

## CHAPTER 10: Basic reactor models and evaluation of rate expressions from experimental data

In spite of the advances made by absolute kinetic rate theories, the ultimate determination of the kinetic rate form and the evaluation of the appropriate kinetic parameters has to be based on experimental results. Only when the rate form has been confirmed in the laboratory and the rate parameters evaluated, preferably at conditions close to those contemplated for the large scale process, can an engineer use with some confidence the rate and its parameters for design purposes or for predictions of events in the atmosphere.

The question then arises, if the reaction rates have to be determined by experiments of what help are the kinetic theories to chemical or environmental engineers? The knowledge of reaction mechanism leads to postulated rate forms. It is always much easier to check a postulated rate form, find out whether the experimental data confirm it in its entirety or indicate that a limiting case is sufficient, than to find what rate form experimental data conform to without the prior knowledge of that form. In other words, it is clear that if one knows the expected rate form one can plan well the experiments, and minimize the number of necessary experiments, in order to confirm the postulated rate expression and determine its parameters. Without "a priori" knowledge of the rate expression more experimentation and more work is necessary in order to extract all the information. At the same time prediction of kinetic constants and activation energies from transition state theory helps in setting up the expected upper limits on the kinetic constants and in assessing the temperature sensitivity of reaction. This also helps in planning properly the experiments.

In order to understand how rate expressions are evaluated from laboratory experimental measurements it is instructive to consider first what types of experiments are usually possible and in what environments and under what conditions are they done. We will restrict ourselves here to experiments performed in homogeneous systems.

### 10.1 Reaction environments and conditions for determination of reaction rates in homogeneous systems

Typically laboratory experiments can be performed in one of the reactor types described below. Each of the reactor types can be operated (more or less successfully) under isothermal, adiabatic, or non-isothermal conditions.

Under **isothermal** experimental conditions the temperature of any point of the reaction mixture in the reactor should be the same and constant (equal to the desired experimental temperature) at all times during the run.

**Adiabatic** experimental conditions are achieved when the reaction mixture does not exchange any heat with the surroundings (other than sensible heat of the inflow and outflow stream in flow reactors) and no work is done on or by the reaction mixture (other than PV work of the fluid entering and leaving the vessel in flow reactors).

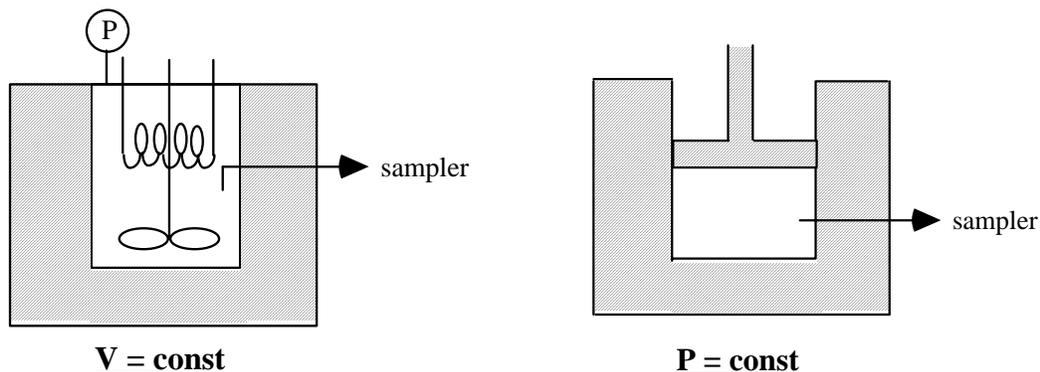
**Non-isothermal** experimental conditions are achieved:

- a. either when a temperature program with respect to time or position in the reactor is established
- b. or when the reactor establishes its own temperature profile in time and space while exchanging heat with the surroundings.

From the point of view of determination of kinetic rates, isothermal conditions are preferred. Kinetic data for simple reactions with well defined stoichiometry can also be obtained from adiabatic runs, but interpretation of non-isothermal runs is usually extremely tedious and is to be avoided.

The typical reactor types in which experiments are performed are:

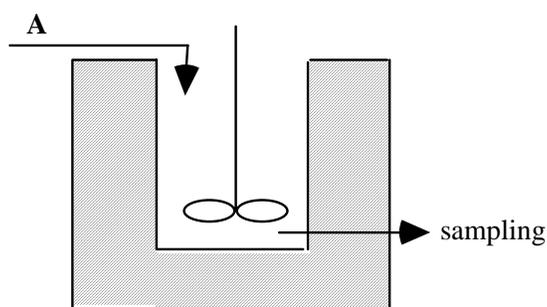
### 10.1.1 BATCH REACTOR



A typical batch reactor ( $V = \text{const}$ ) is a vessel of constant volume (i.e., a flask, autoclave, etc.) into which the reactants are charged at the beginning of the run. The reactor is equipped either with a cooling/heating coil or jacket, or is well insulated, and can be run isothermally (or close to it) or adiabatically. A mixer provides for vigorous agitation of the reaction system. The progress of reaction can be monitored by taking samples of the reaction mixture in specified time intervals and analyzing their composition, i.e. concentrations of certain components are observed as a function of time. In case of gas phase reactions, which proceed with the change in the number of moles, the change of the overall pressure in the system can be monitored in time and tied to reaction progress in case of single reactions.

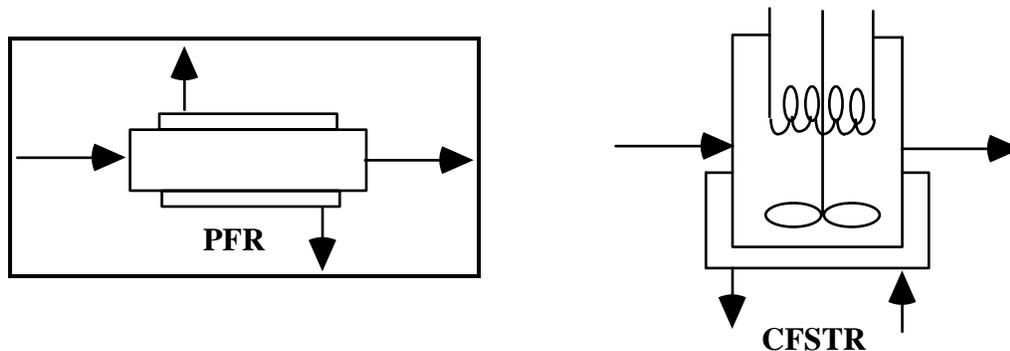
Another type of batch reactor, which is infrequently used in practice to generate rate data but which illustrates an important concept to be used later, is the constant pressure batch system where the volume of the reaction mixture may change in time (i.e. in case of gas phase reactions which proceed with the change in the total number of moles).

### 10.1.2 SEMIBATCH REACTOR:



In the case of a semibatch reactor some of the reactants are charged at the beginning of the run while one or more reactants are added continuously throughout the run. Again, the reactor can be run isothermally or adiabatically, and sampling of the reaction mixture is performed in time in order to monitor the progress of reaction. This reactor type may be quite useful when one is trying to determine the reaction order with respect to say reactant  $B$  and constantly keeps adding reactant  $A$  in large excess. It is also a convenient device in complex reaction systems to study the effect of the order of reactant addition on selectivity and yield etc.

### 10.1.3 CONTINUOUS FLOW REACTOR:



Reaction rates and rate expressions can also be determined in continuous flow systems run at steady state. Two basic types of continuous flow reactors are: the ideal plug flow reactor (PFR) and the ideal continuous flow stirred tank reaction (CFSTR).

#### 10.1.4 PLUG FLOW REACTOR (PFR):

The main assumption of the ideal plug flow reactor is that the fluid is perfectly mixed in the direction perpendicular to main flow and that there is absolutely no mixing in the axial direction, i.e. in the direction of flow. Thus, it is visualized that all fluid molecules move at a uniform velocity  $u$ , i.e. the molecules that enter at  $t = 0$  form a front (plug) that moves at velocity  $u$  all the way to the exit. Therefore, there are no variations in composition and temperature in the direction perpendicular to flow, while concentration changes in the axial or  $z$  direction as one proceeds downstream.

The assumptions of the plug flow reactor are frequently met in industrial practice and in the laboratory. High Reynolds number flow in sufficiently long tubes, i.e. tubes of high  $L/d$ , (length/diameter) ratio, will usually approximate well the plug flow reactor. Flow in packed beds can also be treated as plug flow. This reactor can be operated isothermally or adiabatically.

#### 10.1.5 CONTINUOUS FLOW STIRRED TANK REACTOR (CFSTR):

The CFSTR is also frequently called the backmixed reactor, ideal stirred tank reactor (ISTR), etc. The main assumption is that the reaction mixture in a CFSTR is ideally or perfectly mixed. Thus, when the reactor operates at steady state every point (i.e. every portion) in the reactor has the same composition and temperature. Since there is nothing to distinguish the points in the exit line from the points in the reactor, this implies that the composition and temperature in the exit stream is identical to the composition and temperature of the reaction mixture in the reactor. This ideal reactor in practice is approached by devices that provide a very vigorous mixing of the reaction mixture. It can be operated isothermally or adiabatically.

Other flow type reactors which do not approach a PFR or CFSTR behavior are not useful for evaluation of rate expressions.

