

CE 213A

Introduction to Environmental Science

L3: Unit 1

Chemical kinetics

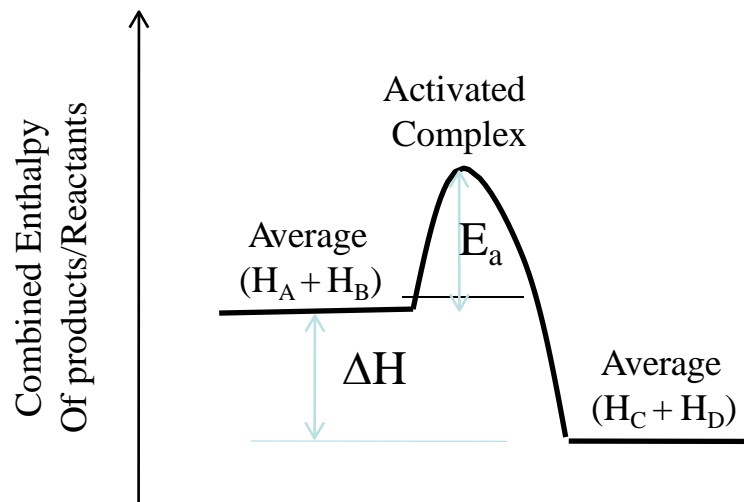
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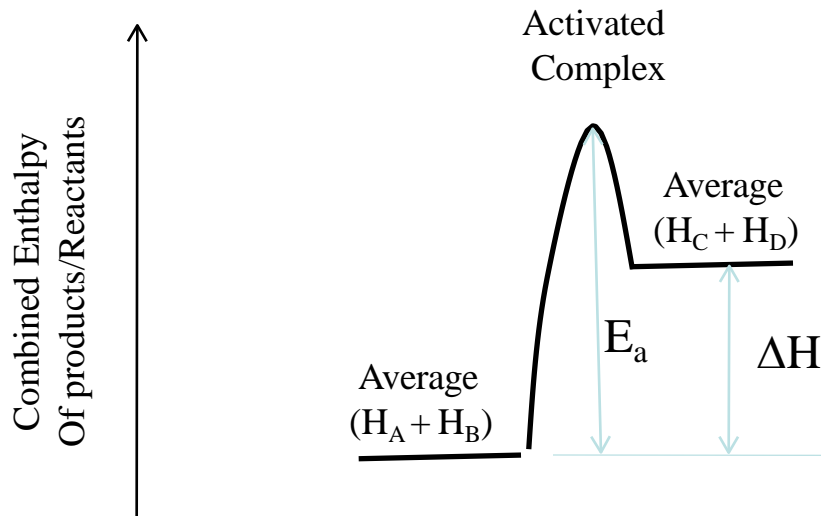
Schedule : LEC Mon Wed Fri 5: - 6pm

Content

- Chemical Kinetics
 - Activation Energy
 - Catalyst
 - Order of Reaction
 - Reaction type
 - Elementary , Complex
 - Kinetics of Elementary Reactions
 - Equilibrium Constant
 - Complex Reactions
 - Empirical Rate Constants
-
- Vapour Pressure
 - Raoult's Law
 - Henry's Law



Exothermic Case



Endothermic Case

A and B will 'react' when molecules of A and B with enthalpies much greater than average enthalpies collide, enabling the formation of the activated complex. If the energy of the activated complex is high (i.e., high activation energy barrier), relatively few high energy collisions will take place and hence the kinetics of the reaction will be slow.

Increasing the temperature will increase average enthalpies of A and B. Hence more high energy collisions can take place, resulting in the increase in the reaction rate.

Chemical kinetics

The study of the **rate of progress of a reaction** towards equilibrium is called **chemical kinetics**. There are various types of reactions,

1. Very fast chemical kinetics: they reach equilibrium in a fraction of a second.
e.g., acid-base reactions and some complexation reactions, etc.
2. Medium to fast kinetics: they tend to reach equilibrium in min. to hours.
e.g. precipitation/dissolution reactions, solid-liquid and liquid-gas mass transfer reactions
3. Slow chemical kinetics: may take months to years to reach equilibrium.
e.g. many oxidation-reduction reactions, crystallization of precipitates etc.

