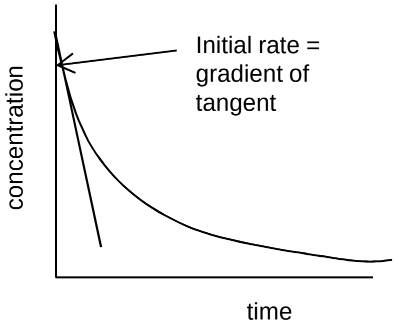
16. Kinetics II

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

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

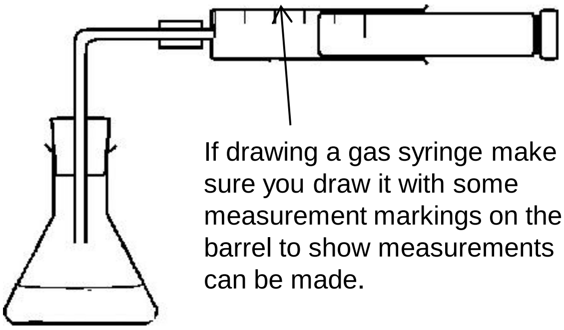
There are several different methods for measuring reactions rates. Some reactions can be measured in several ways

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.

$(CH_3)_2C=CH_2(g) + HI(g) \rightarrow (CH_3)_3CI(g)$

$HCOOH(aq) + Br_2(aq) \rightarrow 2H^+(aq) + 2Br^-(aq) + CO_2(g)$



If drawing a gas syringe make sure you draw it with some measurement markings on the barrel to show measurements can be made.

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

$HCOOH(aq) + Br_2(aq) \rightarrow 2H^+(aq) + 2Br^-(aq) + CO_2(g)$

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.

$HCOOCH_3(aq) + NaOH(aq) \rightarrow HCOONa(aq) + CH_3OH(aq)$	The NaOH could be titrated with an acid
$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$	The H^+ could be titrated with an alkali
$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$	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

$H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow 2H_2O(l) + I_2(aq)$

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

$HCOOH(aq) + Br_2(aq) \rightarrow 2H^+(aq) + 2Br^-(aq) + CO_2(g)$

Measurement of optical activity.

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

$CH_3CHBrCH_3(l) + OH^-(aq) \rightarrow CH_3CH(OH)CH_3(l) + Br^-(aq)$

Rate Equations

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

For the following reaction, aA + bB → products, the generalised rate equation is: $\mathbf{r = k[A]^m[B]^n}$

r is used as symbol for rate

The unit of r is usually **mol dm^{-3} 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

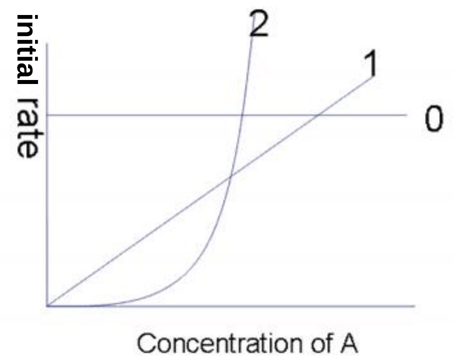
NOTE: the orders have *nothing* to do with the stoichiometric coefficients in the balanced equation. They are worked out experimentally

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



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

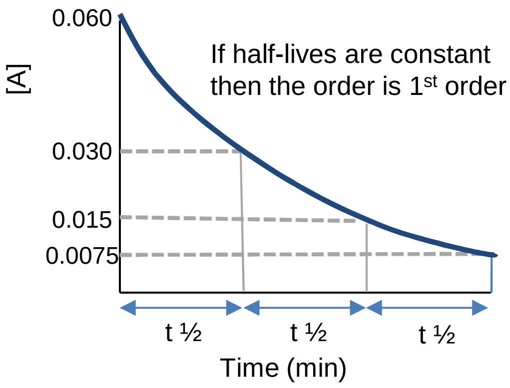
For zero order: the concentration of A has no effect on the rate of reaction **$\mathbf{r = k[A]^0 = k}$**