We have mentioned before that it is desirable to perform kinetic runs at constant temperature. Of the above reactor types CFSTR is the easiest to run at isothermal conditions. When operated at steady state, the composition in the reactor is constant and the heat released (or taken) per unit time is constant and can be readily removed or provided. In contrast, in a batch reactor, since the composition changes in time so will the heat released or absorbed; thus, one must have sufficient flexibility to meet varying heat requirements. Similarly, in a PFR fluid composition changes along the reactor, and thus the heat released or taken per unit reactor length changes along the reactor. Cooling or heating must meet this varying requirements.

It also should be pointed out that flow reactors (especially laboratory ones) operate essentially at constant pressure conditions since the pressure drops are usually negligible. In making energy balances, friction losses, or the work done on the fluid by the impeller, can generally be neglected in comparison to heats of reaction. At the same time, since the volume of the reaction mixture is fixed in flow reactors and also  $P = \text{const}$ , this means that in the case of gas phase reactions which proceed with the changes in the total number of moles there would be a change in the volumetric flow rate of the mixture as it moves through the PFR. For such gas phase reactions the exit and entrance volumetric flow rates in a CFSTR are different.

## 10.2 Determination of the Rate

When we run any of the above reactor types we determine the rate of reaction by making a material balance on the reactor. Let us for simplicity consider a single reaction

$$aA + bB = dD; \quad (1)$$

or

$$\sum_{j=1}^s \nu_j A_j = 0 \quad (1a)$$

Since for a single reaction

$$\frac{N_{Ao} - N_A}{a} = \frac{N_{Bo} - N_B}{b} = \frac{N_D - N_{Do}}{d}; \quad (2)$$

or

$$X = \frac{N_j - N_{jo}}{\nu_j} \quad (2a)$$

it is sufficient to monitor only one variable of the system, i.e. one concentration, or any property of the system such as its pressure, viscosity, refractive index, etc. that is directly and uniquely related to its composition. The rate of reaction  $r(T, C_A, C_B, C_D) = r(T, C_j)$  is a function of temperature and composition.

**NOTE:**  $r$  is the intrinsic or equivalent rate i.e.

$$r = \frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_D}{d} \quad (3)$$

Suppose we run the reaction in a batch reactor from time 0 to time  $t$  and monitor concentration  $C_A$  as a function of time.

The overall material balance on  $A$  gives:

$$\left( \begin{array}{c} \text{Amount of } A \\ \text{charged in} \end{array} \right) - \left( \begin{array}{c} \text{Amount of } A \\ \text{left unreacted} \\ \text{at time } t \end{array} \right) - \left( \begin{array}{c} \text{Amount of } A \\ \text{reacted from} \\ \text{time 0 to time } t \end{array} \right) = 0 \quad (4)$$

$$\left( \begin{array}{c} \text{Amount of } A \\ \text{charged in the reactor} \end{array} \right) = N_{A_0} \text{ (moles)} \quad (5)$$

$$\left( \begin{array}{c} \text{Amount of } A \\ \text{left unreacted at time } t \end{array} \right) = N_A(t) \text{ (moles)} \quad (6)$$

↑ evaluated at  $t$

By definition

$$ar = \left( \frac{\text{moles of } A \text{ reacted}}{\text{unit volume unit time}} \right)$$

Then

$$a \underbrace{\int_V r(T, C_j) dV}_{\downarrow} = \left( \frac{\text{moles of } A \text{ reacted}}{\text{unit time}} \right)$$

(moles reacted per unit volume and unit time summed up over the whole volume of the mixture)

$$\left( \begin{array}{c} \text{Amount of } A \\ \text{reacted from time 0 to time } t \end{array} \right) = a \int_0^t \int_V r(T, C_j) dV dt \quad (7)$$

Thus, substituting eqs. (5-7) into eq. (4) we get:

$$N_{A_0} - N_A(t) - a \int_0^t \int_V r(T, C_j) dV dt = 0 \quad (8)$$

Similarly an energy balance gives:

$$\left( \begin{array}{c} \text{Energy of} \\ \text{the system} \\ \text{at time 0} \end{array} \right) - \left( \begin{array}{c} \text{Energy of} \\ \text{the system} \\ \text{at time } t \end{array} \right) + \left( \begin{array}{c} \text{Heat generated} \\ \text{by reaction from} \\ \text{time 0 to time } t \end{array} \right) - \left( \begin{array}{c} \text{Heat removed} \\ \text{from time} \\ \text{0 to time } t \end{array} \right) = 0 \quad (9)$$

$$(\rho C_v VT)_o - (\rho C_v VT)_t + a \int_0^t \int_V (-\Delta U)_r r(T, C_j) dV dt - \int_0^t UA_h (T - T_c) dt = 0 \quad (9a)$$

- $\rho$  - density of the reaction mixture ( $kg/m^3$ )
- $C_v$  - specific heat of the reaction mixture ( $J/kg \cdot C$ )
- $V$  - reaction mixture volume ( $m^3$ )
- $\Delta U_r$  - heat of reaction ( $J/mol$ )
- $U$  - overall heat transfer coefficient ( $J/m^2 \cdot s \cdot C$ )
- $A_h$  - area for heat transfer ( $m^2$ )

Clearly the equations simplify if the temperature is kept constant ( $T = T_c$ ) in an isothermal system and if the volume of the reaction mixture is constant.

$$N_{Ao} - N_A(t) - aV \int_0^t r(T_c, C_j) dt = 0 \quad (10)$$

Differentiating eq. (10) we get

$$-\frac{dN_A}{dt} - aV r(T_c, C_j) = 0 \quad (11)$$

$$\text{or } \underbrace{ar(C_j, T_c)}_{-r_A(C_j, T_c)} = -\frac{1}{V} \frac{dN_A}{dt} \quad (12)$$

Now if the volume of the reaction mixture is constant  $\frac{N_A}{V} = C_A$   
and the concentrations of all other components can be related to  $C_A$

$$N_B = N_{Bo} - bX \quad (13)$$

$$X = \frac{N_{Ao} - N_A}{a} \quad (13a)$$

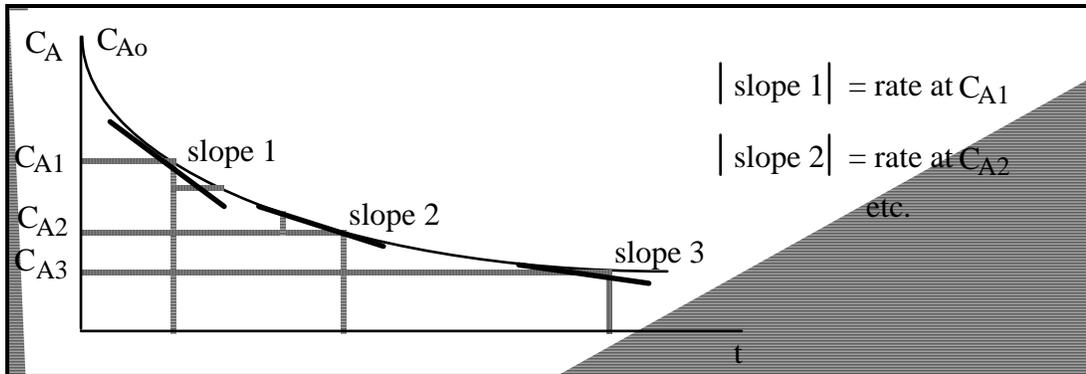
$$\text{If } V = \text{const} \text{ then } \xi = \frac{X}{V} = \frac{C_{Ao} - C_A}{a} \quad (14)$$

$$C_B = C_{Bo} - \frac{b}{a} (C_{Ao} - C_A) \quad (15)$$

$$C_D = C_{Do} - \frac{d}{a} (C_{Ao} - C_A) \quad (16)$$

$$-r_A(C_A, T_c) = -\frac{dC_A}{dt} \quad (17)$$

Since we monitor  $C_A$  as a function of time, the derivative  $\frac{dC_A}{dt}(t)$  gives us the value of the rate at that particular time, i.e. at the concentration  $C_A$  present at time  $t$ .



In this way we could extract the overall order of reaction,  $n$ .

In order to get the reaction order with respect to reactant  $A$  we can use the method of excess, i.e. take initial  $N_{B0}/N_{A0} \gg 1$  so that  $C_B$  stays practically constant during reaction. In order to be able to neglect the effect of product  $D$  on the rate we can use the method of initial rates, i.e. measure the rates only while very little product is present.

Let us briefly consider the material balance for a continuous flow reactor for the same reaction at isothermal conditions and at steady state

$$\left( \begin{array}{c} \text{Rate of molar} \\ \text{input of A} \end{array} \right) - \left( \begin{array}{c} \text{Rate of molar} \\ \text{output of A} \end{array} \right) - \left( \begin{array}{c} \text{Rate of} \\ \text{disappearance} \\ \text{by reaction in} \\ \text{the reactor} \end{array} \right) = 0 \quad (18)$$

$$\begin{array}{c} F_{A0} \\ \left( \frac{\text{mol}}{\text{hr}} \right) \end{array} - \begin{array}{c} F_A \\ \left( \frac{\text{mol}}{\text{hr}} \right) \end{array} - a \int_V r(C_A, T_c) dV = 0 \quad (18a)$$

$\left( \frac{\text{mol}}{\text{lit hr}} \right) \times (\text{lit})$

In terms of conversion:

$$F_A = F_{A0} (1 - x_A) \quad (19)$$

$$F_{A0} x_A - a \int_V r(C_A, T_c) dV = 0 \quad (20)$$

The integral is necessary in the PFR since the concentration of  $A$  changes as one moves down the reactor length and, therefore, so does the rate.

