Lecture 18

Thursday, November 14, 2024 10:07

Last lecture: worked on exercise to find rate constant and reaction order using a combination of the isolation method and the method of initial rates.

Data table: $[I]_0$ and r_0, at several $[Ar]_0$ (refer to Excel attachment).

First, plot $\log r_0$ vs. $\log [I]_0$:

$$r_0 = k_{eff} [I]_0^a$$

$$\log r_0 = \log k_{eff} + a \log [I]_0$$

For three different $[Ar]_0$, we obtain three trendlines, from which we obtain the same slope of 2. This gives us the reaction order in $[I]_0$. The different intercepts give us three values for k_{eff}.

Then, we note that

$$k_{eff} = k[Ar]_0^b$$

where k is the true rate constant for this reaction. Thus,

$$\log k_{eff} = \log k + b \log [Ar]_0$$

Now if we plot $\log k_{eff}$ vs. $\log [Ar]_0$, the slope will tell us the reaction order in $[Ar]_0$ and the intercept will give us the true rate constant.

In conclusion, the initial rate law for the reaction

$$2I(g) + Ar(g) \rightarrow I_2(g) + Ar(g)$$

is $r = k[Ar]_0[I]_0^2$

Topic 17B: Integrated Rate Laws

Zeroth-Order Reactions:

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

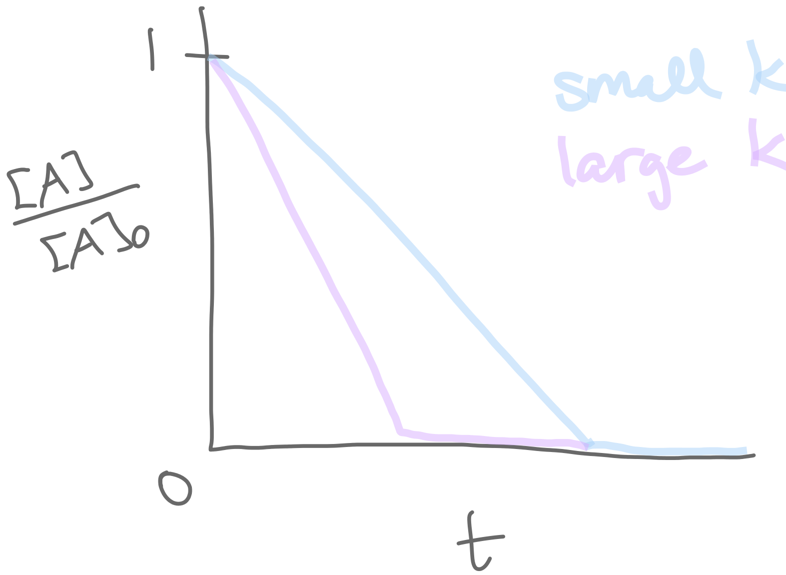
Let $[A]_0$ be the concentration of $[A]$ at time 0.

Then $\frac{d[A]}{dt} = [A] - [A]_0$

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

$$\boxed{[A] = [A]_0 - kt}$$

integrated zeroth-order rate law



First-Order Reactions :

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

$$\frac{1}{[A]} d[A] = -k\,dt$$

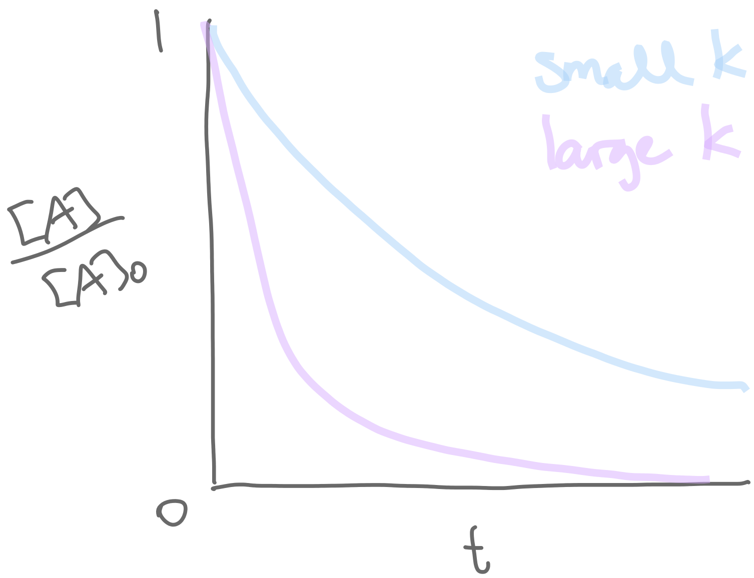
$$\int_{[A]_0}^{[A]} \frac{1}{[A]'} d[A]' = -k \int_0^t dt'$$

