Process Chem and Pharmaceutical Engineering 1

Chemical Reaction Part 2

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http://ocw.ump.edu.my/course/view.php?id=350#section-3

Chapter Description

- **Aims**
  - Define reaction rate and the factors affecting the rate

- **Expected Outcomes**
  - Define reaction rate and the factors affecting the rate
  - Construct mass and mole balances for different types of process corresponding to the stoichiometry and conversion
  - Factors affecting reaction rate

- References
  - Chemistry, A molecular Approach, Nivaldo J. Tro, Pearson, 4th Edition, 2017

The Half-Life of Reaction

- Half-life ($t_{½}$) of a reaction:

  time required for the concentration of a reactant to fall to one-half of its initial value.

- E.g. if a reaction has a half-life of 100 seconds, and if the initial concentration of the reactant is 1.0 M, the concentration will fall to 0.50 M in 100 s.

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First-Order Reaction Half-Life

- The integrated rate law for first-order reaction:
- $ln\frac{[A]_t}{[A]_0} = -kt$
- At a time equal to the half-life ($t=t_{1/2}$), the concentration is exactly half of the initial concentration: ($[A]t_{1/2} = ½[A]_0$). Therefore, when $t=t_{1/2}$ we can write the following expression:
- $ln\frac{\frac{1}{2}\cancel{[A]}_0}{\cancel{[A]}_0} - ln\frac{1}{2} = -kt_{1/2}$
- Solving $t_{1/2}$ and substituting -0.693 for ln ½, the half-life of a first-order reaction:
- $t_{1/2} = \frac{0.693}{k}$

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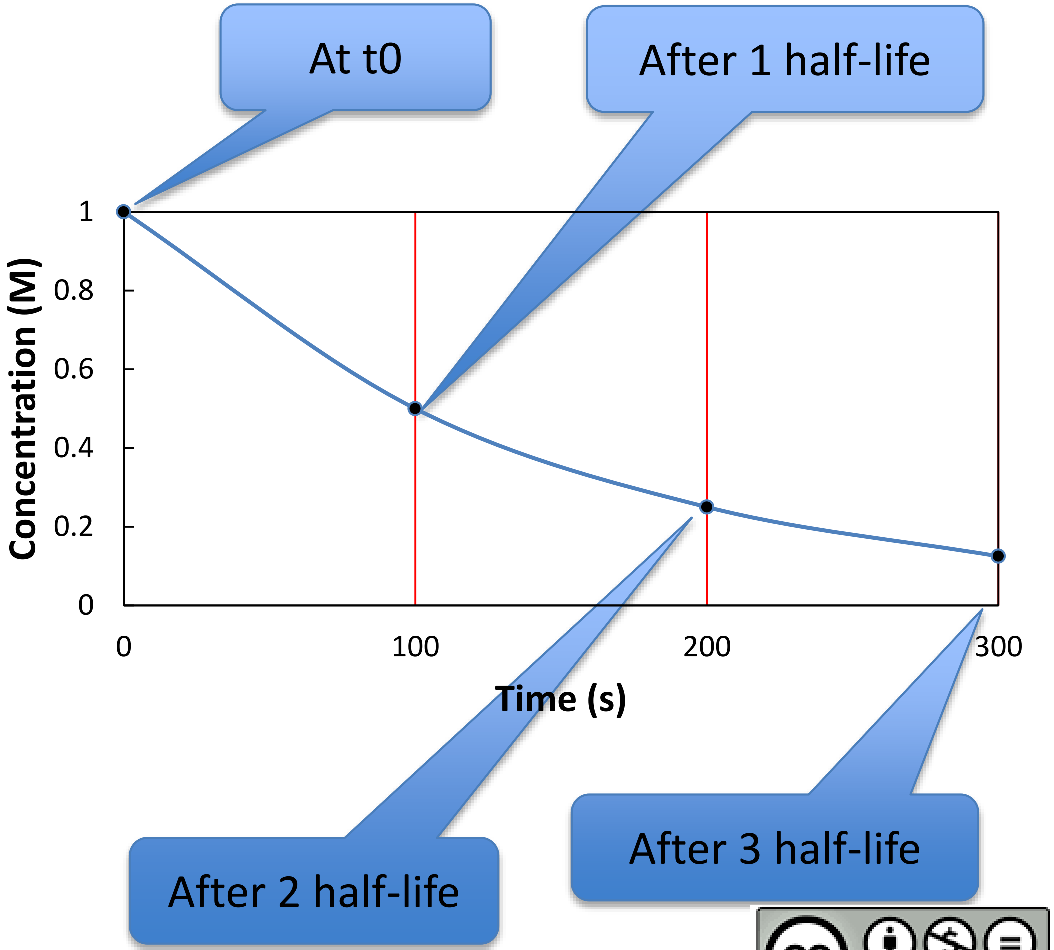
Half-life for a First-Order Reaction



- $t_{1/2}$ is independent of the initial concentration.

