**Reactant Concentrations and Time**

Rate equations (laws) relate rate of reaction to rate constant and reactant concentrations, which enable us to calculate the rate of reaction from the rate constant and reactant concentrations. But it would be useful to know how the concentrations of reactants change during the course of a reaction. Let us consider the simplest case- first-order reaction- to illustrate this application.

First-Order Reaction

In the first-order reaction, only one reactant is involved and the rate depends on the 1st power of the reactant concentration.

A → products
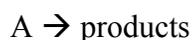
The rate in terms of rate of disappearance of reactant is

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

From the rate law, we know that

$$rate = k\,[A]$$

Therefore,

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

By rearranging this, we get

$$-\frac{\Delta[A]}{[A]} = k\,\Delta t$$

This is a differential equation and can be integrated between the time limit of t=0 and t=t to produce

$$\ln\frac{[A]_t}{[A]_o} = -kt \quad or \quad [A]_t = [A]_0\, e^{-kt} = [A]_0\, \exp(-kt) \tag{1}$$

Where $[A]_0$ is the concentration of A at zero time and $[A]_t$ is the concentration of A at time t=t. The above equation can be rearranged to give the equation of straight line (y = a + b x, where a is an intercept, b is a slope, x is independent variable, and y is dependent variable):

$$\ln [A]_t = \ln A]_0 - k\ t$$
(y   = a   +b x)

When we plot $\ln[A]_t$ against t, we get a straight with slope = k and intercept = $\ln[A]_0$. This is another way of calculating the rate constant k. The Equation (1) is very useful and has some interesting applications, such as,

(a) To calculate the concentration after certain time
(b) To determine how long it takes for a concentration to decrease to a certain amount
(c) To compute the time required to convert certain percentage of original concentration
(d) To calculate the half-life of a reaction

Let us illustrate above four applications with a specific example.

Example

The dissociation of hydrogen peroxide (disinfectant) to water and oxygen

$$2\ H_2O_2\ (l) \rightarrow 2\ H_2O\ (l) + O_2\ (g)$$

is a first order reaction with rate constant $k = 7 \times 10^{-4}$ /s.

(a) If the starting (initial) concentration of H_2O_2 solution is 0.75 M, what will be the concentration after 15 min?

Solution

Here $[A]_0 = 0.75$ M, $k = 7 \times 10^{-5}$ /s, and t= 15 min x 60 s/min = 900 s. Substitute these values into Equation (1) and solve for $[A]_t$

$$[A]_t = 0.75\ \text{M exp} (-7 \times 10^{-4}\ \text{/s} \times 900\ \text{s})$$
$$= 0.75\ \text{M exp}(-0.63)$$
$$= 0.39\ \text{M}$$

(b) How long will it takes for concentration of H_2O_2 decreases from 0.75 M to 0.1M?

Solution

Here $[A]_0 = 0.75$ M, $[A]_t = 0.1$ M, and $k = 7 \times 10^{-5}$ /s. Substitute these values into Equation (1) and solve for t.

$$\ln(0.1\ \text{M} / 0.75\ \text{M}) = -7 \times 10^{-4}\ (\text{M/s}) \times t\ (s)$$
$$-2.015 = -7 \times 10^{-4 \times} t$$
Therefore
$$t = 2878.5\ s = 48\ \text{min}$$

(c) How long will take to dissociate 50 % of the original sample?

Solution

Here $[A]_0 = 0.75$ M
        $[A]_t = [A]_0 - ([A]_0 \times 50\ \%) = 0.75M - (0.75M \times 0.5) = 0.75M - 0.375\ M = 0.375$ M.

Substitute these values into Equation (1)

$$\ln (0.375\ M\ /\ 0.75\ M\ ) = -\ 7 \times 10^{-4}/s\ \ t$$

Therefore
$$t = 990.21\ s = 16.5\ min$$

(d) Half-life

The half-life of a chemical reaction is defined as the time required for the concentration of a reaction to decreases to one-half of its initial concentration, which is usually denoted by either $t_{1/2}$ or $t_{0.5}$. We can formulate the half-life equation starting with Equation (1) in the following manner. Equation(1), after rearranging and solving for t assumes

$$t = \frac{1}{k} \ln \frac{[A]_0}{[A]_t}$$

According to the definition of half-life, we set $t = t_{1/2}$ and $[A]_t = [A]_0 / 2$. Substituting these values into above equation yields

$$t_{1/2} = \frac{1}{k} \ln \frac{[A]_o}{[A]_0 / 2} = \frac{1}{k} \ln 2 = \frac{0.693}{k} \qquad (2)$$

What kind of information we can derive from this equation?

- The half-life of the first order kinetics is independent of the initial concentration of the reactant; it does not matter how much amount you start with, the time required to decrease to one-half is always the same. For examples, the half-life to decrease the concentration from 6M to 3 M or 5M to 2.5M is the same.
- This equation provides another route for calculating the rate constant when $t_{1/2}$ is known.

$$k = \frac{0.693}{t_{1/2}} \qquad (3)$$

- Since $t_{1/2}$ is inversely proportional to k, it gives some idea about the magnitude of the rate constant – longer the $t_{1/2}$, smaller the k , and vice verse.

Example

The half-life for isomerization of gaseous cyclobutane to butadiene is 35 min. Calculate its rate constant.

Solution

The half-life is given in minutes and hence it needs to converted into seconds

$t_{1/2}$ = 35 min = 35 min x 60 s/min = 2100 s

Substitute these values into Equation (3) to calculate k

$$k = \frac{0.693}{t_{1/2}} = 0.693 / 2100 \text{ s} = 3.3 \text{ x } 10^{-3} / \text{s}$$

Something You Should Remember

The first-order rate Equation (1) and half-life Equation (3) have important application in nuclear chemistry in determining the age of an ancient object (Carbon dating technique).