$$\ln \frac{[A]}{\;} = -kt$$

$[A]_0$

$$\boxed{[A] = [A]_0 e^{-kt}}$$

integrated first-order rate law



What about the product concentration?

For a reaction $A \rightarrow P$, where no P is present initially, $[P] = [A]_0 - [A]$.

$$[A] = [A]_0 e^{-kt}$$

$$[A]_0 - [P] = [A]_0 e^{-kt}$$

$$[P] = [A]_0 - [A]_0 e^{-kt}$$

$$\boxed{[P] = [A]_0 (1 - e^{-kt})}$$

Define half-life ($t_{1/2}$) as the time it takes for the concentration of a reactant to fall to half its initial value. Then,

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

$$\ln \frac{1}{2} = -kt_{1/2}$$

$$\ln 2 = kt_{1/2}$$

$$\boxed{t_{1/2} = \frac{\ln 2}{k}}$$

half-life for a first-order reaction

The half-life of a species in a first-order reaction does not depend on its initial concentration.

Second-Order Reactions:

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

$$-\frac{1}{[A]^2}\,d[A] = -k\,dt$$

$$\int_{[A]_0}^{[A]} -\frac{1}{[A]'^2}\,d[A]' = -k\int_0^t dt'$$

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

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

$$[A] = \frac{1}{1/[A]_0 + kt} \cdot \frac{[A]_0}{[A]_0}$$

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

integrated second-order rate law

For a reaction of the form $A \rightarrow P$,

$$[P] = [A]_0 - [A]$$

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

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

$$[P] = \frac{[A]_0 + [A]_0^2 kt - [A]_0}{1 + [A]_0 kt}$$

$$\boxed{[P] = \frac{[A]_0^2 kt}{1 + [A]_0 kt}}$$

For the half-life,

$$\frac{1}{1/2[A]_0} - \frac{1}{[A]_0} = kt_{1/2}$$

$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = kt_{1/2}$$

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

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

half-life for a second-order reaction

Alternate form of a second-order reaction:

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

At time t,

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

$$[B] = [B]_0 - x$$

$$\frac{d[A]}{dt} = -k([A]_0 - x)([B]_0 - x)$$

$$\frac{d[A]}{dt} = -\frac{dx}{dt}, \text{ so}$$

$$\frac{dx}{dt} = k([A]_0 - x)([B]_0 - x)$$

$$\frac{1}{([A]_0 - x)([B]_0 - x)} dx = k\,dt$$

$$\int_0^x \frac{1}{([A]_0 - x')([B]_0 - x')} dx' = k\int_0^t dt'$$

Use integral table:

$$\int \frac{1}{(A-x)(B-x)} dx = \frac{1}{B-A} \ln \frac{B-x}{A-x} + C$$

$$\left[\frac{1}{[B]_0 - [A]_0} \ln \frac{[B]_0 - x'}{[A]_0 - x'}\right]_0^x = kt$$

$$\ln \frac{[B]}{\cdots} - \ln \frac{[B]_0}{\cdots} = ([B]_0 - [A]_0)kt$$

$[A]_0 \neq [B]_0$

$$\boxed{\ln \frac{[B]/[B]_0}{[A]/[A]_0} = ([B]_0 - [A]_0)kt}$$

integrated second-order rate law for a reaction of the type $A + B \rightarrow P$.