

CHAPTER 4 Chemical Kinetics: Rate and Mechanistic Models

4.1 Introduction

By listing the plausible reaction stoichiometries, we can calculate the composition of the closed system in its final state, i.e. at equilibrium, provided that we are given the thermodynamic properties such as heats (enthalpies) of formation, Gibbs free energies of formation, temperature and pressure of the system, as well as the composition of its initial state. As important as this may be, it does not tell us at all how long will it take for the system to transit from its initial to the final state.

Chemicals kinetics deals with the rates of chemical reactions and with how these rates are affected by the composition of the system, temperature and pressure. Kinetic studies are important, since based on them empirical and semi-empirical rate expressions are obtained which then can be used for predictive purposes in analysis of system's dynamic behavior or in design of chemical reactors. Kinetic studies deal with reactions with a wide range of characteristic times. Reactant half-life can vary from a pico second to a period longer than the age of the universe. Reaction speed will often depend on the conditions of the system. For example, O_2 and H_2 at room temperature and pressure left alone at stoichiometric ratio for water production would have a half-life of 10^{25} years or 3×10^{32} seconds. However, a spark causes the half-life to be reduced to 10^{-6} s!

In summary, the scope of kinetic studies is to quantify the rate of reaction as a function of system intensive properties (composition, temperature, etc.) and to suggest a fundamental theory (if possible) for estimation of kinetic parameters. The knowledge of kinetics can answer many important questions related to the environment: For example,

- How fast will a species disappear in a given compartment.
- How much time is needed to oxidize a pollutant in treatment facilities.
- How fast processes take place in natural water, in soil or in the atmosphere..

In the next section, we start with the definition of reaction rate and investigate how concentration, temperature and other system properties affect these rates. The rate constants can be calculated in different ways, such as empirically, mechanistically, and by performing molecular and quantum level calculations. Here, we will focus on estimating these rate constants using empirical and mechanistic approaches. These calculations are provided in a later chapter. The present chapter mainly focuses on how reactor rate can be related as a function of system variables.

4.2 Reaction Rate

Consider an arbitrary mass of the reaction system in its initial state and place an invisible envelope around all the molecules that comprise that mass. This envelope creates the control volume of constant mass within it. The control volume of the system should be large enough to contain a statistically significant number of molecules so that the concept of molar concentration is meaningful. The control volume of the system should also be small enough so that there are no spatial gradients of composition or temperature within this volume. Let us assume that we can observe this control volume at time t and count the molecules N_j of each species j in it. We repeat the observation at time $t + \Delta t$ when the number of molecules of the same species is $N_j + \Delta N_j$. During time Δt the number of molecules crossing the boundary of the control volume is zero or very negligible compared to the change in molecular form due to reaction within the system. The volume of the system can be evaluated at some

time θ ($t \leq \theta \leq t + \Delta t$) so that $V(\theta) = \frac{1}{\Delta t} \int_t^{t+\Delta t} V(t) dt$ is the mean control volume of the system. (Note that while the control volume may change the mass within it is constant). We can relate the number of molecules to the number of moles via Avogadro's constant L , $n_j = \frac{N_j}{L}$. ($L = 6.022 \times 10^{23}$ molecules/mol). Then **the rate of reaction (rate of formation) of species j is defined as the number of moles of j produced by reaction per unit time and unit volume of the system** and is, therefore, given by

$$R_j = \lim_{\Delta t \rightarrow 0} \frac{1}{V(\theta)} \frac{\Delta n_j}{\Delta t} = \frac{1}{V} \frac{dn_j}{dt} \quad (1)$$

Please, note that while our above verbal statement is indeed the general definition of the reaction rate, eq (1) is not - it is subject to the assumptions and scenarios depicted above for an isolated, closed, batch control volume. The point is that **the rate of reaction of j is always the change in the number of moles of j per unit time and unit volume of the system caused by reaction**, but it is only represented mathematically by eq. (1) for a closed batch system without spatial gradients. One should remember that in flow systems, or in macroscopic batch systems with spatial gradients, the number of molecules of a species within an element of volume changes not only due to reaction but also due to species being brought in and out of this element of volume by flow or diffusion. Hence, one must take considerable precautions in obtaining reaction rates from experimental data in order not to attribute rates of other processes to the rate of reaction **i.e.** kinetic rate. Effects of flow and diffusion are considered later.

Our above definition defines reaction rate as an intensive property of the system. If only a single reaction takes place in the system then stoichiometry requires that the rates of various components participating in the reaction are tied as shown by equation (2).

$$\frac{R_j}{\nu_j} = r \quad (2)$$

where r is the intrinsic kinetic rate of reaction. Unfortunately, even r is not uniquely defined for a reaction system since stoichiometric coefficients can be multiplied by any arbitrary constant, while the number of moles of j converted per unit time and unit volume, R_j , only depends on the conditions of the system not on how stoichiometry is written. Thus when we define, r , it is usually with reference to a given stoichiometry for the reaction.

Experience shows that reaction rate is a function of composition, **i.e.** concentrations, temperature, catalyst activity, etc. We will talk about the dependence of rate on concentration in the next section.

4.3 Dependence of rate on concentration

Often, within a narrow range of composition and temperature, the rate can be correlated with a power law dependence on concentration and an exponential dependence on temperature. Hence, for an irreversible reaction $aA + bB \rightarrow pP$ with $K \rightarrow \infty$ an n-th order rate form is frequently fitted to data

$$r = k_o e^{-E/RT} C_A^\alpha C_B^\beta \quad (3)$$

This rate form is a product of a function of temperature with a function of composition.

At constant temperature we speak of a (specific) rate constant $k = k_o e^{-E/RT}$ where k_o is the frequency factor, E is the activation energy, R the ideal gas constant and T absolute temperature. This is an Arrhenius form for the temperature dependence which will be discussed later. The order of reaction with respect to reactant A is α and the order with respect to reactant B is β . The overall reaction order is $n = \alpha + \beta$. If we measure concentrations in (mol/L) then the units of the rate constant for an n-th order reaction are $\{(\text{mol/L})^{1-n}\text{s}^{-1}\}$.

For a reversible single n-th order reaction ($aA + bB = pP$) the rate is given by

$$r = k_{fo} e^{-E_f/RT} C_A^\alpha C_B^\beta - k_{bo} e^{-E_b/RT} C_p^\gamma \quad (4)$$

The rate constant for the forward reaction is $k_f = k_{fo} e^{-E_f/RT}$, where E_f is the activation energy for the forward reaction, and $k_b = k_{bo} e^{-E_b/RT}$ is the rate constant for the reverse reaction and E_b the activation energy for the reverse reaction. Reaction order for the forward reaction is $n = \alpha + \beta$ and for the reverse reaction is γ .

