Physical Chemistry
Chapter 6
Chemical Kinetics

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Chapter Description

- Aims
  - To define rate laws accordingly
  - To determine the reaction order
  - To determine Arrhenius parameters

- Expected Outcomes
  - Student will be able define rate law
  - Student will be able to determine reaction order correctly

- Other related Information

  Problem Analysis - Identify, formulate, research literature and analyse complex engineering problems reaching substantiated conclusions using first principles of mathematics, natural sciences and engineering sciences.

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6.1 Definition of rate

▸ How do we describe the speed at which a reaction occurs?

Rusting Iron

Source:
https://commons.wikimedia.org/wiki/
File:Rust03102006.JPG

Burning coal

Source:
https://commons.wikimedia.org/wiki/File:Charbon_-_charcoal_burning_(3106924114).jpg

Chemical Kinetics

Thermodynamics – does a reaction take place?

Kinetics –   how fast does a reaction proceed?

How the catalyst respond to the rate of reaction?

Identify the mechanism of a reaction.

Procedure to compute the rate and mechanism of a reaction:

1. Determine the overall stoichiometry & any side reactions.
2. Determine how the reactant and products concentration have been changed with time after reaction has been started.

Reaction rate is the change in the concentration of a reactant or a product with time (*M*/s).

$$Rate = \frac{|\Delta[J]|}{\Delta t}$$

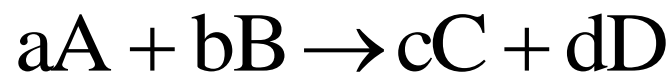$|\Delta[J]| =$ Δ the molar concentration of species J.

Δt = time interval

* All rate are positive

- For the reaction

$$aA + bB \rightarrow cC + dD$$

$$\text{rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$
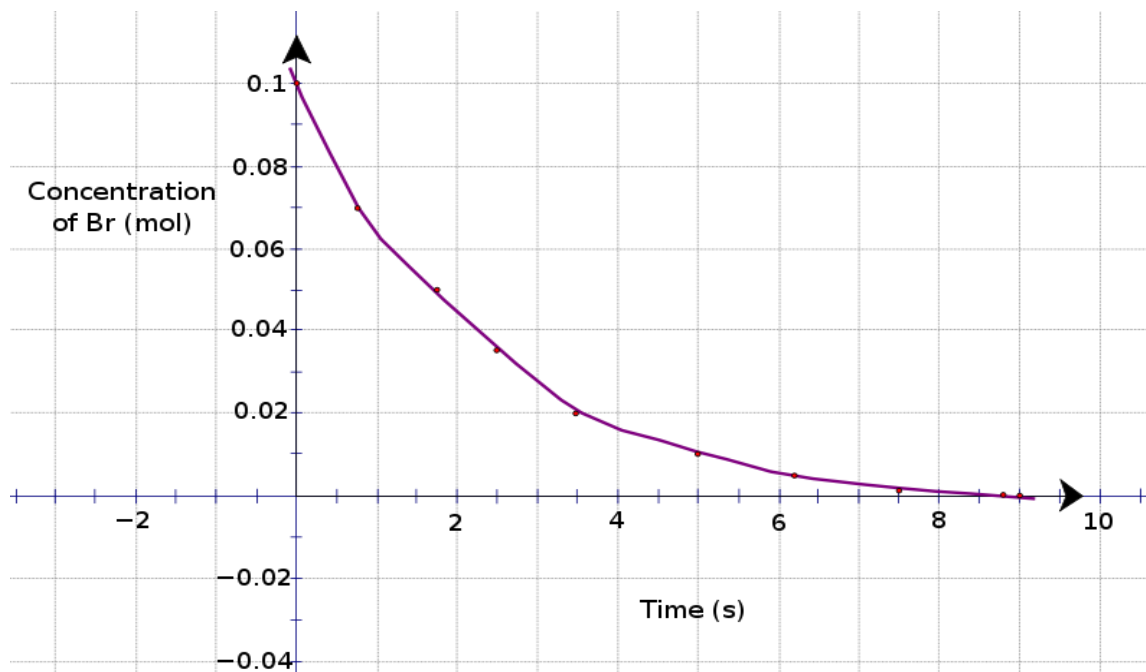
Write the rate expression for the following reaction:

