26. REACTION KINETICS

26.1 Simple rate equations, orders of reaction and rate constants

Nitrosyl chloride, NOC*l*, can be formed by the reaction between nitrogen monoxide and chlorine, as shown.

$$2NO + Cl_2 \rightarrow 2NOCl$$

The initial rate of this reaction is investigated, starting with different concentrations of NO and Cl_2. The results obtained are shown in Table 5.1.

Table 5.1

experiment	[NO] / mol dm^{-3}	[Cl_2] / mol dm^{-3}	initial rate / mol dm^{-3} min^{-1}
1	0.0250	0.0150	3.68×10^{-2}
2	0.0750	0.0150	3.32×10^{-1}
3	0.0500	0.0600	5.89×10^{-1}

Use the data in the table to deduce the rate equation for this reaction. Explain your answer.

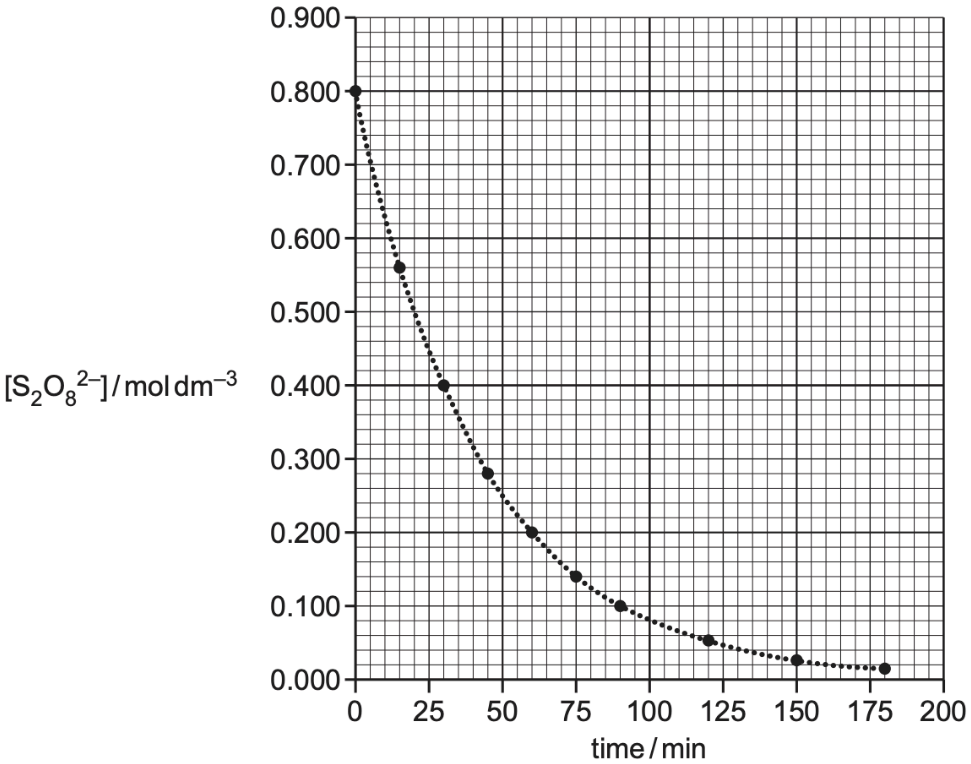
- Using exp 1&2: [NO] x 3, rate x 9, so 2nd order to NO.
- Using exp 1&3: [NO] x2, [Cl2] x 4, rate x 16, so 1st order to Cl2.
- Rate equation: rate = k[NO2]^2 [Cl2]

In aqueous solution, persulfate ions, $S_2O_8^{2-}$, react with iodide ions, as shown in reaction 1.

reaction 1 $$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$$

The rate of reaction 1 is investigated.

A sample of $S_2O_8^{2-}$ is mixed with a large excess of iodide ions of known concentration. The graph in Fig. 5.1 shows the results obtained.