At equilibrium the net rate of reaction is zero and the forward rate equals the reverse rate. Hence, the rate form must be compatible with thermodynamics and this requires that

$$\frac{k_f}{k_b} = \left(\frac{C_p^\gamma}{C_A^\alpha C_B^\beta} \right)_{eq} = K_c^{1/s} \quad (5)$$

so that $p = s\gamma$, $a = s\alpha$, $b = s\beta$ and

and

$$E_f - E_b = \frac{\Delta H_r}{s} \quad (6)$$

where s is the stoichiometric number of the rate limiting step to be discussed later.

One should note that reaction rate is a much stronger function of temperature than of concentration. Activation energies are typically in the range of 10 to 60 kcal/mol (about 40 to 250 kJ/mol). For example, for an irreversible second order reaction, with an activation energy of 40 kcal/mol, doubling the reactant concentration quadruples the reaction rate but raising the temperature by 10°C, from 20°C to 30°C, raises the rate almost tenfold (9.66 times).

Many reaction rates cannot be fitted by the power law form and more complex forms are required to tie reaction rate, temperature and concentrations. Often when the functional dependence on temperature and composition cannot be separated in a convenient product of two functions, then a reaction order and activation energy cannot be separately defined. For example the simplest rate form of the Hougen-Watson or Langmuir-Hinshelwood type is given by

$$r = \frac{k_o e^{-E_1/RT} C_A}{K_o e^{-\Delta E/RT} + C_A} \quad (7)$$

where $E_1, \Delta E, k_o$ and K_o are positive constants. Figure 1a illustrates that reaction order cannot be defined as it is readily seen that the apparent reaction order varies between order one (when at small C_A , $C_A \ll K_o e^{-\Delta E/RT}$) and zero (when $C_A \gg K_o e^{-\Delta E/RT}$). We also see from Figure 1b that the apparent activation energy varies between E_1 at low temperature, when $C_A \gg K_o e^{-\Delta E/RT}$, and $(E_1 - \Delta E)$ at sufficiently high temperature when $C_A \ll K_o e^{-\Delta E/RT}$.

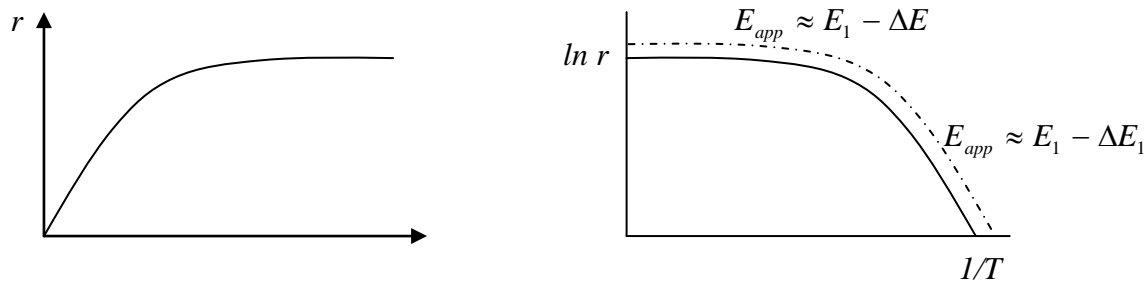


Figure 1: a) Sketch of rate of eq(7) vs. concentration, b) Plot of the $\ln r$ (at fixed C_A vs. reciprocal temperature).

Two additional remarks are in order. The stoichiometry of the reaction for which the rate form, r , is reported should always be clearly stated. Then $R_j = \nu_j r$ and the rate constant for species j is $k_j = \nu_j k$. Forgetting this multiplier is a frequent source of unnecessary errors. Similarly if the rate form for species i is reported, R_i , the rate for species j is

$$R_j = \frac{\nu_j}{\nu_i} R_i. \quad (8)$$

Often in heterogeneous systems it is more practical to utilize rate forms based on unit surface of catalyst, $r' \left(\frac{\text{mol}}{\text{m}^2 \text{ s}} \right)$, or unit mass of the system, instead of using a rate form $r \left(\frac{\text{mol}}{\text{L s}} \right)$, that expresses the rate of change of in moles per unit volume of the system $r'' \left(\text{mol}/\text{kg s} \right)$. One should then incorporate the appropriate conversion of units into the rate constants.

In summary, the intrinsic kinetic rate of reaction can be defined as

$$\left(\text{rate of reaction} \right) = \frac{\left(\text{change in moles of } j \text{ caused by reaction} \right)}{\left(\text{stoichiometric coefficient of } j \right) \left(\text{unit measure of the system} \right) \left(\text{unit time} \right)}$$

where unit measure of the system can be volume, mass, surface, etc. It is usually the volume for homogeneous reaction.

A final word of caution. When one deals with an n -th order reaction the reaction orders with respect to various species are not necessarily related to stoichiometric coefficients unless the reactions are elementary, i.e. proceed in one step. We will talk about the elementary reactions later on.

We wrote that in order to evaluate the rate of reaction at given condition of the system we will need to know the functional dependence of the rate form on composition and temperature. This can be accomplished based on theory or experiments. We will see how far we can get by using the theory for elementary reactions (e.g. those that proceed in one step) to estimate activation energies and reaction order. We will also see how mechanisms, consisting of elementary reactions, can help us derive rate forms for more complex reactions. At the end we will consider establishing rate forms based on experimental evidence, and planning experiments for evaluation of rate forms.

Next we need to examine the temperature dependence of the rate form.

4.4 Temperature Dependence of Reaction Rates

We have already seen that the expression for the reaction rate at fixed temperature may take a relatively simple n-th order form e.g.

$$r = k C_A^\alpha C_B^\beta \quad \text{with} \quad \alpha + \beta = n \quad (3)$$

or it may have a more complex form e.g.

$$r = \frac{k_1 C_A^\alpha}{K + C_A} \quad (7a)$$

In either case the "constants" in the rate expression are functions of temperature. For the n-th order reaction rate, k may not be a rate constant of a particular elementary step of the mechanism. In general it is a combination (product or ratio) of several rate constants of mechanistic steps. The same is true of k_1 , in our Langmuir-Hinshelwood kinetic form of equation (7a), while K in the example given above is also a ratio of some rate constants for elementary steps. (When $\alpha = 1$ the above form is the Michaelis-Menten form for enzyme catalyzed reactions).

