# Concentration – Time and Rate Law

Mathematical expressions allow us to determine the conc. Of a reactant remaining in a system at any particular time in a reaction.

The rate tells us:  How the speed of a reaction varies with the conc. of the reactants.
However we wish to know:  more than how fast a reaction is going.

We wish to know the conc. of the reactants & products at some specified time after the reaction has started so that we can decide if it is time to harvest the products.

We might like to know how much of the reactants remains or how long it would take for the conc. of the reactants to drop to some minimum optimum values so that we could replenish them.

In order to obtain information of this type requires a mathematical expression that relates concentration to time.
The mathematical expression that relates concentration to time can be obtained from the rate law of a reaction, derived using calculus.
The mathematical expressions are always the same for a given order of the reaction, thus they require a knowledge of the order of the reaction.

Suppose that a reaction:      $A \longrightarrow$ products
is first order, then: Rate  $=$  $k[A]^1$          Equation 1

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

Combining equation 1 and 2 ...

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

Integration of this leads to ...

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

Rearranging this equation we obtain ...

$$\mathbf{\ln [A]_t = -kt + \ln [A]_0}$$
$$(y \quad = \quad mx \quad + \quad B)$$

$[A]_0$  =  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, $[A]_t$ .

# Characteristic Properties of Rate Laws

$[A]_t$ = concentration of A after time t,    $[A]_0$ = concentration of A at beginning of reaction.

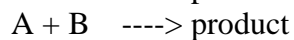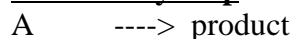| Order | Relative Rate vs. Conc. (mol $dm^{-3}$) | | Rate Law | Integrated Rate Law | Straight Line Plot | Relationship of Rate constant to Slope | Units of Rate Constant | Half - Life: $t_{1/2}$ |
|---|---|---|---|---|---|---|---|---|
| 0 | [A]<br>1<br>2<br>3 | Rate<br>1<br>1<br>1 | $k[A]^0$ | $[A]_t = -kt + [A]_0$ | $[A]_t$ vs t | $-k$ | $mol\ dm^{-3}\ s^{-1}$ | $\dfrac{[A]_0}{2k}$ |
| 1 | [A]<br>1<br>2<br>3 | Rate<br>1<br>2<br>3 | $k[A]^1$ | $\ln[A]_t = -kt + \ln[A]_0$ | $\ln [A]_t$ vs t | $-k$ | $s^{-1}$ | $\dfrac{0.693}{k}$ |
| 2 | [A]<br>1<br>2<br>3 | Rate<br>1<br>4<br>9 | $k[A]^2$ | $\dfrac{1}{[A]_t} - \dfrac{1}{[A]_0} = kt$ | $\dfrac{1}{[A]_t}$ vs t | $k$ | $dm^3 mol^{1-}s^{-1}$ | $\dfrac{1}{k[A]_0}$ |

## Rate Law Summary

1. Rate law is determined experimentally.

2. Rate law is defined in terms of reactant concentration (not product concentration).

3. The order is not related to the stoichiometric coefficients of the reactants in the overall balanced equation, however it is related to the coefficients in the rate determining step.

**Rate Equations for Elementary Steps**

Molecularity is defined as the number of species that must collide to produce the reaction indicated in that step.

The molecularity of an elementary step and its order are the same.

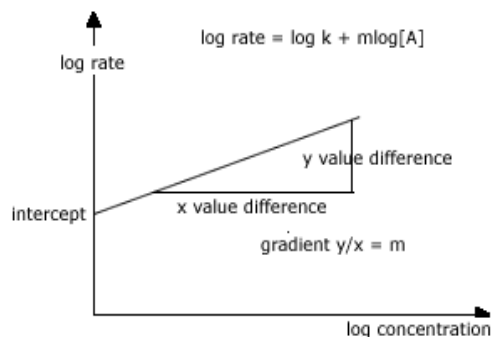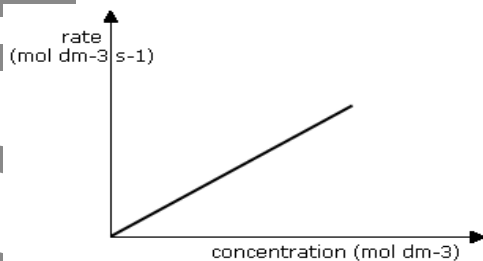| **Elementary Step** | **Molecularity** | **Rate Equation** |
|---|---|---|
| A ----> product | unimolecular | Rate = k [A] |
| A + B ----> product | bimolecular | Rate = k [A][B] |
| A + A ----> product | bimolecular | Rate = k $[A]^2$ |
| | | or k $[B]^2$ |
| 2 A + B ----> product | termolecular | Rate = k $[A]^2$ [B] |
| | | or k $[A][B]^2$ |
| | | or k$[B]^3$ |
| | | or k [A][B][C] |

## Graphical Representation of Rate Law

**Zero Order**

Rate = k $[A]^0$
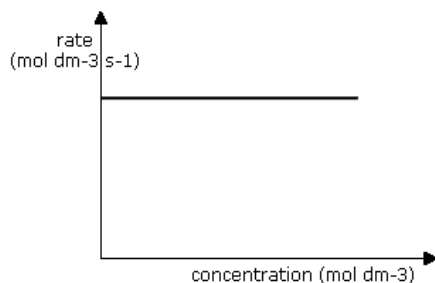


**First Order**

Rate = k $[A]^1$



The gradient (slope) of the graph gives the rate constant k, whose units are s-1

**Second Order**

Rate = k $[A]^2$



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