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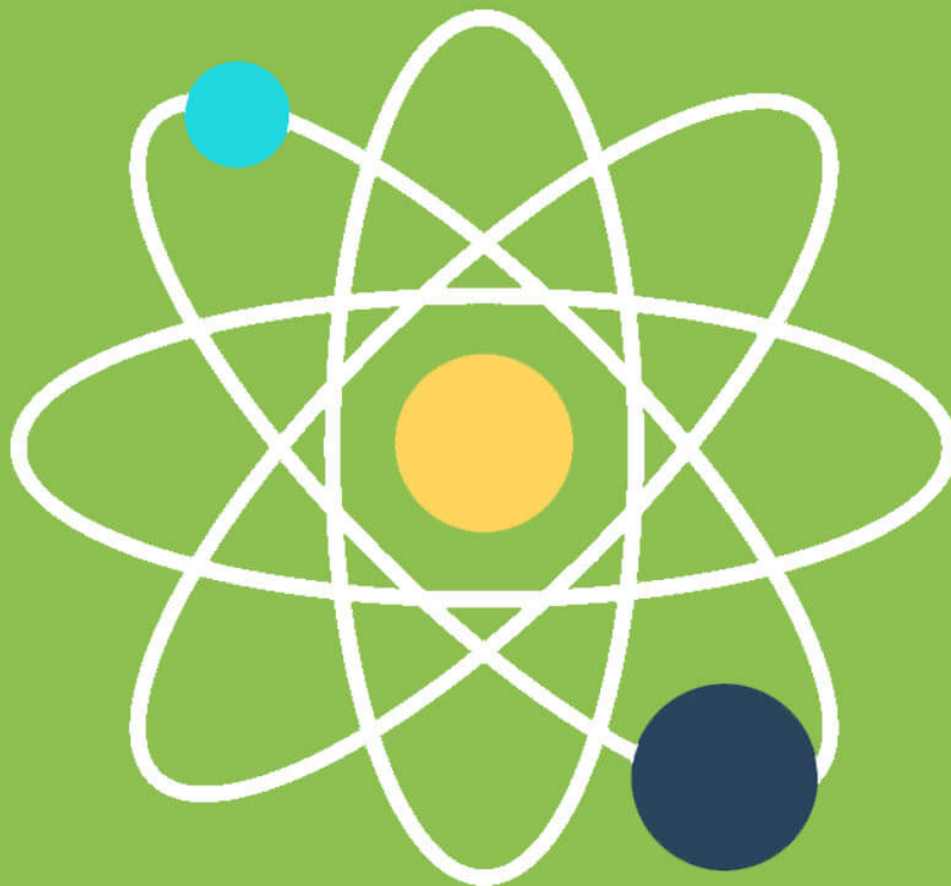
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16.2 Activation Energy



IB Chemistry - Revision Notes

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16.2.1 The Arrhenius Equation

The Arrhenius Equation

- The rate equation shows how each of the reactants in a reaction affects the rate of the reaction and it includes the rate constant, k
- However, k only remains constant if the concentration of the reactants is the only factor which is changed
 - If the temperature is changed or a catalyst is used or changed, then the rate constant, k , changes
- At higher temperatures, a greater proportion of molecules have energy greater than than the activation energy
- Since the **rate constant** and **rate of reaction** are **directly proportional** to the fraction of molecules with energy equal or greater than the activation energy, then at higher temperatures:
 - The **rate of reaction** increases
 - The **rate constant** increases
- The relationship between the rate constant, the temperature and also the activation energy is given by the Arrhenius equation:

$$k = Ae^{\frac{-E_a}{RT}}$$

k = THE RATE CONSTANT

A = ARRHENIUS CONSTANT

(A CONSTANT RELATED TO THE COLLISION FREQUENCY AND ORIENTATION OF THE MOLECULES)

E_a = ACTIVATION ENERGY (J mol^{-1})

R = GAS CONSTANT ($8.31 \text{ J K}^{-1} \text{ mol}^{-1}$)

