Lecture 12
Elementary Chemical Kinetics: Concepts

Is it possible to understand the feasibility of processes?

Yes - thermodynamics - thermodynamic state functions.

Time dependence of chemical processes - chemical kinetics.

A BRIEF HISTORY OF CHEMICAL KINETICS

Ref: "The World of Physical Chemistry," by K. J. Laidler, Oxford Univ. Press, 1993)

- **1850**: Wilhelmy (Germany) studied the rate of inversion of sucrose (hydrolysis into D-(+)-glucose and D-(-)-fructose in the presence of an acid) and found it to be proportional to the concentrations of both the sugar and the acid.

- **1864**: Guldberg and Waage (Norway) formulated their "law of mass action," according to which the reaction "forces" are proportional to the product of the concentrations of the reactants: $K = [R]^r [S]^s / ([A]^a [B]^b)$ where a, b, r and s are the stoichiometric coefficients in the chemical equation A+B=R+S. So the rate of the forward reaction is proportional to $[A]^a [B]^b$ and that of the reverse reaction is proportional to $\{R\}^r [S]^s$.

- **1865**: Harcourt and Esson (UK) analyzed the reactions between H_2O_2 and HI and between $KMnO_4$ and $(COOH)_2$. They wrote the corresponding differential equations, integrated them and determined the concentration vs. time relationships. They also proposed an equation for the temperature dependence of the reaction rate, $k = A T^C$.

- **1884**: van't Hoff (The Netherlands) published his "Studies of Chemical Dynamics" (Études de dynamique chimique), in which he generalized and further developed the work of Wilhelmy, Harcourt and Esson. In particular, he introduced the differential method of analysis. He also analyzed the temperature dependence of the equilibrium constant (now called the "van't Hoff equation") and of forward and reverse reaction rates.

- **1887**: Ostwald (Germany; Latvia) introduces the terms "reaction order" and "half-life" in his "Lehrbuch der allgemeinen Chemie."

- **1889**: Arrhenius (Sweden) further analyzed the temperature dependence of reaction rate, $k = A \exp(-B/T)$, and gave it an "energy barrier" interpretation; this is now called the "Arrhenius equation."

Chemical reactions occur at a definite rate.

Slow… Fast….in kinetics one is concerned with the in-between…

Some of them are very slow…

Neutralisation of an acid by alkali in aqueous solution…. fast

Diamond to graphite… slow

Temperature dependence..

Kinetics refers to a branch of mechanics dealing with the motion of particles without considering any external forces acting on the particles. This differs from dynamics which takes into account of the external forces acting on the particles.

In the gas phase, chemical kinetics can be treated in terms of the kinetic theory of gases and the statistical mechanics of isolated atoms. In the liquid phase, the molecules are closer and applications of molecular theories are difficult. In the liquid phase, many reactions are diffusion controlled and the rate constants depend upon the rate with which the reactants can diffuse together.

Rate of a chemical reaction depends upon the concentration of the reacting substances. In the gas phase, it depends upon the pressure. Since the concentration is decreasing steadily, the rate decreases. A variation of rate with time is shown in the figure.

[C]