The engineer's goal often is to find an empirical n-th order rate expression (such as the first form shown above) since such a form can often match the data reasonably well within the experimental accuracy and is easier to use than the complex rate form. It is further assumed that the temperature dependence can be lumped into the dependence of the rate constant k on temperature. Note: the rate constant is only a constant in the sense that it does not depend on concentrations but it is a function of temperature. Furthermore it is widely assumed that the functional form of the rate constant's dependence on temperature is:

$$k = k_o e^{-E/RT} \quad (9)$$

where E is called the activation energy for the reaction, k_o is the constant independent of temperature (sometimes called frequency factor - a term borrowed from collision theory), R is universal gas constant. Taking logarithms of both sides of the above equation one gets

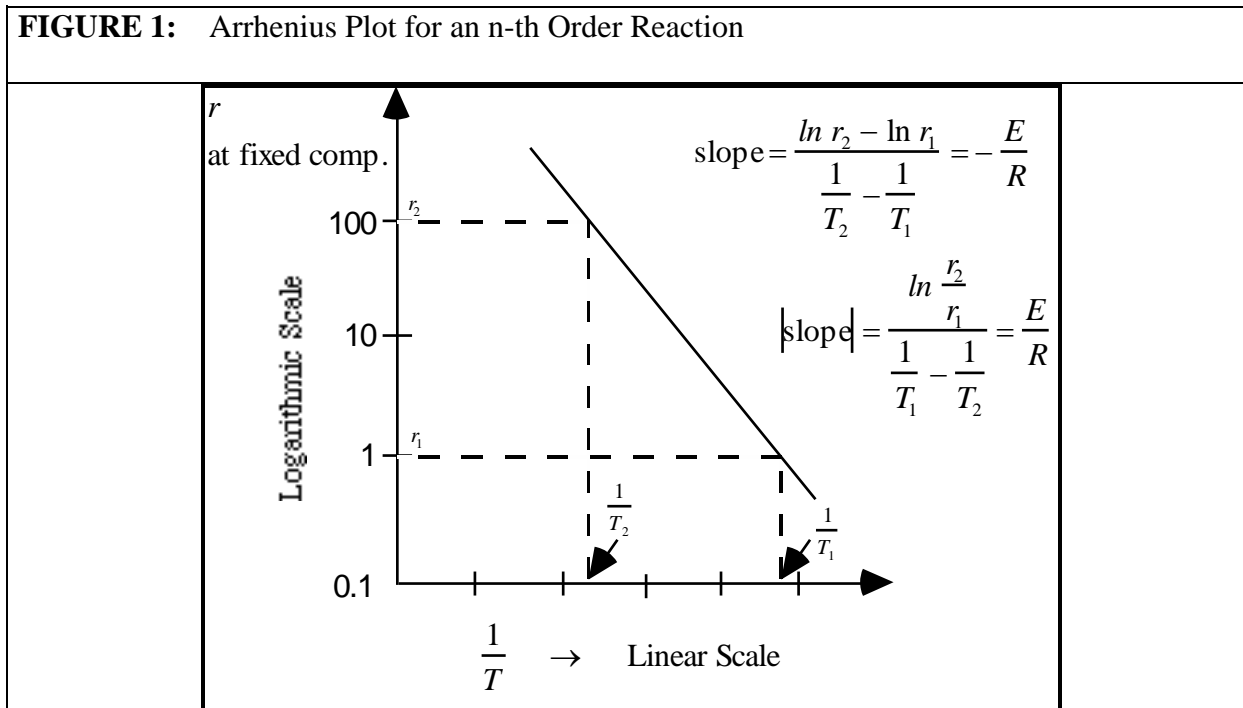
$$\ln k = \ln k_o - \frac{E}{R} \frac{1}{T} \quad \text{or} \quad \log k = \log k_o - \frac{E}{R} \frac{1}{T} \times \overbrace{0.43429}^{\log e}$$

The customary engineering practice is, therefore, to plot k vs $\frac{1}{T}$ on a semilog plot (k is on the logarithmic scale and $\frac{1}{T}$ on the linear). The slope of such a plot can be related to the activation energy.

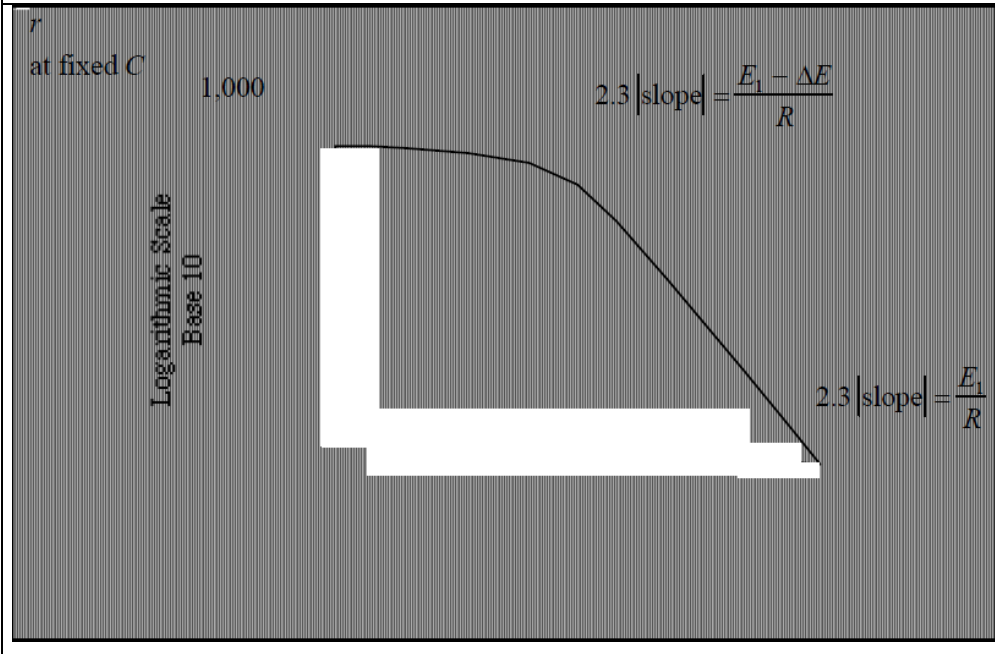
$$\frac{E}{R} = 2.3026 \times |\text{slope}|$$

If semilog paper is unavailable, a plot of $\ln k$ vs $\frac{1}{T}$ yields $|\text{slope}| = \frac{E}{R}$. Furthermore, often it is suggested to plot the log (rate) vs $\frac{1}{T}$ at fixed composition. This is convenient since rate data can be taken at fixed concentrations (e.g. in a differential reactor) at various temperatures. Then a plot of log (r) vs $\frac{1}{T}$ is made and the slope is related to E/R (see Figure 1).

