

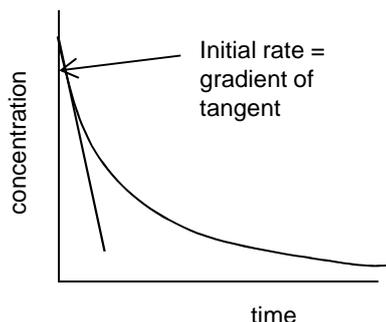
16. Kinetics II

The rate of reaction is defined as the **change in concentration** of a substance in **unit time**
Its usual unit is $\text{mol dm}^{-3}\text{s}^{-1}$

When a graph of concentration of reactant is plotted vs time, the **gradient** of the curve is the rate of reaction.

The **initial rate** is the rate at the start of the reaction where it is fastest

Reaction rates can be calculated from graphs of concentration of reactants **or** products

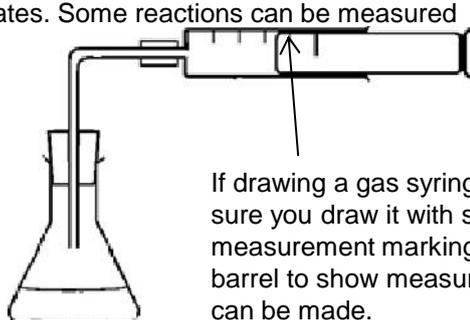
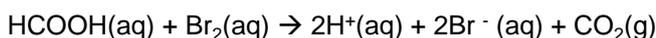
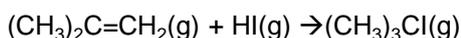


Techniques to investigate rates of reaction

There are several different methods for measuring reactions rates. Some reactions can be measured in several ways

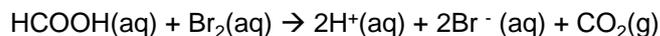
measurement of the change in volume of a gas

This works if there is a change in the number of moles of gas in the reaction. Using a gas syringe is a common way of following this.



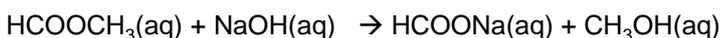
Measurement of change of mass

This works if there is a gas produced which is allowed to escape. Works better with heavy gases such as CO_2



Titrating samples of reaction mixture with acid, alkali, sodium thiosulphate etc

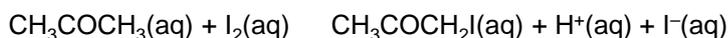
Small samples are removed from the reaction mixture, quenched (which stops the reaction) and the titrated with a suitable reagent.



The NaOH could be titrated with an acid



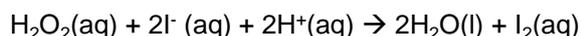
The H^+ could be titrated with an alkali



The I_2 could be titrated with sodium thiosulphate

Colorimetry.

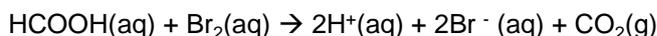
If one of the reactants or products is coloured then colorimetry can be used to measure the change in colour of the reacting mixtures



The I_2 produced is a brown solution

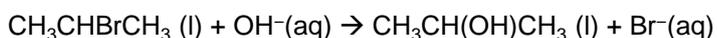
Measuring change in electrical conductivity

Can be used if there is a change in the number of ions in the reaction mixture



Measurement of optical activity.

If there is a change in the optical activity through the reaction this could be followed in a polarimeter



Rate Equations

The rate equation relates mathematically the rate of reaction to the concentration of the reactants.

For the following reaction, $aA + bB \rightarrow$ products, the generalised rate equation is:



r is used as symbol for rate

The unit of r is usually $\text{mol dm}^{-3} \text{s}^{-1}$

m, n are called **reaction orders**

Orders are usually integers 0,1,2

0 means the reaction is zero order with respect to that reactant

1 means first order

2 means second order

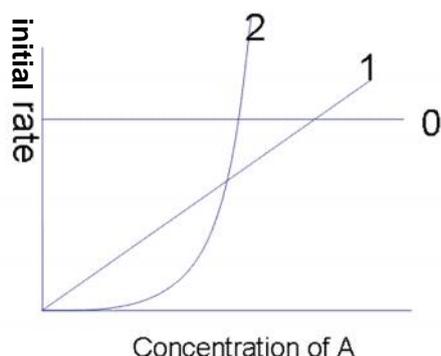
NOTE: the orders have *nothing* to do with the stoichiometric coefficients in the balanced equation. They are worked out experimentally