-dC/dt = rate

time

$N_2O_5 \rightarrow N_2O_4 + O_2$
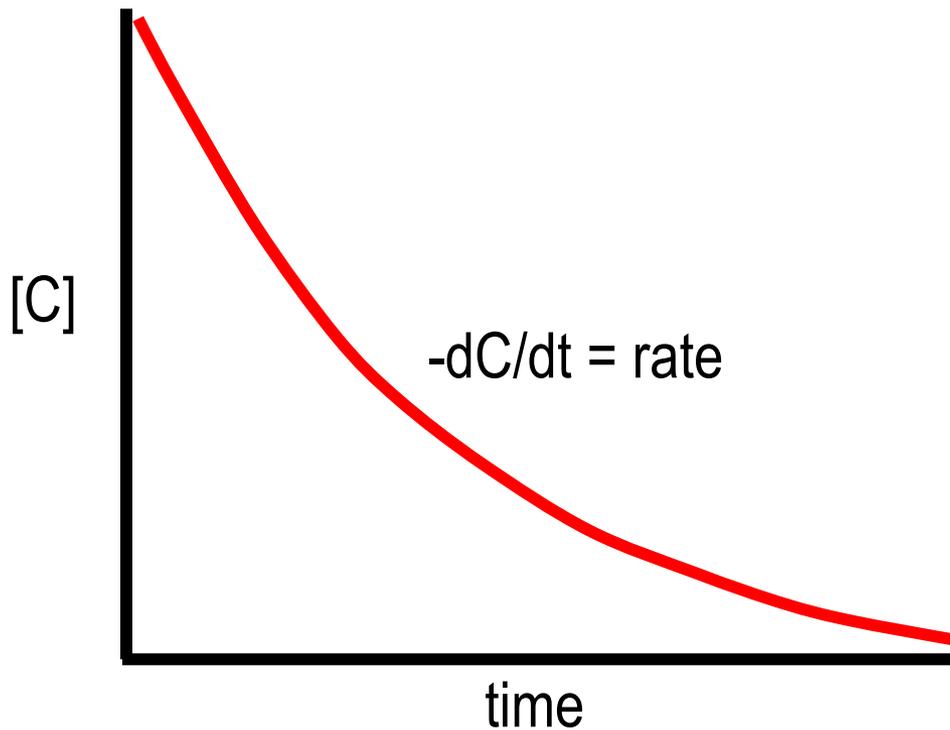
The rate depends only on the concentration of N_2O_5 except at very low pressures.

RCOOR' + H_2O $\rightarrow$ RCOOH + R'OH

Although both ester and water are involved in the reaction, the concentration of water does not undergo any significant change during the reaction. Thus the reaction is first order although there are two reacting species.

Dissociation of HI is second order.

Reaction of NO and O_2 giving NO_2 is third order depending on the square of the NO concentration and the concentration of O_2.

Rate = $KC_1^{n1} C_2^{n2} C_3^{n3}$…
The overall order n is
n = n1 + n2 + n3 + …

The reaction is of order n1 in reactant 1, and n2 in reactant 2, etc.
It may appear that any order is possible, but in reality order does not exceed three.

Chemical reactions can be classified in terms of the molecularity. This number is the number of molecules or atoms taking part in each act of chemical reaction.

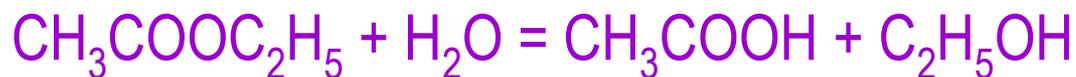The dissociation of nitrogen pentoxide is a unimolecular reaction. This can occur in the gaseous or solution phase.

$$N_2O_5 = N_2O_4 + \tfrac{1}{2} O_2$$

In HI dissociation, two molecules take part.

$$2HI = H_2 + I_2$$

The reaction is not, $HI = \tfrac{1}{2} H_2 + \tfrac{1}{2} I_2$

Another biomolecular reaction is

$$CH_3COOC_2H_5 + H_2O = CH_3COOH + C_2H_5OH$$

If three molecules are involved, the overall process is termolecular.

$2NO + O_2 = 2NO_2$

In simple reactions, the number of reactants appearing in the stoichiometric reaction is the molecularity. However, reactions can occur in multiple steps referred to as elementary processes. Molecularity can be assigned to each individual step, which indicates the species reacting in that step. This form of assignment is possible only if the mechanism is known.

Molecularity is concerned with the mechanism. But the order of a reaction expresses the dependence of measured rate on the concentration of the reactants.

Order and molecularity can be same or different. In reactions where one of the reactant is present in large excess, this is invariably the case. Order of a reaction can be zero and even fractional, but molecularity is never zero and always an integer. The decomposition of gaseous acetaldehyde has been shown to have an order of 3/2. The reaction of H_2 and Br_2 to from HBr has a rate proportional to $(Br_2)^{1/2}$ in the absence HBr and $(Br_2)^{3/2}$ in the presence of sufficient amount of HBr. The rate of formation of phosgene ($COCl_2$) from CO and Cl_2 is given by $k(Cl_2)^{3/2}(CO)$. Order and molecularity are not completely independent, however. Measurements of order are sometimes used to confirm or contradict a proposed mechanism.

