

Kinetics of radicalic chain polymerization-1:

Rate of reaction and kinetic investigations

The **reaction rate** is always defined as the change in the concentration (with an extra minus sign, if we are looking at reactants) divided by the change in time, with an extra term that is 1 divided by the stoichiometric coefficient.



During the course of the reaction shown below, reactants A and B are consumed while the concentration of product AB increases.

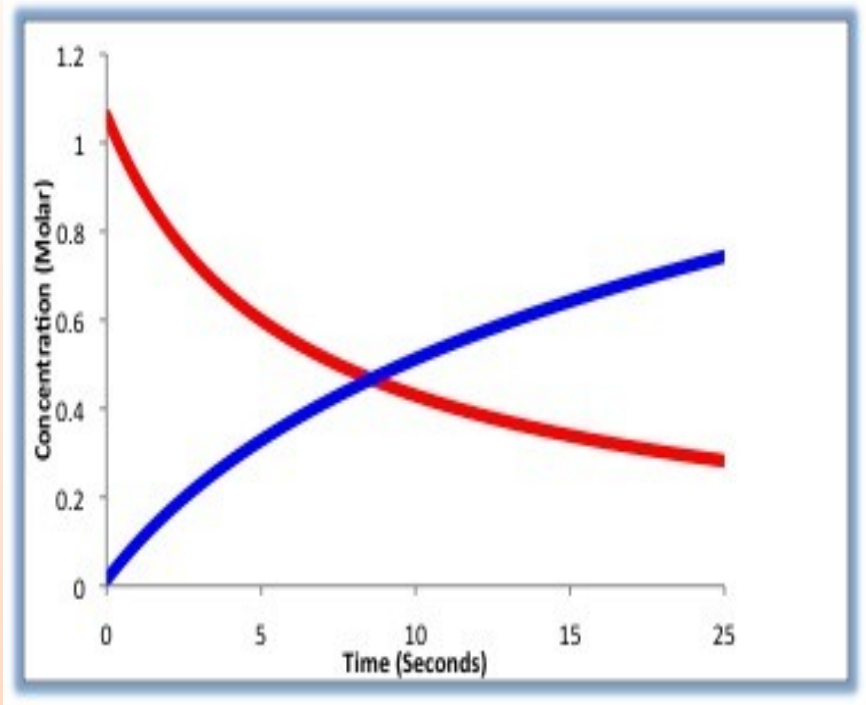
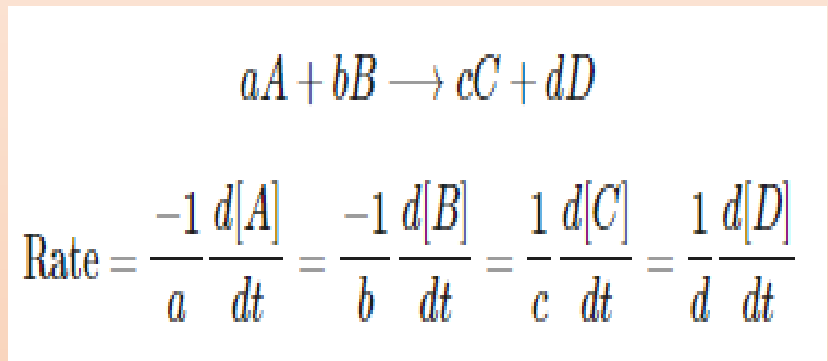


Figure 1: The above picture shows a hypothetical reaction profile in which the reactants (red) decrease in concentration as the products increase in concentration (blue).

The reaction rate can be determined by measuring how fast the concentration of A or B decreases, or by how fast the concentration of AB increases.

For the stoichiometrically complicated Reaction:



Looking at Figure 1 above, we can see that the rate can be measured in terms of either reactant (A or B) or either product (C or D).

Definition of Reaction Rate

The **Reaction Rate** for a given chemical reaction is the measure of the change in concentration of the reactants or the change in concentration of the products per unit time.

The speed of a chemical reaction may be defined as the change in concentration of a substance divided by the time interval during which this change is observed:

$$\text{rate} = \frac{\Delta \text{concentration}}{\Delta \text{time}}$$

For a reaction of the form $A+B \rightarrow C$, the rate can be expressed in terms of the change in concentration of any of its components

$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

$$\text{rate} = -\frac{\Delta[B]}{\Delta t}$$

$$\text{rate} = \frac{\Delta[C]}{\Delta t}$$

$$\Delta[A] = [A]_2 - [A]_1$$

in which $\Delta[A]$ is the difference between the concentration of A over the time interval $t_2 - t_1$:

Notice the minus signs in the first two examples above. The concentration of a reactant always decreases with time, so $\Delta[A]$ is both negative. Since negative rates do not make much sense, rates expressed in terms of a reactant concentration are **always** preceded by a minus sign to make the rate come out positive.

Consider now a reaction in which the coefficients are different:



It is clear that [B] decreases three times as rapidly as [A], so in order to avoid ambiguity when expressing the rate in terms of different components, it is customary to divide each change in concentration by the appropriate coefficient:

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[B]}{3\Delta t} = \frac{\Delta[D]}{2\Delta t}$$

Reaction Order

The reaction rate for a given reaction is a crucial tool that enables us to calculate the specific order of a reaction. The order of a reaction is important in that it enables us to classify specific chemical reactions easily and efficiently. Knowledge of the reaction order quickly allows us to understand numerous factors within the reaction including the rate law, units of the rate constant, half life, and much more. Reaction order can be calculated from the rate law by adding the exponential values of the reactants in the rate law.

$$\text{Rate} = k[\text{A}]^a[\text{B}]^b$$

$$\text{Reaction Order} = a + b$$

It is important to note that although the reaction order can be determined from the rate law, there is in general, **no relationship** between the reaction order and the stoichiometric coefficients in the chemical equation.

Rate Expressions describe reactions in terms of the change in reactant or product concentrations over the change in time. The rate of a reaction can be expressed by any one of the reactants or products in the reaction.

There are a couple of **rules to writing rate** expressions:

- Expressions for reactants are given a negative sign. This is because the reactant is being used up or decreasing.
- Expressions for products are positive. This is because they are increasing.
- All of the rate expressions for the various reactants and products must equal each other to be correct.

CHEMICAL KINETICS FOR DIFFERENT REACTION TYPES

	Zero-Order	First-Order	Second-Order
Rate Law	$R = k$	$R = k [A]$	$R = k [A]^2$
Linear Plot	$[A] = f(t)$	$\ln[A] = f(t)$	$[A]^{-1} = f(t)$
Integrated Law	$[A] = [A]_0 - kt$	$[A] = [A]_0 e^{-kt}$	$[A]^{-1} = [A]_0^{-1} + kt$
Half-life	$[A]_0 / 2k$	$\ln 2 / k$	$1 / k[A]_0$