- Even though the concentration is changing as the reaction proceeds, the half-life is constant and independent of concentration.

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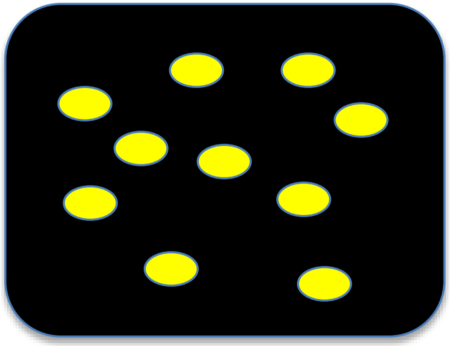
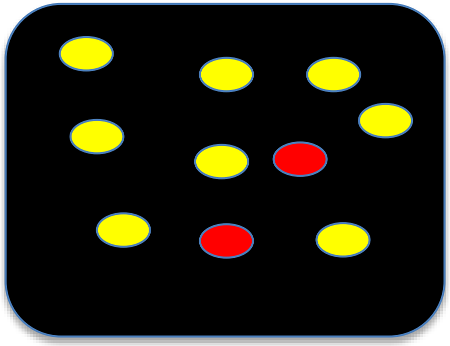
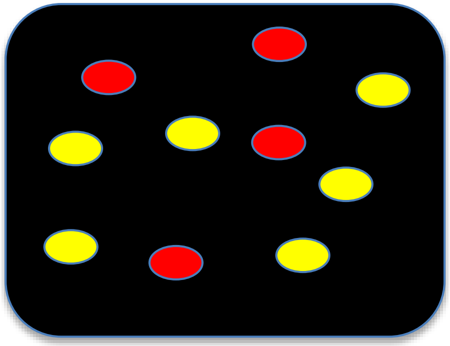
The first-order reaction $A \rightarrow B$ at various times during the reaction process.



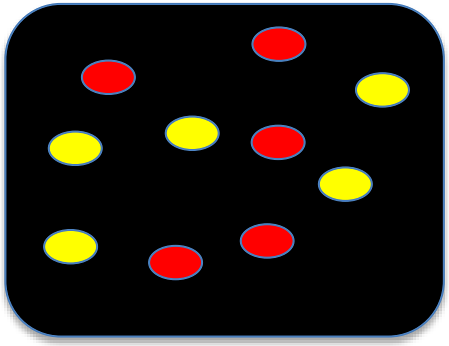
t = 0 s



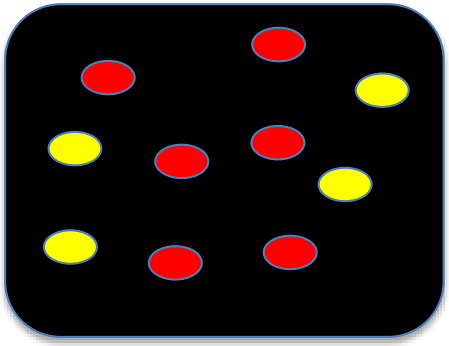
t = 30 s



t = 60 s



t = 90 s



t = 120 s

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Second-Order Reaction Half-Life

- The integrated rate law for second-order reaction:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

- At time equal to t1/2, the concentration is exactly one-half of the initial concentration ([A]t = ½[A]0). Therefore, the following expression at t = t1/2.
- $\frac{1}{\frac{1}{2}[A]_0} = kt_{1/2} + \frac{1}{[A]_0}$
- $t_{1/2} = \frac{1}{k[A]_0}$

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Zero-Order Reaction Half-Life

- The integrated rate law for zero-order reaction:

  $[A]_t = -kt + [A]_0$

- At time equal to t1/2,
- $\frac{1}{2}[A]_0 = -kt_{1/2} + [A]_0$
- $t_{1/2} = \frac{[A]_0}{2k}$
- The half-life depends on the initial concentration.