We shall consider only homogeneous, simple reactions taking place at a constant temperature.

How do you probe the system?

Physical and chemical methods

Physical method is preferred, no variation of concentration.

Pressure of a gas, the conductance of an electrolyte, extent of light absorption, rotation of polarisation of an incident light beam, extent of fluorescence of a species etc. are monitored.

In the chemical method, a small portion of the sample is taken form time to time, and the product concentration is analysed.

First order reaction

In first order, rate is proportional to the concentration of one of the reactants.

$-d[C]/dt = k[C]$

[C] is the concentration of the reactant at time t. k is the proportionality constant or the rate constant or the velocity constant or the specific reaction rate.

When [C] = 1 rate = k. Rate at any concentration C is the product of k and [C].

In practice, it is advantageous to use the relation in a different form.

$-d[C]/[C] = kdt$

 Upon integration,

$-\int_{c_o}^{c} d[C]/[C] = k\int_{o}^{t} dt$

Where $[C]_o$ is the concentration of the reactant at time 0 and [C] at time t

$\ln [C]_o/[C] = kt$

$k = 1/t \ln [C]_o/[C]$

$[C]_o$ is proportional to a and [C] to a-x.

$k = 1/t \ln (a/a-x)$

**Important characteristics of the first order rate equation**

Any unit of concentration could be used as long as both a and a-x are expressed in the same units. The specific reaction rate has unit of time^{-1} and is generally expressed as sec^{-1}.

Important characteristic of a first order reaction is the time taken for the completion of a fraction the reaction. If $t_{0.5}$ is the time required for the completion of half of the reaction,

$t_{0.5}$ = (2.303/k) log 2 = 0.693/k = $t_{0.5}$

This value is called the half-life, which is a constant for the reaction.

Time to complete any definite fraction of the reaction is constant.
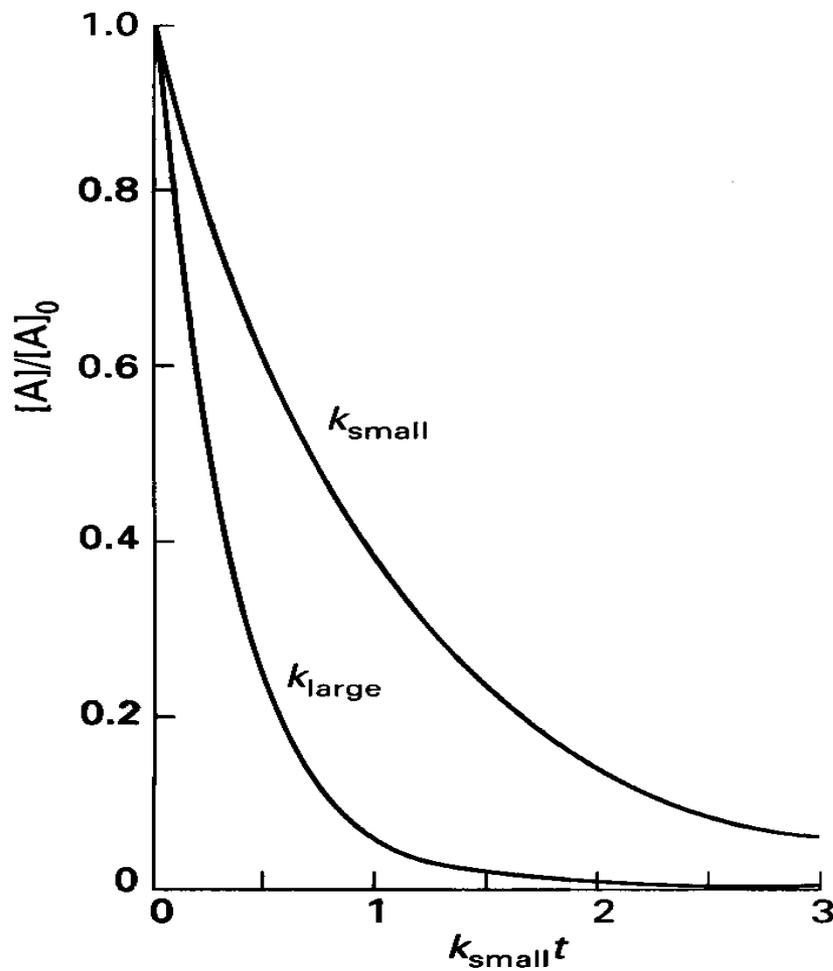
The value of k can tell us quickly the rate at which products are formed.

