

Rates part 3

Rate Determining Step

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

One of those steps **must** be slower than the others. The slowest step is called the rate determining 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)

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

Example: S_N1 versus S_N2

A classic example to illustrate the use of the rate determining step is to look at nucleophilic substitution reactions of haloalkanes.

The '1' (unimolecular) tells you that there is only one reactant in the rate equation:

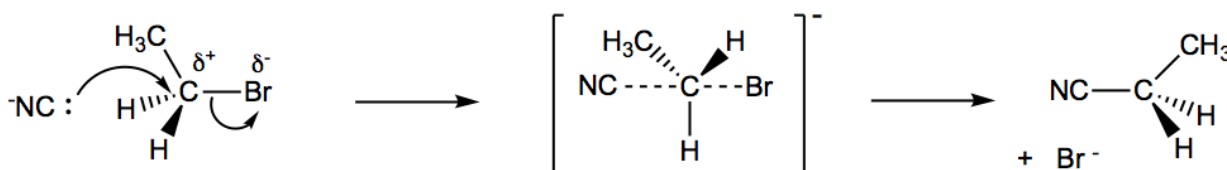
$$\text{Rate} = k[\text{A}]$$

The '2' (bimolecular) tells you that there are two reactants in the rate equation:

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

I won't go into this too much here as it will become all about organic chemistry. Briefly, here are the two mechanisms:

S_N2

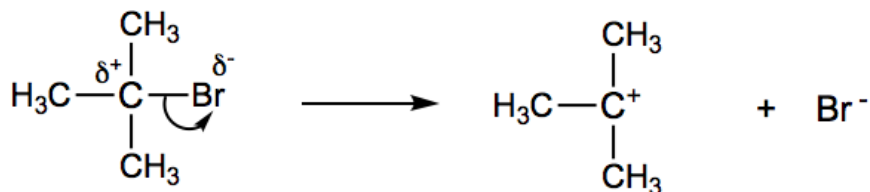


This is a one step reaction and **both** the **nucleophile** and **primary** haloalkane are in the rate equation:

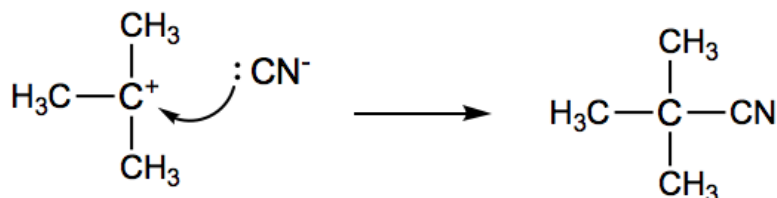
$$\text{Rate} = k[\text{haloalkane}][\text{nucleophile}]$$

S_N1

step 1



step 2



This occurs in two steps where only the haloalkane is in the rate equation, therefore step 1 is the rate determining step:

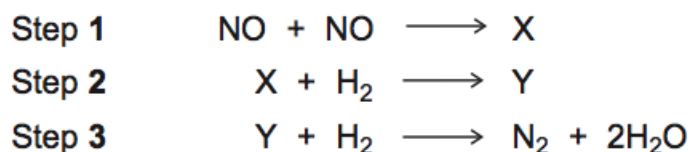
$$\text{Rate} = k[\text{haloalkane}]$$

In summary, rate studies showed that the two reactions proceed by different mechanisms and helped them work out possible mechanisms.

Another type of question

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**.

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

In 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**.

The Arrhenius Equation

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

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:

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

- ✓ They actually give **both** forms of the Arrhenius equation in the data sheet. Nice people at OCR.

The Graph

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 $1/T$** .

$$\text{the gradient} = -E_a/R$$

- ✓ In brief...all you do is plot the graph, get the gradient and multiply by R (8.31) $\rightarrow E_a$.

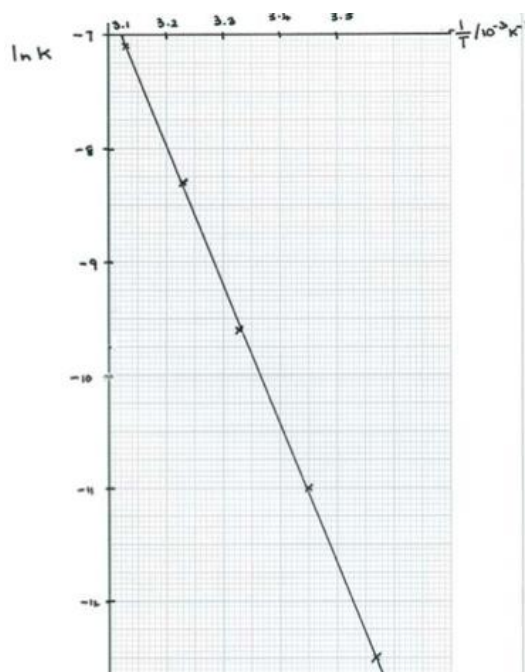
The graph is **always** a **straight line** and should be "upside down" from what you are used to (see below).

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. It might be easier though doing as shown:



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.

lnA

lnA can be found where the graph cuts the y-axis (vertical axis). This would require extrapolating the line backwards i.e. continue the line back until it cuts the y-axis and read the value.

Once you have this value any question will probably ask for the **value of A** and not lnA. So you would need to press the **inverse ln** button on your calculator.

A = pre-exponential factor (Arrhenius constant) and the units depend on the reaction.

A represents the frequency of collisions between reactant molecules