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 **$\mathbf{r = k[A]^2}$**

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



If half-lives are constant then the order is 1st order

Continuous rate data

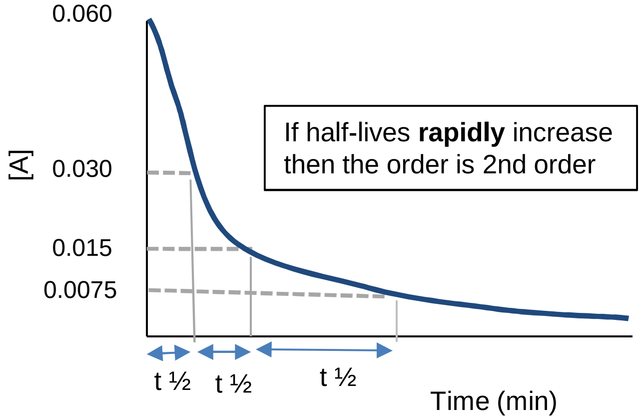
This is data from one experiment where the concentration of one substance is followed throughout the experiment.

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.

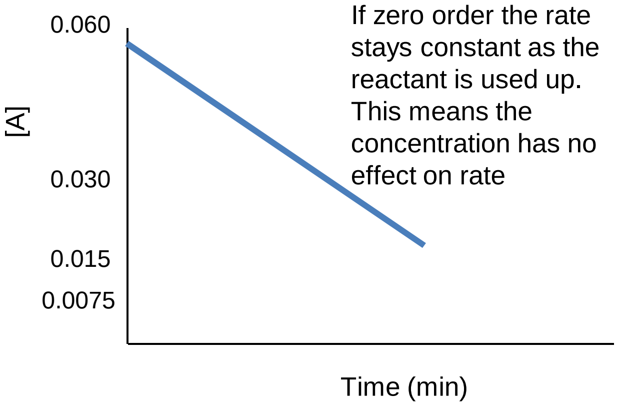
The half-life of a first-order reaction is independent of the concentration and is constant

Second order



If half-lives **rapidly** increase then the order is 2nd order

zero order



If zero order the rate stays constant as the reactant is used up. This means the concentration has no effect on rate

The rate constant (k)

1. The units of k depend on the overall order of reaction. It must be worked out from the rate equation
2. The value of k is independent of concentration and time. It is constant at a fixed temperature.
3. 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 $\mathbf{s^{-1}}$

For a 2nd order overall reaction the unit of k is $\mathbf{mol^{-1}dm^{3}s^{-1}}$

For a 3rd order overall reaction the unit of k is $\mathbf{mol^{-2}dm^{6}s^{-1}}$

Example (first order overall)

Rate = $k[A][B]^0$ m = 1 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

1. Rearrange rate equation to give k as subject

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

2. Insert units and cancel

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

Unit of k = s^{-1}

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

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

Calculate the unit of k

1. Rearrange rate equation to give k as subject

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

2. Insert units and cancel

$$k = \frac{\cancel{mol\ dm}^{-3}s^{-1}}{\cancel{mol\ dm}^{-3}.(moldm^{-3})^2}$$

3. Simplify fraction

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

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

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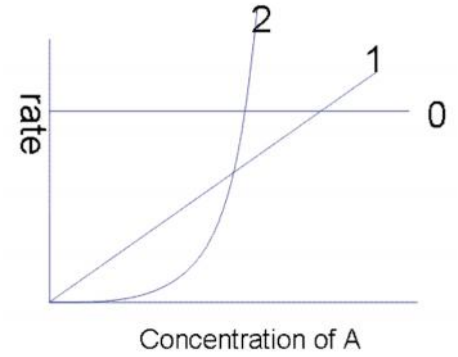