Use Fig. 5.1 to determine the initial rate of reaction 1. Show your working

- tangent drawn at t = 0 AND gradient of tangent calculated at t = 0
- answer between 0.016 to 0.040

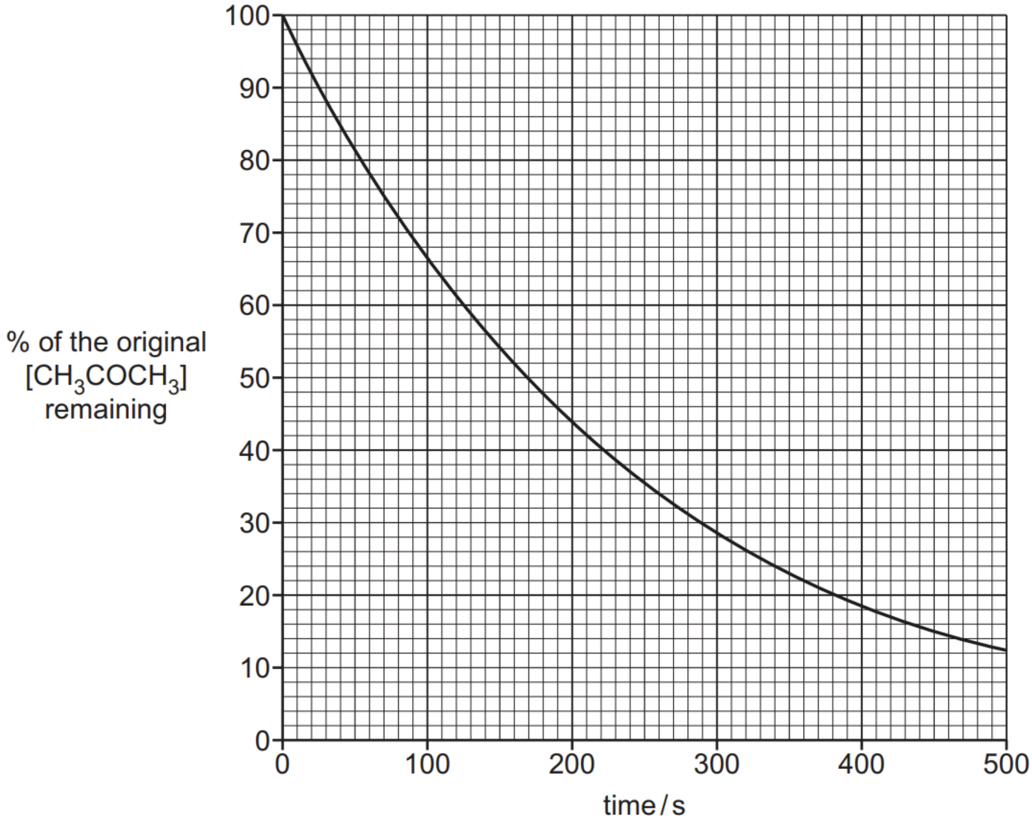
NOTE: for calculation of initial rate from graph, tangent should be at t=0 (0 should be like the midpoint).

The rate equation for reaction 1 is rate = k $[S_2O_8^{2-}]$ $[I^-]$. Suggest why a large excess of iodide ions allows the rate constant to be determined from the half-life in this investigation.

- [I–] is effectively constant / does not change AND doesn't affect the rate.

(iii) In a separate experiment, a large excess of CH_3OH and H^+ ions are added to a solution containing a known concentration of CH_3COCH_3.

Fig. 2.2 shows how $[CH_3COCH_3]$ varies over time.



Use Fig. 2.2 to show how, under these conditions, reaction 1 is first order with respect to CH3COCH3 .

- two quoted half-lives within range / 155–170 s AND (roughly) constant.

REMEMBER:
For first order reactions,
$k = 0.693/t_{1/2}$

The following rate equation is determined for reaction 2.

$$rate = k [CH_3COCH_3] [H^+]$$

Four possible mechanisms for reaction 2 are shown in Table 2.2.

Table 2.2

proposed reaction mechanism		steps
1	fast	$CH_3COCH_3 + H^+ \rightarrow [CH_3C(OH)CH_3]^+$
	slow	$[CH_3C(OH)CH_3]^+ + CN^- \rightarrow CH_3C(OH)(CN)CH_3$
2	fast	$H^+ + CN^- \rightarrow HCN$
	slow	$CH_3COCH_3 + HCN \rightarrow CH_3C(OH)(CN)CH_3$
3	slow	$CH_3COCH_3 + CN^- \rightarrow CH_3C(O^-)(CN)CH_3$
	fast	$CH_3C(O^-)(CN)CH_3 + H^+ \rightarrow CH_3C(OH)(CN)CH_3$
4	slow	$CH_3COCH_3 + H^+ \rightarrow [CH_3C(OH)CH_3]^+$
	fast	$[CH_3C(OH)CH_3]^+ + CN^- \rightarrow CH_3C(OH)(CN)CH_3$

Suggest which of these mechanisms is consistent with the rate equation for reaction 2. Explain your answer.

