 50 cm³ solution containing of 0.40 mol dm⁻³ H_2O_2 takes 20 min to produce 120 cm³ of O_2 gas at room temperature and pressure. How much time is needed for 210 cm³ of O_2 gas to be formed at room temperature and pressure?

Α	20 min	В	35 min	С	40 min	D	60 min

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Exercise 5				

Lead is the final product formed by a series of changes in which the rate-determining stage is the radioactive decay of uranium-238. This radioactive decay is a first-order reaction with a half-life of 4.5×10^9 years.

What would be the age of a rock sample, originally lead-free, in which the molar ratio of uranium to lead is now 1:7?

Α	1.5 × 10 ⁹ years	В	2.25 × 10 ⁹ years

C 9.0×10^9 years **D** 1.35×10^{10} years

4.2.3 Second Order Reaction

For the reaction $\mathbf{A} \rightarrow \mathbf{B} + \mathbf{C}$, if it is a second order,

The rate equation is Rate = $k [A]^2$

the rate of reaction is proportional to the \underline{square} of the concentration of reactant $\pmb{A}.$

A second order reaction can be recognised from the following plots:

What are the units for k?



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4.2.4 Pseudo first–order reaction

The acid catalysed hydrolysis of an ester such as ethyl ethanoate

$$CH_{3}CO_{2}C_{2}H_{5}(I) + H_{2}O(I) \rightarrow CH_{3}CO_{2}H(I) + C_{2}H_{5}OH(I)$$

is <u>first order</u> with respect to ester and <u>first order</u> with respect to water.

rate equation: Rate = _____

However, if <u>water is present in a **large** excess</u>, only a small fraction of the water will be used up in the reaction. The <u>concentration of water is practically constant</u>, and the rate depends on the concentration of ester alone.

The rate equation becomes: Rate = _____

where $k' = k [H_2O] = a$ first order rate constant

The reaction <u>appears to be zero order</u> (pseudo zero order) with respect to water <u>and 1st order</u> (pseudo 1st order) with respect to $CH_3CO_2C_2H_5$. Overall it is a pseudo 1st order reaction although it is actually an overall 2nd order reaction.

Exercise 6:

Phosgene is a toxic gas prepared by the reaction of carbon monoxide with chlorine:

$$CO(g) + Cl_2(g) \rightarrow COCl_2(g)$$

The following data were obtained in a kinetics study of its formation:

Experiment	Initial [CO] / mol dm ⁻³	Initial [Cl ₂] / mol dm ⁻³	Initial Rate / mol dm ⁻³ s ⁻
			1
1	1.00	0.100	1.29 x 10 ⁻²⁹
2	0.100	0.100	1.30 x 10 ⁻³⁰
3	0.100	1.00	1.31 x 10 ⁻²⁹
4	0.100	0.0100	1.28 x 10 ⁻³¹

(a) Write an expression for the rate equation.

- (b) Calculate the rate constant, using Experiment 1.
- (c) Determine the half–life of Experiment 1.

Making Thinking Visible

In the exercise 6, in which of the experiments, will you observe a constant half-life for CO? Why?

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5. Methods to Determine Order of Reaction

5.1 Graphical Method

Order	[] vs time	Rate vs []	Rate vs [] ²
0	Straight line (constant gradient)	Horizontal line – no change in rate	NA
1 st	Curve with <u>constant</u> half life	Straight line through origin, rate ∞ []	NA
2 nd	Curve but half–life is NOT constant	Curve through origin	Straight line through origin, rate $\propto []^2$

Worked Example 4: For the reaction

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

the change in concentration of a reactant/product with time can be obtained and the result is shown in the graph below.



- (i) Indicate the half–life on the graph below, hence determine the order of the reaction with respect to N_2O_5 .
- (ii) Sketch another appropriate graph to confirm order of reaction with respect to N_2O_5 .

