

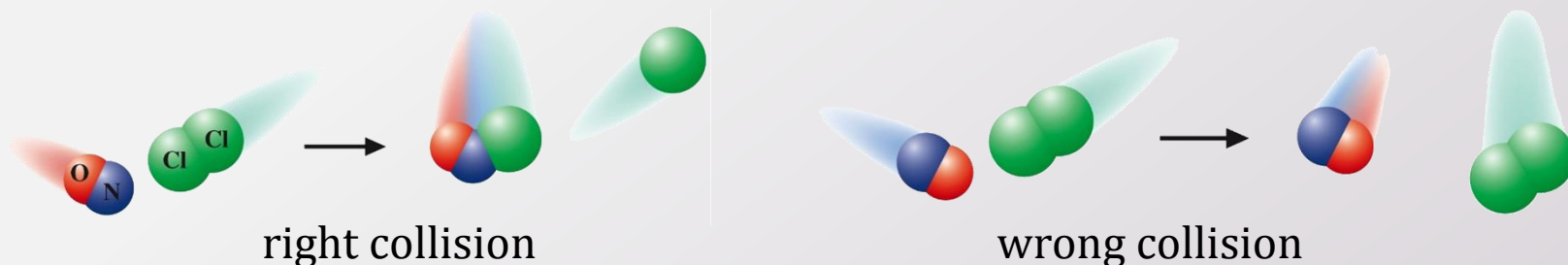
KINETICS -3

**RATE OF REACTION AND ITS
DEPENDENCE ON TEMPERATURE
AND MECHANISM OF REACTION**

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RATE OF REACTION AND TEMPERATURE

- Most reactions will occur faster at a higher temperature.
- To understand this one has to know “Collision Theory” – this states that molecule must undergo collisions in order to react. The higher the collisions the faster the reaction. More energy gives more KE to molecules thus faster reaction.
- Two key parts of collision theory are:
 - **Orientation of molecules**: only molecules in correct orientation will result in product formation; so not all collisions lead to product regardless of the temp. for example below in the reaction of NO with chlorine molecules.



- **Activation Energy**: minimum energy to break the bonds.

TRANSITION STATE THEORY

Transition-state theory states that an activated complex or transition state forms as a result of “correct” collision of molecules forming an unstable grouping of atoms that can break up to form products.

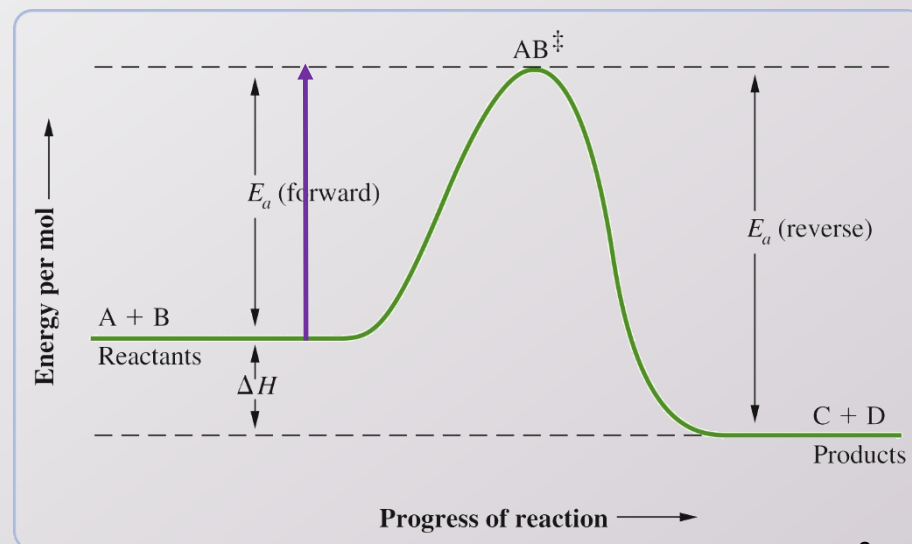
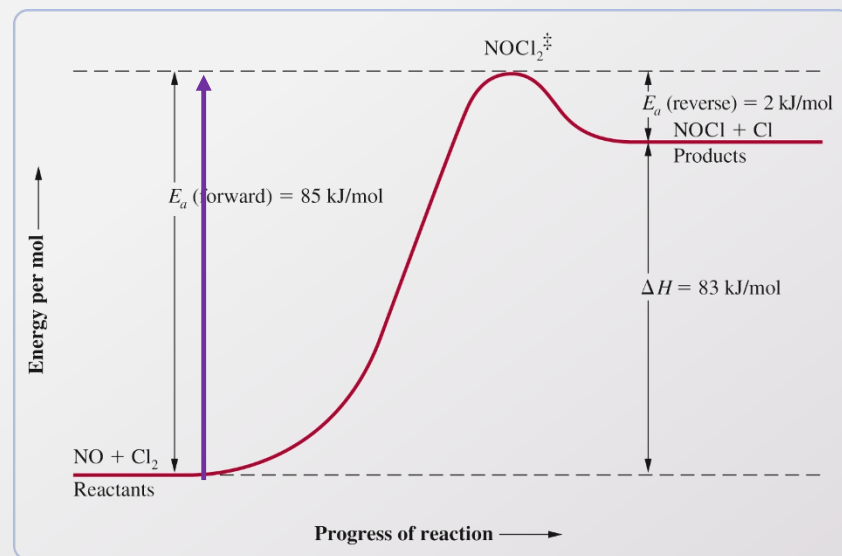
Activation Energy: minimum amount of energy required to form the transition state.

