

RATE EQUATIONS PART 2

RATE-DETERMINING STEPS IN MECHANISMS

Many reactions occur in several steps, i.e. with more than one step in the **reaction mechanism**. For example, there may be an intermediate formed in one step which then turns into the product in a second step. Catalysts may react in one step and then be regenerated in a later step.

In the reaction of X with Y and C to form Z, the reaction mechanism could be:



The rate of the **entire** reaction is equal to the rate of the **slowest** step in a mechanism. The slowest step in a mechanism is called the **rate-determining step**. In the example above:

- Changing the rate of step 2 does **not** change the rate of the reaction
- Changing the rate of step 1 **does** change the rate of the reaction
- Step 1 is the rate-determining step
- The rate is affected by the concentrations of **only** the chemicals involved in this step

EXAM TIP

The steps in the mechanism must add up to give the overall balanced equation

Calculating k

A reaction has $A = 5.02 \times 10^5 \text{ s}^{-1}$. It is performed at 298 K and has an activation energy of 82.4 kJ mol⁻¹. What is the rate constant, k? ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

$$k = Ae^{-E_a/RT} = 5.02 \times 10^5 \times e^{-82400/(8.314 \times 298)} = 0.181 \text{ s}^{-1}$$

EFFECT OF TEMPERATURE ON RATE CONSTANT

The rate of a chemical reaction is affected by temperature. Reactions happen faster when heated and more slowly when cooled. Look back at **Reaction Rates** (Sheet 7) to see how collision theory can explain why this is.

It is not obvious how the rate equation shows that rate depends on temperature. The key is that the rate constant, k, is a constant **only at constant temperature**. When the temperature goes up, k increases, when the temperature goes down, k decreases.

E_a = activation energy

A is called the Arrhenius constant

R = gas constant = $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

If E_a , A and R are constant, as T increases then E_a/RT will decrease and so $e^{-E_a/RT}$ will increase.

EXAM TIP

No need to remember the equation - it's given in exam questions. The value of R will be given also.

RATE EQUATIONS AND MECHANISMS

In a rate equation, the **order** with respect to each reactant must be the same as the number of molecules of that reactant involved in the **rate-determining step** of the mechanism.

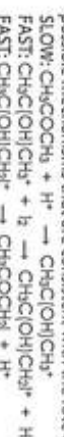
Example 1: The overall reaction $2\text{NO} + 2\text{H}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$ happens in two steps:
SLOW: $2\text{NO} + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}_2$
FAST: $\text{H}_2\text{O}_2 + \text{H}_2 \rightarrow 2\text{H}_2\text{O}$

The rate equation is: $\text{Rate} = k[\text{NO}]^2[\text{H}_2]$. It is **second order** with respect to NO and **first order** with respect to H_2 because there are **two** molecules of NO and **one** molecule of H_2 in the **rate-determining (slow)** step of the mechanism.

Example 2: The rate equation for the acid catalysed reaction $\text{CH}_3\text{COCH}_3 + \text{I}_2 \rightarrow \text{CH}_3\text{COCH}_2\text{I} + \text{HI}$ is: $\text{Rate} = k[\text{CH}_3\text{COCH}_3][\text{H}^+]$.

This tells you that the rate-determining step of the mechanism must involve one catalytic H^+ ion, one molecule of CH_3COCH_3 and **no** I_2 at all.

You cannot be certain what the mechanism is from this information - but you can propose possible mechanisms that are consistent with the rate equation, e.g.



EXAM TIP

Make sure that each step of the mechanism, and especially the rate-determining step, is correctly balanced. The balancing numbers in the rate-determining step give you the powers in the rate equation.

USING A GRAPH TO WORK OUT E_a AND A

The Arrhenius equation is an exponential equation - perhaps it looks more complicated than other equations that you have seen. The trick to dealing with it is to know that the inverse function of exponential e^x is the natural logarithm, $\ln x$, so the Arrhenius equation can be written as:

$$\ln k = -\frac{E_a}{RT} + \ln A \quad \text{or} \quad \ln k = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln A$$

This fits the equations of a straight line: $y = mx + c$ where $y = \ln k$ and $x = \frac{1}{T}$

A plot of $\ln k$ on the y-axis and $\frac{1}{T}$ on the x-axis should give a straight line e.g. the following data produces a graph of $\ln k$ against $\frac{1}{T}$ like this:

T (K)	Rate constant, k (s ⁻¹)	$\frac{1}{T}$ (K ⁻¹)	$\ln k$
298	0.00171	3.36×10^{-3}	-6.37
359	0.0187	2.79×10^{-3}	-3.98
465	0.181	2.15×10^{-3}	-1.71
603	1.44	1.66×10^{-3}	0.37

At the y-axis, $x = 0$, so $1/T = 0$ and $\ln k = \ln A$

By extending the trend line, you can see that it crosses the y-axis at 6.83, so:

$$\ln A = 6.83 \quad \text{and} \quad A = e^{6.83} = 925 \text{ s}^{-1}$$

The gradient of the line is -3920, so $-\frac{E_a}{R} = -3920$

$$E_a = 3920 \times R = 3920 \times 8.314 = 32591 \text{ J mol}^{-1} = 32.6 \text{ kJ mol}^{-1}$$