However, in a CFSTR, by assumption, the mixture is perfectly mixed and at uniform composition. Therefore, every element of the reaction mixture reacts at the same rate and we have ( $q$  - volumetric flow rate of reaction mixture at the exit,  $q_o$  - volumetric flow rate of entrance):

$$-r_A(C_A, T_c) = \frac{F_{Ao} x_A}{V} = \frac{C_{Ao} q_o - C_A q}{V}$$

concentration in the reactor and at the same time in the exit

(21)

Clearly CFSTR is a convenient contacting device for direct measurement of reaction rates (no derivatives needed). A rate at a different  $C_A$  can be found by increasing or decreasing  $q_o$ .

From the above we have seen that PFR operates as an integral reactor, i.e. overall conversion is given by the integral of the rate over the whole reactor volume.

Sometimes the PFR is used as a differential reactor, i.e. overall conversion is kept very low so that the change in concentration is very small from entrance to exit. Then the mean value theorem can be used.

$$F_{Ao} x_A - ar(C_{Am}, T_c) V = 0$$
(22)

$C_{Am}$  - mean value of concentration  $C_{Aexit} < C_{Am} < C_{Ao}$ . Now the rate is obtained directly but the small changes in concentration are difficult to measure accurately.

The CFSTR in contrast can give very large changes in  $C_A$  between inlet and outlet and still the rate is obtained directly.

### 10.3 Evaluations of rate forms using batch (Homogeneous Systems)

We will concentrate now on evaluation of rate expressions in homogeneous systems using batch reactors. The problem, if we start from a simple single reaction, can be stated as follows:

For a reaction  $aA + bB = dD + gG$  find the reaction rate, i.e. find the rate's dependence on concentration and temperature.

The experiments are selected to be performed at isothermal conditions so that the rate's dependence on concentrations is established first. Once the rate form is known, isothermal runs can be repeated at different temperature levels so that the dependence of the specific rate constant(s) on temperature can be established.

Let us assume further that these hypothetical experiments are performed in an enclosed batch vessel so that the volume of the reaction mixture is constant  $V = const$ .

Since  $V = const$  the stoichiometric relationship

$$\frac{N_{Ao} - N_A}{a} = \frac{N_{Bo} - N_B}{b} = \frac{N_D - N_{Do}}{d} = \frac{N_G - N_{Go}}{g} = X$$
(2)

or for a general single reaction  $\sum \nu_j A_j = 0$  (1a)

$$\frac{N_j - N_{j0}}{\nu_j} = X \quad (2a)$$

can be extended by dividing it by  $V$  and since  $\frac{N_{Ao}}{V} = C_{Ao}$ ,  $\frac{N_A}{V} = C_A$  etc., while  $\xi = \frac{X}{V}$  is the extent per unit volume we get

$$\frac{C_{Ao} - C_A}{a} = \frac{C_{Bo} - C_B}{b} = \frac{C_D - C_{Do}}{d} = \frac{C_G - C_{Go}}{g} = \xi \quad (23)$$

or  $\frac{C_j - C_{j0}}{\nu_j} = \xi$  (23a)

Let us that suppose we have charged the reactor with  $N_{Ao}$ ,  $N_{Bo}$  moles of  $A$  and  $B$  and no  $D$  and  $G$ . A balance on  $A$  gives

$$ar (C_j) V = -\frac{dN_A}{dt} \quad (24)$$

But  $N_A = C_A V$  and  $V = const$  so that

$$-r_A = ar (C_j) = -\frac{dC_A}{dt} \quad (25)$$

The rate is in general a function of concentration of all species. Let us assume that we expect to find the rate of the form

$$r = k_f C_A^\alpha C_B^\beta - k_b C_D^\gamma C_G^\delta \quad (26)$$

where  $k_f = k_{f0} e^{-E_f/RT}$  and  $k_b = k_{b0} e^{-E_b/RT}$ . We have assumed the rate constants to obey the Arrhenius form but since we operate at constant temperature (isothermal runs) both  $k_f$ ,  $k_b$  are constants to be determined from the run as well as the powers  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ .

Using the stoichiometric relationship we could eliminate all other concentrations in terms of  $C_A$ .

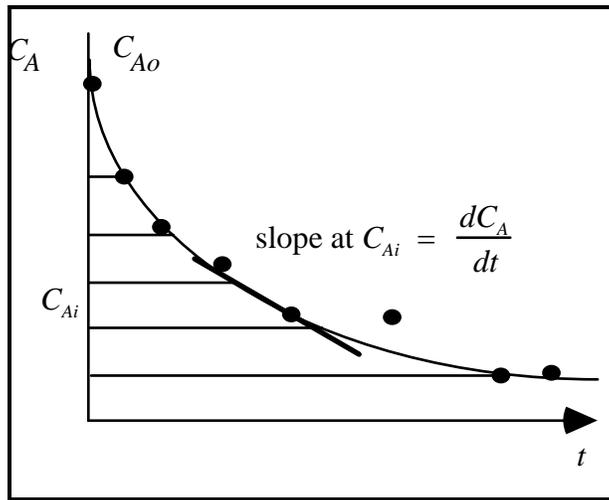
$$\begin{aligned} C_B &= C_{Bo} - \frac{b}{a} (C_{Ao} - C_A) & \text{In General:} \\ C_D &= C_{Do} + \frac{d}{a} (C_{Ao} - C_A) & C_j = C_{j0} + \frac{\nu_j}{\nu_l} (C_l - C_{l0}) \\ C_G &= C_{Go} + \frac{g}{a} (C_{Ao} - C_A) \end{aligned} \quad (27)$$

Thus we would have

$$a \left\{ k_f C_A^\alpha \left[ C_{Bo} - \frac{b}{a} (C_{Ao} - C_A) \right]^\beta - k_b \underbrace{\frac{dg}{a^2} (C_{Ao} - C_A)^{\gamma + \delta}}_{\substack{\text{this follows nice since} \\ C_{Do} = C_{Go} = 0 \text{ were assumed}}} \right\} = -\frac{dC_A}{dt} \quad (28)$$

$$\text{At } t = 0 \quad C_A = C_{Ao} \quad (28a)$$

Clearly, we could monitor the concentration of A,  $C_A$ , in time continuously, or as is more often the case discretely. We can try to evaluate the slope of  $C_A$  vs.  $t$  line,  $\frac{dC_A}{dt}$ , at various values of  $C_A$ .



Plugging the  $C_A$  and corresponding  $\frac{dC_A}{dt}$  values in the above equation we would get a large set of nonlinear equations from which we would have to determine a great number of parameters, namely six (6) all together:  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $k_f$ ,  $k_b$ .

This method of attack due to large errors hidden in experimental data does not seem too fruitful. Instead we can decide to run the experiment only up to low conversions  $x_A = \frac{C_{Ao} - C_A}{C_{Ao}}$ . In this situation we can neglect the rate of the reverse reaction - we are using the method of initial rates.

$$a k_f C_A^\alpha \left[ C_{Bo} - \frac{b}{a} (C_{Ao} - C_A) \right]^\beta = -\frac{dC_A}{dt} \quad (29)$$

Now we would have to determine only three parameters from the experimental run:  $\alpha$ ,  $\beta$ , and  $k_f$ .

In addition, we can decide, if experimentally feasible, to make the job even easier and use reactant B in large excess over the stoichiometrically required amount i.e.  $\frac{C_{Bo}}{C_{Ao}} \gg \frac{b}{a}$ .

The mass balance can be rewritten in the following form:

$$a k_f C_A^\alpha C_{Ao}^\beta \left[ \frac{C_{Bo}}{C_{Ao}} - \frac{b}{a} x_A \right]^\beta = -\frac{dC_A}{dt} \quad (30)$$

but since  $x_A \ll 1$  (low conversion) and  $\frac{C_{Bo}}{C_{Ao}} \gg \frac{b}{a}$  we can safely ignore  $\frac{b}{a} x_A = \frac{b}{a} \frac{C_{Ao} - C_A}{C_{Ao}}$  in comparison to  $\frac{C_{Bo}}{C_{Ao}}$

Thus, we get (with  $k_f^1 = k_f C_{Bo}^\beta$ ):

$$a (k_f C_{Bo}^\beta) C_A^\alpha = -\frac{dC_A}{dt} = a k_f^1 C_A^\alpha \quad (31)$$

and we have used the method of excess in addition to the method of initial rates. Now we have only two parameters to determine:  $\alpha$  and  $k_f^1$ . This seems a reasonable task. We can afterwards proceed to repeat the runs at different temperatures, still measuring rates at small conversions and using *B* in excess, in order to determine  $E_f$  from the Arrhenius plot. After that, experiments can be performed in excess of *A* to determine  $\beta$  and  $k_{fo}$ , and then runs starting with only *C* and *D* can be performed to determine the reverse rate's parameters  $\gamma$ ,  $\delta$ ,  $k_{bo}$ ,  $E_b$ .