The square brackets **[A]** means the concentration of A (unit mol dm^{-3})

k is called the **rate constant**

The **total order** for a reaction is worked out by adding all the individual orders together ($m+n$)

Calculating orders from initial rate data



For zero order: the concentration of A has no effect on the rate of reaction $r = k[A]^0 = k$

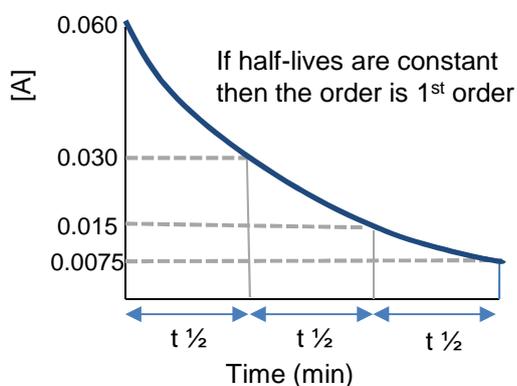
For first order: the rate of reaction is directly proportional to the concentration of A $r = k[A]^1$

For second order: the rate of reaction is proportional to the concentration of A squared $r = k[A]^2$

Graphs of initial rate against concentration show the different orders. The initial rate may have been calculated from taking gradients from concentration /time graphs

For a rate concentration graph to show the order of a particular reactant the concentration of that reactant must be varied whilst the concentrations of the other reactants should be kept constant.

Continuous rate experiments



Continuous rate data

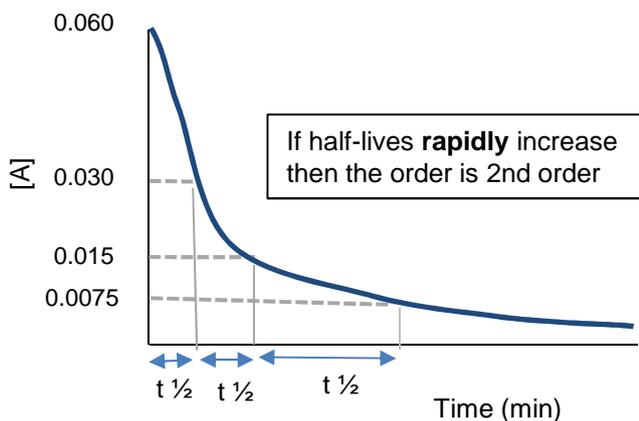
This is data from one experiment where the concentration of one substance is followed throughout the experiment.

For this method to work the concentrations of the reactants not being followed must be in large excess in the experiment so their concentrations stay virtually constant and do not affect rate.

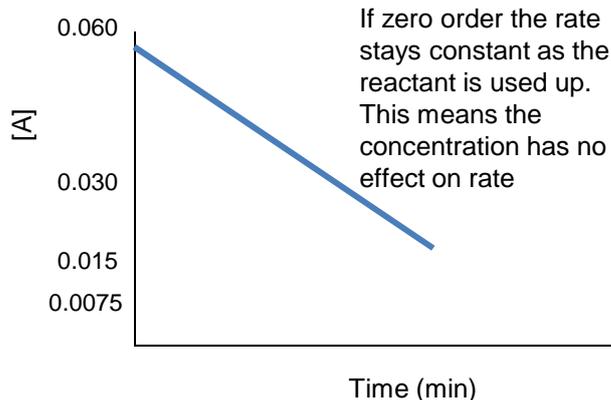
This data is processed by plotting the data and calculating successive half-lives.

The half-life of a first-order reaction is independent of the concentration and is constant

Second order



zero order



The rate constant (k)

- The units of k depend on the overall order of reaction. It must be worked out from the rate equation
- The value of k is independent of concentration and time. It is constant at a fixed temperature.
- The value of k refers to a specific temperature and it **increases** if we **increase temperature**

For a 1st order overall reaction the unit of k is **s⁻¹**

For a 2nd order overall reaction the unit of k is **mol⁻¹dm³s⁻¹**

For a 3rd order overall reaction the unit of k is **mol⁻²dm⁶s⁻¹**

Example (first order overall)

$$\text{Rate} = k[A][B]^0 \quad m = 1 \text{ and } n = 0$$

- reaction is first order in A and zero order in B
- overall order = 1 + 0 = 1
- usually written: Rate = k[A]