$$CH_4\ (g) + 2O_2\ (g) \longrightarrow CO_2\ (g) + 2H_2O\ (g)$$

$$\text{rate} = -\frac{\Delta[CH_4]}{\Delta t} = -\frac{1}{2}\frac{\Delta[O_2]}{\Delta t} = \frac{\Delta[CO_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[H_2O]}{\Delta t}$$

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Source: https://commons.wikimedia.org/wiki/File:Concentration_of_Bromine_vs_Time.svg

$$\textbf{\textit{Average rate}} = - \frac{D[Br_2]}{Dt} = - \frac{[Br_2]_{final} - [Br_2]_{initial}}{t_{final} - t_{initial}}$$

Instantaneous rate:
rate at specific time = slope of graph of its molar
concentration vs time.

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The rate of reactions is proportional to the molar concentrations of the reactants raised to a simple power.

$$Rate = k[A][B]$$

k = Rate constant; independent of concentration but depend on temperature

Rate law: An equation that expresses the rate of a reaction in terms of the molar concentration (or partial pressure) of the species in the overall reaction.

* Unit: mol dm^{-3} s^{-1}

- Overall reaction order can be determined by the unit of k

Reaction Order	Rate Law	k unit
Zero	$-r_A = k_A$	$mol/dm^3.s$
One	$-r_A = k_A C_A$	s^{-1}
Two	$-r_A = k_A C_A^2$	$(dm)^3/mol.s$
Three	$-r_A = k_A C_A^3$	$(dm^3/mol)^2.s^{-1}$

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Rate law and rate constant of reaction:

- Predict the rate of the reaction for any given composition of the reaction mixture.

- Predict the concentrations of the reactants and products at any time after the start of reaction.

- Mechanism of the reaction.

6.3 Reaction Order

Classification of reactions according to kinetics.
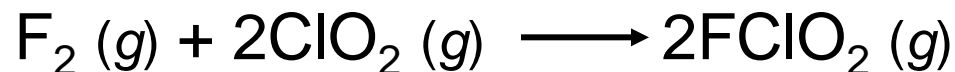
Exp: $$Rate = k[A][B]$$

1st order in A and 1st order in B

Overall order: the sum of the order of all the components.

- Reaction order is **always** defined in terms of reactant (not product) concentrations.

- The order of a reactant **is not** related to the stoichiometric coefficient of the reactant in the balanced chemical equation.

$$F_2 \ (g) + 2ClO_2 \ (g) \longrightarrow 2FClO_2 \ (g)$$

$$rate = k \ [F_2][ClO_2]$$

6.4 The determination of the rate law

- Isolation method
  - All reactants except one are present in large excess
  - If reactant B in large excess, take it concentration as constant throughout the reaction.

$$\mathbf{Rate} = k[A][B]^2$$

  - pseudo is referred as the effective rate law
  - 1st order and k' is the effective rate constant at concentration of B.

$$\mathbf{Rate} = k'[A] \text{ with } k' = k[B]_o^2$$

– If reactant A in large excess, the rate law is simplified to

$$\text{Rate} = k^{''}[B]^2 \text{ with } k^{''} = k[A]_o$$

– This called as pseudo 2nd rate law.

6.4 The determination of the rate law

- Method of initial rates;
  - the instantaneous rate is measured at the beginning of the reaction for several different initial concentrations of reactants.

$$Rate = k'[A]^a$$

$$Rate_0 = k'[A]_o^a$$

$$\log rate_0 = \log k' + a \log[A]_0$$

6.6 Integrated Rate Laws

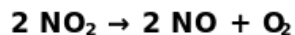- Is defined as the concentration of a species as a function of time.

