<u>Problems: Relationship Between Concentration and Time for a First Order Reaction</u>

Suppose that a reaction: A ---------> products

is first order, then: Rate = $k [A]^1$ Equation 1

Rate = $- \frac{\Delta[A]}{\Delta t}$ Equation 2

Combining equation 1 and 2 ...

$$- \frac{\Delta[A]}{\Delta t} = k [A]^1$$

Integration of this leads to ...

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

Rearranging this equation we obtain ...

$$\mathbf{\ln [A]_t = - k\,t + \ln [A]_0}$$

$$(y = m\,x + B)$$

$[A]_0$ = concentration of reactant A at a time = 0 (i.e when instrument readings started not necessarily at time = 0)

$[A]_t$ = concentration of reactant A at a later time = t

A plot of $\ln [A]_t$ vs time, t will be a linear graph, slope = - k (the rate constant).

This integrated form of the equation is useful in three ways:

1. If $[A]_t / [A]_0$ is known in the lab, then k may be calculated.
2. If $[A]_0$ and k are known the $[A]_t$ of material expected after time t may be determined.
3. If k is known, then the equation can be used to calculate the time elapsed until A achieves some pre-determined concentration, $[A]_t$.

Note from the integrated equation ...

1. $\frac{[A]_t}{[A]_0}$ is the fraction of the material remaining after the specified time period.
2. The negative sign is because the ratio of $[A]_t / [A]_0$ is less than one, because $[A]_t$ is always less than $[A]_0$.

Problems:

1. Cyclopropene, C_3H_6, rearranges to propene by a first order reaction: Rate = k [cyclopropene]^1
Given the rate constant, $k = 5.4 \times 10^{-2}\ h^{-1}$, if the initial concentration of cyclopropene is $0.050\ moldm^{-3}$.
a) How many hours must elapse for the concentration to drop to $0.010\ mol\ dm^{-3}$.
b) What is the concentration after 8.8 min? (answer: (a) t = 30 h, (b) [ ] =)
2. H_2O_2 decomposes in dilute NaOH at 20 ^{0}C in a first order reaction ...
$2 H_2O_2$ --------> $2 H_2O + O_2$ Rate = $k [H_2O_2]$ $k = 1.06 \times 10^{-3}\ min^{-1}$
If the initial concentration of H_2O_2 is $0.020\ moldm^{-3}$. What is the concentration of the H_2O_2 after exactly 100 min? (Answer = $[H_2O_2] = 0.018\ moldm^{-3}$)
3. Methyl isocyanide undergoes a first order isomerization to form methyl cyanide ...
CH_3NC -----------> CH_3CN
The reaction was studied at 199 ^{0}C. The initial concentration of CH_3NC was $0.0258\ moldm^{-3}$ and after 11.4 min, analysis showed the concentration of the product to be $1.30 \times 10^{-3}\ moldm^{-3}$.
a) What is the value of the rate constant? (b) How long will it take for 90 % of CH_3NC to react?
(answer: (a) $k = 4.54 \times 10^{-3}\ min^{-1}$ (b) t = 507 min)