The previous discussion indicates that if we want to determine a rate expression for a single reaction, and we monitor the concentration of one component (one species) as a function of time (say of limiting reactant *A*), we can almost always, by proper selection of experimental conditions, reduce the problem to one of the type:

$$-\frac{dC_A}{dt} = k C_A^\alpha; \quad t = 0 \quad C_A = C_{Ao} \quad (32)$$

where from a set of  $C_A$  vs.  $t$ , i.e.  $C_{Ai}$  vs.  $t_i$ , data parameters  $\alpha$  and  $k$  have to be determined.

For the analysis of this type we can employ two basic methods:

- differential method or
- integral method.

Let us discuss each of them.

### 10.3.1. Differential Method:

**Objective:** given a set of data  $C_A$  vs.  $t$ , i.e.  $C_{Ai}$  vs.  $t_i$ , determine  $\alpha$  and  $k$  in the hypothesized rate form,  $kC_A^\alpha$ .

1. Tabulate the data and evaluate the differences  $\Delta C_{Ai} = C_{Ai+1} - C_{Ai}$  and  $\Delta t_i = t_{i+1} - t_i$ .
2. Evaluate the approximation to the derivative  $\frac{dC_A}{dt}$ .

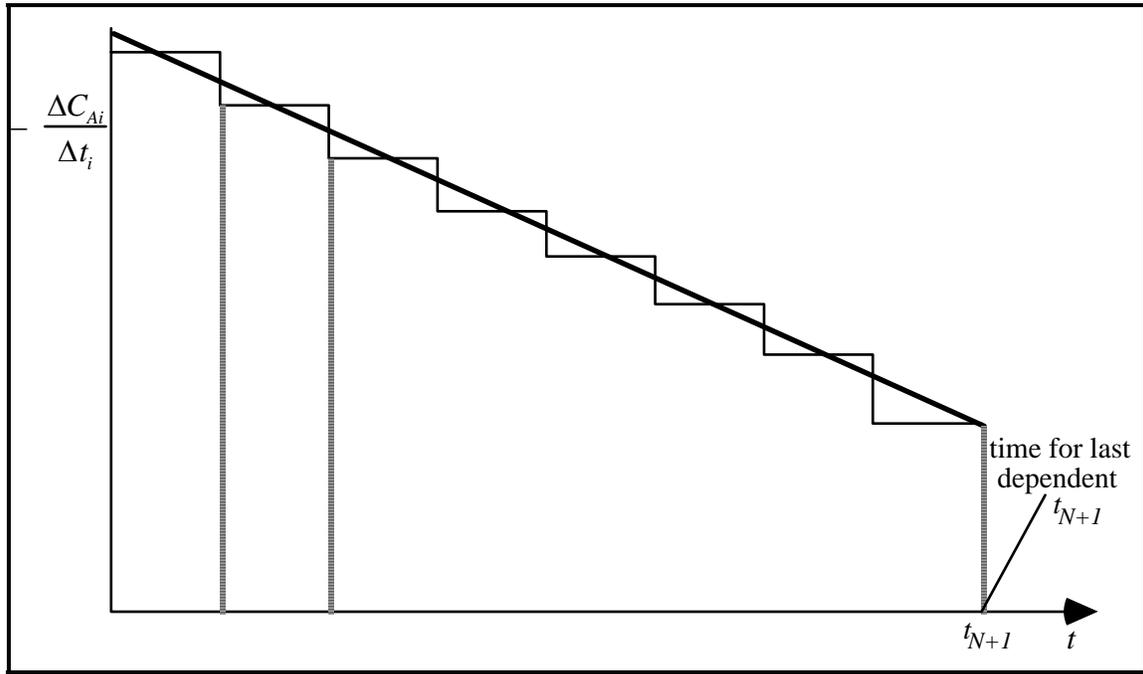
This can be done either directly from the table of differences of the data i.e.

$$\frac{dC_A}{dt}(\tilde{t}_i) \approx \frac{\Delta C_{Ai}}{\Delta t_i} = \frac{C_{Ai+1} - C_{Ai}}{t_{i+1} - t_i}; \quad t_i < \tilde{t} < t_{i+1} \quad (33)$$

or by numerical differentiation of the data, or by plotting a smooth curve through the  $C_A$  vs.  $t$  data and evaluating its slope graphically, or by matching the  $C_A$  vs.  $t$  data by some function and evaluating its derivative. Using the ratio of the differences from the table of data leads to very poor estimates of the derivative when  $\Delta t_i$  are uneven and large and  $\Delta C_{Ai}$  are large. At the same time the question arises to what value of  $\tilde{t}$  ( $t_i < \tilde{t} < t_{i+1}$ ), i.e. to what value of  $\tilde{C}_A$  ( $t_i > \tilde{C}_A > C_{Ai+1}$ ) does the derivative approximation  $\frac{\Delta C_{Ai}}{\Delta t}$  correspond. The quality (i.e., poor quality) of error prone kinetic data usually does not warrant the use of more sophisticated numerical differentiation methods.

The best practical procedure is to plot  $\left(-\frac{\Delta C_{Ai}}{\Delta t_i}\right)$  verses  $t$  as a stepwise curve shown below. Since

$\frac{\Delta C_{Ai}}{\Delta t_i}$  was evaluated by using  $C_{Ai+1}$ ,  $C_{Ai}$  and  $t_{i+1}$ ,  $t_i$  it is valid for the interval  $t_{i+1} - t_i$



The area under every step is the value of the ordinate  $\frac{\Delta C_{Ai}}{\Delta t_i}$  times the value of the corresponding time interval  $t_{i+1} - t_i$ , i.e.,  $-\frac{\Delta C_{Ai}}{\Delta t_i} \Delta t_i = C_{A_i} - C_{A_{i+1}}$  which measures the variation in concentration during one time interval. The area under the whole stepwise curve is:

$$\sum_{i=0}^N \left( -\frac{\Delta C_{Ai}}{\Delta t_i} \right) \Delta t_i = C_{A_0} - C_{A_{N+1}} \quad (34)$$

and measures the overall concentration change of  $A$  during the experiment. Yet we know that the overall concentration change we can obtain by integrating the derivative  $\frac{dC_A}{dt}$  with respect to time:

$$C_{A_0} - C_{A_{N+1}} = \int_{t_0}^{t_{N+1}} \left( -\frac{dC_{Ai}}{dt} \right) dt \quad (35)$$

This tells us to plot a smooth curve on our step-wise plot in such a way that the area under the smooth curve is equal to the area under the stepwise curves. Since both areas are  $C_{A_0} - C_{A_{N+1}}$  the smooth curve gives us our best estimate of  $\left( -\frac{dC_A}{dt} \right)$ . This was done on the figure in the previous page. Now for every  $t_i$  we can read the value of the derivative  $\left( -\frac{dC_A}{dt} (t_i) \right)$  by going to the smooth curve at that

value of  $t_i$  and reading of the corresponding value of the ordinate. Since for every  $t_i$  we have a measured  $C_{Ai}$  value, we can now pair the values  $-\frac{dC_A}{dt}(t_i)$  and  $C_{Ai}$ .

$\underbrace{\hspace{10em}}_{\substack{\text{means } -\frac{dC_A}{dt} \\ \text{evaluated at } t_i}}$

3. Now plot  $-\frac{dC_A}{dt}(t_i)$  versus  $C_{Ai}$  on log-log paper. By doing this

$$\underbrace{\log\left(-\frac{dC_A}{dt}\right)}_y = \underbrace{\log k}_a + \alpha \underbrace{\log C_A}_x \quad (36)$$

we should be able to pass a straight line through the data points provided that the rate indeed was of n-th order form and not of a more complex form.

The slope from the log-log plot gives our  $\alpha$ . From any point then we can determine  $\log k$  and  $k$ . It is advisable to determine  $k$  from a number of points and to take an average value.

The strength of the differential method is that all that we have to assume is that the rate is of a particular form (n-th order form). Both the reaction rate order  $\alpha$  and the kinetic constant  $k$  are then extracted by the method. The main weakness of the method is poor accuracy.

### 10.3.2. Integral Method:

**Objective:** given a set of data  $C_A$  vs.  $t$ , i.e.  $C_{Ai}$  vs.  $t_i$ , determine  $\alpha$  and  $k$  in the hypothesized rate form  $k C_A^\alpha$ .

#### Procedure:

1. Tabulate the  $C_A$  vs.  $t_i$  data.
2. Assume a particular order  $\alpha$ , i.e.  $\alpha = 1$ , or  $\alpha = \frac{1}{2}$  or  $\alpha = 2$ , etc.
3. Integrate the batch mass balance.

$$\underbrace{-\int_{C_{Ao}}^{C_A} \frac{dC_A}{C_A^\alpha}}_{F(C_A, C_{Ao}) = kt} = k \int_0^t dt \quad (37)$$

Note: The form of  $F(C_A, C_{Ao})$  depends on the chosen value of  $\alpha$ :

$$\text{for } \alpha = 1, \quad F(C_A, C_{Ao}) = \ln \frac{C_{Ao}}{C_A} \quad (37a)$$

$$\text{for } \alpha = 2, \quad F(C_A, C_{Ao}) = \frac{1}{C_A} - \frac{1}{C_{Ao}} \text{ etc.} \quad (37b)$$

4. Form the pairs of values  $F(C_{Ai}, C_{Ao})$  vs  $t_i$ , i.e. evaluate the known function  $F(C_A, C_{Ao})$  at all measured values  $C_{Ai}$  and pair them with corresponding  $t_i$  by extending the previous table of data.
5. Plot  $F(C_{Ai}, C_{Ao})$  vs  $t_i$  on a linear plot

$$\underbrace{F(C_A, C_{Ao})}_y = k \underbrace{t}_x \quad (38)$$

If the assumed order  $\alpha$  was correct one will be able to pass a straight line through the above plotted points, the slope of the lines gives  $k$  and the assumed order  $\alpha$  has been confirmed.