Summary of the Kinetics of First-Order and Second-Order Reactions

Order	Rate Law	Concentration-Time Equation	Half-Life
1	rate = k [A]	$\ln[A] = \ln[A]_0 - kt$	$t_{1/2} = \dfrac{\ln 2}{k}$
2	rate = k [A]^2	$\dfrac{1}{[A]} = \dfrac{1}{[A]_0} + kt$	$t_{1/2} = \dfrac{1}{k[A]_0}$

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6.6 The Arrhenius Parameters

Temperature Dependence of the Rate Constant

2 NO$_2$ → 2 NO + O$_2$

$$k = A \cdot \exp(-E_a/RT)$$

(Arrhenius equation)

E_a is the activation energy (J/mol)

R is the gas constant (8.314 J/K•mol)

T is the absolute temperature

A is the frequency factor

$$\ln k = - \frac{E_a}{R} \frac{1}{T} + \ln A$$
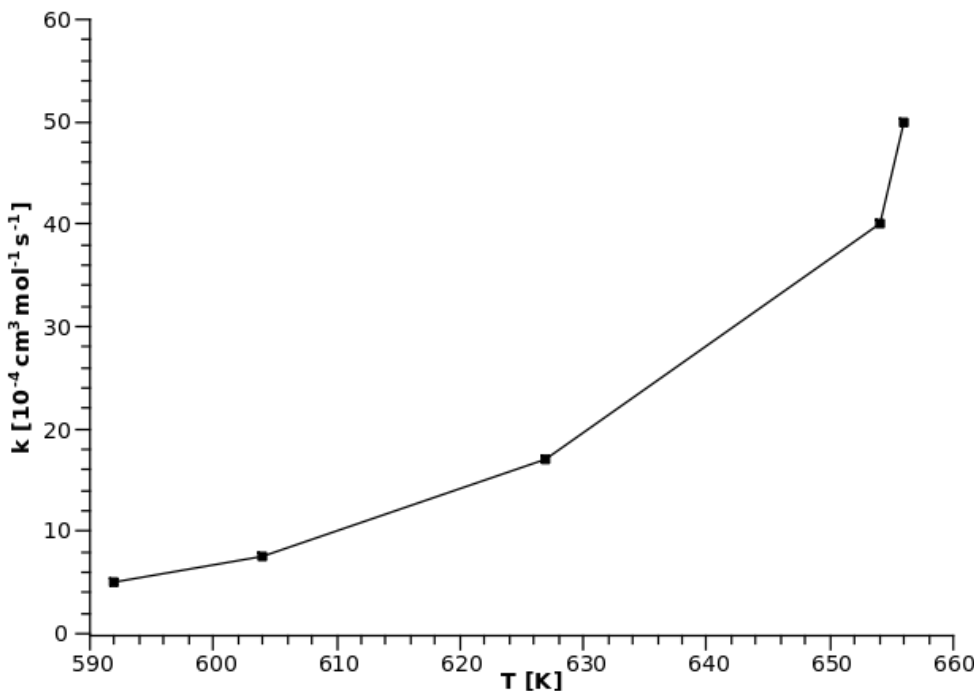
Source:
https://de.wikipedia.org/wiki/Datei:NO2_Arrhenius_k_
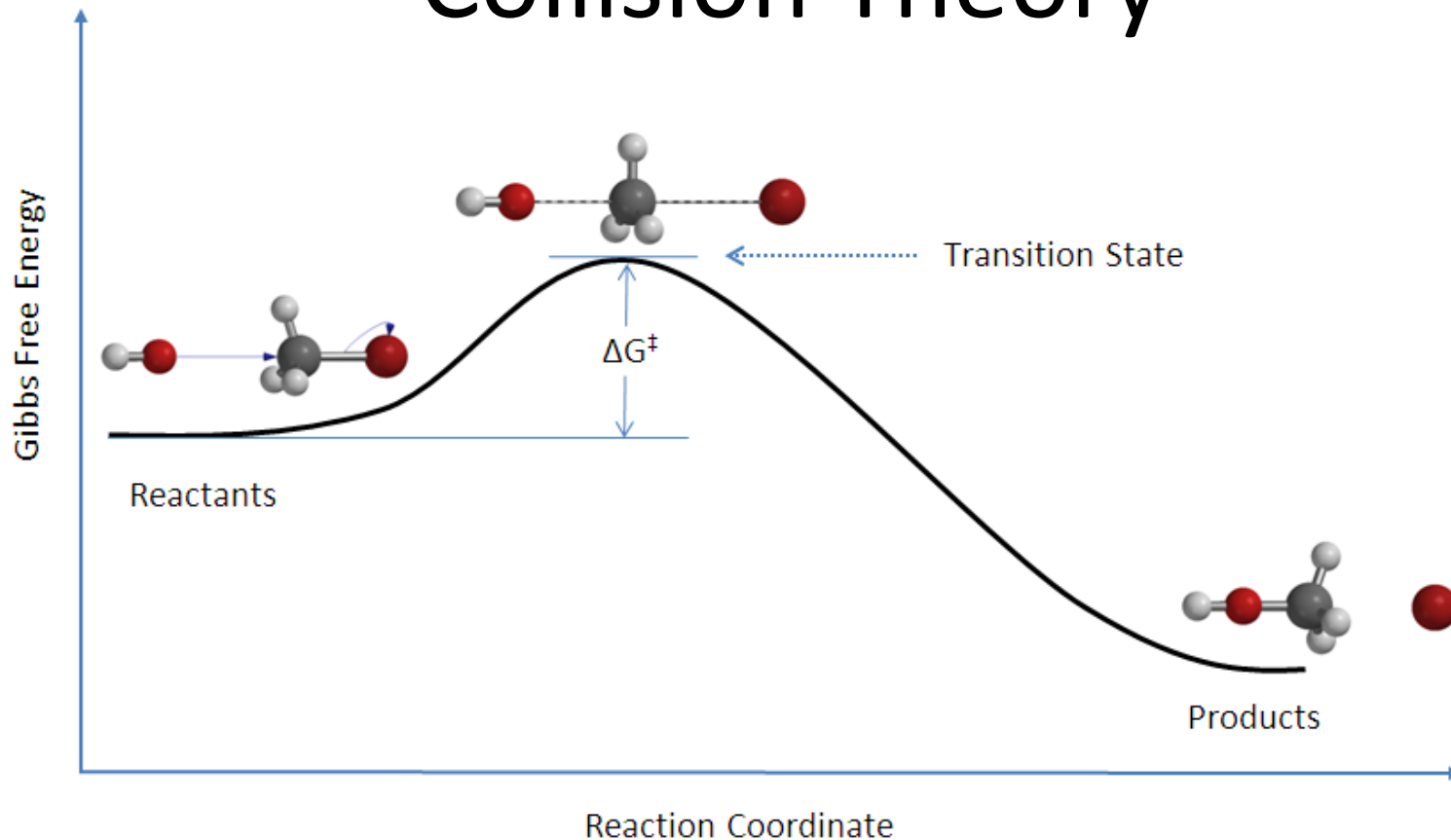against_T.svg

6.7 Collision Theory

- Reaction occurs only if 2 molecules collide with a certain minimum kinetic energy (KE) along their line approach.

- The rate of collision (collision frequency) is proportional to concentration of reactants.

$$\text{Collision frequency} \propto [A][B]$$

- However, not all collisions lead to reactions.