T = TEMPERATURE (KELVIN, K)

e = MATHEMATICAL CONSTANT

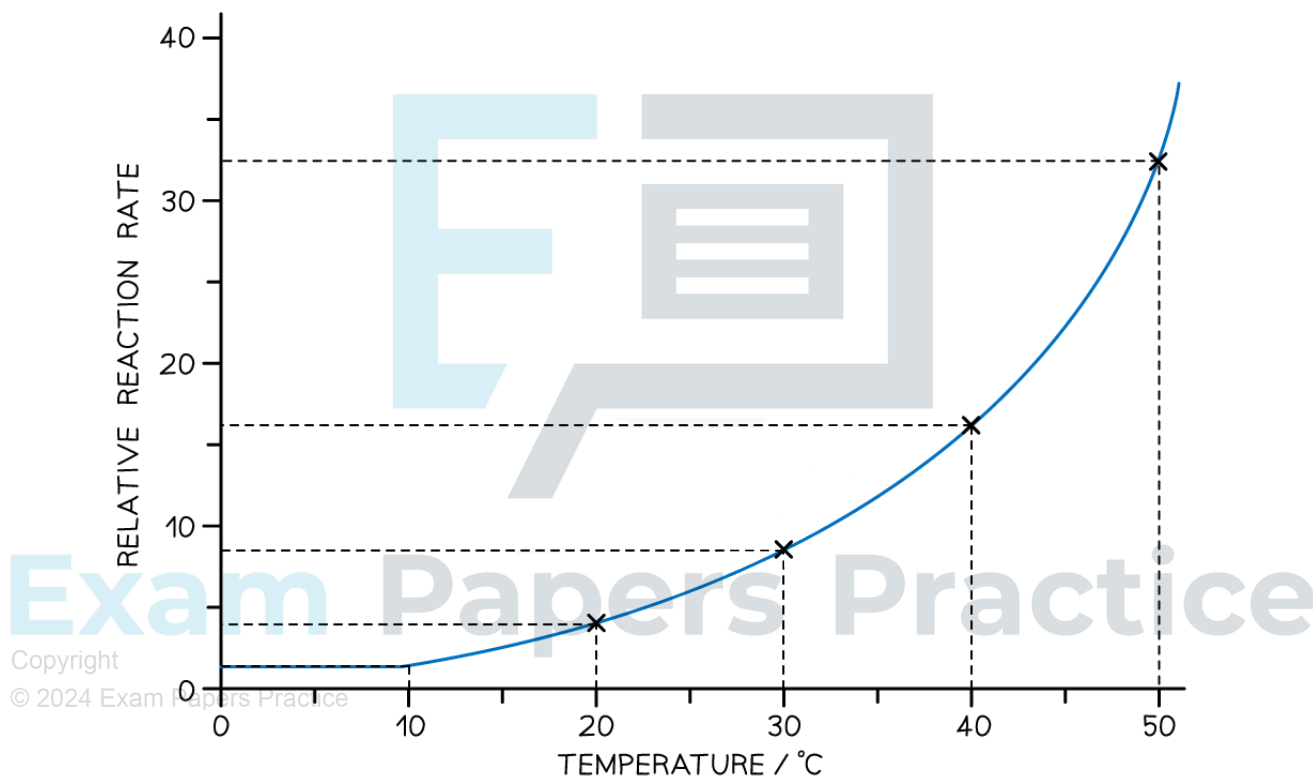
(CAN BE FOUND ON YOUR CALCULATOR – IT HAS AN APPROXIMATE VALUE OF 2.718)

- E_a and A are constants that are characteristic of a specific reaction
 - A does vary slightly with temperature but it can still be considered a constant

- R is a fundamental physical constant for all reactions
- k and T are the only variables in the Arrhenius equation
- The Arrhenius equation is used to describe reactions that involve gases, reactions occurring in solution or reactions that occur on the surface of a catalyst

Temperature Dependence

- The following rate-temperature graph is typical of reactions that have an activation energy, E_a , of around 50 kJ mol^{-1}



Graph showing the temperature dependence of reaction rate in the Arrhenius equation

- The graph shows a generally accepted rule that rate doubles with a temperature increase of approximately 10°C
 - This rule is not an absolute rule as values for the activation energy, E_a , of a reaction vary greatly

Using the Arrhenius Equation

- The Arrhenius equation is easier to use if you take natural logarithms of each side of the equation, which results in the following equation:



$$\ln k = \ln A - \frac{E_a}{RT}$$

- The Arrhenius Equation can be used to show the effect that a change in temperature has on the rate constant, k , and thus on the overall rate of the reaction
 - An increase in temperature (higher value of T) gives a greater value of $\ln k$ and therefore a higher value of k
 - Since the rate of the reaction depends on the rate constant, k , an increase in k also means an increased rate of reaction
- The equation can also be used to show the effect of increasing the activation energy on the value of the rate constant, k
 - An increase in the activation energy, E_a , means that the proportion of molecules which possess at least the activation energy is less
 - This means that the rate of the reaction, and therefore the value of k , will decrease
- The values of k and T for a reaction can be determined experimentally
 - These values of k and T can then be used to calculate the activation energy for a reaction
 - This is the most common type of calculation you will be asked to do on this topic

 **Exam Tip**

In the exam, you could be asked to calculate any part of the Arrhenius Equation Using the equation in its natural logarithm form makes this easier

 **Worked example**

Calculate the activation energy of a reaction which takes place at 400 K, where the rate constant of the reaction is $6.25 \times 10^{-4} \text{ s}^{-1}$.