The Effect of Temperature on Reaction Rate

The rates of chemical reactions are highly sensitive to temperature.

The Arrhenius Equation

- The rate law for a reaction: Rate = $k[A]^n$.
- The temperature dependence of the reaction rate is contained in the rate constant, *k.*
- The Arrhenius Equation:
- $k = Ae^{\frac{-E_a}{RT}}$

Activation energy

Exponential factor

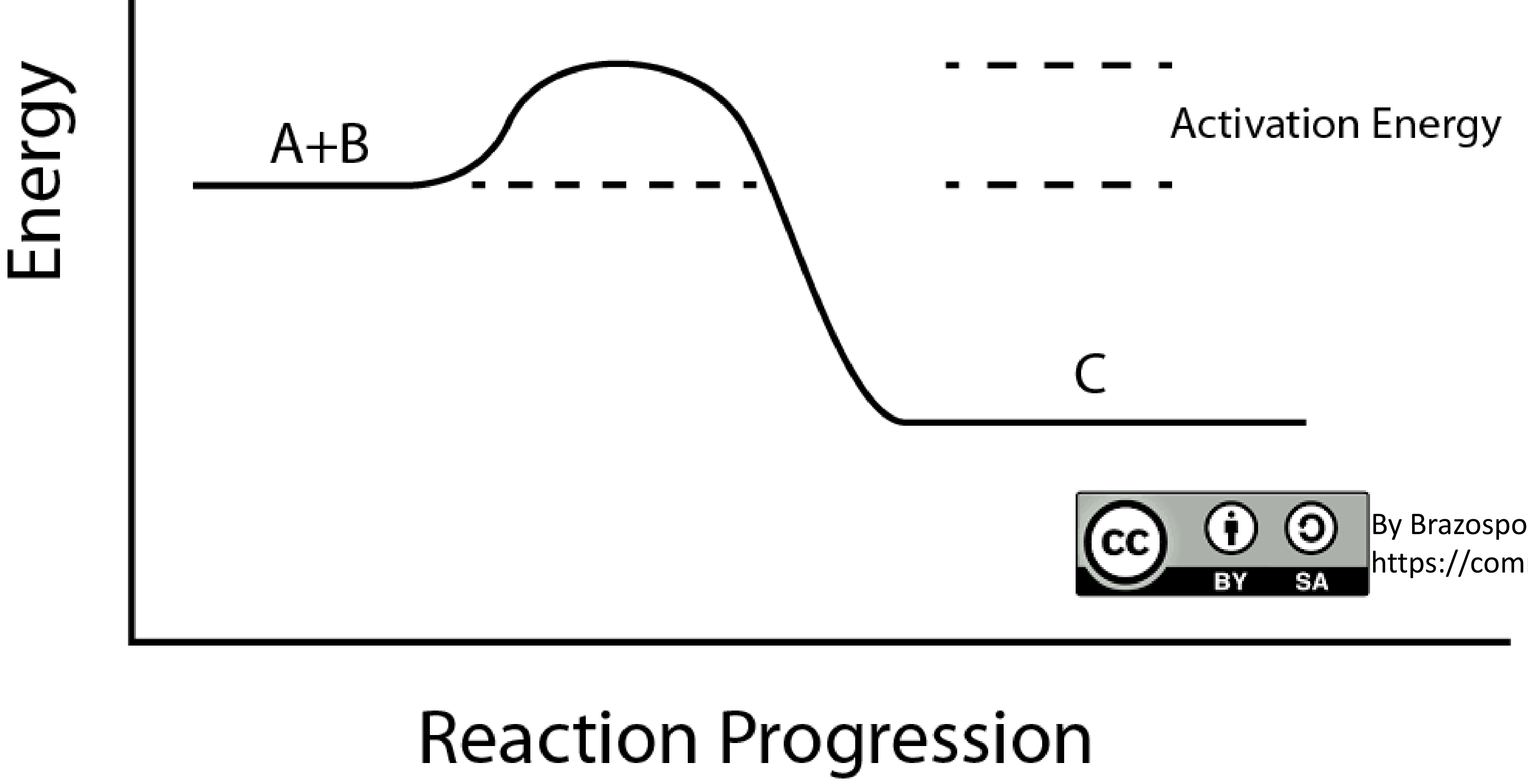
Frequency factor

- $\ln k = \ln A - \frac{E_a}{RT}$

A plot of the ln *k* vs the inverse of the temperature in kelvins(1/T) yields a **straight line** with a slope of $-E_a/R$ and a y-intercept of ln A.