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Unit of k = s^{-1}

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

$r = k[A][B]^2$ **overall order is 3**

Calculate the unit of k

1. Rearrange rate equation to give k as subject

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

2. Insert units and cancel

$$k = \frac{\cancel{mol\ dm^{-3}}s^{-1}}{\cancel{mol\ dm^{-3}}.(moldm^{-3})^2}$$

3. Simplify fraction

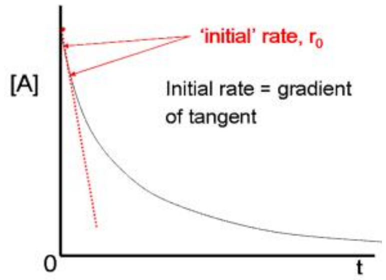
$$k = \frac{s^{-1}}{mol^2dm^{-6}}$$

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

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 → 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 =$mol^{-2}dm^6s^{-1}$

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 $x3^2$= **x9**

If these changes happened at the same time then the rate would x2x9= **x 18**

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 =$mol^{-2}dm^{6}s^{-1}$

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:

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

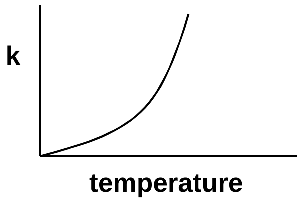
Remember k is the same for all experiments done at the same temperature.

Increasing the temperature increases the value of the rate constant k

Effect of Temperature on rate constant

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** = $Ae^{-Ea/RT}$ where A is a constant R is gas constant and Ea is activation energy.

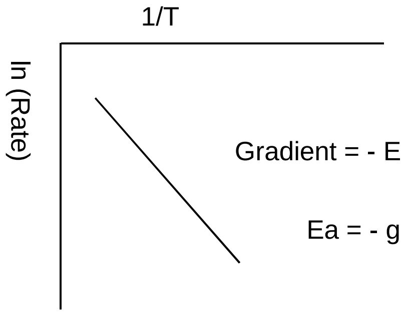


The Arrhenius equation can be rearranged

$$\ln k = \text{constant} - Ea/(RT)$$

k is proportional to the rate of reaction so ln k can be replaced by ln(rate)

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

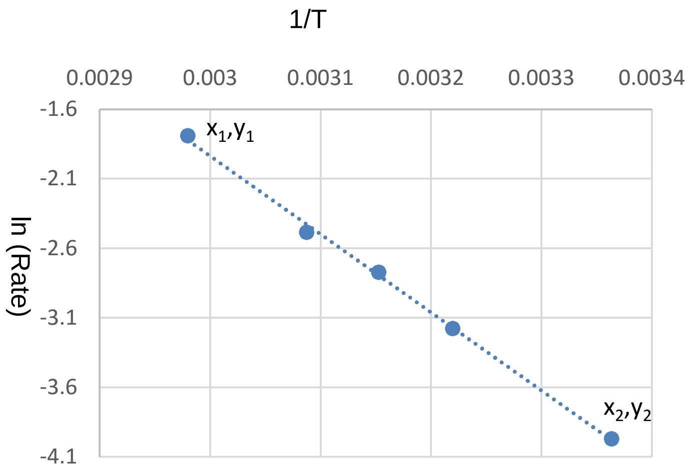


Gradient = - Ea/ R

Ea = - gradient x R

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

use a line of best fit
use all graph paper
choose points far apart on the graph to calculate the gradient

In above example gradient =-5680

Ea = - gradient x R (8.31)
= - -5680 x8.31
= 47200 J mol^{-1}

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

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

$A + 2B + C \rightarrow D + E$

Mechanism

Step 1	**$A + B \rightarrow X + D$**	**slow**
Step 2	$X + C \rightarrow Y$	fast
Step 3	$Y + B \rightarrow E$	fast

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

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

Example 2

overall reaction

$A + 2B + C \rightarrow D + E$

Mechanism

Step 1	$A + B \rightarrow X + D$	fast
Step 2	**$X + C \rightarrow Y$**	**slow**
Step 3	$Y + B \rightarrow E$	fast