$A = 4.6 \times 10^{13}$ and $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$.

Answer



$$\ln k = \ln A - \frac{E_a}{RT}$$

REARRANGE THE EQUATION FOR E_a :

$$\frac{E_a}{RT} + \ln k = \ln A$$

$$\frac{E_a}{RT} = \ln A - \ln k$$

$$\rightarrow E_a = (\ln A - \ln k) \times RT$$

INSERT VALUES FROM THE QUESTION:

$$\begin{aligned} E_a &= [(\ln 4.6 \times 10^{13}) - (\ln 6.25 \times 10^{-4})] \times (8.31 \times 400) \\ &= [(31.4597) - (-7.3778)] \times (3324) \\ &= 129,095.85 \text{ J} \end{aligned}$$

REMEMBER, E_a HAS THE UNIT kJ...

$$E_a = 129 \text{ kJ}$$

16.2.2 Graphing the Arrhenius Equation

Graphing the Arrhenius Equation

Finding the Activation Energy

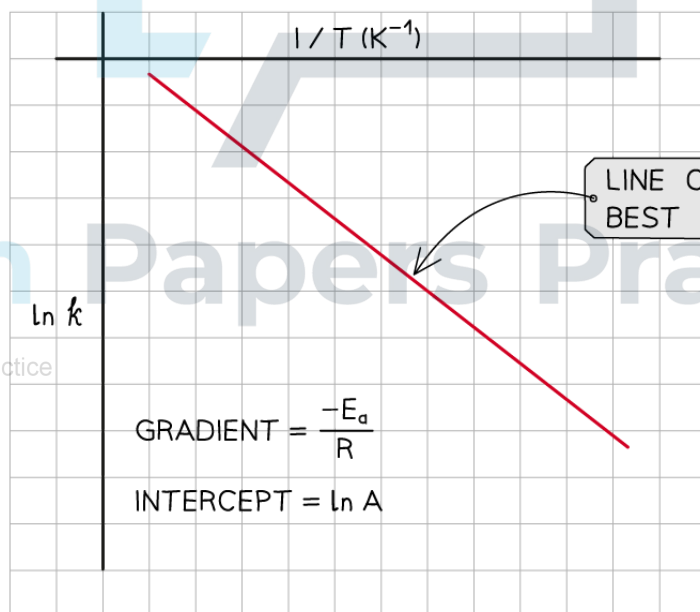
- Very often, the Arrhenius equation is used to calculate the activation energy of a reaction
- A question will either give sufficient information for the Arrhenius equation to be used or a graph can be plotted and the calculation done from the plot

Using the equation:

- Remember, it is usually easier to use the version of the Arrhenius equation after natural logs of each side have been taken

Using an Arrhenius plot:

- A graph of $\ln k$ against $1/T$ can be plotted, and then used to calculate E_a
 - This gives a line which follows the form $y = mx + c$



The graph of $\ln k$ against $1/T$ is a straight line with gradient $-E_a/R$

- From the graph, the equation in the form of $y = mx + c$ is as follows:



$$\ln k = \frac{-E_a}{R} \frac{1}{T} + \ln A$$

$$y = \ln k$$

$$x = \frac{1}{T}$$

$$m = \frac{-E_a}{R} \text{ (THE GRADIENT)}$$

$$c = \ln A \text{ (THE } y \text{ INTERCEPT)}$$

 **Worked example**

1. Complete the following table
2. Plot a graph of $\ln k$ against $1/T$
3. Use this to calculate the activation energy, E_a , and the Arrhenius constant, A , of the reaction.