Examples of first order reactions

N_2O_5 (g) = N_2O_4 (g) + ½ O_2 (g)

For every mole of N_2O_5 decomposed, the number of moles of the system increases by 1½ in a constant volume apparatus, the partial pressure x of N_2O_5 decomposed is equal to double the increase in gas pressure.

 Measurement of pressure will not directly give the amount of N_2O_5 decomposed since N_2O_4 formed will undergo further decomposition to form NO_2. This can however be accounted for by knowing the equilibrium constant of this reaction.

The measured rate constant is approximately constant at 1.3 x 10^{-4} sec^{-1} which shows that the reaction is first order.

N_2O_5 equilibrium has also been studied in solution. By keeping the appropriate solvents it is possible to keep N_2O_4 and NO_2 formed in solution and the volume of oxygen evolved is measured. The amount of O_2 produced corresponds to double the amount of N_2O_5 decomposed. The final O_2 volume will give the value of a.

Instead of individual values of k, a graphical method can be employed.
t = (2.303/k) ln a – (2.303/k) log (a-x)

A plot of t against log (a-x) should give a straight line with – 2.303/k as the slope.

Another first order reaction.

$$N_2O_5 = NO_3 + NO_2$$

The hydrolysis of an ester is very slow if only water is present. In the presence of an acid catalyst, the reaction has a measurable rate. Hydrolysis of methyl acetate in presence of HCl is such a reaction. The concentration of acid is small and it does not change during the reaction. Water concentration is high and it does not change appreciably. Thus the rate depends only on the concentration of methyl acetate and the rate is first order. To follow the reaction, a small volume of the r^n mixture is withdrawn at definite intervals and it is titrated against standard alkali. The volume of alkali consumed at time 0, ∞ and t will give the rate constant of the reaction.

$k = 2.303/t \log (T_\infty - T_{0/}T_\infty - T_t)$
$T_\infty - T_0$ refers to a. $T_t - T_0$ is x.

Experimental studies show that k determined remains a constant.
It has to be said that k does depend upon the amount of water and
the concentration of acid. With these, the value of k will change.

Another example is the inversion of sucrose. This is also catalysed
by acid. The course of the reaction can be measured by determining
the angle of rotation of polarised light. Sucrose rotates it to right and
a mixture of dextrose and laevulose makes it to left. If α_0 and α_∞
and α_t are the angles of rotation including the sign, $\alpha_0 - \alpha_\infty$ is
proportional to a and $\alpha_t - \alpha_\infty$ is proportional to a-x.

Thus, $k = 2.303/t \log(\alpha_0 - \alpha_\infty / \alpha_t - \alpha_\infty)$

Here again the value of k depends on the concentration of water and acid.

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$$
Sucrose   Dextrose   Laevulose

A typical decomposition reaction is that of azomethane.