Other reactions may have such slow kinetics that they may never proceed unless **high temperature and pressure is or catalysts/enzymes** are provided. Many chemical reactions important in chemical engineering, will not be possible without application of high temperature/pressure and/or catalysts.

Order of a reaction

The **order** of a chemical **reaction** is defined as the **sum of the powers** of the concentration of the reactants in **the rate equation** of that particular chemical **reaction**

A **first-order reaction** is a **reaction** that proceeds at a rate that depends linearly on only one reactant concentration.

A **zero-order reaction** has a rate that is independent of the concentration of the reactant(s).

Zero-order reactions are typically found when a material that is required for the **reaction** to proceed, such as a surface or a catalyst, is saturated by the reactants.

A **second order reaction** is a type of chemical **reaction** that depends on the concentrations of one **second order** reactant or on two first **order** reactants.

This **reaction** proceeds at a rate proportional to the square of the concentration of one reactant or the product of the concentrations of two reactants.

Reaction types

1. Elementary Reactions

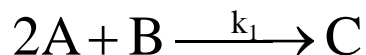
- Elementary reactions are those whose rate expression can be written based on the reaction stoichiometry.
 - Irreversible
 - Reversible
- Reaction rate can be easily computed

1. Complex Reactions

- Complex reactions consist of a series of elementary reactions, i.e., the reactants first combine to form intermediate product(s) through one or more elementary reaction steps. These intermediate product(s) then transform into the final products.
- Empirical measurements needed to compute Reaction rates

Kinetics of Elementary Reactions: Irreversible Reactions

Consider the elementary irreversible reaction between two species A and B in a solution,



Thus,

$$\text{Rate of decline in } [A] = \frac{d[A]}{dt} = -2.k_1.[A]^2.[B]$$

$$\text{Rate of decline in } [B] = \frac{d[B]}{dt} = -k_1.[A]^2.[B]$$

$$\text{Rate of formation of } [C] = \frac{d[C]}{dt} = k_1.[A]^2.[B]$$

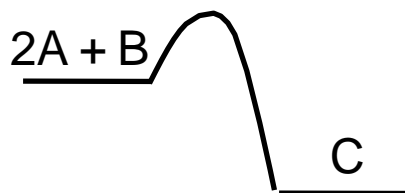
$$R = \text{Rate of Reaction} = k_1.[A]_a.[B]_b$$

The order of the reaction with respect to A is 'a', the order of the reaction with respect to B is 'b'.

For elementary reactions, 'a' and 'b' may be assumed to be the same as the stoichiometric coefficients of the reaction.

If initial conditions and k_1 are known, the differential equations may be solved simultaneously to obtain the variation of A and B with time.

The value of the reaction rate constant (k_1) depends on the activation energy barrier.

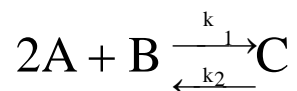


Reaction from left to right is possible due to relatively low activation energy barrier.

Reaction from right to left is not possible due to high activation energy barrier

Kinetics of Elementary Reactions: Reversible Reactions

Consider the reversible elementary reaction between species A, B and C in a solution,



$$\frac{d[A]}{dt} = -2.k_1.[A]^2.[B] + 2.k_2.[C]$$

$$\text{Rate of forward reaction} = k_1.[A]^2[B]$$

$$\frac{d[B]}{dt} = -k_1.[A]^2[B] + k_2.[C]$$

$$\text{Rate of backward reaction} = k_2.[C]$$

$$\frac{d[C]}{dt} = k_1.[A]^2[B] - k_2.[C]$$

In the above expressions, k_1 is the rate of the forward reaction, while k_2 is the rate of the backward reaction.

If initial conditions, k_1 and k_2 are known, the differential equations may be solved simultaneously to obtain the variation of A, B and C with time.