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5.2 Initial rate method

This method is **based on inspection of experimental data**. It measures the rate at the beginning of the reaction. This rate is called the initial rate. The idea is to determine the rate before the initial concentrations of the reactants have changed significantly.

Several experiments are carried out using different initial concentrations and the initial rate is determined for each run.

Worked Example 5:

Find the rate equation and **k**, the rate constant, for the following reaction:

	NH₄⁺(aq)	+ NO₂⁻ (a	aq) \rightarrow N ₂ (g) +	2H ₂ O(<i>I</i>)
[Exp.	Initial [NH ₄⁺]	Initial [NO₂ ⁻]	Initial rate (moldm ⁻³ s ⁻¹)
	1	0.100	0.0050	1.35 x 10 ⁻⁷
	2	0.100	0.010	2.70 x 10 ⁻⁷
	3	0.200	0.010	5.40 x 10 ⁻⁷
Rate	equation:	rate = k [NH ₄*	⁺] ⁿ [NO ₂ [−]] ^m	
Com	pare experin	nents 1 and 2		
Rate: Rate	<u>2</u> =	<u>2.70 x 10⁻⁷</u> 1.35 x 10 ⁻⁷ 2.00 m	$= \frac{k [0.100]^{n} [0.010]}{k [0.100]^{n} [0.000]}$ = 2 ^m = 1	<u>)]</u> m 50] ^m
<u>Com</u>	pare experin	nents 3 and 2		
<u>Rate</u> Rate	<u>3</u> =	<u>5.40 x 10⁻⁷</u> 2.70 x 10 ⁻⁷ 2.00 n	$= \frac{k [0.200]^{n} [0.010]}{k [0.100]^{n} [0.010]}$ = 2 ⁿ = 1	<u>)]m</u>)]m
Rate	=			
Find	k			

Making Thinking Visible

1. Why is initial rate used instead of the rate of reaction after some time?

2. How can initial rate be determined experimentally?

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Worked Example 6:

Find how the rate depends on [Na₂S₂O₃] for the following reaction

$Na_2S_2O_3 \quad + \quad 2HC/ \quad \rightarrow \quad 2NaC/ \ + \quad H_2O \ + \quad S \ \ + \quad SO_2$

$Na_2S_2O_3$,	H ₂ O	HC/	Time,t	1/ t	Vt	V ² t
V (cm ³)	(cm ³)	(cm³)	(s)	(S ⁻¹)	(cm ³ s)	(cm ⁶ s)
20	5	5	24	0.042	480	9600
10	15	5	49	0.020	490	4900
5	20	5	94	0.011	470	2350

where **t** is the time taken for the sulfur produced to obscure the marked cross.

♦ Rate ∞

Total volume of mixture is the same, hence,

no. of moles of $Na_2S_2O_3 \propto$ volume of $Na_2S_2O_3$ solution

if Rate = $k [Na_2S_2O_3]^n$

 \Rightarrow then,1/t = k Vⁿ



Constant value	Order with respect to the reactant
t	zero order, n = 0
V ¹ t	
V ² t	

From the table, Vt = constant

i.e. order of reaction with respect to $Na_2S_2O_3$ is 1.

Making Thinking Visible

1. When 1/t is used to estimate the initial rate, what is the assumption made?

2. Is variable time, t used the example 6 the same as the time used in example 4?

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Exercise 6:

One reaction which occurs in air polluted with nitrogen oxides is shown below.

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

Five experiments were carried out to find the relationship between the initial concentration of NO and of O_2 , and the initial rate of formation of NO_2 .

Expt. No.	[NO] / mol dm ⁻³	[O ₂] / mol dm ⁻³	Initial rate of production of NO ₂ /
			mol dm ⁻³ s ⁻¹
1	1 x 10 ⁻³	1 x 10 ⁻³	7 x 10 ⁻⁶
2	1 x 10 ⁻³	2 x 10 ⁻³	14 x 10 ⁻⁶
3	1 x 10 ⁻³	3 x 10 ⁻³	21 x 10 ⁻⁶
4	2 x 10 ⁻³	3 x 10 ⁻³	84 x 10 ⁻⁶
5	3 x 10 ⁻³	3 x 10 ⁻³	189 x 10 ⁻⁶

a) Find the order of reaction with respect to NO

b) Find the order of reaction with respect to **O**₂.

