Module 2, Lecture 6
Chemical Kinetics
Part 3

Learning objectives:

- Understand the terms 'molecularity', 'activation energy' and 'transition state'
- Understand that a system of molecules will have a range of energies and this range is dependent on the temperature of the system
- Use the Arrhenius equation to calculate the activation energy or rate constants

Textbook: Chapter 14

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Temperature dependence of rate

Experiments show that an increase in **temperature** speeds up **all** reactions

$$\text{rate} = k[A]^a[B]^b$$

k is the only term in the rate law that depends on T therefore k is given for a certain temperature.

Why does temperature speed up the reaction?

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The collision model

Consider: **$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$**

break N-O bond and **form** C-O bond

- Kinetic theory of gases indicates all molecules are in constant motion.
- Molecules constantly collide $\Rightarrow$ energy transferred from one molecule to another
- Three factors affect rate at which molecules react:

    1. **Collision rate**
    2. **Collision effectiveness**
    3. **Collision orientation**

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1. Collision rate

Molecules must collide to react

More collisions = increased reaction rate

Collision rate measures, at the molecular level, the number of collisions per second between species.

This is how the terms [A] and [B] get into the rate law.
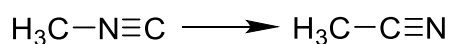
<u>What factors affect collision rate?</u>

| ↑ Temperature = ↑ Kinetic energy = ↑ Frequency of collisions |

- Higher concentrations = more collisions
- Greater speed (kinetic energy) = more collisions

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2. Collision effectiveness

Collision must yield enough **energy** for bond breaking or formation.

$$H_3C-N\equiv C \longrightarrow H_3C-C\equiv N$$

- Even if ΔG is -ve, E is required for reaction

- Energy threshold for reaction to occur is called **activation energy E_a**

- Not all collisions lead to a reaction

- Only those with sufficient energy are successful

Also called:
transition state
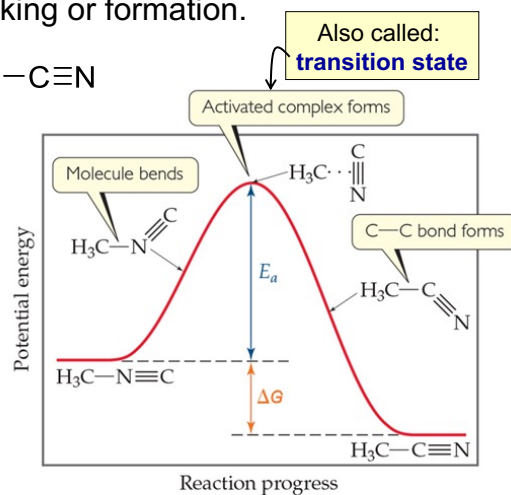
▲ FIGURE 15.17 Energy profile for conversion of methyl isonitrile (H_3CNC) to its isomer acetonitrile (H_3CCN).

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Collision effectiveness and temperature

- An increase in temperature causes molecules to **move faster and hence with more energy.**
- Distribution of kinetic energy is exponential **(Boltzmann Distribution)**
- Fraction of molecules with $E > E_a = e^{-Ea/RT}$
- As T increases, more molecules have $E > E_a$ i.e **greater fraction of collisions effective.**
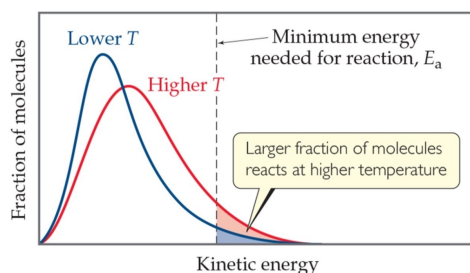
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Temperature and reaction rate

• Experiments show that an increase in T speeds up **all** reactions.

• Approximate 'rule of thumb':

'For every 10ºC rise in T, the rate doubles.'

• Temperature affects reaction rate both because of its effect on **collision frequency** & **collision effectiveness**.
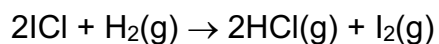
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3. Collision orientation