If the assumed order  $\alpha$  was incorrect, a straight line plot cannot be obtained, and one has to go back to step 2 and assume another  $\alpha$  and repeat all other steps.

The strength of the integral method is that the integration procedure smoothes the error of experimental data and allows more accurate evaluation of  $k$ 's. The main weakness is that the method is very tedious to use unless one has a good indication of what  $\alpha$  may be. Clearly the knowledge of the mechanism would help.

In general, if one does not have any idea what  $\alpha$  may be, it is advisable to get an estimate of  $\alpha$  and  $k$  using the differential method, and then retest the found  $\alpha$  and upgrade the accuracy of the  $k$  value by the integral method.

In the above discussion we have assumed that the concentration of a reactant was monitored in time. Naturally, all the above procedures hold if instead a product concentration is monitored, or a physical quantity proportional to the composition of the system, or total pressure of the system (in case of gas phase reactions which proceed with the change in the total number of moles). Let us consider this last case:

$$aA + bB = dD + gG \quad \text{or} \quad \sum_{j=1}^S \nu_j A_j = 0 \quad (1a)$$

$$\Delta n = d + g - a - b \quad \Delta n = \sum_{j=1}^S \nu_j \quad (39)$$

Let us assume a rate of the form:

$$-r_A = k C_A^\alpha C_B^\beta \quad (40)$$

Assuming ideal gases

$$C_{Ao} = \frac{P_{Ao}}{RT} \quad C_{Bo} = \frac{P_{Bo}}{RT} \quad (41)$$

The total initial pressure, if there were no inerts and products present, is given by:

$$C_{Ao} + C_{Bo} = \frac{P_{Ao} + P_{Bo}}{RT} = C_{To} = \frac{P_{To}}{RT} \quad (42)$$

Concentrations are related to extent per unit volume  $\xi$ , as shown below:

$$\begin{aligned}
 C_A &= \frac{P_A}{RT} = \frac{N_A}{V} = \frac{N_{A_0} + aX}{v} = C_{A_0} - a\xi \\
 C_B &= \frac{P_B}{RT} = C_{B_0} - b\xi \\
 C_D &= \frac{P_D}{RT} = d\xi \\
 C_G &= \frac{P_G}{RT} = g\xi \\
 C_T &= (C_A + C_B + C_D + C_G) = \frac{(P_A + P_B + P_D + P_G)}{RT} = \frac{P_T}{RT} = C_{T_0} + (\Delta n)\xi \\
 C_T &= \frac{P_T}{RT} = \frac{P_{T_0}}{RT} + (\Delta n)\xi \Rightarrow \xi = \frac{P_T - P_{T_0}}{(\Delta n) RT}
 \end{aligned} \tag{43}$$

or in general

$$C_T = C_{T_0} + \sum_{j=1}^s \nu_j \xi \quad \xi = \frac{P_T - P_{T_0}}{\sum \nu_j RT} \tag{44}$$

Now let us get an equation in terms of total pressure:

$$- \frac{dC_A}{dt} = k C_A^\alpha C_B^\beta \tag{45}$$

$$- \frac{1}{RT} \frac{dP_A}{dt} = k P_A^\alpha P_B^\beta \frac{1}{(RT)^{\alpha+\beta}}$$

$$- \frac{dP_A}{dt} = \underbrace{\left[ k (RT) \right]^{1-(\alpha+\beta)}}_{k_p} P_A^\alpha P_B^\beta \tag{46}$$

$$P_A = P_{A_0} - a\xi = P_{A_0} - \frac{a}{\Delta n} (P_T - P_{T_0}) \tag{47}$$

$$P_{A_0} = y_{A_0} P_{T_0} \tag{48}$$

↑ Mole fraction of A initially

$$\frac{dP_A}{dt} = - \frac{a}{\Delta n} \frac{dP_T}{dt} \tag{49}$$

$$\frac{a}{\Delta n} \frac{dP_T}{dt} = k_p \left[ y_{A_0} P_{T_0} - \frac{a}{\Delta n} (P_T - P_{T_0}) \right]^\alpha \left[ y_{B_0} P_{T_0} - \frac{b}{\Delta n} (P_T - P_{T_0}) \right]^\beta \tag{50}$$

$$\boxed{\frac{dP_T}{dt} = \left( \frac{k_p \Delta n}{a} \right) \left[ y_{A_0} P_{T_0} - \frac{a}{\Delta n} (P_T - P_{T_0}) \right]^\alpha \left[ y_{B_0} P_{T_0} - \frac{b}{\Delta n} (P_T - P_{T_0}) \right]^\beta} \tag{51}$$

This equation relates now the change of total pressure  $P_T$  with time and from the  $P_T (t_i)$  vs.  $t_i$  data  $\alpha$ ,  $\beta$ ,  $k_p$  can be determined by the previously outlined methods. Method of excess can be again used in order to further simplify the apparent rate form.

Clearly, both the integral and differential method have one thing in common - they attempt to find a relationship between properly arranged experimental data which is linear. The key is to find and plot a straight line relationship.

Differential method (n-th order reaction)

$$\underbrace{\log \left( -\frac{dC_A}{dt} \right)}_y = \log k + n \underbrace{\log C_A}_x \quad (52)$$

Integral method (n-th order reaction)

$$F(C_{A1}) = F(C_{Ao}) + kt f(n) \quad (53)$$

$$\underbrace{\frac{1}{C_A^{n+1}}}_y = \frac{1}{C_{Ao}^{n+1}} + k(n+1) \underbrace{t}_x \quad (53a)$$

For rate forms other than n-th order straight line relationships are also sought. For example for Michaelis-Menten rate form:

$$-\frac{dC_A}{dt} = -r_A = \frac{k C_A}{K + C_A} \quad (54)$$

**Differential Analysis:**

$$\underbrace{\left[ \frac{1}{\left( -\frac{dC_A}{dt} \right)} \right]}_y = \frac{1}{k} + \frac{K}{k} \underbrace{\left( \frac{1}{C_A} \right)}_x \quad \text{or} \quad \underbrace{\left[ \frac{C_A}{\left( -\frac{dC_A}{dt} \right)} \right]}_y = \frac{K}{k} + \frac{1}{k} \underbrace{C_A}_x \quad (55)$$

**Integral Analysis:**

$$\underbrace{\left( \frac{\ln \frac{C_{Ao}}{C_A}}{C_{Ao} - C_A} \right)}_y = \frac{k}{K} \underbrace{\left( \frac{t}{C_{Ao} - C_A} \right)}_x - \frac{1}{K} \quad (56)$$

Thus any combination that yields a straight line relationship is sought.

## 10.4 Examples of evaluation of rate forms from kinetic data in batch systems

EXAMPLE 1: Determine the reaction order and the rate constant for a single reaction of the type  $A \rightarrow$  products based on the following experimental information obtained at isothermal conditions at  $V = \text{const.}$

$t \text{ (min)}$	0	5	10	15	20	25	30	35	40	$\infty$
$C_A \left( \frac{\text{mol}}{\text{lit}} \right)$	1	0.58	0.41	0.32	0.25	0.22	0.19	0.16	0.14	$\approx 0$

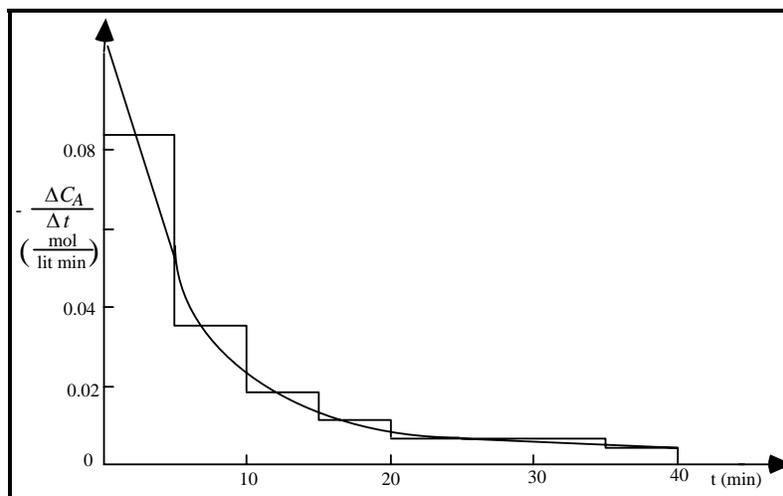
The last data point simply indicates that after a very long time (several hours as compared to minutes) practically no  $A$  is found. Thus, at the experimental conditions used the reaction is practically irreversible.