- c) Write an expression for the rate equation.
- d) Calculate the rate constant and give its units.

Worked Example 7:

lodine and propanone react together in aqueous solution according to the equation

$\mathsf{CH}_3\mathsf{COCH}_3(\mathsf{aq}) + \mathbf{I}_2(\mathsf{aq}) \xrightarrow{\mathsf{H}^+} \mathsf{CH}_3\mathsf{COCH}_2\mathbf{I}(\mathsf{aq}) + \mathsf{HI}(\mathsf{aq})$

The rate of reaction can be measured by recording the reduction of the concentration of the iodine by the decrease in the intensity of its color as measured in a colorimeter. Three sets of separate experiments were performed in which the initial concentration of each of the reactants; iodine, propanone and acid was varied in turn, the other two being kept constant.

The results are shown below in graphical form.

Note: All the graphs are straight lines or pseudo-order graphs of concentration versus time. The reactant that is monitored, iodine, is used in small amounts, while propanone and acid are used in large quantities.

a) How is the rate of reaction found from a graph of concentration of reagent against time?

Rate = $\underline{\text{change in } [l_2]}$ and since graph is a straight line Time

rate = gradient of the straight line = constant

|--|

b) Use the graphs to find how the rate of reaction varies with the concentration of (i) iodine (ii) propanone and (iii) acid.

Express your answer in the form rate \propto [X]ⁿ where X is the reactant.



Let rate = k $[I_2]^a$ $[CH_3COCH_3]^b[H^+]^c$

The reaction <u>appears to be</u> a zero order reaction. (propanone and acid are in excess). The straight line graph shows that gradient is constant hence rate is constant. Even when concentration of iodine is changed, the same gradient (lines are parallel) is obtained hence rate is unchanged even when $[I_2]$ has changed.

Hence Rate = $k'[I_2]^0$, where $k' = k[H^+]^c [CH_3COCH_3]^b$



2nd set of graphs

Magnitude of gradient/rate of reaction doubles when initial [CH₃COCH₃] doubles.

Show working:

Hence, Rate \propto [CH₃COCH₃]; order of reaction w.r.t. CH₃COCH₃ is 1.

3rd set of graphs



(c) Write the full expression for the rate equation, using k as the rate constant.

- (d) What is the total order of the reaction?
- (e) Give the units for the rate constant.

Worked Example 8:

Solutions of known concentrations of the ether and chlorine are mixed and the time is noted. Samples of the reaction mixture were withdrawn at different times and run into excess **KI** solution. $[CI_2]$ is subsequently determined by a suitable method.

The following results were obtained from 2 experiments on the chlorination of ether. In each experiment, the overall [ether] can be assumed to remain constant.

Time/min	[Cl₂]/moldm ⁻³ when	[Cl ₂]/moldm ⁻³ when
	$[ether] = 0.10 \text{ moldm}^{-3}$	$[ether] = 0.15 \text{ moldm}^{-3}$
0	0.0100	0.0100
40	0.0079	0.0070
80	0.0062	0.0049
120	0.0049	0.0034
160	0.0038	0.0024
200	0.0030	0.0017

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Plot these data and use your graphs to find

(i) The order of reaction w.r.t. chlorine using the half–life method.



Using only one of the graphs, show at least 2 half-lives to check whether they are constant.

For [ether]= 0.15 moldm⁻³, $t_{1/2}$ = 78 mins

Note : If 2 half-lives are not exactly equal, take the average but show working.

Since the half–life is constant, the reaction is 1st order with respect to chlorine Note: For [ether]= 0.10 moldm^{-3} , t _{1/2} of chlorine = 110 mins

THINK! Why is there a difference in the value of t 1/2 for different [ether]?