Remember: the values of the reaction orders must be determined from experiment; they cannot be found by looking at the balanced reaction equation

Calculating units of k

- Rearrange rate equation to give k as subject

$$k = \frac{\text{Rate}}{[A]}$$

- Insert units and cancel

$$k = \frac{\text{mol dm}^{-3}\text{s}^{-1}}{\text{mol dm}^{-3}}$$

$$\text{Unit of } k = \text{s}^{-1}$$

Example: Write the rate equation for the reaction between A and B where A is 1st order and B is 2nd order.

$$r = k[A][B]^2 \quad \text{overall order is 3}$$

Calculate the unit of k

- Rearrange rate equation to give k as subject

$$k = \frac{\text{Rate}}{[A][B]^2}$$

- Insert units and cancel

$$k = \frac{\text{mol dm}^{-3}\text{s}^{-1}}{\text{mol dm}^{-3} \cdot (\text{mol dm}^{-3})^2}$$

- Simplify fraction

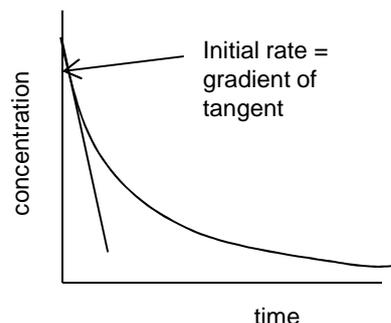
$$k = \frac{\text{s}^{-1}}{\text{mol}^2\text{dm}^{-6}}$$

$$\text{Unit of } k = \text{mol}^{-2}\text{dm}^6\text{s}^{-1}$$

Working out orders from experimental initial rate data

The initial rate is the rate at the start of the reaction, where it is fastest. It is often obtained by taking the gradient of the conc vs time graph.

Normally to work out the rate equation we do a series of experiments where the initial concentrations of reactants are changed (one at a time) and measure the initial rate each time. This data is normally presented in a table.



Example: work out the rate equation for the following reaction, $A + B + 2C \rightarrow D + 2E$, using the initial rate data in the table

Experiment	[A] mol dm ⁻³	[B] mol dm ⁻³	[C] mol dm ⁻³	Rate mol dm ⁻³ s ⁻¹
1	0.1	0.5	0.25	0.1
2	0.2	0.5	0.25	0.2
3	0.1	1.0	0.25	0.4
4	0.1	0.5	0.5	0.1

In order to calculate the order for a particular reactant it is easiest to compare two experiments where **only that reactant** is being changed

If conc is doubled and rate stays the same: order= 0

If conc is doubled and rate doubles: order= 1

If conc is doubled and rate quadruples : order= 2

For reactant A compare between experiments **1 and 2**

For reactant A as the concentration **doubles** (B and C staying constant) so does the rate. Therefore the order with respect to reactant **A is first order**

For reactant B compare between experiments **1 and 3** :

As the concentration of B **doubles** (A and C staying constant) the rate **quadruples**.

Therefore the order with respect to **B is 2nd order**

For reactant C compare between experiments **1 and 4** :

As the concentration of C **doubles** (A and B staying constant) the rate **stays the same**.

Therefore the order with respect to C is zero order

The overall rate equation is $r = k [A] [B]^2$

The reaction is 3rd order overall and the unit of the rate constant = mol⁻²dm⁶s⁻¹

Working out orders when two reactant concentrations are changed simultaneously

In most questions it is possible to compare between two experiments where only one reactant has its initial concentration changed. If, however, both reactants are changed then the effect of both individual changes on concentration are multiplied together to give the effect on rate.

In a reaction where the rate equation is $r = k [A] [B]^2$

If the [A] is x2 that rate would **x2**

If the [B] is x3 that rate would $x3^2 = \mathbf{x9}$

If these changes happened at the same time then the rate would $x2x9 = \mathbf{x18}$

Example work out the rate equation for the reaction, between X and Y, using the initial rate data in the table

Experiment	Initial concentration of X/ mol dm ⁻³	Initial concentration of Y/ mol dm ⁻³	Initial rate/ mol dm ⁻³ s ⁻¹
1	0.05	0.1	0.15×10^{-6}
2	0.10	0.1	0.30×10^{-6}
3	0.20	0.2	2.40×10^{-6}

For reactant X compare between experiments **1 and 2**

For reactant X as the concentration **doubles** (Y staying constant) so does the rate. Therefore the order with respect to reactant **X is first order**

Comparing between experiments 2 and 3 :

Both **X and Y double** and the **rate goes up by 8**

We know X is first order so that will have doubled rate

The effect of Y, therefore, on rate is to have quadrupled it.

