

STABILITY SYSTEM

ScienTek Software, Inc.

This short discussion is an excerpt from "A Crash Course on Chemical Kinetics and Statistical Data Treatment" that is part of the documentation for STABILITY SYSTEM program from ScienTek Software, Inc.

Simple Reactions

We now consider some simple reactions whose rate laws can be easily solved. They will serve to introduce and illustrate some very important kinetic parameters and features.

Zero-Order Reactions

When the reaction rate is independent of the concentration of the reacting substances, it is dependent on the zero power of the reactant concentration. Thus the reaction is considered to be a *zero-order reaction*. This type of reaction can be described by:

$$-\frac{dA}{dt} = k_o \quad (1)$$

where the negative sign indicates that the concentration of the reactant A is decreasing as the reaction proceeds and k_o is the *zero-order rate constant*.

An analytical form of EQ(1), expressing A as a function of t , is often more convenient to comprehend the kinetic data. This can be derived by solving the differential equation (1). In this case, the variables can be separated and integrated separately:

$$-\int_{A_o}^A dA = k_o \int_0^t dt \quad (2)$$

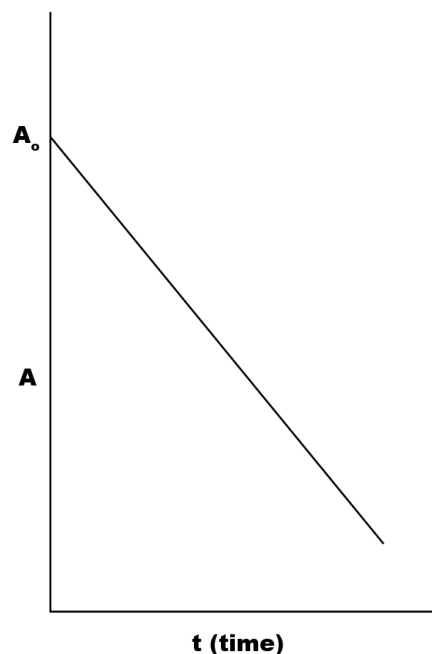
where A_o is the initial concentration and A is the concentration at time t . The integration of EQ(2) leads to:

$$A = A_o - k_o t \quad (3)$$

It is apparent from EQ(3) that the concentration-time profile is linear (Figure 1). The rate constant k_o can be obtained from the slope of the straight line in Figure 1 (i.e., slope = $-k_o$).

In a zero-order reaction, the rate is determined by some limiting factors. Examples are the amount of light absorption in a photochemical reaction and amount of catalyst in a catalytic reaction.

Figure 1: Concentration-time profile of a zero-order reaction



First-Order Reactions

Consider the following reaction:



We have a first-order reaction when the rate law is:

$$-\frac{dA}{dt} = k_1 A \quad (5)$$

where k_1 is the *first-order rate constant*. The concentration-time relationship can be obtained by solving EQ(5), again by separating the variables and integrating. The convenient forms of the solution for EQ(5) are:

linear form:

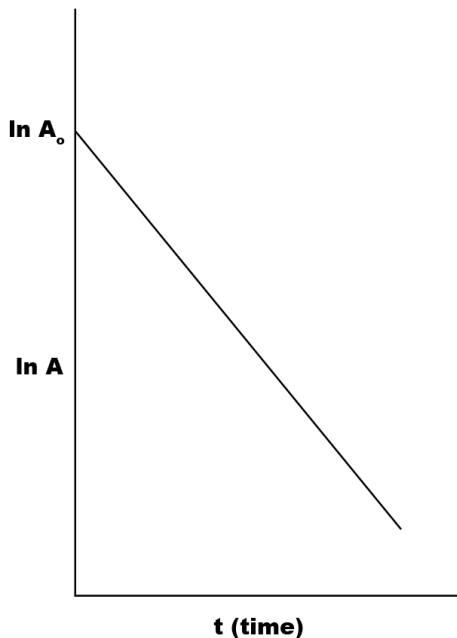
$$\ln A = \ln A_o - k_1 t \quad (6)$$

non-linear form:

$$A = A_o e^{-k_1 t} \quad (7)$$

The $\ln A$ vs. t kinetic profile is shown in Figure 2. The rate constant k_1 can be obtained from the slope of the straight line in Figure 2 using EQ(6).

Figure 2: Linear concentration-time profiles of a first-order reaction



Second-Order Reactions

Consider the following reaction:



We have a second-order reaction when the rate law is:

$$-\frac{dA}{dt} = k_2 A^2 \quad (9)$$

where k_2 is the *second-order rate constant*. The concentration-time relationship can be obtained by

solving EQ(9), again by separating the variables and integrating. A convenient form of the solution for EQ(9) is:

$$\frac{1}{A} = \frac{1}{A_0} + k_2 t \quad (10)$$

The $\frac{1}{A}$ vs. t kinetic profile is shown in Figure 3. The rate constant k_2 can be obtained from the slope of the straight line in Figure 3 using EQ(10).

Figure 3: Concentration-time profiles of a second-order reaction