(ii) The order of reaction w.r.t. the ether using the initial rates method.

For [ether]= 0.10 moldm^{-3} , magnitude of gradient = $0.0000588 \text{ mol dm}^{-3} \text{ min}^{-1}$ For [ether]= 0.15 moldm^{-3} , magnitude of gradient = $0.0000833 \text{ mol dm}^{-3} \text{ min}^{-1}$

Rate = k[Cl₂][ether]^x

Draw tangents at t= 0

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(iii)	Construct a	rate equation for the reaction	and calculate the rate constant.		

- (iv) Based on your answer for the half–life of chlorine in a(i) for the expt with [ether]= 0.15 moldm⁻³, predict the half–life of chlorine if [ether] is increased to 0.30 mol dm⁻³.

6. <u>Theories of Reaction Rates</u>

6.1 <u>The collision theory</u>

The collision theory was developed from the kinetic theory of gases to account for the influence of temperature and concentration on reaction rates. The theory is based on three postulates:

- Reaction occurs due to the collision of reactant particles.
- A collision only results in a reaction if a certain minimum energy known as the activation energy, Ea is exceeded.
- A collision will not result in a reaction unless the colliding particles are correctly orientated to one another.



Which would result in an effective collision?

 $2NOBr \rightarrow 2NO + Br_2$

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The collision theory does not necessarily apply to the reactant species represented by the stoichiometric equation. The stoichiometric equation represents the overall reaction. The mechanism of the reaction may involve a number of steps.

The <u>collision theory only applies to a specific step</u> – <u>the rate determining step or the slowest</u> <u>step in the reaction mechanism.</u>

6.2 Transition State Theory

The transition state theory treats reacting molecules as a single entity. It deals with changes in the geometric arrangements of the atoms involved as the system changes from reactants to products. A geometric arrangement of atoms is called a configuration. As the reactant configurations change towards product configuration, there is an increase in potential energy until a maximum is reached. At this energy, molecules have a critical configuration known as the transition state or activated complex. Only molecules with adequate total energy can attain this critical configuration. As the critical configuration changes to the product configuration, the potential energy decreases.

The reaction coordinate represents the changes in geometric arrangement of the atoms in the reacting molecules taken as a whole entity. Any reactive intermediate involved in the reaction appears at a minimum on the energy profile.



7 Factors Affecting the Rate of a Reaction

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7.1 Concentration

Rate of reaction generally increases with an increase in concentration of one or more of the reactant species.

Reason: According to the collision theory, as concentration increases, the <u>number of particles in</u> <u>a given volume increases</u>.

Number of collisions per unit time increases and frequency of effective collisions (collisions with energy $>= E_a$) increases.

The degree to which the concentration of a particular reactant affects the rate of reaction depends on the rate equation.

If rate = $k[\mathbf{A}][\mathbf{B}]^2$, then changing the $[\mathbf{B}]$ has a greater impact.

7.2 <u>Temperature</u>

Rate of reaction generally increases with temperature regardless of whether the reaction is exothermic or endothermic. For every 10°C rise in temperature, the reaction rate would <u>double</u>.

Reason: The kinetic energy of molecules is spread over a wide range known as the **Maxwell – Boltzmann distribution**. As temperature increases, this spread shifts to higher energies. Hence an increase in temperature increases the no of reactant molecules with sufficient to overcome the E_a and form new products.

Increasing T also results in an increase in the total no. of collisions per sec (collision frequency) but this reason is insignificant compared to previous reason.



The diagram shows the distribution of collision energies with respect to collision frequency. The shaded area represents the probability that the energy of the collision will exceed the activation energy (minimum energy that a molecule must have to break the original bonds before a reaction can occur). As temperature increases, this area increases. Hence by the collision theory, the **number of effective collisions per unit time increase** and the rate of reaction therefore increases.

Temperature affects different types of reactions differently.