For most reactions, molecules must also be oriented correctly during the collision for the reaction to occur.
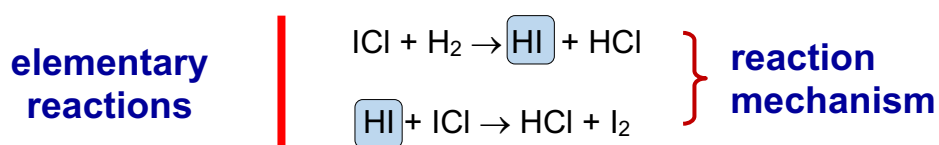
e.g. Cl + ONCl → Cl_2 + NO
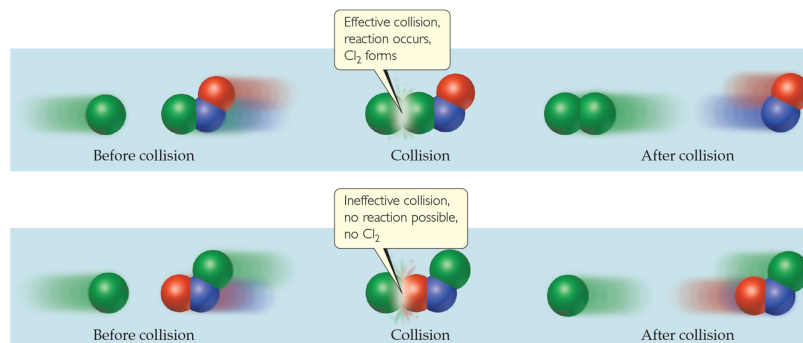
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Molecularity

Used to classify **elementary reactions**

$$2ICl + H_2(g) \rightarrow 2HCl(g) + I_2(g)$$

chance of three molecules coming together in correct way to react very low.

Instead:

elementary reactions | $ICl + H_2 \rightarrow$ HI $+ HCl$ } **reaction mechanism**
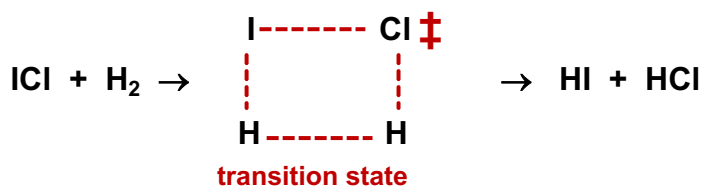HI $+ ICl \rightarrow HCl + I_2$

Molecularity

Molecularity: the total number of species involved in a single collision leading to reaction.

molecularity	classification
1	unimolecular
2	bimolecular
3	termolecular (**unlikely**)

Transition state (activated complex)

Collision forms loosely bound 'complex' containing **partly broken and partly formed bonds** e.g

$$ICl + H_2 \rightarrow \quad \begin{array}{ccc} I\text{-------}Cl & \ddagger \\ | & | \\ | & | \\ H\text{-------}H \end{array} \quad \rightarrow \quad HI + HCl$$

transition state

Transition state, denoted by superscript $\ddagger$ exists for a very short time – can not be isolated (i.e. different from a reaction intermediate e.g. HI)

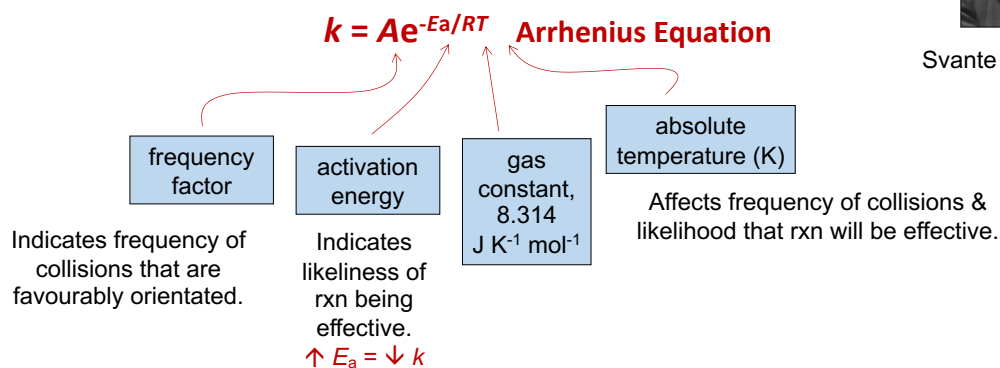**Either** forms products (effective collision) **or** returns to reactants (ineffective collision)