FIGURE 1: Arrhenius Plot for an n-th Order Reaction



However, occasionally a situation presented in Figure 2b is encountered. A single value of activation energy cannot be extracted.

FIGURE 2: Arrhenius Plot for the L-H Reaction

This shows that the habit of plotting the logarithm of the rate vs $\frac{1}{T}$ is a bad one unless one is sure that the rate form has an n-th order form, i.e. that the temperature and composition dependence of the rate are separable. If this is the case, then at fixed concentrations the rate ($r = k_o e^{-E/RT} C_A^\alpha C_B^\beta$) can be evaluated at two temperatures T_1 and T_2 and the logarithm taken.

$$\log r_2 = \log [k_o (C_A^\alpha C_B^\beta)] - \frac{E}{RT_2} \quad \times \quad 0.434$$

$$\log r_1 = \log [k_o (C_A^\alpha C_B^\beta)] - \frac{E}{RT_1} \quad \times \quad 0.434$$

Thus

$$\log r_2 - \log r_1 = \log \frac{r_2}{r_1} = \frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \times \quad 0.434 \quad (9a)$$

and

$$\frac{E}{R} = \frac{2.3026 \log \frac{r_2}{r_1}}{\frac{1}{T_1} - \frac{1}{T_2}} = \frac{\ln \frac{r_2}{r_1}}{\frac{1}{T_1} - \frac{1}{T_2}} = |\text{slope}|$$

as shown in Figure 2a.

However if the rate form is complex, as illustrated below and shown in Figure 2b

$$r = \frac{k_{o1} e^{-E_1/RT} C_A^\alpha}{K_o e^{-\frac{\Delta E}{RT}} + C_A} ; \quad k_1 = k_{o1} e^{-E_1/RT} \\ K = K_o e^{-\Delta E/RT}$$

then clearly even at fixed composition plotting $\log(r)$ vs $\frac{1}{T}$ will not yield a straight line.

Indeed an activation energy does not exist for the above rate form. One can only talk about the apparent activation energy E_{app} . Usually for gas phase reactions, at high enough temperatures

$K_o e^{-\frac{\Delta E}{RT}} \gg C_A$ and the apparent activation energy is $E_{app} = E_1 - \Delta E$ since the apparent rate constant is $\frac{k_{o1}}{K_o} e^{-\frac{(E_1 - \Delta E)}{RT}}$. At low enough temperatures $K_o e^{-E/RT} \ll C_A$ and the apparent activation energy is $E_{app} = E_1$ as shown in Figure 2b.

In conclusion, a plot of $\log(r)$ vs $\frac{1}{T}$ will yield an activation energy only if the rate is of the n -th order type. Even then, if as a result of a particular mechanism the rate constant is actually a combination of constants for elementary steps, for example $k = \frac{k'_1}{k'_2 + k'_3}$, this may not be true. It is also misleading to do this in heterogeneous systems where mass transfer effects (to be shown later) can mask the kinetic activation energy. Clearly, the above method fails for complex rate forms.

The advisable procedure is as follows. Once a rate form is identified, evaluate at each temperature all of the constants that appear in the rate form and plot them individually as $\log(k)$ vs $\frac{1}{T}$ to extract the activation energy for each of them.

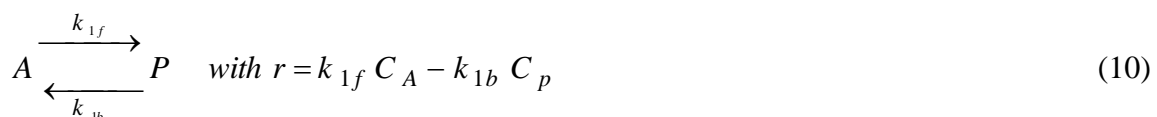
Plotting $\log(r)$ vs $\frac{1}{T}$ often saves time for the engineer but has to be done with due caution.

We have mentioned that it is a custom to expect the constants in any rate form to show an exponential dependence on temperature of the form $k = k_o e^{-E/RT}$.

We will now show which theories suggested that particular form.

4.4.1 Arrhenius Law

Arrhenius considered in 1889 reversible elementary reactions



He argued that since for an elementary reaction the equilibrium constant is given by

$$K_c = \frac{k_{1f}}{k_{1b}} = \left(\frac{C_p}{C_A} \right)_{eq} \quad (11)$$

and since van't Hoff's equation for the variation of the thermodynamic equilibrium constant with temperature is

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \quad (12)$$

it is reasonable to assume that the rate constants follow the same type of temperature dependence:

$$\frac{d \ln k_{1f}}{dT} = \frac{E_f}{RT^2} \quad (13a) \quad ; \quad \frac{d \ln k_{1b}}{dT} = \frac{E_b}{RT^2} \quad (13b)$$

We recall that

$$K = \left(\frac{a_p}{a_A} \right)_{eq} = \left(\frac{\gamma_p}{\gamma_A} \right)_{eq} \left(\frac{C_p}{C_A} \right)_{eq} = K_\gamma K_c = e^{-\frac{\Delta G^\circ}{RT}} \quad (14)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (15)$$

Integration of the above derivatives for the rate constants, with E_f and E_b kept constant, gives:

$$k_{1f} = k_{of} e^{-E_f/RT} \quad ; \quad k_{1b} = k_{ob} e^{-E_b/RT} \quad (16)$$

E_f - activation energy for the step forward

E_b - activation energy for the reverse step

k_{of} , k_{ob} - frequency factors for the forward and reverse reaction, respectively.

In view of the Arrhenius theory, molecules must acquire a certain critical energy level before they can react. E_f is the activation energy for the forward step viewed as the difference between the mean energy level of reactant molecules prone to react (i.e. in excited state susceptible to reaction) and the mean energy level of other reactant molecules which are not ready to react. Similarly, E_b is the activation energy for the reverse step, i.e. the difference in mean energy of "excited" product molecules and "base" product molecules. The factor $e^{-E/RT}$ is the familiar Boltzmann factor (see any physical chemistry book and the chapter on kinetic theory of gases) which yields the fraction of molecules that managed to acquire sufficient energy level above the mean.

