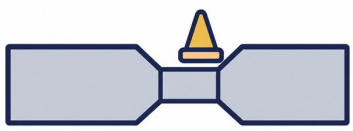
Mechanisms and Temperature Map

AQA A-level Chemistry (7405) · 3.1.9 Mechanisms and temperature

1 The slow step

3.1.9.2 vi

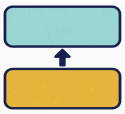
- Slowest step: **rate-determining**
- Its species: in the rate equation
- Later steps: not counted
- **Intermediate**: made, then used



2 Rate equation → mechanism

3.1.9.2 vii

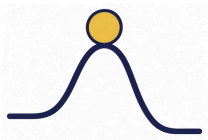
- Slow step: the rate-equation species
- Other reactants: **fast** steps after
- Steps **add up** to the equation
- Intermediates cancel

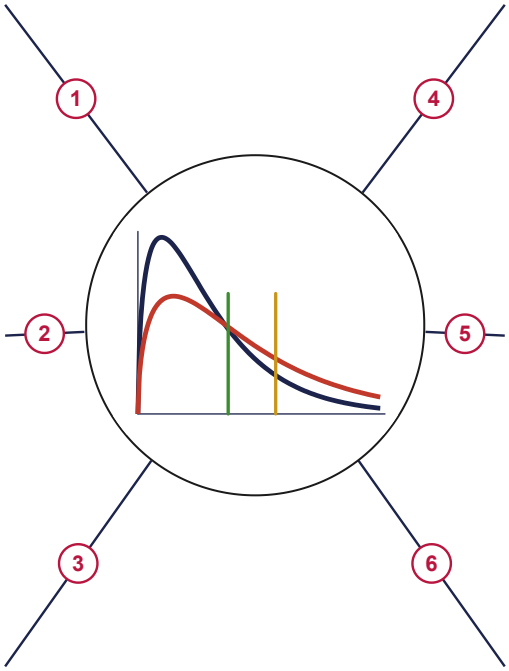


3 E_a and temperature

3.1.5.2-3

- **E_a**: minimum energy to react
- Higher T: curve flatter, to the right
- More molecules with $E \geq E_a$
- k rises; rate equation unchanged





4 The Arrhenius equation

3.1.9.1 v-vii

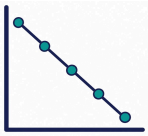
- **$k = Ae^{(-E_a/RT)}$**
- E_a in J mol^{-1}, T in K
- R = 8.31 J K^{-1} mol^{-1}
- $\ln k = -E_a/RT + \ln A$



5 Arrhenius plot

3.1.9.1 viii

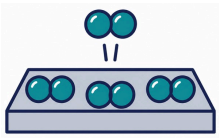
- ln k against **1/T**
- Gradient = **$-E_a/R$**
- Clock at several T: **$1/t \propto k$**
- Intercept = ln A



6 Catalysts

3.1.5.5, 3.2.5.5

- Route of **lower E_a**
- More molecules with $E \geq E_a$(cat)
- Homogeneous: same phase, intermediate
- Heterogeneous: **adsorb**, **desorb**



Rate equation to mechanism

the species in the rate equation are the species up to and including the slow step

Reaction	Rate equation	Slow step holds	Mechanism
$NO_2 + CO \rightarrow NO + CO_2$	rate = $k[NO_2]^2$	2 NO_2, no CO	two steps, NO_3 intermediate
$2NO + O_2 \rightarrow 2NO_2$	rate = $k[NO]^2[O_2]$	2 NO and O_2	fast $2NO \rightleftharpoons N_2O_2$ first
$CH_3CH_2Br + OH^-$	rate = $k[RBr][OH^-]$	RBr and OH^-	one step
$(CH_3)_3CBr + OH^-$	rate = k[RBr]	RBr only	two steps, carbocation

Worked examples

Rate to mechanism

- $2NO_2 + O_3$, rate = $k[NO_2][O_3]$
- slow: $NO_2 + O_3 \rightarrow NO_3 + O_2$
- fast: $NO_3 + NO_2 \rightarrow N_2O_5$

k from E_a

- E_a 50 kJ, A 4.0×10^{10} s^{-1}
- E_a/RT at 300 K = 20.06
- **k = 78 s^{-1}**

E_a from a gradient

- gradient -7.22×10^3 K
- × 8.31
- **E_a = 60.0 kJ mol^{-1}**

Catalysts return with the transition metals (3.2.5.5); the rate equation for nucleophilic substitution returns in 3.3.3.

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