Collision Theory
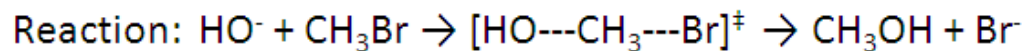
Reaction: $HO^- + CH_3Br \rightarrow [HO\text{---}CH_3\text{---}Br]^{\ddagger} \rightarrow CH_3OH + Br^-$

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- Colliding molecules - total kinetic energy equal to or greater than the activation energy, E_a.
- The species temporarily formed by the reactant molecules as a result of the collision before they form the product is called the **transition state** or **activated complex**.
- If the products more stable than reactant, then the reaction will be accompanied by a release of heat.
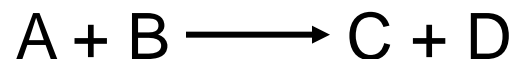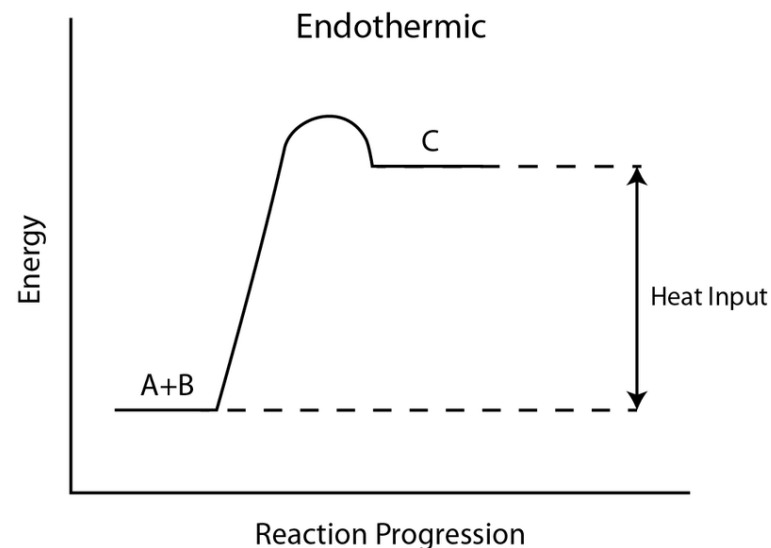
$$A + B \longrightarrow C + D$$

Exothermic Reaction
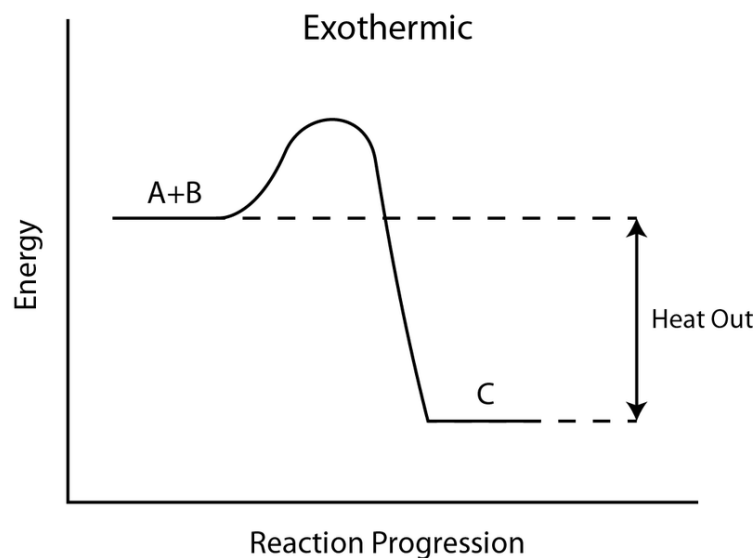
Exothermic

Endothermic Reaction

Endothermic

The **activation energy (E_a)** is the minimum amount of energy required to initiate a chemical reaction.

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- Conclusion
  - Develop and calculate the path of Gibbs Energy
  - The **activation energy (E_a)** is the minimum amount of energy required to initiate a chemical reaction.

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Authors Information

Credit to the authors: Dr Suriati Ghazali, Dr Sunarti Abd Rahman, Dr Norhayati Abdullah, Dr Izirwan Izhab

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