Substituting eqs. (11) and (15) into eq (14) yields the following form:

$$K = K_\gamma K_c = K_\gamma \frac{k_{of}}{k_{ob}} e^{-\frac{(E_f - E_b)}{RT}} = e^{-\frac{\Delta H^\circ}{RT}} e^{\frac{\Delta S^\circ}{R}} \quad (17)$$

Thus

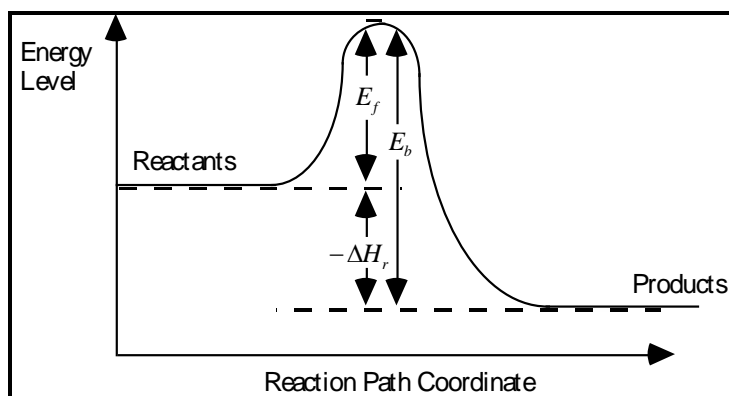
$$K \gamma \frac{k_{of}}{k_{ob}} = e^{\frac{\Delta S^\circ}{R}} \quad (17a)$$

and

$$E_f - E_b = \Delta H^\circ \quad \text{heat of reaction} \quad (18)$$

According to Arrhenius theory the difference between the activation energy for the forward and reverse reaction equals the heat of reaction. (This is illustrated in the figure below for an exothermic reaction $\Delta H^\circ < 0$).

FIGURE 3: Arrhenius Theory Interpretation of the Energy Diagram. (The fraction of reactant molecules that have energies in excess of E_f given by Boltzmann factor $e^{-E_f/RT}$)



The so often used (equation (18)) has two drawbacks. First, activation energies are supposed to be independent of temperature. Yet it is well known from thermodynamics that the heat of reaction varies with temperature. Formally one can assign (lump) the variation of the heat of reaction with temperature with the $\exp\left(\frac{\Delta S^\circ}{R}\right)$ term, but then the question remains as to what heat of reaction, i.e. evaluated at what temperature, is $E_f - E_b$ equal to and why? We mention this question so that one is aware of it although an engineer need not be overly concerned with it.

The second drawback of the above equation is something that an engineer should be fully aware of. Activation energies are independent of stoichiometry. For elementary reactions reaction stoichiometry can be written in one unique way only, since the stoichiometric coefficients are dictated by reaction mechanism. Thus $\Delta H^\circ = \sum_{j=1}^s \nu_j \Delta H_{f_j}^\circ$ has a unique value for an elementary reaction. However,

for a general reaction, which is not elementary, i.e. the kind that we deal with most often, the stoichiometry can be written in a number of ways, i.e. all the stoichiometric coefficients can be multiplied by any number. Naturally that changes the value of the heat of reaction by the multiplier factor, and $E_f - E_b$ cannot possibly be equal to the heat of reaction since the heat of reaction now depends on stoichiometry while the activation energies do not!

In order to avoid this difficulty an effort is sometimes made to report the activation energy per mole of a component, and to require that the heat of reaction be reported per mole of the same component. But activation energies are numbers determined from experiments, while the heat of reaction will again depend if we choose A or B or Q to have a stoichiometric coefficient of magnitude one as shown below.

- a) $3A + B = 2Q$
 b) $A + \frac{1}{3}B = \frac{2}{3}Q$
 c) $\frac{3}{2}A + \frac{1}{2}B = Q$

If by convention we then require that stoichiometry be written with all stoichiometric coefficients as integers, with no common factor among them, then in the situation above only case a) would be an acceptable representation of stoichiometry. Then

$$(K_c)^{1/s} = \frac{k_{1f}}{k_{1b}} \quad K_c = K / K_\gamma$$

$$\left[\left(\frac{e^{\frac{\Delta S^\circ}{R}}}{K_\gamma} \right) e^{-\frac{\Delta H^\circ}{RT}} \right]^{1/s} = \frac{k_{of}}{k_{ob}} e^{-\frac{E_f - E_b}{RT}}$$

and therefore $E_f - E_b = \frac{\Delta H^\circ}{s}$ (19)

where s is the stoichiometric number of the rate determining step.

The most useful aspect of the Arrhenius theory is the functional form of the dependence of k on T , i.e. $k = k_o e^{-E/RT}$. However, one should be aware that by assigning such a form to the rate constant irrespective of variables that are used as a "driving force" for the rate (i.e. concentration, partial pressure, mole fraction, etc.) the activation energy E , i.e. its numerical value, becomes dependent on the choice of variables used in the "driving force". For example consider the rate form for an n-th order reaction:

$$r \left(\frac{\text{mol}}{\text{lit s}} \right) = k_c \left[\left(\frac{\text{mol}}{\text{lit}} \right)^{1-n} s^{-1} \right] C_A^n \left(\frac{\text{mol}}{\text{lit}} \right)^n \quad (20)$$

Suppose then $k_c = k_{co} e^{-E_c/RT}$ where E_c is the numerical value of the activation energy.

If we deal with gas reaction it is often more useful to express the rate as

$$r \left(\frac{\text{mol}}{\text{lit s}} \right) = k_p \left[\left(\frac{\text{mol}}{\text{lit}} \right) (\text{atm})^{-n} s^{-1} \right] P_A^n (\text{atm})^n \quad (21)$$

and the driving force is now expressed in partial pressures.

If we now take $k_p = k_{po} e^{-E_p/RT}$ (and there is nothing in Arrhenius theory to prevent us from doing it) the question arises whether $E_p = E_c$, as it should be if the activation energy is a unique number for the reaction.

For simplicity we will assume ideal gas behavior $P_A = C_A RT$. By comparison of the two rate forms we conclude: $k_c = k_p (RT)^n$. Then, from the Arrhenius temperature dependence of the rate constants

$$\frac{d \ln k_c}{dT} = \frac{E_c}{RT^2} \quad ; \quad \frac{d \ln [k_p (RT)^n]}{dT} = \frac{E_p}{RT^2} + \frac{n}{T}$$

we get the following relationship between activation energies

$$E_c = E_p + n RT \quad (22)$$

The relationship between k_{co} , and k_{po} is:

$$k_{co} = k_{po} (RT)^n e^n \quad (23)$$

Clearly the value of the activation energy does depend on the quantities used in the driving force term.