Y must be second order

The overall rate equation is $r = k [X] [Y]^2$

The reaction is 3rd order overall and the unit of the rate constant = mol⁻²dm⁶s⁻¹

Calculating a value for k using initial rate data

Using the above example, choose any one of the experiments and put the values into the rate equation that has been rearranged to give k. Using experiment 3:

$$r = k [X] [Y]^2 \longrightarrow k = \frac{r}{[X] [Y]^2} \quad k = \frac{2.40 \times 10^{-6}}{0.2 \times 0.2^2} \quad k = \mathbf{3.0 \times 10^{-4} \text{ mol}^{-2}\text{dm}^6\text{s}^{-1}}$$

Remember k is the same for all experiments done at the same temperature.

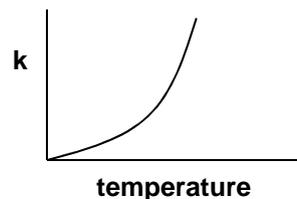
Increasing the temperature increases the value of the rate constant k

Effect of Temperature on Rate Constant: The Arrhenius Equation

Increasing the temperature increases the value of the rate constant k

Increasing temperature increases the rate constant k .

The relationship is given by the Arrhenius equation $k = Ae^{-E_A/RT}$ where A is the Arrhenius constant, R is the gas constant, and E_A is activation energy.



Using the Arrhenius equation (equations will be given in the exam)

$$k = Ae^{-E_A/RT}$$

The Arrhenius equation is usually rearranged to (You don't need to know how)

$$\ln k = \ln A - E_A/(RT)$$

You should be able to do rearrangements and substitute values into both these equations.

Units

Temperature uses the unit **K**

$R = 8.31 \text{ J mol}^{-1}\text{K}^{-1}$

Activation energy will need to be in **J mol^{-1}** to match the units of R

The unit of the Arrhenius constant A will be the same as the unit of the rate constant k

Example

A reaction carried out at 30°C has a value of $k = 4.26 \times 10^{-8} \text{ s}^{-1}$

The activation energy $E_a = 95.8 \text{ kJ mol}^{-1}$

The gas constant $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$

Calculate a value for the Arrhenius constant, A , for the reaction.

Using Equation $k = Ae^{-E_A/RT}$

$$\begin{aligned} \text{Rearrange to } A &= \frac{k}{e^{-E_A/RT}} = \frac{4.26 \times 10^{-8}}{e^{-95800/(8.31 \times 308)}} = \frac{4.26 \times 10^{-8}}{e^{-37.4}} = \frac{4.26 \times 10^{-8}}{5.55 \times 10^{-17}} \\ &= 7.67 \times 10^8 \text{ s}^{-1} \end{aligned}$$

Example

A reaction carried out at 25°C has a value of $k = 3.3 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$

$\ln A = 17.1$

The gas constant $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$

Calculate a value for the activation energy in kJ mol^{-1}

Using Equation $\ln k = \ln A - E_A/(RT)$

$$\begin{aligned} \text{Rearrange to } E_A &= (\ln A - \ln k) \times RT = (17.1 - 5.71) \times 8.31 \times 298 \\ &= 56486 \text{ J mol}^{-1} \\ &= 56.5 \text{ kJ mol}^{-1} \end{aligned}$$

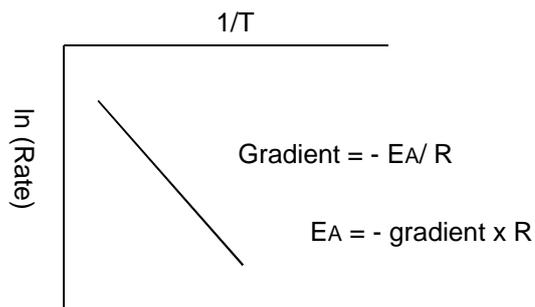
Calculating the activation energy graphically from experimental data

Using the rearranged version

$$\ln k = \ln A - EA/(RT)$$

k is proportional to the rate of reaction so $\ln k$ can be replaced by $\ln(\text{rate})$

From plotting a graph of $\ln(\text{rate})$ or $\ln k$ against $1/T$ the activation energy can be calculated from measuring the gradient of the line.



