

PHYSICAL CHEMISTRY

CHEMICAL KINETICS

Integrated rate laws

Because rate laws are differential equations, we must integrate them if we want to find the concentrations as a function of time. A number of simple cases analytical solutions are easily obtained, and prove to be very useful. We examine a few of these simple cases here.

(A) Zero-order Reaction

A reactant whose concentration does not affect the reaction rate is not included in the rate law. In effect, the concentration of such a reactant has the power 0. Thus $[A]^0 = 1$. A zero order reaction is one whose rate is independent of concentration.

$A \longrightarrow \text{Products}$

Rate of reaction =

$$= \frac{-d[A]}{dt} = k_0 [A]^0$$

$$d[A]/dt = K_0$$

This expression can be integrated directly because k is a constant independent of t . Initially (at $t = 0$) the concentration of A is $[A]_0$, and at a later time t it is $[A]$, so we make these values the limits of the integrals and write

$$\int_{[A]_0}^{[A]} d[A] = -K \int_{t=0}^t dt$$

Integration of the expression gives:

$$[A] - [A]_0 = -k_0 t \quad \text{.....7-1}$$

Thus the units of k are $\text{mol l}^{-1} \text{time}^{-1}$

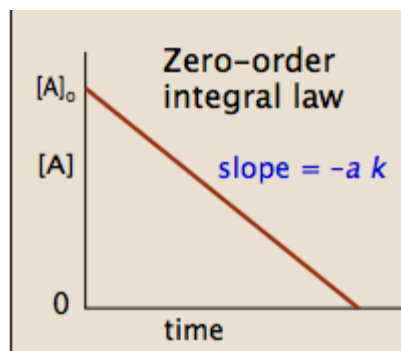


Figure 1: Rate vs. time (A) and Concentration vs. time for a zero order reaction.

$$[A]_0 - [A] = k_0 t$$

Half-lives time :

A useful indication of the rate of a first-order chemical reaction is the half-life, $t_{1/2}$, of a substance, the time taken for the concentration of a reactant to fall to half its initial value. The time for $[A]$ to decrease from $[A]_0$ to $1/2 [A]_0$ in a first-order reaction is given by eqn. 7-1 as :

$$[A]_0 - 1/2 [A]_0 = k_0 t_{1/2}$$

$$1/2 [A]_0 = k_0 t_{1/2}$$

$$\text{Hence: } t_{1/2} = \frac{[A]_0}{2K}$$

(B) First-order reactions

For the reaction

$A \longrightarrow \text{products}$

The rate law

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

This expression can be integrated directly because k is a constant independent of t . Initially (at $t = 0$) the concentration of A is $[A]_0$, and at a later time t it is $[A]$, so we make these values the limits of the integrals and write

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -K \int_{t=0}^t dt$$

$[A]_0$ = initial conc. , $[A] = [A]_0 - x$

$[A]_0 = a$, $[A] = a - x$

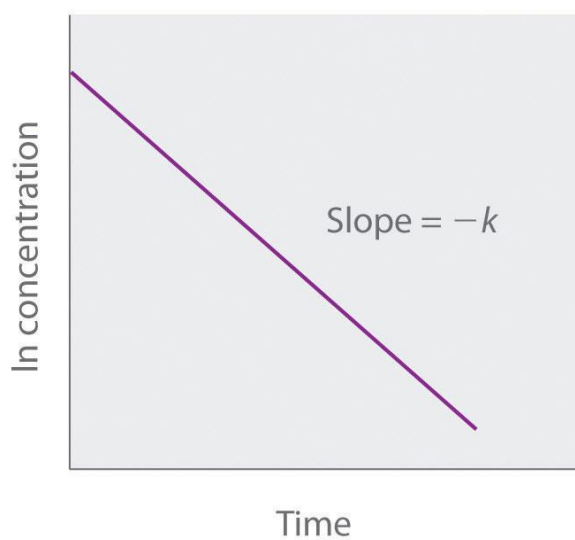
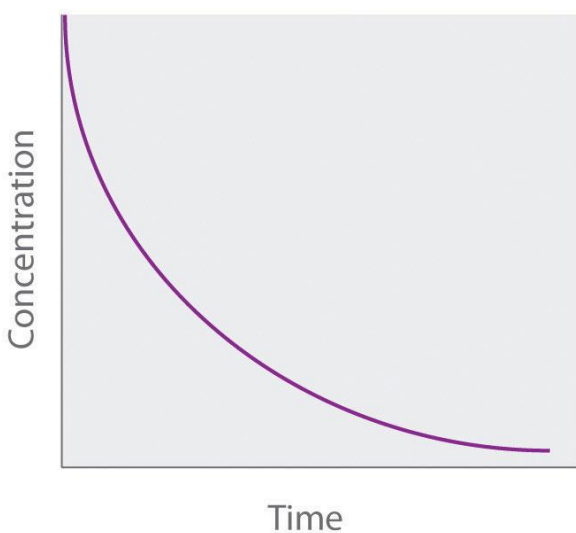
Integration of the expression gives:

$$\ln \frac{[A]}{[A]_0} = -Kt \quad \text{or} \quad [A] = [A]_0 e^{-Kt} \quad \dots\dots 7-2$$

$$\ln \frac{[A]_0}{[A]} = Kt$$

the concentration of A is a moles litre⁻¹. after time t, x moles of A have changed, the concentration of A is a - x , eq. (1) will be

$$\ln \frac{a}{a-x} = kt$$



Half-lives time :

$$kt_{1/2} = -\ln \left(\frac{\frac{1}{2}[A]_0}{[A]_0} \right) = -\ln \frac{1}{2} = \ln 2$$

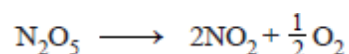
Hence:

$$t_{1/2} = \frac{\ln 2}{k} \quad (\ln 2 = 0.693.)$$

Examples of First order Reactions

Some common reactions which follow first order kinetics are listed below :

(1) **Decomposition of N₂O₅ in CCl₄ solution.** Nitrogen pentoxide in carbon tetrachloride solution decomposes to form oxygen gas,

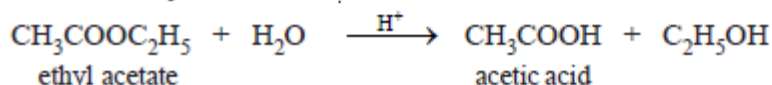


The progress of the reaction is monitored by measuring the volume of oxygen evolved from time to time. If V_t be the volume of O₂ at any time t and V_∞ the final volume of oxygen when the reaction is completed, the V_∞ is a measure of the initial concentration of N₂O₅ and $(V_\infty - V_t)$ is a measure of undecomposed N₂O₅ ($a - x$) remaining at time t . Thus,

$$k = \frac{2.303}{t} \log_{10} \frac{V_\infty}{V_\infty - V_t}$$

On substituting values of V_∞ , $(V_\infty - V_t)$ at different time intervals, t , the value of k is found to be constant. Thus it is a reaction of the first order.

(3) **Hydrolysis of an Ester.** The hydrolysis of ethyl acetate or methyl acetate in the presence of a mineral acid as catalyst, is a first order reaction.



For studying the kinetics of the reaction, a known volume of ethyl acetate is mixed with a relatively large quantity of acid solution, say N/2 HCl. At various intervals of time, a known volume of the reaction mixture is titrated against a standard alkali solution. Hydrolysis of the ester produces acetic acid. Therefore as the reaction proceeds, the volume of alkali required for titration goes on increasing.

SOLVED PROBLEM. The following data was obtained on hydrolysis of methyl acetate at 25°C in 0.35N hydrochloric acid. Establish that it is a first order reaction.

t (secs)	0	4500	7140	∞
ml alkali used	24.36	29.32	31.72	47.15

SOLUTION

For a first order reaction,

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

At any time, the volume of alkali used is needed for the acid present as catalyst and the acid produced by hydrolysis.