$$CH_3N_2CH_3 \text{ (g)} \rightarrow CH_3CH_3 \text{ (g)} + N_2 \text{ (g)}$$

This reaction can be monitored by measuring the total pressure as a function of time. Since all the species are in the gas phase, the pressure is a direct measure of the concentration. This is depicted below.
The shape of the graph (logarithm of concentration is linear with time) illustrates that the reaction is first order.
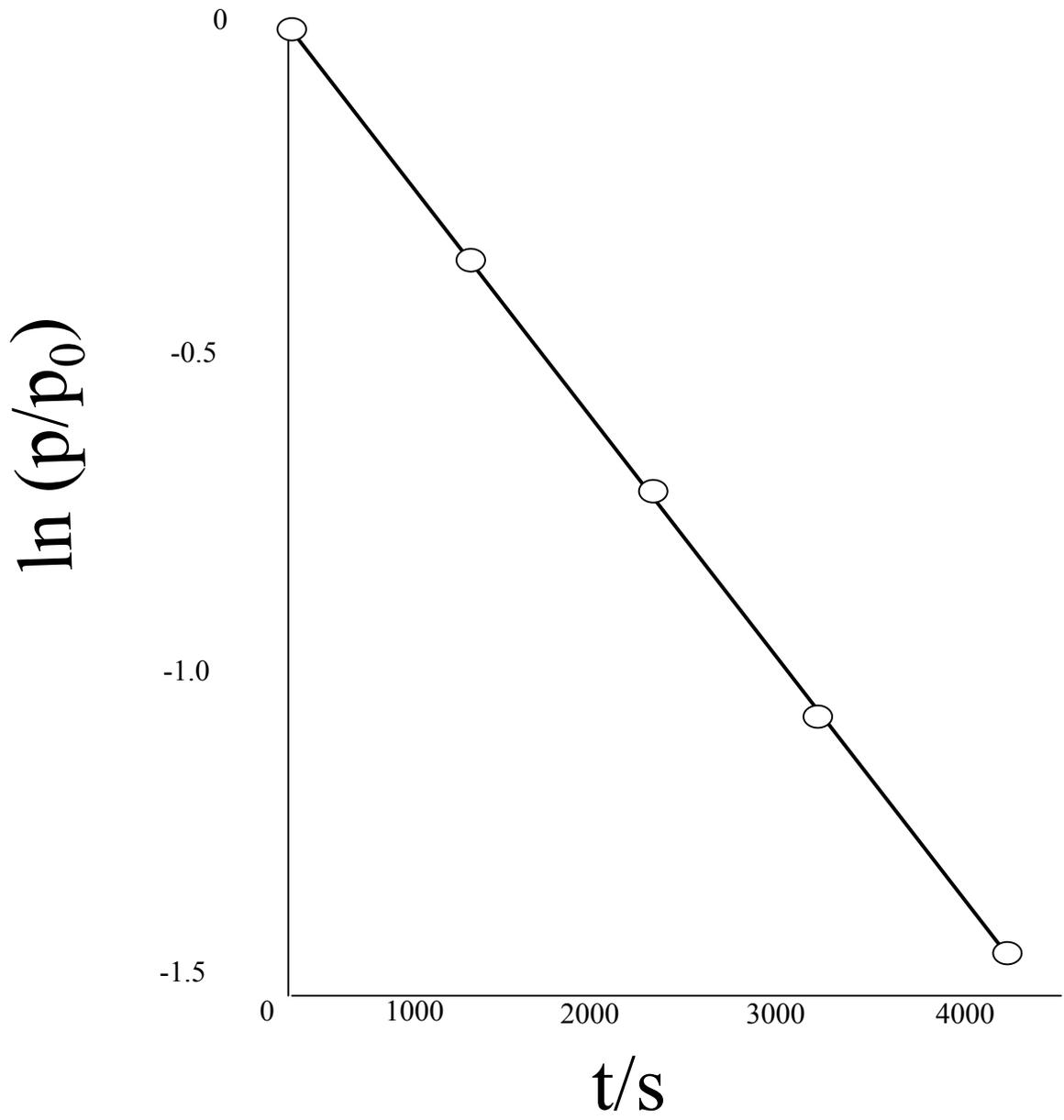
Second order reactions

The rate of a second order reaction depends upon two concentration
 terms. It can be