Activation energy:

energy barrier that must be surmounted in order for the reactants to transform onto products



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The Collision Model

- In order to react, the colliding molecules must have a total kinetic energy equal to or greater than the activation energy (Ea), which is the minimum amount of energy required to initiate a chemical reaction.
- When molecules collide, they form an activated complex (transition state), a temporary species formed by the reactant molecules as a result of the collision before they form the product.
- $A + B \rightarrow AB \rightarrow C + D$
- AB denotes an activated complex formed by the collision between A and B. AB is a highly unstable species with a high potential energy
- If the products are more stable than the reactants, the reaction will be accompanied by a release of heat (EXOTHERMIC). If the products are less stabke than the reactants, the heat will be absorbed by the reacting mixture from the surroundings (ENDOTHERMIC).

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Stoichiometry is the theory of the proportions in which chemical species combine with one another.

- The stoichiometric equation of a chemical reaction is a statement of the relative number of molecules or moles of reactants and products that participate in the reaction
- For example, $2SO_2 + O_2 \rightarrow 2SO_3$ indicates that for every two molecules (g-moles, lb-mole) of O_2 reacts to produce two molecules (g-moles, lb-moles) of SO_3. A valid stoichiometric must be balanced.
- The stoichiometric ratio of two molecular species participating in a reaction is the ratio of their stoichiometric coefficients in the balanced reaction. This ratio can be used as a conversion factor to calculate the amount of a particular reactant (or product) that was consumed (or produced), given a quantity of another reactant of product that participated in the reaction

For $2SO_2 + O_2 \rightarrow 2SO_3$, you can write the stoichiometric ratios

- $$\frac{2\ mol\ SO_3 generated}{1\ mol\ O_2\ consumed}\ or\ \frac{2\ lb - moles\ SO_2 consumed}{1\ mol\ SO_3\ generated}$$

Limiting and Excess Reactant, Fractional Conversion and Extent of Reaction

- Two reactants, A and B are said to be present in stoichiometric proportion if the ratio (moles A present)/(moles B present) equals the stoichiometric ratio obtained from the balanced reaction.
- E.g: $2SO_2 + O_2 \rightarrow 2SO_3$
- If 200 mol of SO2 and 100 mol of O2 are initially present, and the reaction proceeds to completion, the SO2 and O2 would disappear at the same instant.
- The reactant that would run out if a reaction proceededto completion is called the limiting reactant, and the other reactants are termed excess reactants.
- If all reactants are present in stoichiometric proportion, then no reactant is limiting.

Limiting and Excess Reactant, Fractional Conversion and Extent of Reaction

- Suppose n_A feed is the number of moles of an excess reactant, A, present in the feed to a reactor that (n_A)stoich is the stoichiometric requirement of A, or the amount needed to react completely with the limiting reactant.
- Then (n_A)feed - (n_A)stoich is the amount by which the A in the feed exceeds the amount needed to react completely if the reaction goes to completion.
- The fractional excess of the reactant is the ratio of the excess to the stoichiometric requirement:
- $Fractional\ excess\ of\ A = \frac{(nA)_{feed} - (nA)_{stoich}}{(nA)_{stoich}}$
- Percentage excess of A is 100 times the fractional excess

- Chemical reactions do not take place instantaneously and indeed often proceed rather slowly. In such cases, it is not practical to design the reactor for complete conversion of the limiting reactant; instead, the reactor effluent emerges with some of the limiting reactant still present and is then usually subjected to a separation process to remove the unconverted reactant from product.
- The separated reactant is then recycled to the reactor inlet. The fractional conversion of a reactant is the ratio:
- $f = \frac{moles\ reacted}{moles\ fed}$
- The fraction unreacted is accordingly 1- f. If 100 moles of a reactant are fed and 90 moles react, the fractional conversion is 0.90 (the percentage conversion is 90%) and the fraction unreacted is 0.10.
- If 20 mol/min of a reactant is fed and the percentage conversion is 80%, then (20)(0.80) = 16mol/min has reacted and (20)(1-0.80) = 4 mol/min remains unreacted.

Conclusion of The Chapter

This chapter discussed about half-life, the effect of temperature on reaction rate, the Arrhenius equation, the collision model, limiting and excess reactant, fractional conversion and extent of reaction.

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