Rate and orde of reaction

Science Background

Reaction rate

A chemical reaction is a process in which one or more substances (reactants) change into one or more new substances (products).

The rate of a chemical reaction indicates how fast a reaction takes place. In other words the reaction rate is the 'rate of formation of product' or the 'rate of removal of reactant'.

For a one-step reaction $A \rightarrow B$ the reaction rate at which A transforms in B, is the change in concentration of A with time, mathematically expressed as:

$$rate = -\frac{\Delta[A]}{\Delta t} \text{ or } rate = \frac{\Delta[B]}{\Delta t}$$

For a general reaction with stoichiometric coefficients (represented by lowercase letters)

$$aA + bB \rightarrow pP + qQ$$

The reaction rate is:

$$rate = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{p}\frac{d[P]}{dt} = \frac{1}{q}\frac{d[Q]}{dt}$$

with a negative sign for reactants and a positive signs for products.

The reaction rate can be measured by using different experimental techniques. These include, but are not limited to, the following:

- by measuring a change of volume of a gas which is formed during a reaction,
- by measuring a change of pressure of a gas which is formed during a reaction,
- by measuring a change of colour during a reaction,
- by measuring a change of conductivity during a reaction.

Rate law

Experimentally it is found that reaction rate depends on the concentration of the species involved in the reaction. The relation between the rate and these concentrations can be expressed mathematically in the form of an equation called a *rate law*.

For a reaction $aA + bB \rightarrow pP + qQ$, the rate equation is of the form $r = k[A]^a[B]^b$

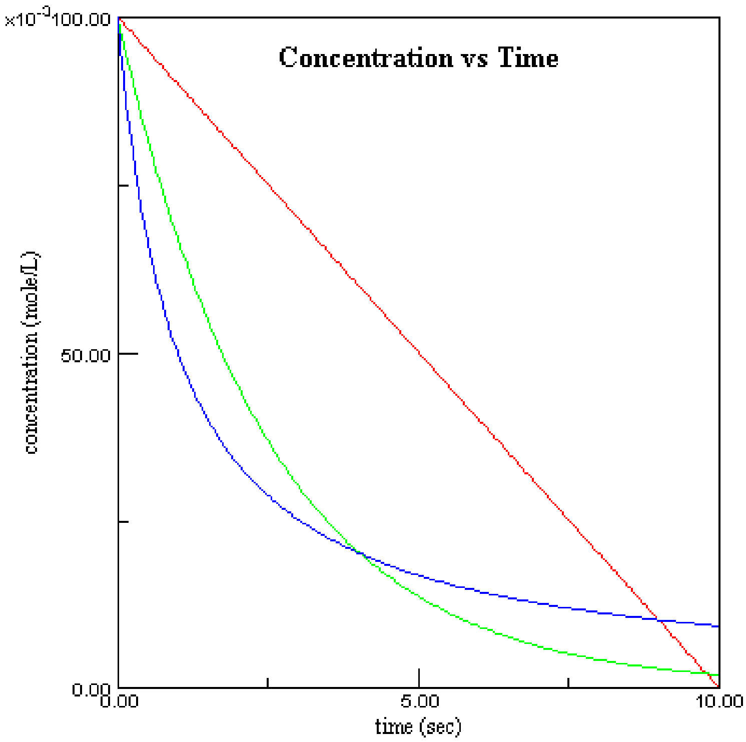
In this equation k is the *reaction rate coefficient* or *rate constant*, although it is not really a constant. It depends on several factors, such as temperature, surface area, etc.

The exponents a and b are called the reaction orders and depend on the reaction mechanism. They reaction orders must be determined experimentally.

For a zero-order reaction (red line), the rate of reaction is constant as the reaction progresses.

For a first-order reaction (green line), the rate of reaction is directly proportional to the concentration. As the reactant is consumed during the reaction, the concentration drops and so does the rate of reaction.

For a second-order reaction (blue line), the rate of reaction decreases with the square of the concentration, producing an upward curving line in the rate-concentration plot. For this type of reaction, the rate of reaction decreases rapidly (faster than linearly) as the concentration of the reactant decreases.



Order of reaction of thiosulphate with hydrochloric acid

When sodium thiosulphate reacts with a hydrochloric acid, a yellow precipitate of sulphur is formed:

$$Na_2S_2O_3\,(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + SO_2\,(aq) + H_2O(l) + S(s)$$

sodium thiosulphate + hydrochloric acid → sodium chloride + sulphur dioxide + water + sulphur

According to the rate law the rate equation for this reaction is:

$$r = k[HCl]^m[thiosulphate]^n$$

where m is the reaction order with respect to HCl, and n is the reaction order with respect to sodium thiosulphate. Assuming that the concentration of thiosulphate is constant and the concentration of hydrochloric acid varies, the rate equation becomes:

$$r = const \cdot [HCl]^n$$

Taking logarithms of both sides of the rate equation gives:

$$\ln(r) = \ln(const) + n * \ln([HCl])$$

When ln(r) is plotted against ln([HCl]) the result is a straight line whatever the order of the reaction. The gradient of this line, which is n, gives the order of the reaction with respect to hydrochloric acid. In similar way the order of reaction with respect to sodium thiosuphate can be found.