

Rate Determining Step & Arrhenius

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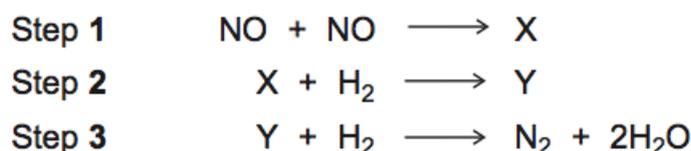
The phrase rate determining step implies that a reaction has **more than one step**.

One of those steps **must** be slower than the others. This is the rate determining step and the step from which the rate equation is derived.

if something is in the rate equation, it is also in the rate determining step (and vice-versa)

They often give you a proposed mechanism for a reaction and ask which step is the rate determining step.

The rate equation for the following reaction is: $\text{Rate} = k[\text{NO}]^2[\text{H}_2]$



From the rate equation, we can see that we must have **one H₂** in the rate determining step and **2 x NO**.

Step 1, we have 2 x NO but **no H₂**, therefore step 1 is ruled out.

Step 2, we have H₂ and X. From step 1, X is *likely* to be 2NO or N₂O₂, it doesn't really matter exactly what it is. But **X** must contain two N atoms and two O atoms. So you can think of X being like 2 x NO in "disguise". Therefore, the rate determining step is **step 2**.

Step 3 would have 2 x H₂, one from step 2 and one from step 3. But we can only have one H₂ in the rate determining step. Therefore step 3 can't be the rate determining step.

The rate determining step is often used to give information about the mechanism of a reaction.

Working out a mechanism

The aim is to write out a two step mechanism (two equations) based on the equations below and they said that the rate determining step is step 1:



$$\text{Rate} = k[\text{H}_2(\text{g})][\text{ICl}(\text{g})]$$

Step 1

As this is the rate determining step, we need to use **H₂ and ICl** from the rate equation. You get a mark for this alone:



Now you have options:

Option 1:

Using the chemical equation we could form HI and HCl for example:



Option 2:

If you're not sure what products to make, a good method is just put it all together:



- ✓ It doesn't matter that H₂ICl is a made up product. In fact, it's about the only time it's ok to make it up!

Step 2

Option 1:

We need use the other compounds we haven't used yet in the chemical equation. We have one ICl still to use and **whatever product we made in step 1** that is **not in the chemical equation** we need to use that too:



Option 2:

Using the made up H₂ICl and the ICl we haven't used yet:



Overall

Adding our two equations together gives us the original overall equation. Therefore we need to cancel the compounds that are not in the overall equation:

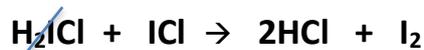
Option 1:





✓ HI's must cancel as not in overall equation

Option 2:



✓ H₂CI's must cancel as not in overall equation

The Arrhenius Equation

$$k = \text{Ae}^{-E_a/RT}$$

This equation just shows how the rate constant, k , varies with E_a and T . But you know this already! i.e. increase T then you increase k , increase E_a then you decrease k .

This form of the equation is not that useful so they remove the 'e' (exponential). This is a bit mathsy but don't worry about it at all. Just know the end result:

$$\ln k = \ln A - E_a/RT$$

The Graph

The purpose of this is to **calculate E_a**

Almost all questions involve plotting a graph to calculate the **activation energy**. It all goes back to the equation of a straight line:

$$y = mx + c$$

$$\ln k = -E_a/RT + \ln A$$

We usually plot **$\ln k$ versus $1/T$** .

the gradient = **$-E_a/R$**

In brief:

- **plot** the graph
- get the **gradient**
- multiply by R (8.31) $\rightarrow E_a$.

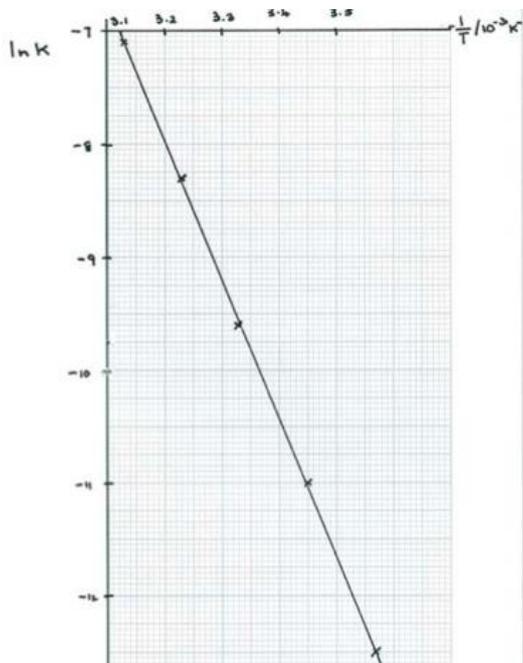
The graph is **always** a **straight line** and should be “upside down” from what you are used to (see below).

Pay attention to the “negative” values on the y-axis. The values become more negative as you go down the y-axis.

Also be careful with the scale. It is recommended that your graph covers at least half of the space available.

Remember you don't need to start the scale at 0 on both or either of the axes. Start it at any value you want!

The $1/T$ axis can go at the top of the graph paper (as shown below) or in the usual place at the bottom.



✓ $\ln A$ has never been asked *so far*. This can be found where the graph **cuts the y-axis**.

The Gradient

Just work out the gradient from the graph or from the values that they give you. The gradient should be a **negative** value.

Then use: **gradient = $-E_a/R$**

As R is the gas constant, we can then multiply the gradient by R to get the activation energy.

- ✓ Activation energies are always + **values**. Just be careful as it is easy to get confused here with the negative signs. The negative gradient and $-E_a$, should cancel out → a positive value.

Rearranging the equation

As AQA can be quite “mathsy” in places, they often ask you to calculate E_a or T without using a graph, which means rearranging the ln form of the equation. This might be quite difficult for non-maths students so here are the equations below:

$$E_a = (\ln A - \ln k) \times RT \quad \text{and} \quad T = E_a / (\ln A - \ln k) \times R$$

- ✓ If you can rearrange to get E_a , then it is very easy from there to rearrange for T: just take the whole $(\ln A - \ln k) \times R$ part to the bottom line on the other side.

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