At equilibrium, rate of forward reaction = rate of backward reaction. Hence, at equilibrium,

$$k_1.[A]_2.[B] = k_2.[C]$$

$$\text{or, } \frac{[C]}{[A]^2[B]} = \frac{k_1}{k_2} = K$$

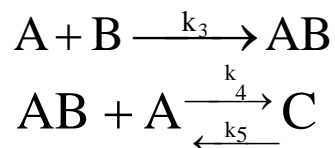
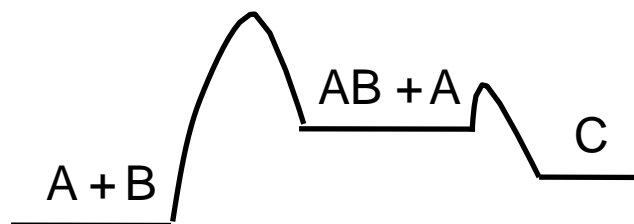
Thus, the equilibrium constant of an elementary reversible reaction is the ratio between the forward and backward reaction rates.

Complex Reactions

Elementary reactions are relatively few. Complex reactions between reacting species are more common.

Complex reactions consist of a series of elementary reactions, i.e., the reactants first combine to form **intermediate product(s)** through one or more elementary reaction steps. These intermediate product(s) then transform into the final products.

The reaction rates of such reactions cannot be written as in case of elementary reactions. For example, consider the following reactions,



AB in this case is a **intermediate** product, which is formed through an initial reaction between A and B. AB combines further with A to produce the end product C.

$$\frac{d[A]}{dt} = -k_3[A].[B] - k_4[AB].[A] + k_5[C]$$

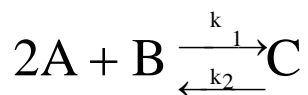
$$\frac{d[AB]}{dt} = k_3[A].[B] - k_4[AB].[A] + k_5.[C]$$

$$\frac{d[B]}{dt} = -k_3[B].[A]$$

$$\frac{d[C]}{dt} = k_4.[A].[AB] - k_5.[C]$$

Comparison: Elementary vs Complex Reaction Kinetics

Elementary:

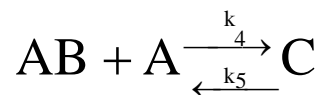
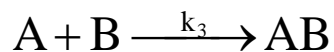


$$\frac{d[A]}{dt} = -2.k_1.[A]^2.[B] + 2.k_2.[C]$$

$$\frac{d[B]}{dt} = -k_1.[A]^2[B] + k_2.[C]$$

$$\frac{d[C]}{dt} = k_1.[A]^2[B] - k_2.[C]$$

Complex:



$$\frac{d[A]}{dt} = -k_3[A].[B] - k_4[AB].[A] + k_5[C]$$

$$\frac{d[B]}{dt} = -k_3.[B].[A]$$

$$\frac{d[AB]}{dt} = k_3.[A].[B] - k_4.[AB].[A] + k_5.[C]$$

$$\frac{d[C]}{dt} = k_4[A].[AB] - k_5[C]$$

Note that the **Equilibrium Constant (K)** of $2A + B \xrightleftharpoons{K} C$ is the same in both cases

However, the reaction kinetics are completely different. So, both reactions will ultimately reach the same equilibrium state, but probably at very different rates.

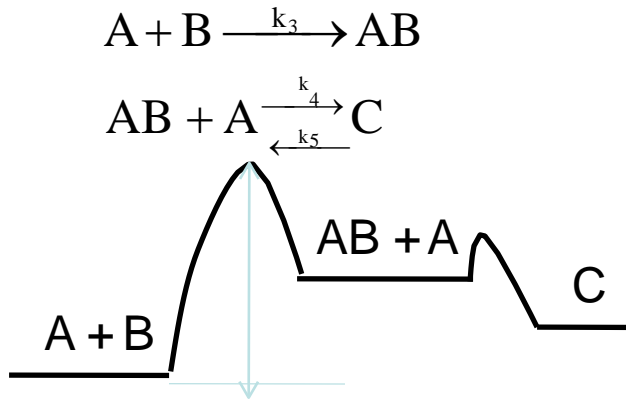
In case the intermediate steps are not fully understood, mechanistic analysis of the chemical kinetics of complex reactions is often not possible.