Example

Temperature T (K)	1/T	time t (s)	1/t	Ln (1/t)
297.3	0.003364	53	0.018868	-3.9703
310.6	0.00322	24	0.041667	-3.1781
317.2	0.003153	16	0.0625	-2.7726
323.9	0.003087	12	0.083333	-2.4849
335.6	0.00298	6	0.166667	-1.7918

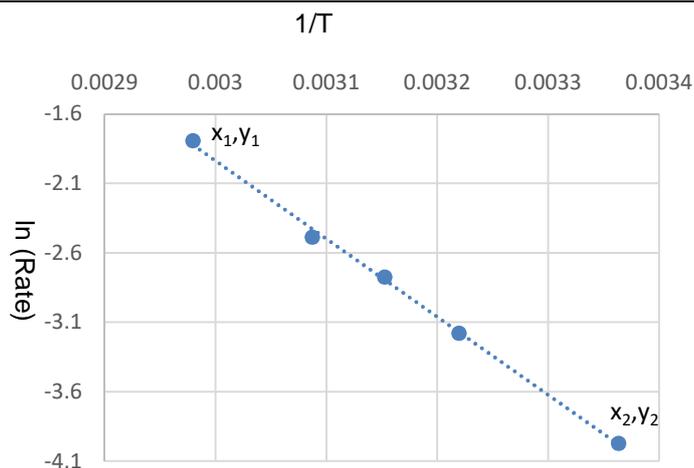
$$\text{gradient} = \frac{y_2 - y_1}{x_2 - x_1}$$

The gradient should always be -ve

In above example gradient = -5680

$$\begin{aligned} EA &= - \text{gradient} \times R \quad (8.31) \\ &= - (-5680) \times 8.31 \\ &= 47200 \text{ J mol}^{-1} \end{aligned}$$

The unit of EA using this equation will be J mol^{-1} .
Convert into kJ mol^{-1} by dividing 1000
 $EA = +47.2 \text{ kJ mol}^{-1}$



- use a line of best fit
- the plotted points should fill all graph paper (generally don't start at the origin)
- choose points far apart on the graph to calculate the gradient

Rate Equations and Mechanisms

A mechanism is a series of steps through which the reaction progresses, often forming intermediate compounds. If all the steps are added together they will add up to the overall equation for the reaction

Each step can have a different rate of reaction. The slowest step will control the overall rate of reaction. **The slowest step is called the rate-determining step.**

The molecularity (number of moles of each substance) of the molecules in the slowest step will be the same as the order of reaction for each substance.

e.g. 0 moles of A in slow step would mean A is zero order.

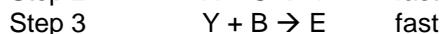
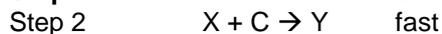
1 mole of A in the slow step would mean A is first order

Example 1

overall reaction



Mechanism



$$r = k [A]^1[B]^1[C]^0$$

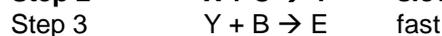
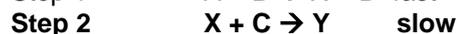
C is zero order as it appears in the mechanism in a fast step after the slow step

Example 2

overall reaction

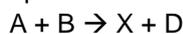


Mechanism



$$r = k [X]^1[C]^1$$

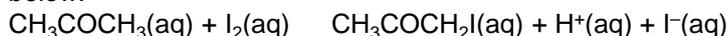
The intermediate X is not one of the reactants so must be replaced with the substances that make up the intermediate in a previous step



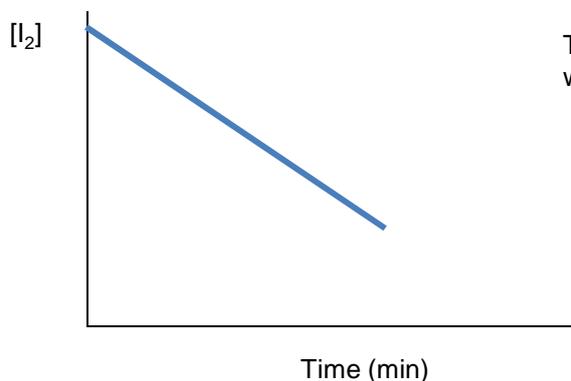
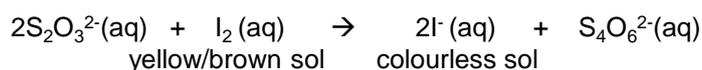
$$r = k[A]^1[B]^1[C]^1$$

Investigating the rate of reaction between iodine and propanone

Propanone reacts with iodine in acidic solution (the acid is a catalyst) as shown in the equation below.



