

Lecture No: 5

5. Zero-Order Reactions

A reaction is zero-order if the rate is independent of the concentration of the reactant;

$$-\frac{d[A]}{dt} = k$$

Integration of the above equation gives;

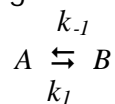
$$[A] = -kt + [A]_0$$

This equation shows that a plot of [A] versus t gives a straight line with a slope equal to -k.

6. Complex Reactions

6.1 Reversible First-Order Reactions:

When a reaction occurs in both directions, we say that the reaction is reversible. To indicate that a reaction is reversible, we draw two arrows, one representing the forward reaction and one representing the reverse reaction. The general reaction scheme is;



For any initial concentrations, $[A]_0$ and $[B]_0$ the chemical system must go to equilibrium. At equilibrium, the concentrations of A and B remain constant at their equilibrium values, so both $d[A]/dt$ and $d[B]/dt$ are equal to zero. The ratio of the equilibrium concentrations of A and B is equal to the equilibrium constant;

$$K = \frac{[A]_{eq}}{[B]_{eq}}$$

The rate law for the above reaction is first-order in both A and B. The differential rate equation then may be written as;

$$-\frac{d[A]}{dt} = k_1[A] - k_{-1}[B]$$

At $t = 0$, $[A] = [A]_0$ and $[B] = 0$. The conservation of mass requires that;

$$[B] = [A]_0 - [A]$$

Substituting this expression into the differential rate equation yields;

$$-\frac{d[A]}{dt} = (k_1 + k_{-1})[A] - k_{-1}[A]_0$$

Integrating the above equation gives;

$$\ln([A] - [A]_{eq}) = \ln([A]_0 - [A]_{eq}) - (k_1 + k_{-1})t$$

A plot of $\ln([A] - [A]_{eq})$ as a function of time is linear with a slope of $-(k_1 + k_{-1})$ and an intercept $\ln([A]_0 - [A]_{eq})$.

From such an analysis, the sum of the rate constants is determined. In order to determine k_1 and k_{-1} individually, we connect the rate law with the equilibrium constant. At equilibrium;

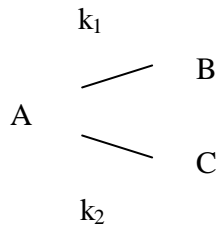
$$-\frac{d[A]}{dt} = 0 = k_1[A]_{eq} - k_{-1}[B]_{eq}$$

$$K = \frac{k_1}{k_{-1}} = \frac{[B]_{eq}}{[A]_{eq}}$$

If we know the sum and the equilibrium constant, we may calculate k_1 and k_{-1} .

6.2 Parallel First-Order Reactions :

If there are more than one reaction path for the reactant, we call such reactions "parallel reactions". For a two path case;



The rate equations for A are;

$$-\frac{d[A]}{dt} = k_1[A] + k_2[A] = (k_1 + k_2)[A]$$

$$[A] = [A]_0 e^{-(k_1+k_2)t}$$

If $[B]=0$ at $t = 0$, then the rate equations for B may be written as;

$$\frac{d[B]}{dt} = k_1[A] = k_1[A]_0 e^{-(k_1+k_2)t}$$

$$[B] = \frac{k_1[A]_0}{(k_1 + k_2)} [1 - e^{-(k_1+k_2)t}]$$

[C] may be calculated by using the conservation of mass equation;

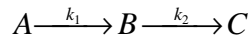
$$\begin{aligned}
 [C] &= [A]_0 - [B] - [C] \\
 &= \frac{k_2[A]_0}{(k_1 + k_2)} [1 - e^{-(k_1+k_2)t}]
 \end{aligned}$$

It is clear from the above equations that;

- The ratio of the concentrations of B and C is equal to k_1/k_2
- The fraction of A that is converted to B is $k_1/(k_1 + k_2)$
- The fraction of A that is converted to C is $k_2/(k_1 + k_2)$

6.3 Consecutive First-Order Reactions:

Consecutive reactions occur when the product of a reaction undergoes further reaction. Two consecutive irreversible reactions may be represented by;



The rate equations for each of them are;

$$\frac{d[A]}{dt} = -k_1[A]$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

$$\frac{d[C]}{dt} = k_2[B]$$

We may assume that at $t = 0$ $[A]=[A]_0$, $[B]=0$ and $[C]=0$. The integral rate equations then may be written as;

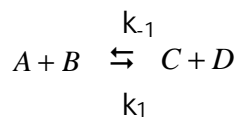
$$[A] = [A]_0 e^{-k_1 t}$$

$$[B] = \frac{k_1 [A]_0}{(k_2 - k_1)} (e^{-k_1 t} - e^{-k_2 t})$$

$$[C] = [A]_0 \left[1 + \frac{1}{(k_1 - k_2)} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right]$$

7. Principal of Detailed Balance

The equilibrium constant for an elementary reaction is equal to the ratio of the forward and reverse rate constants. For the general reversible reaction;



the rates of the forward and reverse reactions are equal to each other at equilibrium.

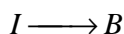
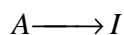
$$\frac{k_1}{k_{-1}} = \frac{[C]_{eq} [D]_{eq}}{[A]_{eq} [B]_{eq}} = K$$

The relationship $K = k_1 / k_{-1}$ holds for all reversible elementary reactions and is called "the principle of detailed balance".

This principle applies only to elementary reactions at equilibrium. For complex reactions, the principle of detailed balance applies to each step of the mechanism. The result is that the rate constants of the steps are not independent of one another.