Temperature / K	$\frac{1}{T} / \text{K}^{-1}$	Time (t) / s	Rate constant (k) / s^{-1}	$\ln k$
310	3.23×10^{-3}	57		-9.2
335		31	3.01×10^{-4}	-8.1
360	2.78×10^{-3}	19	5.37×10^{-4}	-7.5
385	2.60×10^{-3}	7	9.12×10^{-4}	

Answers

Answer 1:

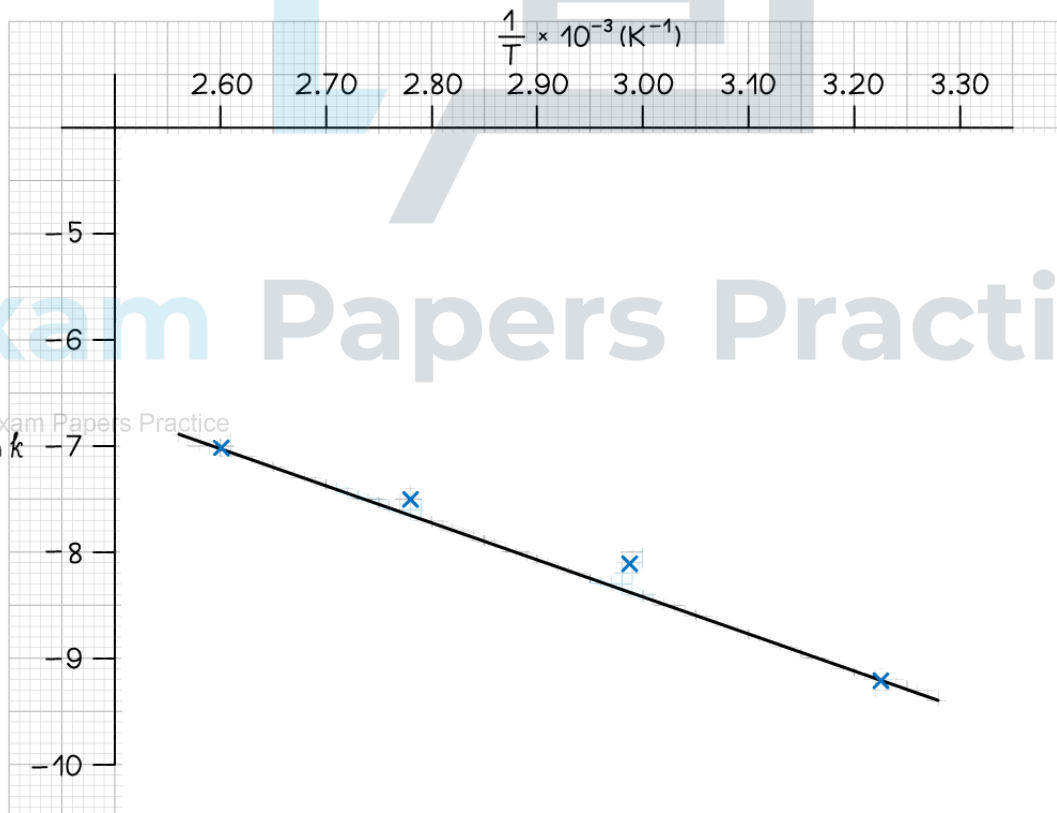
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Temperature / K	$\frac{1}{T} / \text{K}^{-1}$	Time (t) / s	Rate constant (k) / s ⁻¹	ln k
310	3.23×10^{-3}	57	1.01×10^{-4}	-9.2
335	2.99×10^{-3}	31	3.01×10^{-4}	-8.1
360	2.78×10^{-3}	19	5.37×10^{-4}	-7.5
385	2.60×10^{-3}	7	9.12×10^{-4}	-7.0