- **Endothermic Reaction:**

Energy of products is more than reactants

- **Exothermic Reaction:**

Energy of products is less than reactants



ARRHENIUS EQUATION

- The dependence of the rate constant of a reaction on temperature is:

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

E_a = activation energy

R = universal gas constant

A = frequency factor

T = Kelvin temp

- The natural log equation (for graphing purpose) $\ln(k) = -\frac{E_a}{R} \left(\frac{1}{T}\right) + \ln(A)$
 - A plot of $\ln k$ vs $1/T$ will give a straight line
 - The slope of line will equal $-E_a/R$
 - The activation energy may be found by multiplying the slope by “ R ”
- Another way of using Arrhenius equation is at two different temperatures where then you would also have two k values.

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

EXAMPLE USING ARRHENIUS EQ. 2ND WAY

Use the data to calculate activation energy of the reaction.

T (Kelvin)	k (s^{-1})
400	2.9×10^{-3}
450	6.1×10^{-2}
500	7.0×10^{-1}

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

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

Solution:

$$E_a = 8.3145 \text{ J/Kmol} \left(\frac{\ln \frac{2.9 \times 10^{-3}}{6.1 \times 10^{-2}}}{\frac{1}{450} - \frac{1}{400}} \right)$$
$$= 91 \text{ kJ/mol}$$

EXAMPLE: ARRHENIUS EQUATION

In a series of experiments on the decomposition of dinitrogen pentoxide, N_2O_5 , rate constants were determined at two different temperatures:

- At $35^\circ C$, the rate constant was $1.4 \times 10^{-4}/s$.
- At $45^\circ C$, the rate constant was $5.0 \times 10^{-4}/s$.

What is the activation energy? What is the value of the rate constant at $55^\circ C$?

Solution:

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

$$T_1 = 35^\circ C = 308 K; T_2 = 45^\circ C = 318 K$$

$$k_1 = 1.4 \times 10^{-4}/s; k_2 = 5.0 \times 10^{-4}/s$$

$$\ln\left(\frac{5.0 \times 10^{-4}/s}{1.4 \times 10^{-4}/s}\right) = \frac{E_a}{8.315 \frac{J}{mol \cdot K}} \left(\frac{1}{308 K} - \frac{1}{318 K}\right)$$

$$1.273 = E_a \left(\frac{10 K}{\left(8.315 \frac{J}{mol \cdot K}\right)(318 K)(308 K)} \right)$$

$$E_a = \frac{1.273 \left(8.315 \frac{J}{mol \cdot K}\right)(318 K)(308 K)}{10 K}$$

$E_a = 1.0 \times 10^5 J/mol$

CONTD....