$2A \rightarrow$ Products or

$A + B \rightarrow$ Products

$-dC_A/dt = kC_A^2$ or $-dC_A/dt = -dC_B/dt = kC_AC_B$

In general,

$-dC/dt = kC^n$ or

$-dC/C^n = kdt$

$-C^{-n}dC = kdt$

$-[C^{-n+1}/-n+1]_C^{Co} = kt$

$1/n-1 \ [\ 1/C^{n-1} - 1/C_o^{n-1}] = kt$

For a second order reaction,

$k = 1/t \, (1/C - 1/C_o)$

If C_o is a, and C is a-x

$K = 1/t \, (1/a\text{-}x - 1/a) = 1/t \, [x/(a\text{-}x)a]$

Let us consider,

$A + B \rightarrow$ Products

$-dC_A/dt = -dC_B/dt = kC_AC_B$

If a and b represents initial moles of A and B and x represents the amount of each that has reacted after time t,

$dx/dt = k \, (a\text{-}x) \, (b\text{-}x)$ \qquad\qquad (1)

If a = b i.e. A and B are present in equimolar amounts,

$dx/dt = k(a\text{-}x)^2 = k(b\text{-}x)^2$

Integration of (1) yields (by the method of partial functions).

$k = [1/t(a\text{-}b)] \ln [b(a\text{-}x)/a(b\text{-}x)]$ \qquad (what happens when a=b??)

The rate constant depends upon the units employed to express concentrations.

The units of k are con^{-1} time^{-1}. If the concentration is moles/litre, k will be (moles/litre)$^{-1}$ sec^{-1}

$k = 1/t\,(x/a(a-x))$

When x is a/2,

$t_{0.5} = 1/ka$, the time is inversely proportional to initial concentration, in sharp difference with the first order reactions. For any other fraction, a similar relation exists.

Examples

The decomposition of HI is a second order reaction. However, the study of this reaction is difficult since the reaction is reversible.
One reaction that is second order is $H_2 + C_2H_4 = C_2H_6$.
The reaction can be studied by determining the pressure at various times.

Reaction of isobutyl bromide and sodium ethoxide is second order.
$C_4H_9Br + OEt^- \rightarrow C_4H_9OE + Br^-$

Saponification of an ester is a second order reaction.

$CH_3COOC_2H_5 + OH^- = CH_3 COO^- + C_2H_5OH$
This is different from the acid hydrolysis since both reactants are present in similar amounts.

The reaction can be studied by a number of methods. The first method is by conductance measurements. The replacement of OH^- ions by CH_3COO^- ions will change the conductance of the solution.
This change can be correlated with the extent of the reaction.
In the second, definite quantities of the reaction mixture are withdrawn at intervals and the amount of alkali left out is determined. If the initial concentrations of alkali and ester are known, the rate constant can be determined.

Rate can also be treated graphically.
$t=[2.030/k(a-b)]$ log b/a + $[2.303/k(a-b)]$ log $a-x/b-x$
Plot of t against log $[a-x/b-x]$ will give a straight line with slope $[2.303/k(a-b)]$
Reactions of alkyl iodides with tertiary amines is also second order.
$C_2H_5I + C_6H_5N(CH_3)_2 \rightarrow C_6H_5N(CH_3)_2C_2H_5^+ + I^-$

Third order reactions

A+B+C $\rightarrow$ Products

2A+B $\rightarrow$ Products

3A $\rightarrow$ Products

-dC/dt = kC^3

K=1/(2t) (1/C^2 – 1/Co^2)

=1/(2t) [(1/$(a-x)^2$ – 1/a^2]

Unit con^{-2} time^{-1}

For order n, k is conc.$^{n-1}$ time^{-1}

For completing half of the reaction,

k=1/(2t) 3/a^2

$t_{0.5}$ = 3/(2ka^2)

Time to complete a fraction is inversely proportional to the square of the initial concentration.

There are five gas phase reactions which are definitively third order. These are the termolecular reactions involving two molecules of nitric oxide and one molecule of Cl_2, H_2, D_2, O_2 or Br_2.

$2NO + Cl_2 = 2NOCl$
For reactions of the type,
$2A + B \rightarrow$ Products

If x is the amount of B reacted after time t,
$dx/dt = k (a - 2x)^2 (b-x)$
$k = 1/t(2b-a)^2 [(2b-a)^2 2x/a(a-2x) + \ln [b(a-2x)/a(b-x)]]$
Although a number of third order reactions in solution are reported, none of them is proven.