The volume of alkali used for total change from t_0 to t_∞ gives the initial concentration of ester. Thus,

$$a = 47.15 - 24.36 = 22.79 \text{ ml}$$

$$(a-x) \text{ after } 4500 \text{ sec} = 47.15 - 29.32 = 17.83 \text{ ml}$$

$$(a-x) \text{ after } 7140 \text{ sec} = 47.15 - 31.72 = 15.43 \text{ ml}$$

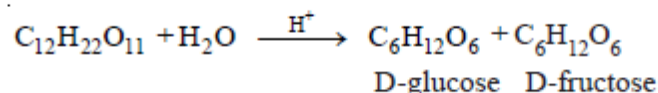
Substituting values in the rate equation above, we have

$$k = \frac{2.303}{4500} \log \frac{22.79}{17.83} = 0.00005455$$

$$k = \frac{2.303}{7140} \log \frac{22.79}{15.43} = 0.0000546$$

Since the values of k in the two experiments are fairly constant, the reaction is of the first order.

(4) **Inversion of Cane sugar (sucrose).** The inversion of cane sugar or sucrose catalyzed with dil HCl



follows the first order kinetics. The progress of the reaction is followed by noting the optical rotation of the reaction mixture with the help of a polarimeter at different time intervals. The optical rotation

goes on changing since D-glucose rotates the plane of polarised light to the right and D-fructose to the left. **The change in rotation is proportional to the amount of sugar decomposed.**

Let the final rotation be r_{∞} , the initial rotation r_0 while the rotation at any time t is r_t

The initial concentration, a is $\propto (r_0 - r_{\infty})$.

The concentration at time t , $(a - x)$ is $\propto (r_t - r_{\infty})$

Substituting in the first order rate equation,

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a - x}$$

we have

$$k = \frac{2.303}{t} \log_{10} \frac{(r_0 - r_{\infty})}{(r_t - r_{\infty})}$$

If the experimental values of t , $(r_0 - r_{\infty})$ and $(r_t - r_{\infty})$ are substituted in the above equation, a constant value of k is obtained.

SOLVED PROBLEM. The optical rotation of sucrose in 0.9N HCl at various time intervals is given in the table below.

time (min)	0	7.18	18	27.1	∞
rotation (degree)	+24.09	+21.4	+17.7	+15	-10.74

Show that inversion of sucrose is a first order reaction.

SOLUTION

The available data is substituted in the first order rate equation for different time intervals.

$$k = \frac{2.303}{t} \log_{10} \frac{r_0 - r_{\infty}}{r_t - r_{\infty}}$$

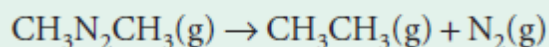
$r_0 - r_{\infty} = 24.09 - (-10.74) = 34.83$ for all time intervals. Thus, the value of rate constant can be found.

time (t)	$r_t = r_{\infty}$	$k = \frac{1}{t} \log \frac{(r_0 - r_{\infty})}{(r_t - r_{\infty})}$
7.18	32.14	$k = \frac{1}{7.18} \log \frac{34.83}{32.14} = 0.0047$
18	28.44	$k = \frac{1}{18} \log \frac{34.83}{28.44} = 0.0048$
27.1	25.74	$k = \frac{1}{27.1} \log \frac{34.83}{25.74} = 0.0048$

Since the value of k comes out to be constant, the inversion of sucrose is a **first order reaction**.

Example/

The variation in the partial pressure of azomethane with time was followed at 600 K, with the results given below. Confirm that the decomposition



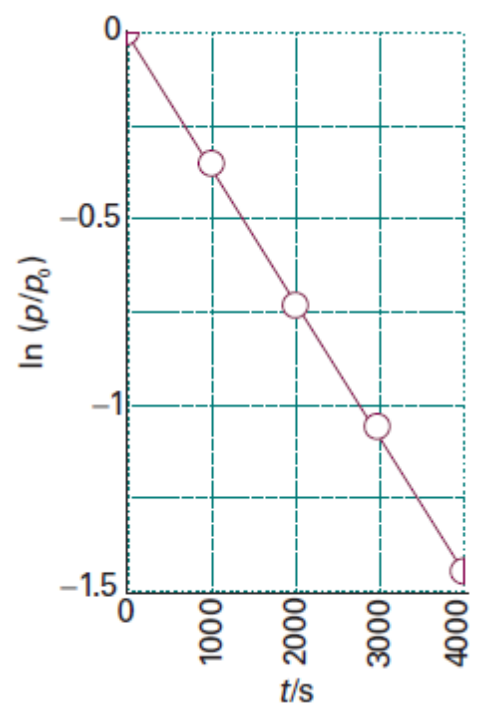
is first-order in azomethane, and find the rate constant at 600 K.