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The exponential effect of temperature on reaction rate – the Arrhenius Equation					

As a general rule of thumb, the **rate of reaction doubles for every 10** °**C rise in temperature**. This means that there is an exponential relationship between rate and temperature. The exact relationship is given by the Arrhenius equation which is



where A = constant for a given reaction; R = gas constant, T = temperature in K.

 $\mathbf{k} \propto \mathbf{e}^{-1/T}$

Reaction rates increase with temperature <u>because rate constant k increases with temperature T.</u> Increase in T causes an increase in the proportion of collisions with energy > E_a i.e. ($e^{-Ea/RT}$)

As E_a affects the rate constant, the use of a catalyst which lowers the E_a , would therefore change the value of k and hence the rate.

7.3 <u>Light</u>

Reactions which are light – sensitive are called **photochemical reactions**. Examples are photosynthesis and photography. Other reactions such as the chlorination of methane in the presence of sunlight involve free radicals. The presence of light splits bonds homolytically to form free radicals which then lead to a chain reaction. Hydrogen and chlorine react slowly in the dark unless heated above 200 °C. However, in the presence of sunlight, the reaction takes place rapidly at room temperature.

7.4 Surface area or particle size

The reaction of solids takes place faster when the solids are in a finely divided state. For example, powdered zinc reacts much more vigorously than a piece of zinc strip.

Reason: The **ratio of surface area to mass** is greater in small particles than in large particles. Also the area over which the solid can come into contact with the liquid or gaseous reactants is much greater.

7.5 Catalysis

What is a catalyst?

Catalyst is a substance that alters the rate of a chemical reaction without itself undergoing any permanent chemical change. It can undergo physical change, e.g. solid MnO_2 used as catalyst in decomposition of H_2O_2 would become very powdery at the end of reaction.

(I) <u>Characteristics of Catalysts</u>

- (a) A catalyst does **NOT** affect the <u>enthalpy change</u>, ΔH of a reaction.
- (b) A catalyst speeds up the rates of both the <u>forward</u> and <u>backward</u> reactions. It thus speeds up the rate at which equilibrium is attained but does not affect the <u>equilibrium</u> position. A catalyst <u>does not</u> alter the <u> $K_c \text{ or } K_p$ </u> of a reaction.



Both k_1 and k_{-1} increase to same extent when catalyst is added

{refer to the Arrhenius equation: \downarrow in **E**_a results in \uparrow in **k**}, **K**_c remains constant.

- (c) A catalyst provides an <u>alternative reaction pathway</u>. The activation energy of this alternative route is <u>lower</u>. Hence by the collision theory, more molecules are able to possess the energy required for a successful collision. The total number of collisions resulting in a reaction increases per unit time and the rate of reaction thus increases.
- (d) A catalyst is often **specific.** It increases the rate of one reaction but not that of a similar reaction.
- (e) A catalyst is chemically involved in a reaction. It is consumed in one step and **regenerated** in a subsequent step. It can thus be used repeatedly without undergoing any permanent change. It may, however, change its physical form.



At the same temperature T₁, a catalyst provides an alternative reaction pathway such that the new activation energy E_a ' is lower. Thus, there is a larger number of molecules with energy $\geq E_a$ '. Hence, no. of effective collisions per unit time increases, and rate increases.

(II) <u>Types of Catalysts</u>

Catalysts can be classified under three main types:

- Homogeneous catalysts (NOT for H1);
- Heterogeneous catalysts;
- Biological catalysts (enzymes)

(a) <u>Homogeneous catalysts</u>

The <u>catalyst and the reactants</u> are in the <u>same physical state/ phase</u> Many redox reactions in solutions are catalysed by d–block transition metal ions.