### A. Differential Analysis:

We can form  $\Delta t_i$  and  $-\Delta C_{A_i} = C_{A_i} - C_{A_{i+1}}$  from the table, and  $-\frac{\Delta C_{A_i}}{\Delta t_i}$

$\Delta t = 5$	0-5	5-10	10-15	15-20	20-25	25-30	30-35	35-40
$-\frac{\Delta C_{A_i}}{\Delta t_i}$	0.084	0.034	0.018	0.014	0.006	0.006	0.006	0.004

We can plot now  $-\frac{\Delta C_{A_i}}{\Delta t}$  vs.  $t_i$  as a stepwise curve shown below. Now we have to pass a smooth curve so that



the area under the stepwise curve and the smooth curve are approximately equal. From the smooth curve we now read of the corresponding values of  $-\frac{dC_A}{dt}$  at desired measured concentrations  $C_{A_i}$ .

$t$	5	10	15	20	25	30	35
$C_{Ai}$	0.58	0.41	0.32	0.25	0.22	0.19	0.16
$-\frac{dC_A}{dt}$	0.055	0.024	0.015	0.0105	0.0065	0.005	0.004

Now we can plot

$$\log \left( -\frac{dC_A}{dt} \right) = \log k + \alpha \log C_A \text{ i.e. we plot } -\frac{dC_A}{dt} \text{ vs. } C_A \text{ on a log-log plot.}$$

From the slope of the straight line that we managed to pass through the data points we find that  $\alpha = 2.05$ . From any point of the line now we could determine  $k$ . For example:

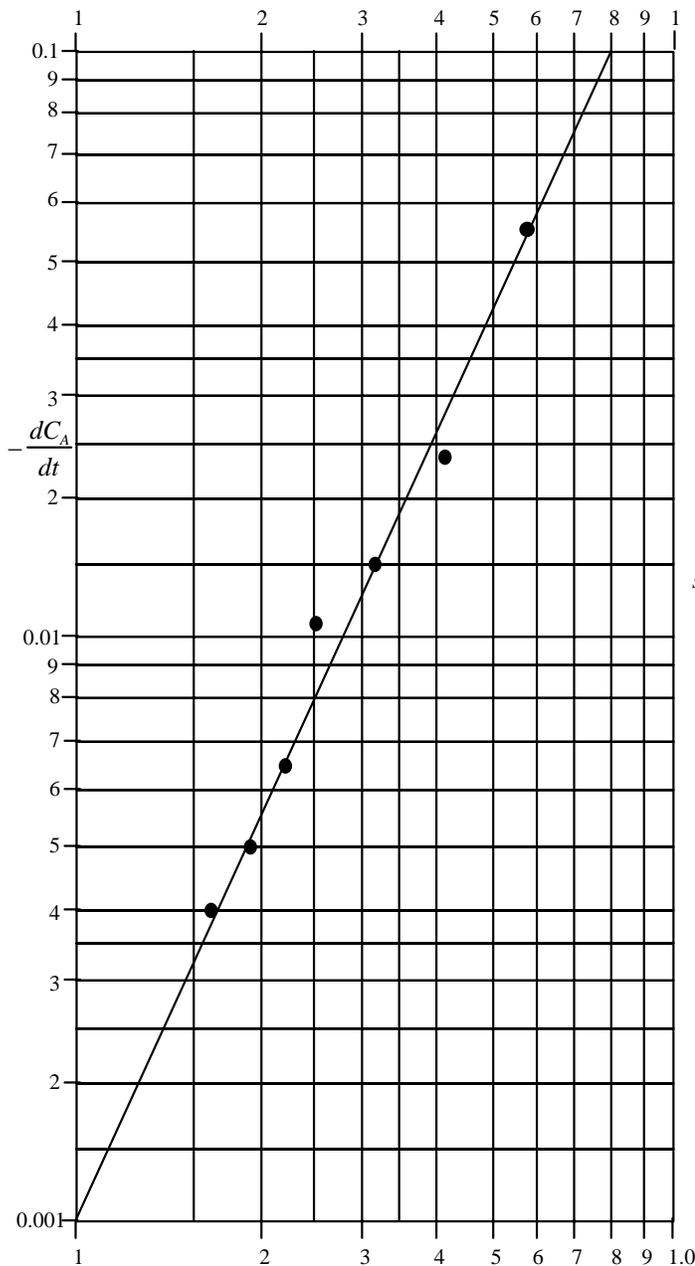
$$\log (0.0014) = \log k + 2.05 \log 0.1$$

$$\log k = \log (0.0014) - 2.05 \log 0.1$$

$$k = 10^{-0.8039} = 0.157 \left( \frac{\text{lit}}{\text{mol min}} \right)$$

However, we should quickly realize that the estimated order is only 2.5% from 2nd order and, thus, most likely the reaction is of order two.  $\alpha \equiv 2$ .  $-\frac{dC_A}{dt} = k C_A^2$ . We can now evaluate  $k$  for every data point and then average them out.

$$k = \frac{-\frac{dC_A}{dt}}{C_A^2} \quad \begin{array}{c|c|c|c|c|c|c|c} C_A & 0.58 & 0.41 & 0.32 & 0.25 & 0.22 & 0.19 & 0.16 \\ \hline k & 0.163 & 0.143 & 0.146 & 0.168 & 0.134 & 0.139 & 0.156 \end{array}$$



$$slope = \frac{\log\left(\frac{0.1}{0.0014}\right)}{\log\left(\frac{0.8}{0.1}\right)} = 2.05$$

The mean value of  $k$  turns out to be  $k = 0.150 \left(\frac{lit}{mol \min}\right)$ . Thus at the temperature of the experiment we have determined

$$-r_A \left(\frac{mol}{lit \min}\right) = 0.150 C_A^2$$

**Note:** Although the values of the rate constants calculated from various data points vary considerably, the variation is random and shows no trend with concentration level indicating that the selected order is correct.

### Integral Method:

Suppose that we have attempted to solve the same problem by the integral method. Since the stoichiometry is  $A \rightarrow \text{products}$ , we will try first whether a first order rate form can fit the data (hoping for an elementary reaction).

Assume  $\alpha = 1$ :

$$-\frac{dC_A}{dt} = k C_A$$

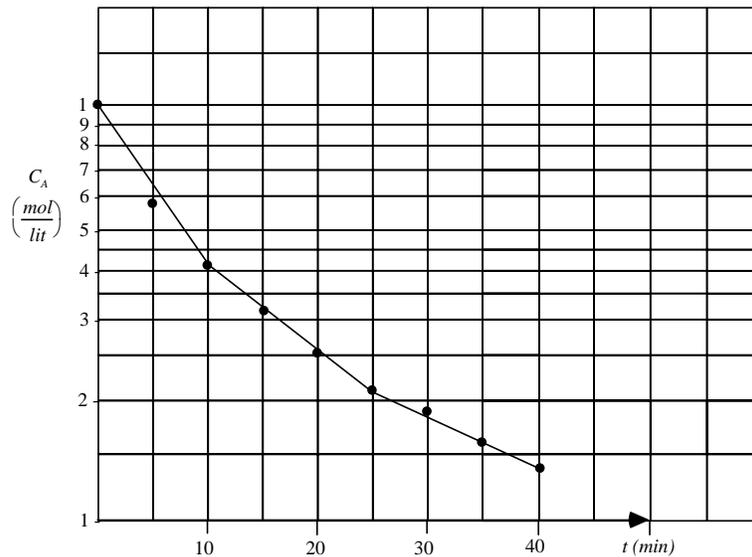
$$-\int_{C_{Ao}}^{C_A} \frac{dC_A}{C_A} = k \int_0^t dt$$

$$\ln \frac{C_{Ao}}{C_A} = kt$$

$$\log \frac{C_{Ao}}{C_A} = (2.3026)^{-1} k t$$

$$\log C_A = \log C_{Ao} - (2.3026)^{-1} k t$$

We should then plot the experimental data on a semi log plot ( $C_A$  on the log scale and  $t$  on the linear scale). If the assumed order of one is correct we should be able to obtain a straight line through the data points. It is clear from the enclosed figure that a straight line cannot be obtained since the data show a definite curve here - convex towards the bottom. If we connect the first and the last data point by a straight line all the other data are below the line indicating that the concentration drop is faster than predicted by first order behavior.



Try 2nd order  $\alpha = 2$

$$-\frac{dC_A}{dt} = k C_A^2$$

$$\frac{1}{C_A} = \frac{1}{C_{Ao}} + kt$$

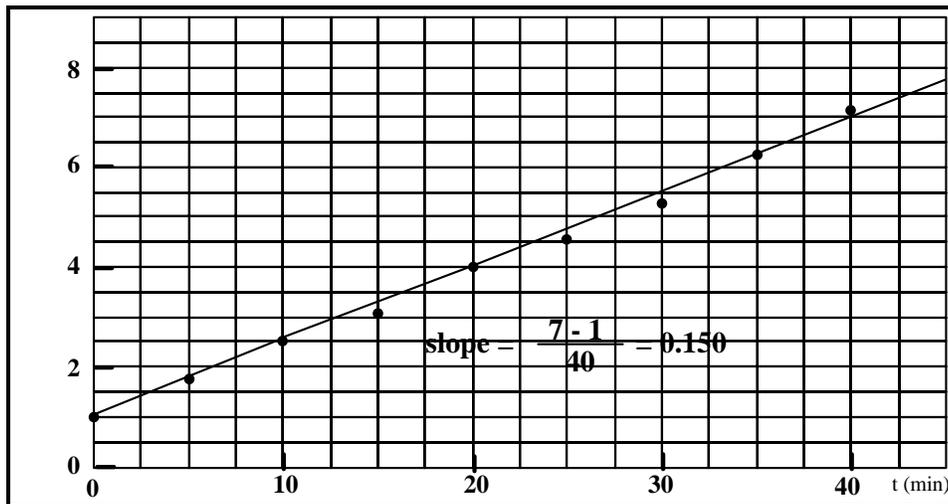
Plot  $\frac{1}{C_A}$  vs.  $t$  on a linear plot.

