KINETICS
4: TEMPERATURE CONSIDERATION AND MECHANISM OF REACTION

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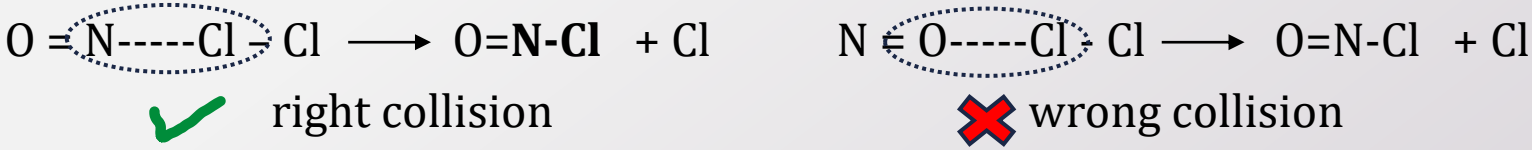
RATE OF REACTION AND TEMPERATURE

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 kinetic energy 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. Not all collisions lead to product regardless of the temperature as shown in the example below in the reaction of NO with chlorine molecules.



right collision

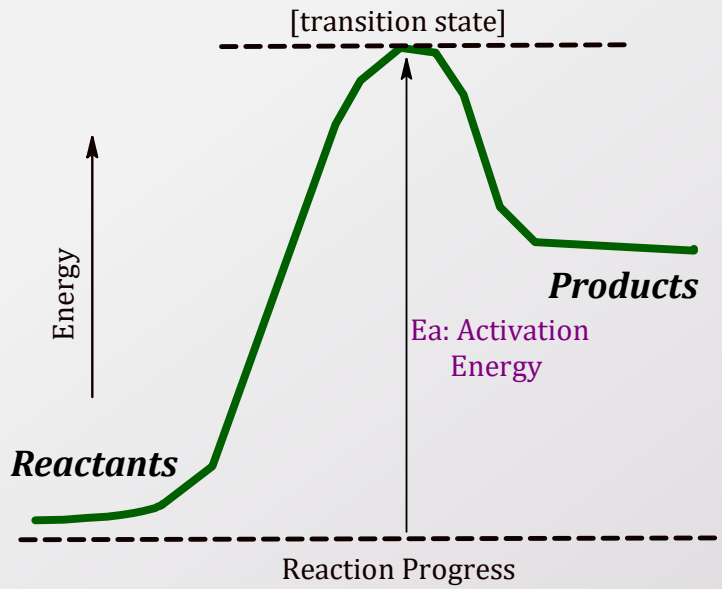
wrong collision

  - **Activation Energy**: Is the minimum energy required 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.

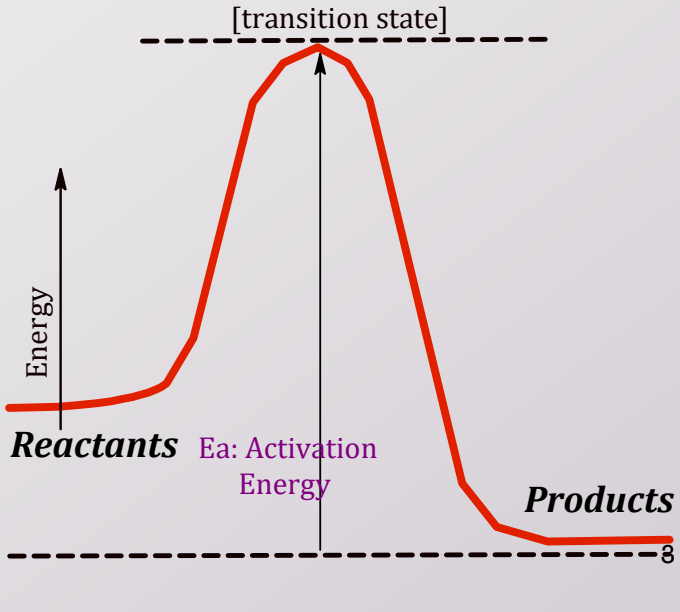


- **Endothermic Reaction:**

Energy of products is more than reactants (top graph)

- **Exothermic Reaction:**

Energy of products is less than reactants (graph on the right)



ARRHENIUS EQUATION

The dependence of the rate constant (k) of a reaction on temperature is given by the Arrhenius equation.

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

E_a = activation energy
R = universal gas constant (8.32 J/mol K)
A = frequency factor
T = Kelvin temp

- The natural log equation (for graphing purpose)
  - 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"

$$\ln(k) = -\frac{E_a}{R}\left(\frac{1}{t}\right) + \ln(A)$$

- Arrhenius equation can also be used to determine a k values at two different temperatures where then you would also have two k values. This indicates also that rate of reaction is dependent on temperature.

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

EXAMPLE 1: 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°C, the rate constant was 1.4×10^{-4}/s.
- At 45°C, the rate constant was 5.0×10^{-4}/s.

What is the activation energy? What is the value of the rate constant at 55°C?

Answer: Convert temperature to K. Use the k_1/k_2 equation. *Note here that the equation has the $k_{1/2}$ inversed from the previous slide.*

$T_1 = 35°C = 308\ K$; $T_2 = 45°C = 318\ K$; $k_1 = 1.4 \times 10^{-4}/s$; $k_2 = 5.0 \times 10^{-4}/s$

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

$$\ln\left(\frac{5.0 \times 10^{-4}/s}{1.4 \times 10^{-4}/s}\right) = \frac{E_a}{8.32\ \frac{J}{mol \bullet K}}\left(\frac{1}{308\ K} - \frac{1}{318\ K}\right)$$

$$1.273 = E_a\left(\frac{10\ K}{\left(8.32\ \frac{J}{mol \bullet K}\right)(318\ K)(308\ K)}\right)$$

$$E_a = \frac{1.273\left(8.32\ \frac{J}{mol \bullet K}\right)(318\ K)(308\ K)}{10\ K} = \boldsymbol{1.0 \times 10^5\ J/mol}$$

continued on next slide...

CONTD....

$T_1 = 35°C = 308\ K$ $\qquad$ $T_2 = 55°C = 328\ K$

$k_1 = 1.4 \times 10^{-4}/s$ $\qquad$ $k_2 = ?$

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

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

$$\ln\left(\frac{k_2}{1.4 \times 10^{-4}/s}\right) = \frac{1.04 \times 10^5 \ \frac{J}{mol}}{8.32 \ \frac{J}{mol \bullet K}}\left(\frac{1}{308\ K} - \frac{1}{328\ K}\right)$$

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

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

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

EXAMPLE 2: CALCULATING ACTIVATION ENERGY

Use the data to calculate activation energy of the reaction.

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

Answer: Use the equation for the two temperatures and k values since we have data for that equation.

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

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

$$E_a = 8.32\ \text{J/mol K}\left(\frac{\ln\frac{2.9 \times 10^{-3}}{6.1 \times 10^{-2}}}{\frac{1}{450} - \frac{1}{400}}\right)$$

$$= \boxed{\textbf{91 kJ/mol}}$$

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.
- There are 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 are found in nature: 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.

Consider: $2NO_{(g)} + O_{2\,(g)} \longrightarrow 2NO_{2\,(g)}$

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

Step 1: $NO + NO \longrightarrow N_2O_2$

Step 2: $N_2O_2 + O_2 \longrightarrow 2NO_2$

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.

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