Empirical reaction rates are computed for describing the chemical kinetics of complex rxn

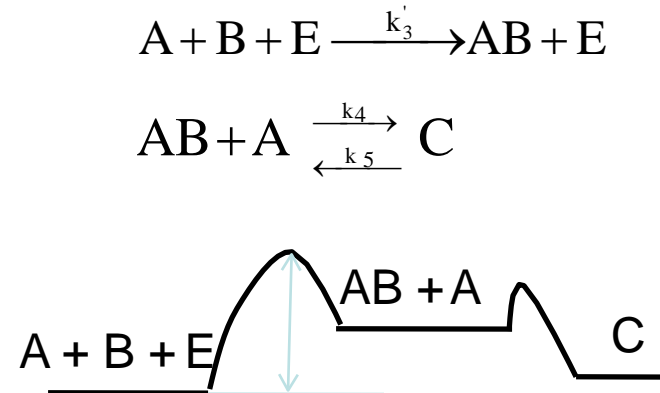
Catalysis

A catalyst (E) helps in the formation of an activated complex at a lower free energy level, without being consumed itself,

Without Catalyst



With Catalyst



Thus the rate of formation of AB is faster (k'_3 is more than k_3) due to mediation by the catalyst.

- **A catalyst can quicken a reaction, it cannot alter the extent (i.e., cannot change the equilibrium constant) of the reaction.**
- Most biological reactions are **catalyzed by enzymes**. Many chemical reactions also occur faster in the presence of catalysts.
- Indeed, many chemical or biochemical reactions will not proceed at all, except in the presence of catalysts/enzymes.

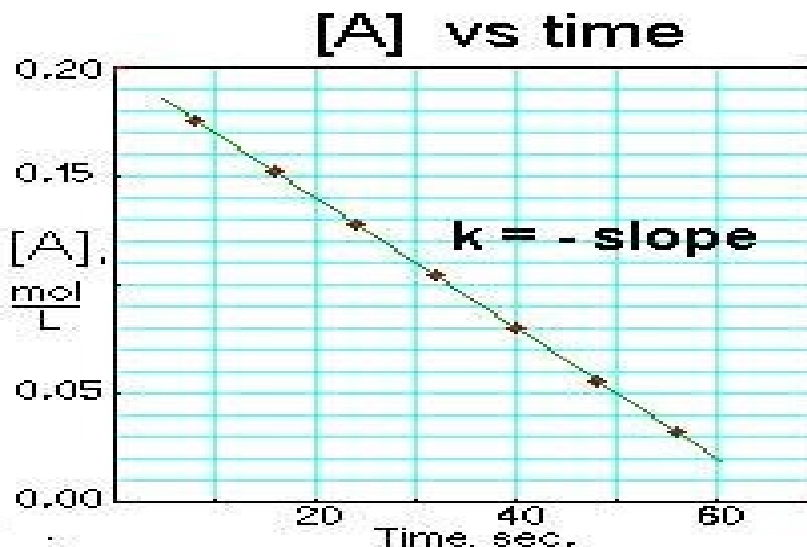
Empirical Reaction Rates

If the mechanism of a complex reaction is not known, empirical rate constants are often used. Suppose experimental data regarding the degradation of A with time (A vs t data) is available. Assuming that degradation of A is through a complex reaction, the apparent reaction order (n) and degradation rate constant (k) for the reaction has to be determined from the experimental data.

Zero Order Reaction

For a zero order reaction, $\frac{dA}{dt} = -k$. If, at $t = 0$, $A = A_0$, then $A = A_0 - kt$.