However, for high activation energies, moderate temperatures ($T < 500^\circ \text{K}$) and reasonable orders of reaction, $n \leq 2$, the relative error made is usually within 10% which is well within the customary experimental uncertainty in this kind of problems. We will define here

$$\text{relative error} = \frac{E_c - E_p}{E_c} = \frac{n RT}{E_c}$$

In spite of all its deficiencies Arrhenius law is used almost exclusively for engineering purposes due to its simplicity. Thus, Arrhenius plots of $\ln k$ vs $\frac{1}{T}$ are usually made of experimental data, and that is the simplest and most useful form for engineering work. However, Arrhenius law cannot predict the values of the rate constants even when activation energy is known. This is the ultimate goal of rate theories to be discussed next.

Note: Sometimes rates are given in $\left(\frac{\text{atm}}{\text{s}}\right)$ especially for gas phase reactions that proceed with the change in the number of moles, as the change in partial pressure or total pressure is monitored.

$$\tilde{r} \left(\frac{\text{atm}}{\text{s}}\right) = k'_p \left[(\text{atm})^{1-n} \text{s}^{-1} \right] P_A^n (\text{atm})^n \quad (24)$$

Then:

$$E_c = E'_p + (n-1) RT \quad (25)$$

and

$$k_{co} = k'_{po} (RT)^{n-1} e^{n-1} \quad \text{for} \quad k'_p \left[(\text{atm})^{1-n} \text{s}^{-1} \right] \text{ and } k_c \left[(\text{mol/L})^{1-n} \text{s}^{-1} \right] \quad (26)$$

Example 1. For the reaction $2\text{NO} + \text{Cl}_2 = 2\text{NOCl}$

$$\log k_c = \frac{-803}{T} + 3.66 \quad \text{where } k_c \text{ and } k_{co} \text{ are in } [(\text{lit/mol})^2 \text{ s}^{-1}]$$

Calculate the rate constant in $[\text{torr}^{-2} \text{ s}^{-1}]$. Use 400K as the mean reaction temperature.

Note first that $n = 3$.

$$E'_p = E_c - (n-1)RT$$

$$E'_p = \underbrace{803}_{\text{given}} \times \underbrace{1.987}_R \times \underbrace{2.3025}_{\text{conversion of log s}} - \underbrace{(3-1)}_{n-1} \times \underbrace{1.987}_R \times \underbrace{400}_T$$

$$E'_p = 3673.8 - 1589.6 = 2084.2 \frac{\text{cal}}{\text{mol}}$$

$$E_c = 3674 \frac{\text{cal}}{\text{mol}} \quad E'_p = 2084 \frac{\text{cal}}{\text{mol}}$$

In reactions with low activation energies the difference in activation energy depending on the choice of units is considerable. The difference above is 43% based on E_c . Now $k_{co} = 10^{3.66}$ so that

$$k'_{po} = k_{co} (R'T)^{1-n} e^{1-n}$$

$$k'_{po} = 10^{3.66} (760 \times 0.0821 \times 400)^{1-3} e^{1-3}$$

Note that here we needed R' in units of (torr L/mol K) and we obtain it by taking $R = 0.0821$ (L atm/mol K) and multiplying it by 760 (torr/atm).

$$k'_{po} = 9.93 \times 10^{-7} [\text{torr}^{-2} \text{ s}^{-1}]$$

$$k_{co} = 10^{3.66} = 4.57 \times 10^3 \left[\left(\frac{\text{lit}}{\text{mol}} \right)^2 \text{ s}^{-1} \right]$$

The last example demonstrates that if say k_{co} , E_c are assumed to be independent of temperature, then k'_{po} , E'_p and E_p would vary with temperature.

The realization that these parameters may indeed be a function of temperature, especially over a broad temperature range, led to the use of the modified Arrhenius equation.

$$k = k'_o T^m e^{-E'/RT} \quad (27)$$

The relationship to the usual form of Arrhenius equation $k = k_o e^{-E/RT}$ is as follows:

$$k_o = k_o' T^m e^{-E'/RT} \quad (28a)$$

$$E = E' + m R\bar{T} \quad (28b)$$

\bar{T} is the mean temperature for the range of experiments, E' , k_o' are constants independent of temperature, m is a parameter proportional to the ratio $\frac{C_{pact}}{R}$ where C_{pact} is the molal heat capacity for activation. Hence, m is small for gas phase reactions but may be as high as 40 for ionic reactions in solution.

Several times on the last few pages we have presented the relationships between activation energies and frequency factors of the rate constant for different representations of the rate forms. These relationships are the result of simple mathematical manipulations which for completeness are outlined in detail below.

Assume that we want to relate the kinetic constants and their activation energies for the rate form expressed by equation (20) and that expressed by equation (24) for the same reaction.

$$r\left(\frac{\text{mol}}{\text{Ls}}\right) = k_{co} e^{-E_c/RT} C_A^n \quad (20)$$

$$\tilde{r}\left(\frac{\text{atm}}{\text{s}}\right) = k_{po} e^{-E_p/RT} p_A^n \quad (24)$$

We need an equation of state, in this case the ideal gas law $p_A = C_A RT$. By multiplying equation (20) with RT we convert the form r into \tilde{r} as shown below:

$$r\left(\frac{\text{mol}}{\text{Ls}}\right) RT\left(\frac{\text{atm L}}{\text{mol}}\right) = \tilde{r}\left(\frac{\text{atm}}{\text{s}}\right) \quad (29)$$

The above equality can be represented by

$$k_{co} e^{-E_c/RT} C_A^n RT = k_{po} e^{-E_p/RT} C_A^n (RT)^n \quad (29a)$$

Upon canceling the common factors we have

$$k_{co} e^{-E_c/RT} = k_{po} e^{-E_p/RT} (RT)^{n-1} \quad (29b)$$

We require now that the derivative with respect to temperature T of the natural logarithm of the left hand side (LHS) and the right hand side (RHS) are equal. This is essentially equivalent to requiring that the Van't Hoff's equation applied to the representation of the rate constant on the LHS and on the RHS is identical. This yields

$$\frac{d}{dT} \left[\ln(k_{co} e^{-E_c/RT}) \right] = \frac{d}{dT} \left[\ln(k_{po} e^{-E_p/RT} (RT)^{n-1}) \right] \quad (30)$$

$$\frac{E_c}{RT^2} = \frac{E_p'}{RT^2} + \frac{n-1}{T} = \frac{E_p' + (n-1)RT}{RT^2} \quad (30a)$$

This yields equation (25)

$$E_c = E_p' + (n-1)RT \quad (25)$$

Now substituting E_p' in terms of E_c from equation (25) e.g. $E_p' = E_c - (n-1)RT$, into equation (29b) we get

$$k_{co} e^{-E_c/RT} = k_{po}' e^{-E_c/RT} e^{(n-1)} (RT)^{n-1} \quad (31)$$

which upon canceling the common factor $e^{-E_c/RT}$ yields equation (26)

$$k_{co} = k_{po}' (RT)^{n-1} e^{(n-1)} \quad (26)$$

Clearly, equations (25) and (26) cannot be satisfied at every temperature! Usually some reference temperature or the mean temperature in the region of interest is used. So these equations hold at $T = \bar{T}$.