t/s	0	1000	2000	3000	4000
p/Pa	10.9	7.63	5.32	3.71	2.59

Answer We draw up the following table:

t/s	0	1000	2000	3000	4000
$\ln(p/p_0)$	1	-0.360	-0.720	-1.082	-1.441

Figure 22.6 shows the plot of $\ln(p/p_0)$ against t . The plot is straight, confirming a first-order reaction, and its slope is -3.6×10^{-4} . Therefore, $k = 3.6 \times 10^{-4} \text{ s}^{-1}$.



(c) Second-order reactions

1- For the reaction

$A \longrightarrow \text{products}$

The rate law:

$$\frac{d[A]}{dt} = -k[A]^2$$

The concentration of A is $[A_0]$ at $t = 0$ and $[A]$ at a general time t later. Therefore,

$$-\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = \int_{t=0}^t K dt$$

is either of the following two forms:

Because the integral of $1/x^2$ is $-1/x$

$$\frac{1}{[A]} - \frac{1}{[A]_0} = Kt \quad \text{.....(7-3)}$$

Or

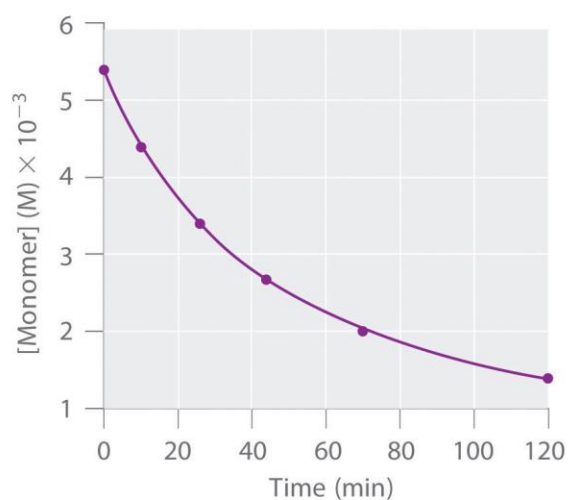
$$[A] = \frac{[A]_0}{1 + Kt [A]_0}$$

The units for K for second order reactions are $(\text{mol}^{-1} \text{ L time}^{-1})$, in some references Eq. (7-3) will be

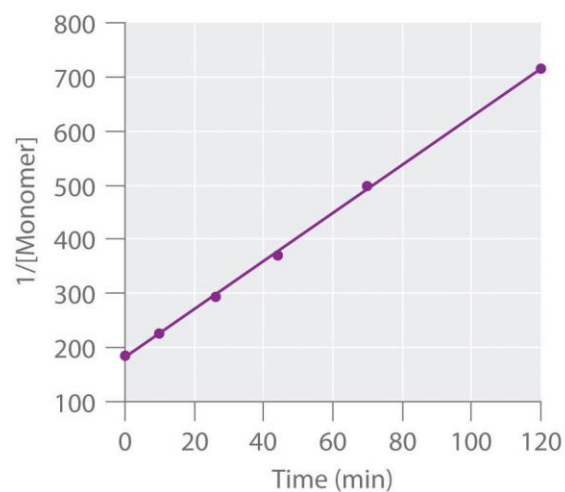
$$\frac{1}{a-x} - \frac{1}{a} = Kt$$

The half-life for this reaction:

$$t_{1/2} = \frac{1}{k[A]_0}$$



(a)



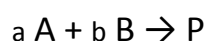
(b)

Fig.: (a) the experimentally determined concentration of monomer versus time and (b) $1/[\text{monomer}]$ versus time. The straight line in (b) is expected for a simple second-order reaction.