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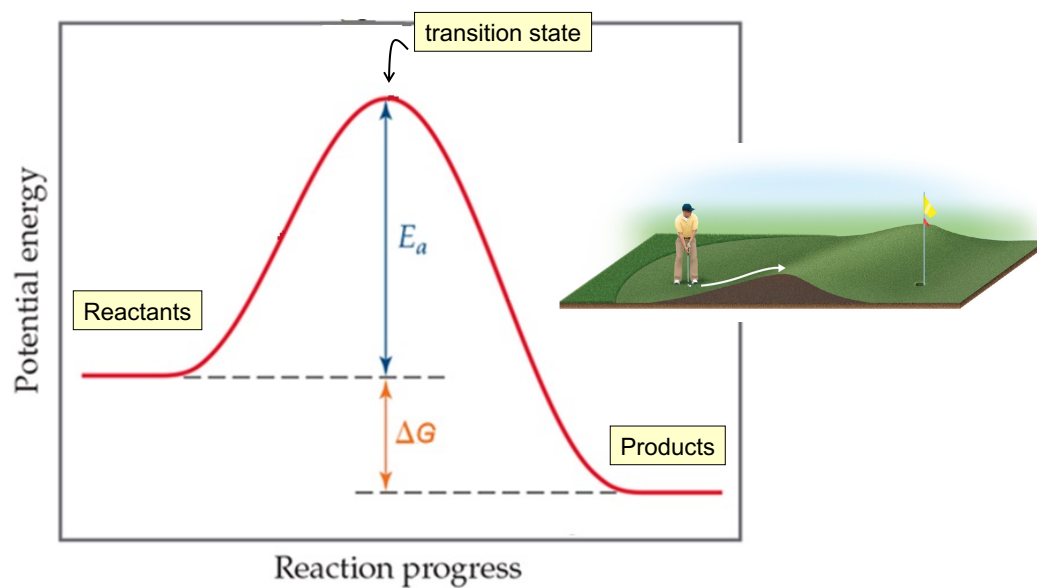
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Arrhenius equation

Arrhenius incorporated the three factors that affect rate into the following equation for the rate constant:

$$k = Ae^{-Ea/RT}$$ **Arrhenius Equation**

Svante Arrhenius

| frequency factor | activation energy | gas constant, 8.314 J K^{-1} mol^{-1} | absolute temperature (K) |

Indicates frequency of collisions that are favourably orientated.

Indicates likeliness of rxn being effective.
$\uparrow E_a = \downarrow k$

Affects frequency of collisions & likelihood that rxn will be effective.

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Another useful form of the Arrhenius equation

Often we want to find E_a. This is tricky to do as it is stuck inside the exponential so we can re-express the Arrhenius equation in log form:

1. $k = Ae^{-Ea/RT}$ Original

2. $\ln k = \ln A - \dfrac{E_a}{RT}$ After taking ln of both sides

$\ln e^x = x \ln e$ and $\ln e = 1$ ∴ $\ln e^x = x$ Math note

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Experimental determination of A and E_a

Approach #1

Measure k at two different temperatures and substitute into logarithmic form of the Arrhenius equation.

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \qquad (1)$$

$$-(\ln k_2 = \ln A - \frac{E_a}{RT_2}) \qquad (2)$$

Add Eqs. (1) and (2): $\quad \ln k_1 - \ln k_2 = \ln \frac{k_1}{k_2} = -\frac{E_a}{R}(\frac{1}{T_1} - \frac{1}{T_2}) \qquad (3)$

| ln a – ln b = ln (a/b) |

| Math note |

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Example calculation of E_a

For the reaction:

$CH_3COOC_2H_5(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + C_2H_5OH(aq)$

$k = 0.0521$ mol^{-1} L s^{-1} at 15°C and 0.332 mol^{-1} L s^{-1} at 45°C.

Calculate E_a for the reaction.

$k_1 = 0.0521 \quad T_1 = (15 + 273) = 288$ K

$k_2 = 0.332 \quad\; T_2 = (45 + 273) = 318$ K

Careful! Make sure T is in K!

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Example calculation of E_a

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

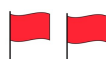$$\ln 0.0521 - \ln 0.332 = -\frac{E_a}{8.314}\left(\frac{1}{288} - \frac{1}{318}\right)$$

$$-1.852 = -\frac{E_a}{8.314}(3.28 \times 10^{-4})$$

$$E_a = \frac{1.852 \times 8.314 \,\mathrm{J\,K^{-1}\,mol^{-1}}}{3.28 \times 10^{-4}\,\mathrm{K^{-1}}}$$

Careful! Answer will be in J mol^{-1} if R is J K^{-1} mol^{-1}

= 46944 J mol^{-1}
= 46.9 kJ mol^{-1}

Watch negatives, E_a should always be positive

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Experimental determination of A and E_a

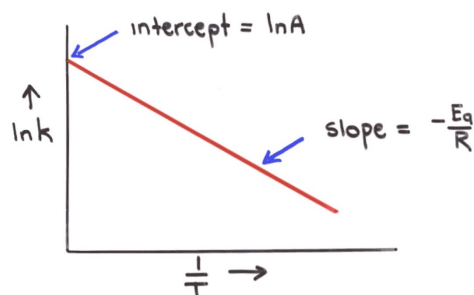**Approach #2**

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

y = m x + c

Measure k at various T and plot **ln k** versus **1/T**

This Arrhenius plot is linear with:

intercept = ln A

slope = $\dfrac{-E_a}{R}$

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✱ **Homework** ✱

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Brown et al.

Problems 14.31 14.32

Answers on Blackboard

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