This reaction can be followed by removing small samples from the reaction mixture with a volumetric pipette. The sample is then quenched by adding excess sodium hydrogencarbonate to neutralize acid catalyst which stops the reaction. Then the sample can be titrated with sodium thiosulfate using a starch catalyst



This reaction is zero order with respect to I₂ but 1st order with respect to the propanone and acid catalyst

The rate equation for the reaction is

$$\text{Rate} = k[CH_3COCH_3(aq)][H^+(aq)]$$

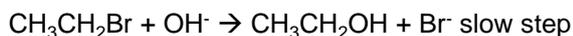
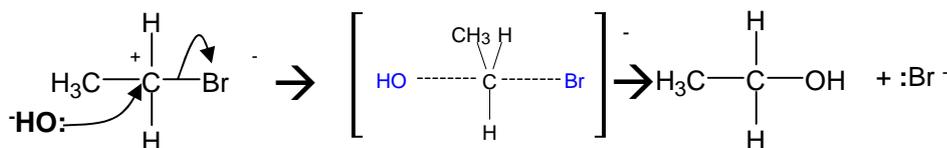
If there is a zero order reactant there must be at least two steps in the mechanism because the rate determining step will not involve the zero order reactant

The rate determining step of this reaction must therefore contain one propanone molecule and one H⁺ ion forming an intermediate. The iodine will be involved in a subsequent faster step.

Example 3: S_N1 or S_N2?

Remember the nucleophilic substitution reaction of halogenoalkanes and hydroxide ions.

This is a one step mechanism



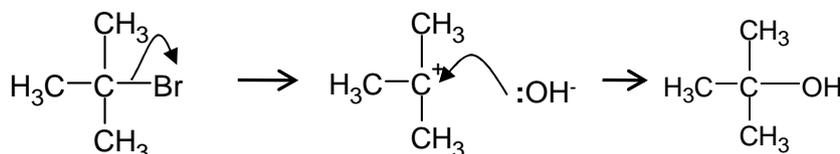
The rate equation is



This is called S_N2.
Substitution, Nucleophilic,
2 molecules in rate
determining step

Primary halogenoalkanes tend to
react via the SN2 mechanism

SN₁ nucleophilic substitution mechanism for tertiary halogenoalkanes



The Br first breaks away
from the halogenoalkane
to form a carbocation
intermediate

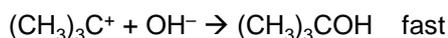
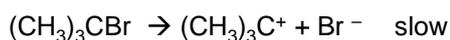
The hydroxide
nucleophile then attacks
the positive carbon

Tertiary halogenoalkanes
undergo this mechanism as the
tertiary carbocation is made
stabilised by the electron
releasing methyl groups around it.
(see alkenes topic for another
example of this).
Also the bulky methyl groups
prevent the hydroxide ion from
attacking the halogenoalkane in
the same way as the mechanism
above

Overall Reaction



Mechanism:



The rate equation is

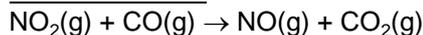


This is called S_N1.
Substitution, Nucleophilic,
1 molecule in rate
determining step

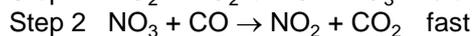
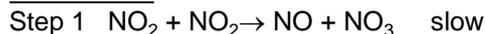
Primary halogenoalkanes do not do the SN₁ mechanism
because they would only form an unstable primary
carbocation.

Example 4

Overall Reaction



Mechanism:



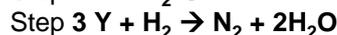
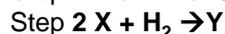
- NO₃ is a reaction intermediate

NO₂ appears twice in the slow steps so it
is second order. CO does not appear in
the slow step so is zero order.



Example 5

Using the rate equation $\text{rate} = k[\text{NO}]^2[\text{H}_2]$ and
the overall equation $2\text{NO}(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$, the
following three-step mechanism for the reaction was
suggested. X and Y are intermediate species.



Which **one of the three steps is the rate-determining step?**

Step 2 – as H₂ appears in rate equation and
combination of step 1 and 2 is the ratio that
appears in the rate equation.