This time a straight line is obtained which properly intersects the ordinate at  $1 \left( \frac{1}{C_{Ao}} = 1 \right)$ . From the

slope of the line we get  $k = 0.150 \left( \frac{\text{lit}}{\text{mol min}} \right)$ .

It is instructive again to evaluate  $k$ 's from the individual data points.

$$k = \frac{1}{C_A} - \frac{1}{C_{Ao}} \quad \begin{array}{c|c|c|c|c|c|c|c|c} C_A & 0.58 & 0.41 & 0.32 & 0.25 & 0.22 & 0.19 & 0.16 & 0.14 \\ \hline k & 0.145 & 0.144 & 0.142 & 0.150 & 0.142 & 0.142 & 0.150 & 0.154 \end{array}$$



The mean value of  $k$  turns to be  $\bar{k} = 0.146 \left( \frac{\text{lit}}{\text{mol min}} \right)$  the difference between this mean value and the one obtained by "eye fitting" the line through data points is 2.7% and is negligible as far as engineering applications are concerned. Notice that the difference between the largest  $k = 0.154$  and smallest  $k = 0.142$  is only 0.012 or less than 8.5% based on the smallest  $k$ -value. For the same data the  $k$ 's evaluated by the differential method varied between a low of 0.134 and a high of 0.168, the difference being 0.034 or 25% based on the smallest  $k$ .

Thus, for the same quality data the integral method tends to smooth out the errors and give more consistent estimates for the rate constant.

Here by integral method we have determined also:

$$-r_A \left( \frac{\text{mol}}{\text{lit min}} \right) = 0.150 C_A^2$$

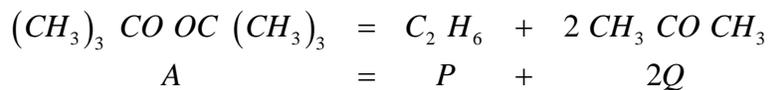
### **EXAMPLE 2:**

Gas phase decomposition of di-*t*-butyl peroxide is monitored in a batch reactor of constant volume at isothermal conditions of 170°C. The run is started with pure di-*t*-butyl peroxide and the change of total

pressure of the system was recorded in time. From the data below find the rate expression and the rate constant.

time (min)	0.0	2.5	5.0	10.0	15.0	20.0
$P(\text{mm Hg})$	7.5	10.5	12.5	15.8	17.9	19.4

The reaction is:



$$V = \text{const}, \quad T = \text{const}$$

The hypothesized rate is of the form:

$$-r_A \left( \frac{\text{mol}}{\text{lit min}} \right) = k C_A^\alpha$$

We have seen before that we can also express the rate in terms of change of the partial pressure:

$$-\tilde{r}_A \left( \frac{\text{mm Hg}}{\text{min}} \right) = k_p P_A^\alpha$$

where

$$k_p = k (RT)^{1-\alpha}$$

In a batch system of constant volume:

$$-\tilde{r}_A = - \frac{dP_A}{dt} = k_p P_A^\alpha$$

We have shown before that

$$\begin{array}{l}
 C_A = C_{A0} - \xi = \frac{P_A}{RT} \\
 C_T = C_{T0} + \left( \sum_{j=1}^s \nu_j \right) \xi = \frac{P_T}{RT} \quad \text{here} \\
 P_A = P_{A0} - \frac{P_T - P_{T0}}{2} \quad \sum \nu_j = 3 - 1 = 2
 \end{array}$$

Since in this case  $P_{A0} = P_{T0}$

$$P_A = \frac{3 P_{T_0} - P_T}{2}$$

$$\frac{1}{2} \frac{dP_T}{dt} = k_p \left( \frac{3 P_{T_0} - P_T}{2} \right)^\alpha$$

$$\boxed{\frac{dP_T}{dt} = (2^{1-\alpha} k_p) [3 P_{T_0} - P_T]^\alpha}$$

### DIFFERENTIAL ANALYSIS:

Evaluate  $\frac{\Delta P_T}{\Delta t}$ , plot vs.  $t$  a stepwise curve, from a smooth curve that has the same area underneath as the stepwise curve. Evaluate  $\frac{dP_T}{dt}$  and calculate the corresponding  $3 P_{T_0} - P_T$ . Plot  $\frac{dP_T}{dt}$  vs.  $3 P_{T_0} - P_T$  on a log-log scale. The slope gives  $\alpha$ ; from the data find  $k_p$  and  $k$  and their mean value.

The augmented table is shown below as well as the two figures (next page)

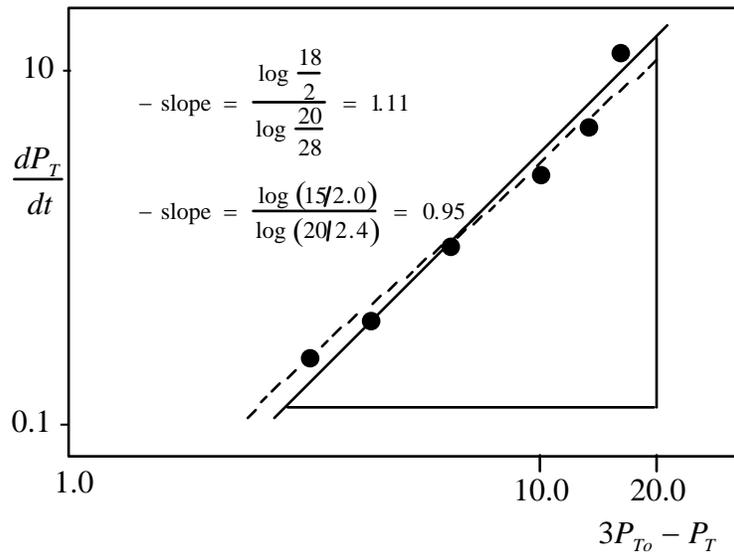
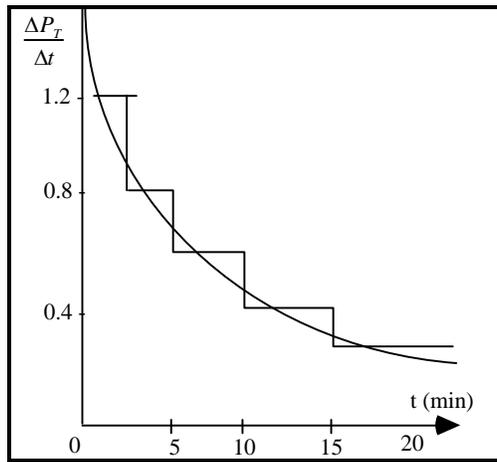
$t$	$P_T$	$\frac{\Delta P_T}{\Delta t}$	$\frac{dP_T}{dt}$	$3 P_{T_0} - P_T$	$kp$
0	7.5		1.48	15.0	0.0987
2.5	10.5	1.20	0.95	12.0	0.0792
5.0	12.5	0.80	0.75	10.0	0.0750
10.0	15.8	0.66	0.52	6.7	0.0776
15.0	17.9	0.42	0.35	4.6	0.0761
20.0	19.4	0.30	0.25	3.1	0.0806

$\bar{k}_p = 0.0812(\text{min}^{-1})$

It seems that more than one straight line can be passed through the points on the  $\log \frac{dP_T}{dt}$  vs.  $(3 P_{T_0} - P_T)$  plot. The maximum slope seems to be 1.11 and the minimum 0.95. This indicates that probably  $\alpha = 1.0$ .

$$k_p = \frac{\frac{dP_T}{dt}}{3 P_{T_0} - P_T}$$

These values are given in the last column of the above table.