- proposed mechanism = 4
- slow step contains only species from the rate equation/law OR slow step contains CH3COCH3 and H+ from the rate equation/law
- Stoichiometric / (mole) ratio / amounts corresponds to order of reaction / to that in the rate equation

Describe the effect of an increase in temperature on the rate constant and the rate of reaction.

- the rate constant and rate of reaction will both increase.

Describe the effect of an increase in temperature on the rate of reaction.

- greater proportion of particles have E ⩾ EA
- frequency of (effective) collisions increases AND rate increases OR rate of collisions increases AND rate increases.

Explain what is meant by order of reaction.

- The power to which the concentration of a reactant is raised in the rate equation.

REMEMBER: when asked to deduce the unit for rate constant, remember to include the unit for time!!! Since rate is given as conc/time.

In aqueous solution, iron(III) ions react with iodide ions, as shown.

$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$

The initial rate of reaction is first order with respect to Fe3+ and second order with respect to I–.
The mechanism for this reaction has three steps.
Each step involves only two ions reacting together.
Suggest equations for the three steps of this mechanism. Identify the rate-determining step.

step 1 $Fe^{3+} + I^- \longrightarrow FeI^{2+}$ ✓

step 2 $FeI^{2+} + I^- \longrightarrow FeI_2^{+}$ ✓

step 3 $FeI_2^{+} + Fe^{3+} \longrightarrow 2Fe^{2+} + I_2$ ✓

Rate-determining step: 2

$$\text{rate} \propto [FeI^{2+}][I^-]$$

But **FeI²⁺ is an intermediate**, so we must rewrite it in terms of **reactants**.

The rate equation for the reaction between CH_3CHO and NO_2 is shown.

$$\text{rate} = k[CH_3CHO][NO_2]$$

The reaction mixture described in is monitored over a period of time. Predict whether the graph of [NO2] against time shows a constant half-life. Explain your answer.

- No constant half-life, because the overall order of the reaction is 2nd order.

NOTE: constant half-life only occurs when overall order of the reaction is 1!!

Nitrogen monoxide, NO, reacts with hydrogen, as shown in reaction 3.

reaction 3 $2NO + 2H_2 \rightarrow N_2 + 2H_2O$

(i) The rate equation for reaction 3 is shown.

$$rate = k[H_2][NO]^2$$

Suggest why reaction 3 is unlikely to proceed by a mechanism involving only a single step.

- Because a four-particle collision is unlikely.

Suggest equations for the **three** steps of the reaction mechanism for reaction 3.

Each step involves a reaction between **two** molecules.

step 1 .... → ....

step 2 .... + ... → N_2O + ...

step 3 N_2O + ... → .... + ...

Ans:

step 1 $2NO \rightarrow N_2O_2$

step 2 $N_2O_2 + H_2 \rightarrow N_2O + H_2O$

step 3 $N_2O + H_2 \rightarrow N_2 + H_2O$

NOTE: Here they've given only one blank in reactants and products for step 1. For the others there are clear blanks with + sign in between. Thus, use only one reactant.

26.2 Homogeneous and heterogeneous catalysts

Write two equations to show how Fe2+ catalyses iodine-peroxydisulfate reaction.

- equation 1: $2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$
  equation 2: $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$

NOTE: remember to write 2Fe2+ and 2Fe3+ to make sure the charges are balanced.

Suggest why this reaction is slow in the absence of Fe3+ (aq)

- repulsion of two negative / same charge ions slows the reaction / raises EA

Name the 3 metal catalysts used in catalytic converters.

- Palladium

- Platinum
- Rhodium

Describe the mode of action of a heterogeneous catalyst.

- reactants are adsorbed onto the catalyst surface
- bonds within reactant molecules are weakened
- products are desorbed from catalyst surface