The same procedure is used to relate the rate constants predicted by collision theory and transition state theory, discussed in the next chapter, to the parameters k_{co} and E_c of the Arrhenius form.

4.3 Elementary Reactions

For elementary reactions, the one to one correspondence exists between order and molecularity of reaction. Unimolecular reactions are first order, bimolecular are second order, etc.

Elementary reactions are those that proceed in one step (a rather loose definition since possibilities of the intermediate on the way from reactants to product is allowed in many theories as we will see later). The stoichiometry of elementary reactions is not arbitrary and the stoichiometric coefficients must be integers reflecting the molecularity of the process. Molecularity of an elementary reaction is identified by the number of elementary particles involved in the event leading to reaction. Molecularity with respect to species j is the number of molecules of that species involved in the event leading to the reaction. Stoichiometric coefficients are now equal to molecularity of the species involved. Only for elementary reactions the law of mass action applies, and the rate of the forward reaction equals the product of reactant concentrations raised to their respective stoichiometric coefficients, (e.g. for $A+B \rightarrow P$ the rate forward is $r_f = k_1 C_A C_B$). The same rule holds for the reverse reaction (e.g. for $P \rightarrow A+B$ reverse rate is $r_b = k_2 C_P$).

In this section, we will give examples of elementary gas-phase reactions and we will classify these as unimolecular, bimolecular, and trimolecular.

Unimolecular elementary gas-phase reactions

Originally simple decompositions were thought to be elementary unimolecular reactions such as



but this was later proven to be untrue. However, examples of unimolecular (hence first order reactions) do exist such as isomerization of cyclopropane to propylene, dissociation of molecular bromine and

decomposition of sulfuryl chloride (i.e. $SO_2Cl_2 \rightarrow SO_2 + Cl_2$).

Unfortunately, the original simple hypothesis that unimolecular reactions do not depend on molecular collisions and, hence, occur only by absorbing energy and forming an activated complex was later disproven by showing that believed unimolecular reactions do not remain first order at very low pressures. Hence, although a unimolecular reaction is supposed by definition to involve one molecule of the reactant species only, and proceed in one step, the definition was broadened to allow mechanisms for explanation of unimolecular reactions. A mechanism is a postulated sequence of elementary steps that leads from reactants to products.

Lindemann-Christansen (L-C) Hypothesis asserts the following mechanism for a unimolecular reaction of the type $A \rightarrow P + R$.



Since $[A^*] \ll [A]$ its rate of change is very small so that

$$R_{A^*} = k_1 [A]^2 - k_{-1} [A^*][A] - k_2 [A^*] = 0$$

$$[A^*] = \frac{k_1 [A]^2}{k_{-1} [A] + k_2}$$

Now from stoichiometry $R_p = R_{A^*}$ so that

$$R_p = k_2 [A^*] = \frac{k_1 k_2 [A]^2}{k_{-1} [A] + k_2} = k^1 [A] \quad (33)$$

When pressure is not too low $k_{-1} [A] \gg k_2$ and

$$R_p = \frac{k_1 k_2}{k_{-1}} [A] = k_\infty^1 [A] \quad (34)$$

If pressure is sufficiently low $k_{-1} [A] \ll k_2$

$$R_p = k_1 [A]^2 \quad (35)$$

and second order is observed. This analysis indicates that the observed rate constant k^1 for the unimolecular reaction is pressure, i.e. concentration of A, dependent since

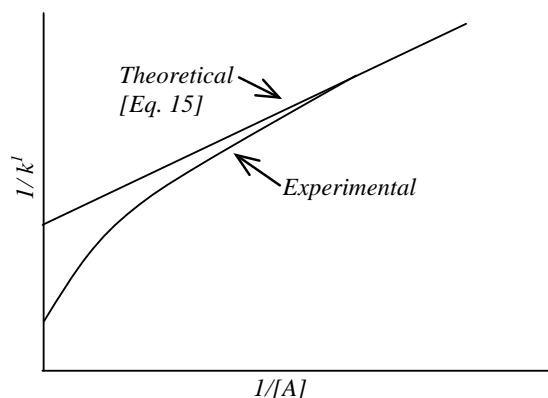
$$k^1 = \frac{k_1 k_2 [A]}{k_{-1} [A] + k_2} = \frac{k_2 \left(\frac{k_1}{k_{-1}} \right)}{1 + \frac{k_2}{k_{-1} [A]}} \quad (36)$$

The plot of $\frac{1}{k^1}$ vs $\frac{1}{[A]}$ should be a straight line

$$\frac{1}{k^1} = \frac{k_{-1}}{k_1 k_2} + \frac{1}{k_1 [A]} \quad (37)$$

which unfortunately is not quantitatively confirmed as evident from Figure 2. However the dependence of the "first order" rate constant k^1 on pressure is evident. This means that while Lindemann's theory qualitatively predicts correctly the change in reaction order with pressure it does not explain it quantitatively. However, Lindemann- Cristensen's theory holds when the proper estimates of the rate constants are arrived at by using quantum mechanics and statistical mechanics calculations as shown in the approach of Rice, Ramsberger, kassel and Marcus (the RRKM theory). Professor Marcus at Caltech was a Nobel prize recipient. Those interested for a more in debt discussion of unimolecular reactions or RRKM theory should consult the literature (e.g. W. Frost, "Theory of Univmolecular reactions").