8. Steady-State Approximation

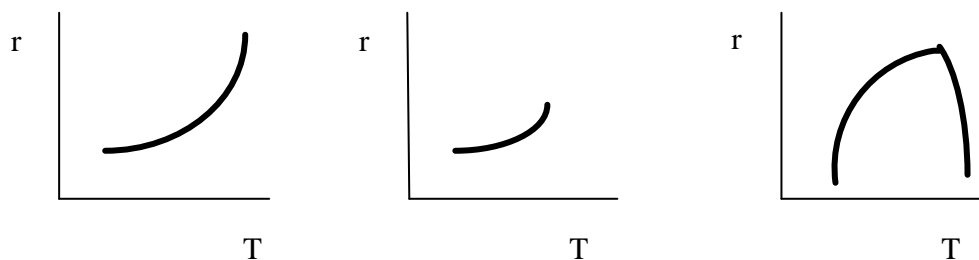
Steady-state approximation is used for complex reactions to simplify the mathematics of the kinetic equations. In the below mechanism;



I is an intermediate. For an intermediate that forms in some elementary steps and decays in others, the concentration change is equal to zero at steady state.

9. Temperature Dependence of the Rate Constant

The rates of chemical reactions depend strongly upon temperature. With very few exceptions, the rate increases with increase in temperature as seen in



the first figure. The second figure illustrates a chemical reaction that becomes explosive at a certain temperature. The second figure illustrates an enzyme-catalysed reaction. The rate increases up to a certain temperature at which the enzyme becomes deactivated.

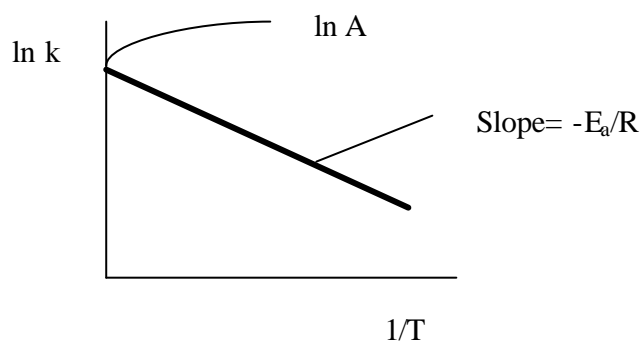
The temperature dependence of the rate of a reaction is due to the temperature dependence of the rate constant. The relation between the rate constant and temperature is expressed by Arrhenius equation;

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

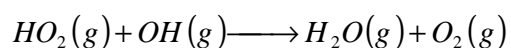
The constant A is called *the frequency factor* and E_a is *the activation energy*. A is the probability of occurrence of the reaction. It slightly depends upon temperature but we may ignore this effect. The activation energy is the energy that must be provided in order to enable the reactants to react. Converting the Arrhenius equation into logarithmic form, we have;

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

A plot of $\ln k$ versus $1/T$ yields a straight line with a slope $-E_a/R$ and an intercept $\ln A$.



Example 3. The Arrhenius parameters for the reaction described by;



are $A = 5.01 \times 10^{10} \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ and $E_a = 4.18 \text{ KJ} \cdot \text{mol}^{-1}$. Determine the value of the rate constant for this reaction at 298 K. At what temperature will the reaction have a rate constant that is twice that at 298 K?

Solution :

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

$$= (5.01 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) \exp \left[-\frac{4180 \text{ J} \cdot \text{mol}^{-1}}{(8.315 \text{ J} \cdot \text{K}^{-1})(298 \text{ K})} \right]$$

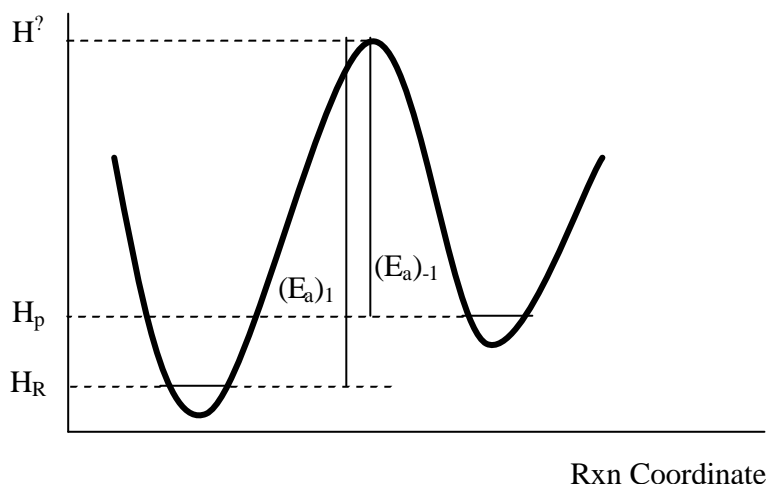
$$= 9.27 \times 10^9 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$$

$$T = \frac{-E_a}{R} \frac{1}{\ln(k/A)}$$

$$= \frac{-4180 \text{ J} \cdot \text{mol}^{-1}}{8.3145 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}} \frac{1}{\ln[2(9.27 \times 10^9) / 5.01 \times 10^{10}]}$$

$$= 506 \text{ K}$$

We can describe a chemical reaction by a simple energy diagram. The reaction proceeds from reactant to product along a reaction coordinate. The reaction coordinate may be a bond length, a bond angle associated with the reaction.



As seen in the above figure, there is an energy barrier which separates the reactants from the products. The reactants must have sufficient energy to surmount this barrier. The height of the barrier ($H^? - H_R$) is the activation energy for the forward reaction. Whereas, the height of the barrier ($H^? - H_P$) is the activation energy for the reverse reaction. The relation between the two activation energies is;

$$(E_a)_{-1} = (E_a)_1 - \Delta H$$

where $\Delta H (= H_P - H_R)$ is the heat of reaction.