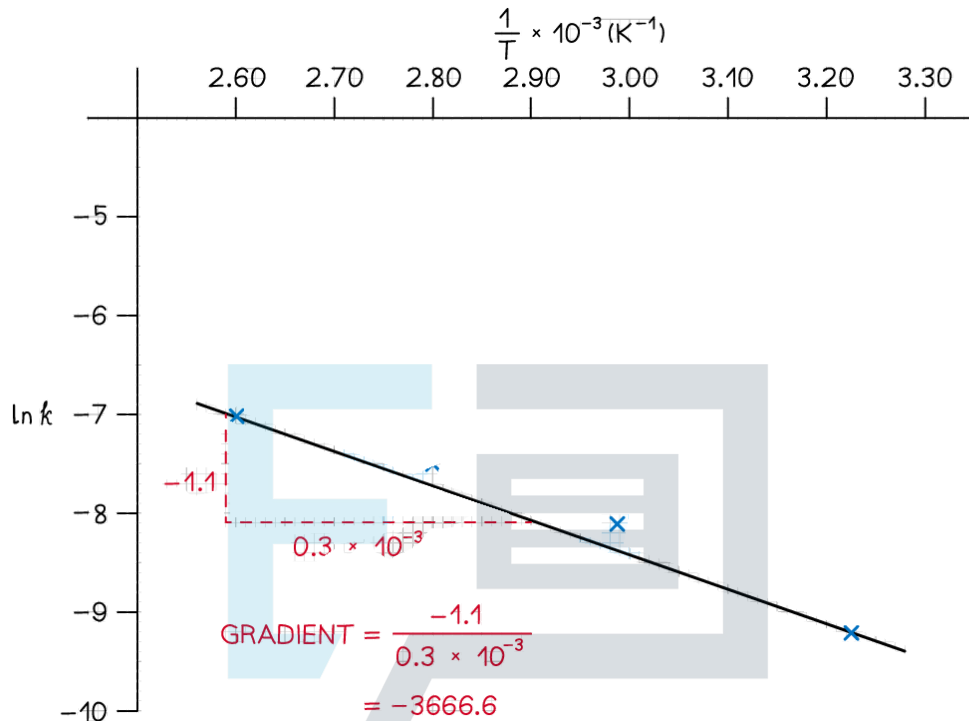
Answer 2:





Answer 3:

CALCULATE THE ACTIVATION ENERGY:



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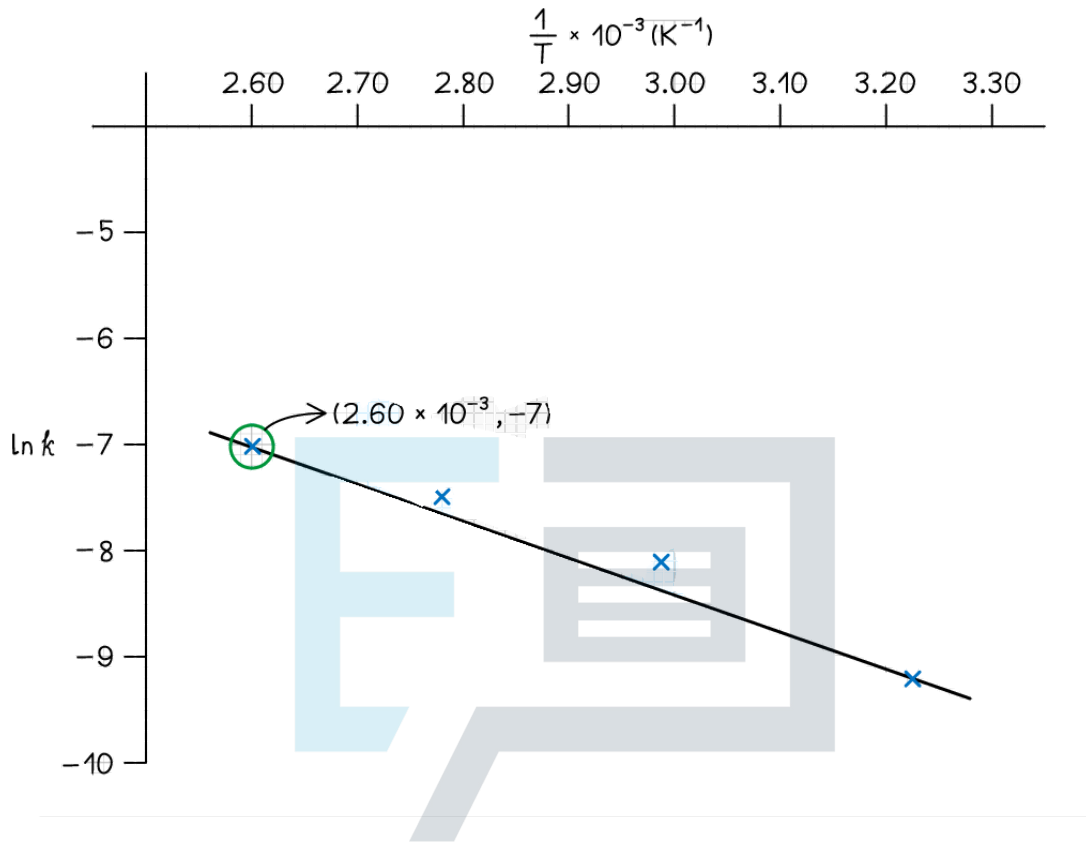
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$$\text{GRADIENT} = \frac{-E_a}{R} = -3666.6$$

$$\begin{aligned} E_a &= -(-3666.6 \times 8.31) \\ &= 30,469 \text{ J mol}^{-1} \\ &= 30.5 \text{ kJ mol}^{-1} \end{aligned}$$