Example a: The reaction between two anions is slow-

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

But addition of \mathbf{Fe}^{2+} (aq) would speed up the reaction:



Progress of reaction

Example b: catalytic oxidation of atmospheric sulfur dioxide by atmospheric oxides of nitrogen

Uncatalysed reaction: $SO_2(g) + \frac{1}{2}O_2(g) \longrightarrow SO_3(g)$

The reaction is slow due to high activation energy because energy is needed to break the strong covalent bonds in the reactants.

In the presence of NO₂, the reaction occurs in two steps.

Step 1: $SO_2(g) + NO_2(g) \longrightarrow SO_3(g) + NO(g)$

Step 2: $NO(g) + \frac{1}{2}O_2(g) \longrightarrow NO_2(g)$

(b) <u>Heterogeneous catalysis</u>

The <u>catalyst and the reactants</u> are in <u>different physical states</u>. All heterogeneous processes occur at the phase boundary. The catalysis at a solid surface can be explained in terms of the **adsorption theory**.

e.g. Haber process, Contact process and Hydrogenation of alkene.

 $\begin{array}{rcl} Fe(s) & & \\ Fe(s) & & \\ 2 & &$

The Adsorption Theory of Heterogeneous Catalysis

Adsorption is the accumulation of molecules at the surface. **Physical adsorption** occurs when the molecules are bound to the active sites at the surface by **van der Waals forces**.

Chemical adsorption occurs when molecules are held on the surface by **chemical bonds**. This weakens the bonds in the original molecule, thus less energy needed to form the activated complex for the reaction. Heterogeneous catalysis usually involves both physical and chemical adsorption. The general mechanism can be represented schematically by five steps as shown:



Application: Catalytic Converters

A catalytic converter is used in some exhaust systems to convert gases that are environmentally harmful into harmless gases. A honeycomb of small beads coated with platinum and palladium catalysts convert <u>unburned hydrocarbons</u> and <u>carbon</u> <u>monoxide</u> into <u>harmless water and carbon dioxide gas</u>. This is done when the catalytic converter is heated and extra air is pumped into it. The <u>nitrogen oxides</u> are converted into <u>harmless nitrogen gas</u>. Cars fitted with catalytic converters in their exhaust systems must use **lead – free** petrol to prevent the catalyst from being coated with lead. A diagram of a typical catalytic converter is as shown:





Autocatalysis

This is the catalysis of a reaction by one of the products of the reaction. The reaction is initially slow but as the products are formed, the reaction is speeded up.

e.g. The autocatalytic oxidation of ethanedioic acid by potassium manganate (VII).

$$2MnO_4^{2-}(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$$

The autocatalyst is the **Mn²⁺** ions.

Sketch the graph of reaction rate versus time; on a separate axis, sketch a graph of concentration of MnO_4^- versus time.

Why does the rate decrease at the end of the reaction?



Enzymes are proteins which catalyse the chemical reactions in living systems. Without them, most biochemical reactions will be too slow to sustain life. In industries enzymes are used in the manufacture and preparation of foods, wine and beer, pharmaceuticals, detergents, textiles, leather and paper.

The general characteristics of enzymes are:

- Enzymes are **neither** homogeneous nor heterogeneous catalysts as they are **colloidal** in nature.
- Enzymes are highly selective and would only catalyse a specific reaction or type of reaction.
- A typical enzyme molecule can be generated a million times in one minute and are highly efficient.
- Enzymes operate most efficiently at **body temperature** i.e. 37°C.



When the temperature rises above 50°C or 60°C, they are destroyed and become ineffective. They are also sensitive to poisons.



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Promoters and poisons

A **promoter enhances** the performance of a catalyst. For example, aluminium oxide is a promoter for the iron catalyst used in the Haber Process for manufacture of ammonia. A **poison inhibits** the effectiveness of a catalyst. For example, carbon monoxide inhibits the action of nickel in the hydrogenation of alkenes.