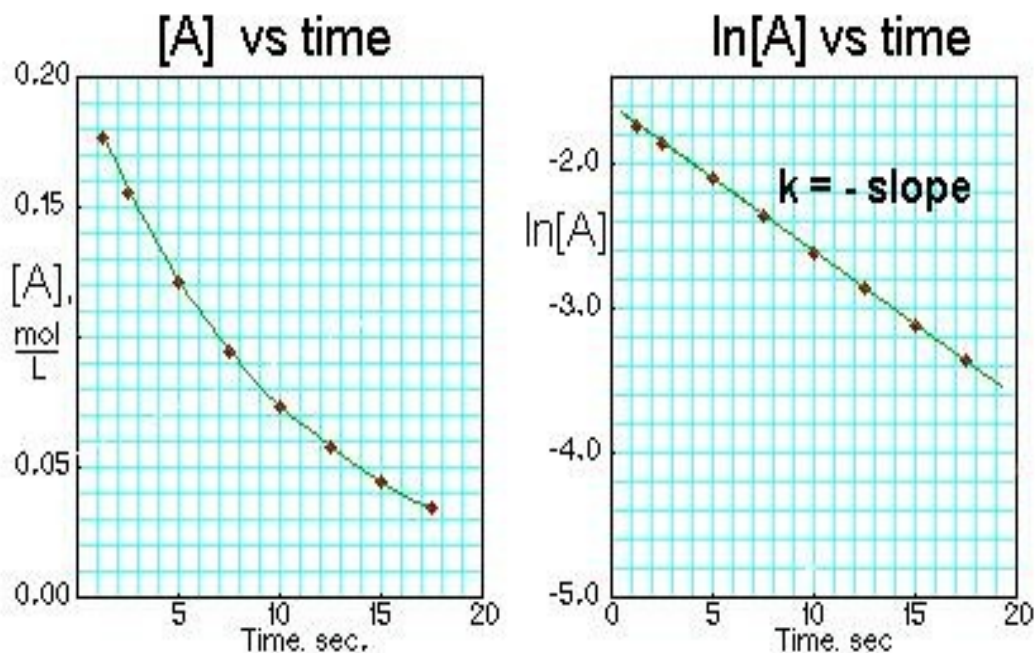
So if a linear fit is obtained when experimental data on decline in concentration of A is plotted vs t, the reaction may be considered to be zero order ($n = 0$) and k may be determined as the slope of the line of best fit.



First Order Reaction

For a first order reaction, $\frac{dA}{dt} = -k[A]$. If, at $t = 0$, $A = A_0$, then integrating, $A = A_0 \cdot \exp(-kt)$.

So if a linear fit is obtained when $\ln(A)$ is plotted vs t , the reaction may be considered to be first order ($n = 1$) and k may be determined as the slope of the line of best fit.



What is Vapour pressure ?



- Vapour pressure is defined as the pressure exerted by a vapour in thermodynamic equilibrium with its condensed phases (solid or liquid) at a given temperature in a closed system.
- Vapour pressure is nothing but the tendency of particles to escape from the liquid (or a solid).
- At normal temperatures, substance with a high vapour pressure is often referred to as volatile.

Raoult's Law (1887)

- Partial vapour pressure of each volatile constituent is equal to the vapour pressure of the pure constituent multiplied by its mole fraction in the solution. Thus, for two constituents A and B,

$$P_A = P_A^\circ X_A$$

$$P_B = P_B^\circ X_B$$

P_A and P_B – partial vapour pressure

X_A and X_B – mole fraction concentration

P_A° and P_B° - vapour pressure of pure components

- The total vapour pressure of the mixture is equal to the sum of the individual partial pressures.

$$\text{Total Vapour Pressure} = P_A + P_B$$

Question

Calculate the expected vapor pressure at 25 °C for a solution prepared by dissolving 97.4 g of common table sugar (sucrose $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, MW = 342) in 453 mL of water. At 25 °C the density of water is approximately 1.00 g/mL and the vapor pressure is 23.76 mm of Hg.

Solution

We will use Raoult's law in the form

$$P_{\text{soln}} = \chi(\text{H}_2\text{O})P^\circ(\text{H}_2\text{O})$$

We need to determine the mol fraction of water

$$97.4 \text{ g} \left(\frac{1 \text{ mol}}{342 \text{ g}} \right) = 0.285 \text{ mol sucrose}$$

$$453 \text{ mL} \left(\frac{1.00 \text{ g}}{1 \text{ mL}} \right) \left(\frac{1 \text{ mol}}{18 \text{ g}} \right) = 25.2 \text{ mol H}_2\text{O}$$

$$\chi(\text{H}_2\text{O}) = \frac{25.2 \text{ mol}}{(25.2 \text{ mol} + 0.285 \text{ mol})}$$

$$\chi(\text{H}_2\text{O}) = .989$$

$$P_{\text{soln}} = .989 (23.76 \text{ mm}) = 23.5 \text{ mm of Hg}$$

Henry's Law



- Henry's law describes the relationship between the solubility of a gas in a solvent and pressure.

$$c = k P$$

Where c = molar concentration of gas dissolved in the solvent in mol / L, P is pressure in atm and k is a constant.

- This makes sense. At higher pressures more gas particles strike the surface of the solution and enter the solvent meaning the concentration of the gas is higher.
- Note: Gas solubility usually decreases with increase in temperature since the gas particles have more energy and can escape from the solvent meaning less gas is dissolved in solution.