FIGURE 4: Schematic plot of $1/k^1$ versus $1/[A]$



Bimolecular elementary gas-phase reactions

Bimolecular gas phase reactions can occur:

- between two molecules
- between a free radical and a molecule
- between an ion and a molecule
- between two free radicals

Kinetic results are also available for bimolecular reactions involving atoms and free radicals. Many of these are abstraction (e.g. metathetical) reactions such as



For all bimolecular reactions the rate is second order and given by:

$$r = A e^{-E/RT} C_A C_B \quad (39a)$$

or

$$r = A' e^{-E_p/RT} p_A p_B \quad (39b)$$

The pre-exponential factor can be estimated from collision or transition state theory as will be discussed later. At that time some typical bimolecular gas phase reactions and values of their kinetic parameters will be presented.

Trimolecular elementary gas-phase reactions

The first gas phase reaction of this type that was observed was



Later it was found that indeed all reactions of the type



with $X = Cl, O, Br$, etc. are trimolecular and occur in one step. Hence, the rate is third order, second order in NO and first order in X_2 . At constant temperature the rate is given by

$$r = k[NO]^2[X_2] \quad (42)$$

where $[NO]$ and $[X_2]$ indicates the concentration of NO and X_2 respectively. Of course the rate can also be represented in terms of partial pressures but overall reaction order is always 3 (three).

Combination and Disproportionation Gas Phase Reactions

Examples of these are

- reactions between atoms



- reactions between free radicals



These have essentially zero activation energy and occur due to every collision.

- free radical-molecule reaction



- disproportionation



These are not simple bimolecular reactions since many are the reverse of unimolecular reactions and hence have special features. If the rate of the reverse reaction is known or calculable by RRKM theory, then the equilibrium constant can be used to derive the rate form and kinetic constants for the forward reaction.

Consider



$$\text{with } K_c = \frac{[C_2H_6]}{[CH_3^*]^2} \quad (47b)$$

The reverse decomposition reaction



at sufficiently high pressure is 1-st order by LC mechanism:

$$r_{-1} = k_{-1} [C_2H_6] \quad (48)$$

At equilibrium it follows that:

$$r_1 = r_{-1} \quad (49a)$$

$$k_1 [CH_3^*]^\alpha = k_{-1} [C_2H_6] \quad (49b)$$

Since

$$\frac{k_1}{k_2} = \frac{[C_2H_6]}{[CH_3^*]^\alpha} \quad (49c)$$

and due to equation (47b)

and the fact that we must have $\frac{k_1}{k_2} = K_c$, it follows that $\alpha = 2$. Then,

$$r_1 = k_1 [CH_3^*]^2 \quad (50)$$

On the other hand at very low pressure the decomposition is 2nd order (due to LC mechanism)

$$r_{-1} = k_{-1} [C_2H_6]^2 \quad (51)$$

which implies that

$$r_1 = k_1 [CH_3^*]^2 [C_2H_6] \quad (52)$$

The forward rate is now third order.

Mechanisms of Atom and Radical Combinations

In the dissociation of a molecule R_2 into two radicals R^* the initial step is the energy demanding process



the second step is the dissociation



The initial step (initiation) was brought about by a molecule M which may be R_2 itself or an added substance (third body).

Termination of the free radical R^* follows then the reverse of the above process



For combination (termination) reactions the third body M is known as the chaperon. The energy of R_2^* is transferred to M , which provides the energy transfer mechanism.

Using the fact that the net rate of R_2^* formation is zero, $R_{R_2^*} = 0$, the concentration of R_2^* can be found as shown below:

$$k_1 [R^*]^2 - k_{-1} [R_2^*] - k_2 [R_2^*] [M] = 0 \quad (55a)$$

$$[R_2^*] = \frac{k_1 [R^*]^2}{k_{-1} + k_2 [M]} \quad (55b)$$

The rate of R^* termination is twice the rate of R_2 formation since the overall stoichiometry is $2R^* = R_2$:

$$-R_{R^*} = 2 k_2 [R_2^*] [M] = \frac{2 k_1 k_2 [R^*]^2 [M]}{k_{-1} + k_2 [M]} \quad (56)$$

Hence, at sufficiently high pressures and

$$k_{-1} \ll k_2 [M] \quad (57)$$

$$-R_{R^*} = 2 k_1 [R^*]^2$$

second order termination rate is observed.

At sufficiently low pressures

$$k_{-1} \gg k_2 [M] \quad (58)$$

$$-R_{R^*} = 2 K_1 k_2 [R^*]^2 [M]$$

and third order termination is observed. Here $K_1 = k_1/k_{-1}$ is the equilibrium constant for the first step. Combination and termination of free radicals most likely follows the above mechanism.

The combination of atoms represents an extreme situation. If energy transfer applies two atoms will come together and separate within the period of first vibration $\sim 10^{-13}$ s unless an effective chaperon molecule arrives and collides with the complex within such short a time. Only at gas pressures of 10^4 to 10^5 atm are collision frequencies high enough for them to be likely. Hence, the atom combination rates are low and 3rd order.

However, an alternative mechanism often plays a role, that is the atom-molecule complexation mechanism.



The predicted rate is

$$-R_{R^*} = 2k_3 K_1 K_2 [R^*]^2 [M] \quad (60)$$

where $K_1 = k_1/k_{-1}$ and $K_2 = k_2/k_{-2}$.

The kinetics remains third order at all pressures. This mechanism is favored if k_1 is large, RM^* is a strong complex.

How to derive rate forms from a postulated mechanism in a systematic way will be discussed in the later chapters.

Elementary reactions in solution

Elementary reactions also occur in the liquid phase. They can be reactions between two species dissolved in a solvent or reactions of solute with the solvent. These reactions are quite different from gas phase reactions, since the medium (solvent) is considerably denser and more viscous. The solvent may and may not participate in the stoichiometry of the reaction. In either event, since the concentration of the solvent is much greater than that of the solute reactants, the solvent concentration does not change due to reaction. Some new concepts, yet to be introduced, will be needed, to handle even elementary reactions in solution. This will be postponed for a later chapter, after our treatment of elementary gas phase reactions via collision and transition complex theory.

4.4 Non-elementary Reactions

Composite or complex reactions consist of a sequence of elementary steps and speaking of the molecularity for the overall reaction has no meaning. Reaction order and stoichiometry are now unrelated.

Many reactions proceed via chain mechanisms that induce a closed loop catalytic sequence. Catalysts can be generated by initiation steps of the chain reaction or are unchanging species that speed up reaction rates. Inhibition of the rate, i.e. slow down, is catalyzed by inhibitors - negative catalysts. We will consider next how to evaluate rate forms for gas phase reactions based on proposed mechanisms consisting of sequences of elementary steps.