Summary of the factors that affect the rate of a reaction

Factor	Effect on rate when factor is increased	Reason
Concentration or pressure	Increases	More particles come into contact, implying more effective collisions between particles.
Temperature	Increases	Average kinetic energy of particles increases, resulting in more energetic collisions hence more molecules can overcome the E _{act} for reaction. Freq of effective collisions increases so rate increases.
Surface area	Increases	Larger surface area of particles, implying more contact between reactants, therefore more effective collisions per unit time.
Catalysis	Increases	Catalyst lowers the E _{act} for reaction, implying more molecules can overcome the energy barrier (E _{act}) for reaction. Freq of effective collisions increases so rate increases.

8. <u>Reaction Mechanisms (NOT FOR H1)</u>

- A chemical reaction may involve a sequence of individual reaction steps. This sequence of steps is called the **reaction mechanism**.
- A mechanism is usually proposed on the basis of experimentally determined reaction rate data and also on the experimental detection of short–lived species which are not represented in the stoichiometric equation. These **short–lived intermediates** are called **reactive intermediates**.
- The **number of reacting species** (molecules, atoms, ions or free radicals) that take part in a reaction step is called the **molecularity** of the that step.
- Reaction steps can be described as unimolecular, bimolecular or termolecular.

Examples:

1. Iodination of propanone in an acidic solution.

CH_3COCH_3 (aq) + I_2 (aq) $\rightarrow CH_2ICOCH_3$ (aq) + HI (aq)

The experimentally derived rate equation is given by

The rate of reaction is thus independent of the concentration of iodine and does not correspond to the stoichiometry of the overall equation.

The reaction can be explained in terms of the following mechanism:

Step 1 $CH_3COCH_3(aq) + H_3O^+(aq) \longrightarrow CH_3COH^+CH_3(aq) + H_2O(I)$ (slow) Step 2 $CH_3COH^+CH_3(aq) + H_2O(I) \longrightarrow CH_2COHCH_3(aq) + H_3O^+(aq)$ (fast) Step 3 $CH_2COHCH_3(aq) + I_2(aq) \longrightarrow CH_2ICOCH_3(aq) + HI(aq)$ (fast)

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Note:				

- All three steps are bimolecular.
- Since the first step is the **slowest**, it is the bottleneck. It would therefore control and determine the overall rate of the reaction.
- The **slow step** in a reaction mechanism is called the **rate-determining step**
- reactants involved in the rate determining step will be involved in the rate equation.
- Rate equation follows the molecularity of the rate determining step. It means that the **coefficient of the substance in the rate-determining step** is the **order of reaction** with respect to that substance in the rate equation.
- Only **reactants or catalyst** can be present in the rate equation. Reactive intermediates should **not** be in the rate equation.
- 2. In the gaseous reaction $X + 2Y \rightarrow XY_2$

Two possible mechanisms have been proposed, suggest the rate equation corresponds to each mechanism.

Mechanism 1	Mechanism 2	
step I $X + Y \rightarrow XY$ (slow)	step I $X + Y \rightarrow XY$ (fast)	
step II $XY + Y \rightarrow XY_2$ (fast)	step II $XY + Y \rightarrow XY_2$ (slow)	
Deduce the rate equation	Deduce the rate equation From the rate-determining step: Rate =k'[XY][Y] Since XY is a reactive intermediate and it should not appear in the rate equation. From step 1: $[XY] \propto [X][Y]$ Hence, Rate = k'[XY][Y] = k([X][Y])([Y]) = k[X][Y] ²	

 Given the following reaction mechanism, write down the corresponding rate equation for the reaction. RBr + OH⁻ → ROH + Br⁻

Reaction mechanism	Corresponding rate equation
RBr + OH [–] → RBrOH [–] (slow) RBrOH [–] → ROH + Br [–] (fast)	rate =
$\begin{array}{lll} RBr & \to \ R^+ \ + \ Br^- & (slow) \\ R^+ \ + \ OH^- & \to \ ROH & (fast) \end{array}$	rate =
RBr + OH ⁻ → RBrOH ⁻ (fast) RBrOH ⁻ → ROH + Br ⁻ (slow)	rate =