B) A reaction that occurs in solution that is first order in two reactants is second order overall.

$$d[A]/dt = -k[A][B] \quad \text{----- (7-4)}$$

If the reaction has the stoichiometry



$[A]_0$: Initial conc. of A, $[B]_0$: Initial conc. of A

a : no. of moles of A, b : no. of moles of B

X : No. of reactant moles, the conc. Of **A** after t time

$$[A] = [A]_0 - x \quad \text{----- (7-5)}$$

The no. of moles of **B** after t time will proportional with $x(\frac{b}{a})$ will be:

$$[B] = [B]_0 - x \left(\frac{b}{a} \right) \quad \text{----- (7-6)}$$

X = $[A]_0 - [A]$ from eq. (7-5), by substitution of x in eq. (7-6)

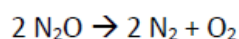
$$[B] = [B]_0 - ba^{-1}([A]_0 - [A])$$

For this type of reactions the integrated rate equation is:

$$\frac{1}{a[B]_0 - b[A]_0} \ln \frac{[B]/[B]_0}{[A]/[A]_0} = Kt \quad \text{-----(7-7)}$$

Example:

The decomposition of nitrous oxide at 565 °C



is second order in N_2O with a rate constant of $1.10 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$. If the reaction is initiated with $[\text{N}_2\text{O}]$ equal to 0.108 M, what will its concentration be after 1250 s have elapsed?

Solution

Because the reaction is first order, we use the first order integrated rate equation.

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

We know $[\text{N}_2\text{O}]_0$, k , and t . We solve for $[\text{N}_2\text{O}]_t$.

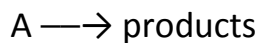
$$\frac{1}{[\text{N}_2\text{O}]_t} - \frac{1}{0.108M} = (1.10 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}) 1250 \text{ s}$$

$$\frac{1}{[\text{N}_2\text{O}]_t} = 9.26 \text{ M}^{-1} + 1.38 \text{ M}^{-1}$$

$$[\text{N}_2\text{O}]_t = 0.940 \text{ M}$$

(D) Third -order reactions:

1- Let us consider a simple third order reaction of the type



$$d[A]/dt = K [A]^3$$

$$\int_{A_0}^A \frac{d[A]}{[A]^3} = - \int_{t=0}^t K dt$$

The integrated rate equation is:

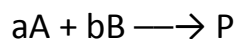
$$\frac{1}{[A]^2} - \frac{1}{[A]_0^2} = 2Kt \quad \text{-----(7-8)}$$

The unit of K ($\text{mol}^{-2} \text{L}^{-2} \text{Min.}^{-1}$)

The $t_{1/2}$ for this reaction :

$$t_{1/2} = \frac{3}{2 [A]_0^2 K}$$

2- For the reaction:



The rate law

$$-d[A]/dt = K [A]^2 [B]$$

The integrated rate equation is:

$$\frac{1}{a[B]_0 - b[A]_0} \left(\frac{1}{[A]_0} - \frac{1}{[A]} + \frac{b}{a[B]_0 - b[A]_0} \ln \frac{[B]/[B]_0}{[A]/[A]_0} \right) = K t \quad \text{-----(7-9)}$$

SOLVED PROBLEM 5. For a certain first order reaction $t_{0.5}$ is 100 sec. How long will it take for the reaction to be completed 75% ?

SOLUTION

Calculation of k

For a first order reaction

$$t_{1/2} = \frac{0.693}{k}$$

or
$$100 = \frac{0.693}{k}$$

$$\therefore k = \frac{0.693}{100} = 0.00693 \text{ sec}^{-1}$$

Calculation of time for 75% completion of reaction

The integrated rate equation for a first order reaction is

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

or
$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

When $\frac{3}{4}$ initial concentration has reacted, it is reduced to $\frac{1}{4}$

Substituting values in the rate equation

$$\begin{aligned} t_{3/4} &= \frac{2.303}{0.00693} \log \frac{[A]_0}{\frac{1}{4}[A]_0} \\ &= \frac{2.303}{0.00693} \log 4 = 200 \text{ sec} \end{aligned}$$