$$T_1 = 35^\circ\text{C} = 308 \text{ K}$$

$$k_1 = 1.4 \times 10^{-4}/\text{s}$$

$$E_a = 1.04 \times 10^5 \text{ J/mol}$$

$$T_2 = 55^\circ\text{C} = 328 \text{ K}$$

$$k_2 = ?$$

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

$$\ln\left(\frac{k_2}{1.4 \times 10^{-4}/\text{s}}\right) = \frac{1.04 \times 10^5 \frac{\text{J}}{\text{mol}}}{8.315 \frac{\text{J}}{\text{mol}\cdot\text{K}}} \left(\frac{1}{308 \text{ K}} - \frac{1}{328 \text{ K}}\right)$$

$$\ln\left(\frac{k_2}{1.4 \times 10^{-4}/\text{s}}\right) = 2.476$$

$$\frac{k_2}{1.4 \times 10^{-4}/\text{s}} = 11.90$$

$$k_2 = 1.7 \times 10^{-3}/\text{s}$$

FACTORS AFFECTING RATE OF REACTION

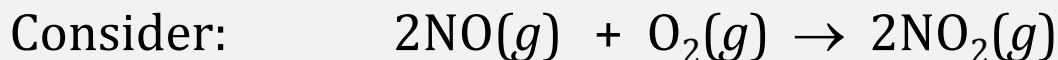
1. **The concentrations of the reactants**: The initial rate of reaction is always higher than as the reaction progresses; this means that the more the concentration the faster the reaction. (As long as the reaction order is more than zero order).
2. **The surface area of the solid reactant or catalyst**: The larger the surface area the more surface to react – so liquids react faster than solid; powder solid has more surface area than block.
3. **Temperature of the reaction**: As temperature increases the collisions of molecules thus increases rate of reaction.
4. **The presence of a catalyst**: A catalyst reduces the activation energy, hence the reaction goes faster. Key point: catalyst does not get consumed in the reaction.

CATALYSTS

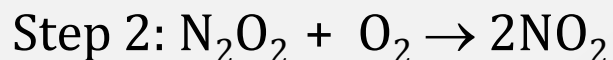
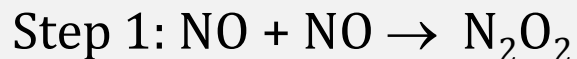
- Again: catalysts speed up reactions without getting consumed in the process.
- The method of working is usually by decreasing the activation energy.
- Two kinds of catalysts:
 - Homogeneous: mix completely with the reactions, e.g. an aq. acid in an aq. Reaction system. These are cheaper and easier to work with.
 - Heterogeneous: has a different phase than reactants, e.g. a solid in gas reaction system. (e.g. catalytic converter in the car)
- Biological catalysts: e.g. enzymes – speed up synthesis, digestion etc. most enzymes are very specific for a particular reaction.

REACTION MECHANISM

- Most reactions occur in a series of steps.
- Order of reaction, activation energy etc. give an idea of how reaction proceeds.



The reaction cannot occur in a single step. One proposed mechanism:



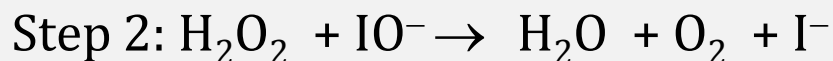
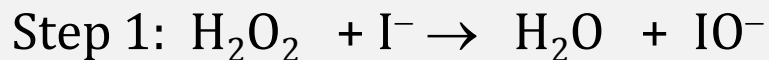
N_2O_2 is an intermediate in the reaction mechanism.

Intermediate: a substance that is produced in an early step and consumed in a later step

- For mechanism:
 - Sum of all steps must equal to the balanced equation.
 - The rate law must be same as the experimental rate law.

EXAMPLE: REACTION MECHANISM

The decomposition of hydrogen peroxide ($2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$) may occur in the following two steps



Step 1 is the rate-determining step, then the rate law is $\text{rate} = k_1[\text{H}_2\text{O}_2][\text{I}^-]$

Explain the role of all the species in the mechanism.

Solution:

- I^- does not appear in the overall balanced equation so I^- serves as a **catalyst** in the reaction - it is present at the start of the reaction and is present at the end
- IO^- is an intermediate (not in the overall balanced equation)

REACTION MOLECULARITY

- **Molecularity:** the number of reactant molecules involved in the collision
- **Unimolecular:** one reactant molecule
- **Bimolecular:** two reactant molecules
- **Termolecular:** three reactant molecules (fairly rare)

- **Rate-determining step:** the slowest step in the mechanism

KEY CONCEPTS

- Calculate activation energy
- Predict rate of reaction when comparing two reactions
- Understand mechanism of reactions