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

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

$A + B \rightarrow X + D$

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

Investigating the rate of reaction between Iodine and propanone

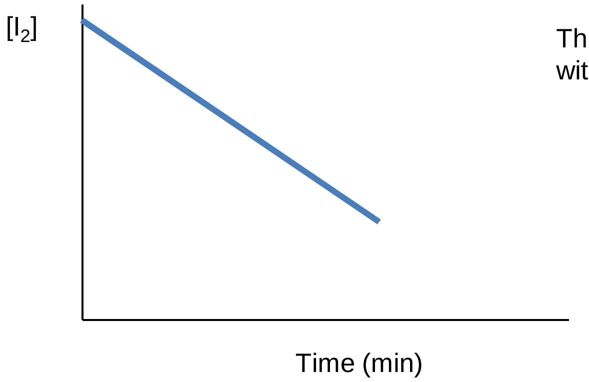
Propanone reacts with iodine in acidic solution (the acid is a catalyst) as shown in the equation below.

$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$

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 thiosulphate using a starch catalyst

$$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

yellow/brown sol colourless sol



This reaction is zero order with respect to I_2 but 1st order with respect to the propanone and acid catalyst

The rate equation for the reaction is
Rate = $k[CH_3COCH_3(aq)][H^+(aq)]$

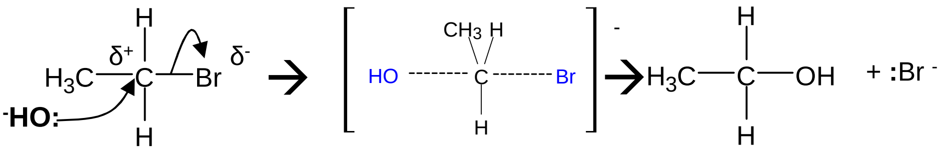
If there is a zero order reactant there must be at least two steps in the mechanism because the rate determining step will not involve the zero order reactant

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



$CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$ slow step

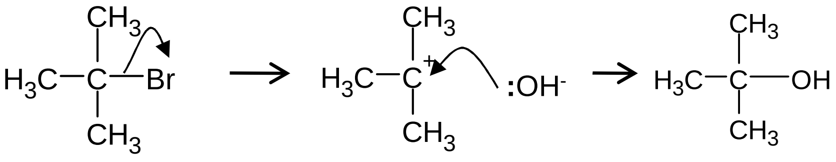
The rate equation is

$r = k\,[CH_3CH_2Br]\,[OH^-]$

This is called S_N2.
Substitution, **N**ucleophilic, **2** molecules in rate determining step

Primary halogenalkanes tend to react via the SN2 mechanism

SN_1 nucleophilic substitution mechanism for tertiary halogenoalkanes



The Br first breaks away from the haloalkane 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

$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$

Mechanism:

$(CH_3)_3CBr \rightarrow (CH_3)_3C^+ + Br^-$ slow

$(CH_3)_3C^+ + OH^- \rightarrow (CH_3)_3COH$ fast

The rate equation is

$r = k\,[(CH_3)_3CBr]$

This is called S_N1.
Substitution, **N**ucleophilic, **1** molecule in rate determining step

Primary halogenoalkanes don't do the SN_1 mechanism because they would only form an unstable primary carbocation.

Example 4

Overall Reaction
$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

Mechanism:
Step 1 $NO_2 + NO_2 \rightarrow NO + NO_3$ slow
Step 2 $NO_3 + CO \rightarrow NO_2 + CO_2$ fast
- NO_3 is a reaction intermediate

NO_2 appears twice in the slow steps so it is second order. CO does not appear in the slow step so is zero order.

$r = k\,[NO_2]^2$

Example 5

Using the rate equation rate = $k[NO]^2[H_2]$ and the overall equation $2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$, the following three-step mechanism for the reaction was suggested. X and Y are intermediate species.
Step **1 NO + NO → X**
Step **2 X + H_2 → Y**
Step **3 Y + H_2 → N_2 + $2H_2O$**

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

Step 2 – as H_2 appears in rate equation and combination of step 1 and 2 is the ratio that appears in the rate equation.