CALCULATE A:



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CHOOSE A POINT ON THE GRAPH
(2.60×10^{-3} , -7.0)

USE THE FOLLOWING EQUATION:

$$y = m x + c$$
$$\rightarrow \ln k = \frac{-E_a}{R} \frac{1}{T} + \ln A$$

$$\ln k = -7.0$$

$$\frac{1}{T} = 2.60 \times 10^{-3}$$

FROM THE POINT
CHOSEN ON THE GRAPH

$$\frac{-E_a}{R} = \frac{-1.1}{0.3 \times 10^{-3}}$$
$$= -3666.6$$

$$\text{SO: } -7.0 = (-3666.6 \times 2.60 \times 10^{-3}) + \ln A$$

$$-7.0 = -9.53 + \ln A$$

$$\therefore \ln A = -7.0 + 9.53$$
$$= 2.53$$

$$A = e^{2.53}$$

$$A = 12.55$$

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 **Exam Tip**

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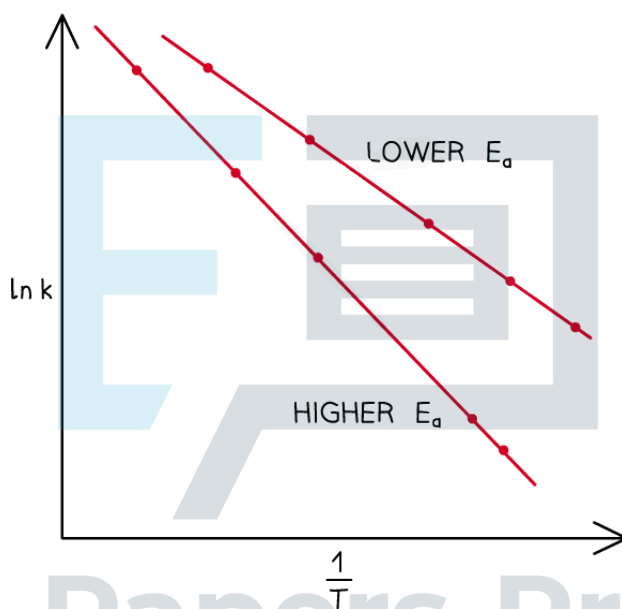
You are not required to learn these equations. However, you do need to be able to rearrange them, and knowing them is helpful in understanding the effects of temperature on the rate constant.

16.2.3 Activation Energy from Rate Constants

Activation Energy from Rate Constants at Different Temperatures

Arrhenius Plots

- Arrhenius plots for two reactions with different activation energies can be drawn on the same graph



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Arrhenius plots for two reactions with different activation energies

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- The reaction with a steeper gradient has the higher activation energy, E_a
- This indicates that the rate constant, and therefore rate, will change quicker with temperature changes

Calculating the Activation Energy

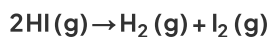
- The activation energy, E_a , can be calculated using rate constant values, k_1 and k_2 , for two given temperatures, T_1 and T_2
- This requires the use of the following equation that is given in the data booklet:



$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Worked example

Hydrogen iodide decomposes in the gas phase to form hydrogen and iodine



At 283 °C, the rate constant is $3.52 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$ At 508 °C, the rate constant is $3.95 \times 10^{-2} \text{ mol dm}^{-3} \text{ s}^{-1}$ Calculate the activation energy, E_a , for the reaction

Answer

1. Convert the temperatures from °C to K:

- $T_1: 283 + 273 = 556 \text{ K}$
- $T_2: 508 + 273 = 781 \text{ K}$

2. Write the appropriate Arrhenius equation from the data booklet

3. Substitute the values

4. Evaluate the equation to get the activation energy, E_a

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

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$$\ln\left(\frac{3.52 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}}{3.95 \times 10^{-2} \text{ mol dm}^{-3} \text{ s}^{-1}}\right) = \frac{E_a}{8.31 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{781 \text{ K}} - \frac{1}{556 \text{ K}}\right)$$

$$-11.6281 = \frac{E_a}{8.31} \times -5.1815 \times 10^{-4}$$

$$\frac{-11.6281}{-5.1815 \times 10^{-4}} = \frac{E_a}{8.31}$$

$$\frac{-11.6281}{-5.1815 \times 10^{-4}} \times 8.31 = E_a$$

$$E_a = 1.87 \times 10^5 \text{ J mol}^{-1}$$