From the above figures and table we find

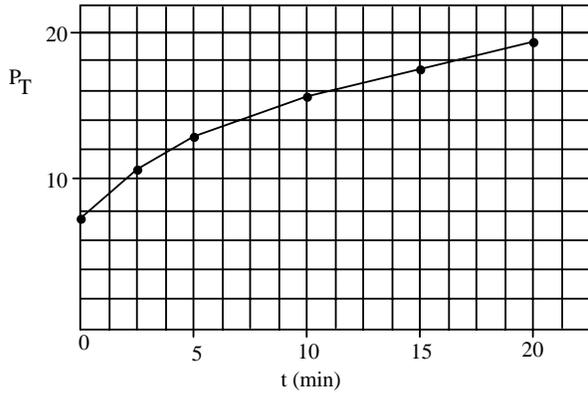
$$-\tilde{r}_A \left( \frac{\text{mm Hg}}{\text{min}} \right) = 0.0812 P_A = 0.08 P_A \text{ or } -r_A \left( \frac{\text{mol}}{\text{lit min}} \right) = 0.0812 C_A = 0.0022 P_A$$

### INTEGRAL METHOD:

Suppose we assumed zero-th order

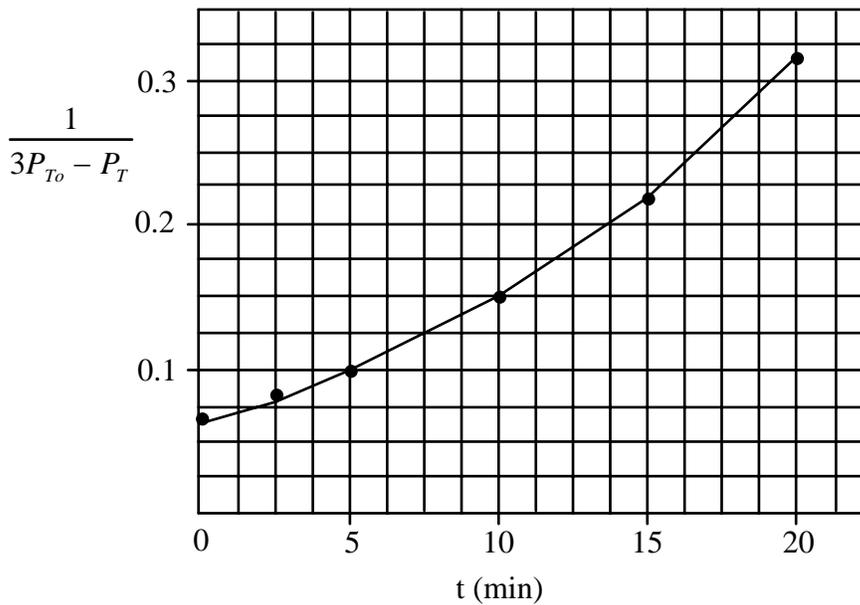
$$\frac{dP_T}{dt} = k'' \quad P_T = P_{T_0} + k'' t$$

Data shows definite curvature and reaction is not zero-th order.



Assume 2nd order:

$$\frac{dP_T}{dt} = k'' (3 P_{T_0} - P_T)^2$$
$$\frac{1}{\underbrace{3 P_{T_0} - P_T}_y} = \frac{1}{2 P_{T_0}} + k'' \frac{t}{x}$$



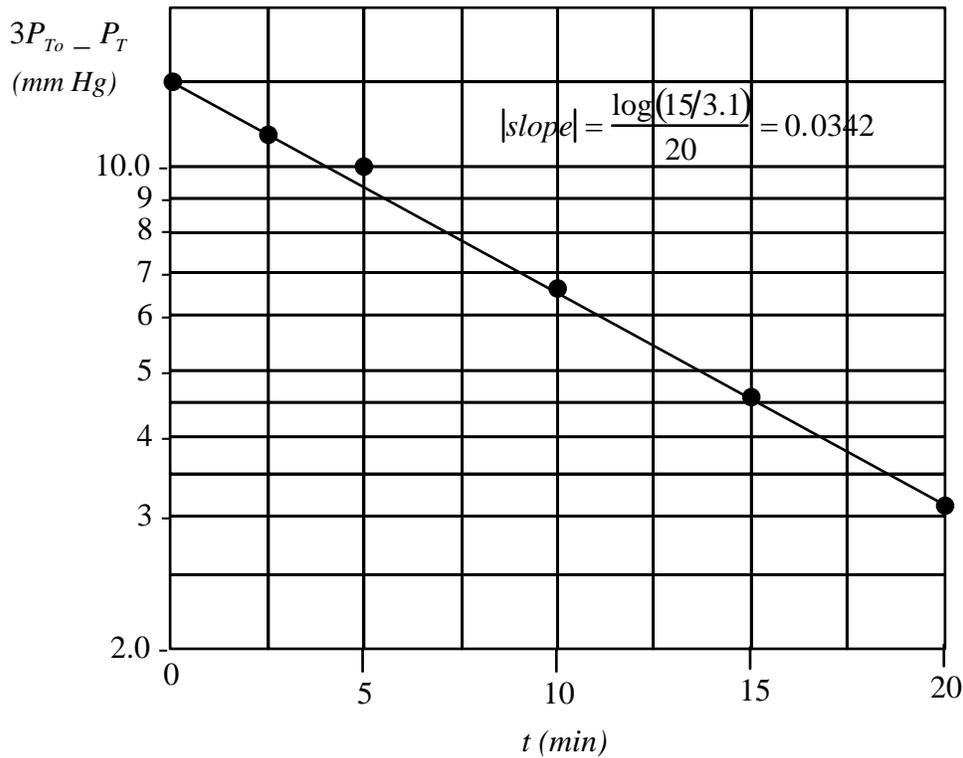
Again data show a definite curvature and the reaction is not 2nd order.

Assume 1st order

$$\frac{dP_T}{dt} = k'' (3 P_{T_0} - P_T)$$

$$\ln \left( \frac{2 P_{T_0}}{3 P_{T_0} - P_T} \right) = k'' t \quad |slope| = \frac{\log(15/3.1)}{20} = 0.0342$$

$$\log (3 P_{T_0} - P_T) = \log (2 P_{T_0}) - (2.3026)^{-1} k'' t$$



Now we do get a straight line.

$$k'' = 2.3026 |slope| = 2.3026 \times 0.0342 = 0.0787 \text{ (min}^{-1}\text{)}$$

Directly from data

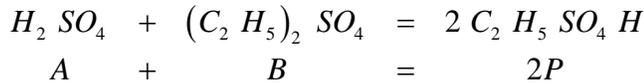
$$k_p = \frac{1}{t} \ln \frac{2 P_{T_0}}{3 P_{T_0} - P_T} = \begin{cases} 0.0893 \\ 0.0811 \\ 0.0806 \\ 0.0788 \\ 0.0788 \end{cases} \quad \bar{k}_p = 0.0817 \text{ min}^{-1}$$

$$-r_A \left( \frac{\text{mol}}{\text{lit min}} \right) = 0.08 C_A = 0.0022 P_A$$

$$-\tilde{r}_A \left( \frac{\text{mm Hg}}{\text{min}} \right) = 0.08 P_A$$

**Notice** again that the variation in the rate constant based on integral method is much less than if differential method is used.

**Example 3:** Consider the reaction between sulfuric acid and diethylsulfate in aqueous solution



At isothermal conditions ( $T = 22.9^\circ C$ ) starting with equimolar mixture of the reactants and with no product the data presented below were obtained. Initial reactant concentration was  $5.5 \text{ (mol/lit)}$  for each of them. Find the rate expression.

$t \text{ (min)}$	0	41	48	55	75	96	127	146	162
$C_p \left( \frac{\text{mol}}{\text{lit}} \right)$	0	1.18	1.38	1.63	2.24	2.75	3.31	3.76	3.81

$t \text{ (min)}$	180	194	212	267	318	368	379	410	several days
$C_p \left( \frac{\text{mol}}{\text{lit}} \right)$	4.11	4.31	4.45	4.86	5.15	5.32	5.35	5.42	5.80

Since for each mole of  $A$  reacted one gets two moles of  $P$  if the reaction went to completion one would find  $11 \text{ (mol/lit)}$  of  $P$ . Since only  $5.80 \text{ (mol/lit)}$  of  $P$  are found this indicates that the reaction is reversible.

$$C_{P_{eq}} = 5.80 \quad C_{A_{eq}} = C_{B_{eq}} = C_{A_0} - \frac{C_{P_{eq}}}{2} = 2.6$$

$$\frac{C_{A_0} - C_{A_{eq}}}{1} = \frac{C_{P_{eq}}}{2}$$

$$x_{A_e} = \frac{C_{A_0} - C_{A_{ie}}}{C_{A_0}} = \frac{C_{P_{eq}}}{2 C_{A_0}} = \frac{5.8}{2 \times 5.5} = 0.527$$

Let us assume that the reaction is 2nd order in both directions

$$R_p = \frac{dC_p}{dt} = k_f C_A C_B - k_b C_p^2$$

Since we start in stoichiometric ratio

$$C_{A_0} = C_{B_0} \text{ therefore } C_A = C_B = C_{A_0} - \frac{C_p}{2}$$

$$\frac{dC_p}{dt} = k_f \left( C_{A_0} - \frac{C_p}{2} \right)^2 - k_b C_p^2 ; t = 0 \quad C_p = 0$$

Let us use integral analysis. From the above rate expression at equilibrium

$$\left( \frac{C_p^2}{C_A C_B} \right)_{eq} = \frac{k_f}{k_b} = K = \frac{4 x_{A_e}^2}{(1 - x_{A_e})^2} = 4.98$$

We can separate the variables in the above differential equation:

$$\int_0^{C_p} \frac{dC_p}{\left( C_{A_0} - \frac{C_p}{2} \right)^2 - \frac{k_b}{k_f} C_p^2} = k_f \int_0^t dt$$

The integral on the left hand side can be promptly evaluated by using a set of integration tables. For an exercise we will integrate it here:

$$\frac{k_b}{k_f} = \frac{1}{K}$$

$$\left( \frac{1}{4} - \frac{1}{K} \right) C_p^2 - C_{A_0} C_p + C_{A_0}^2 = 0$$

Find the roots of the denominator:

$$C_{p_{1,2}} = \frac{2 C_{A_0}}{1 \mp \sqrt{\frac{4}{K}}}$$

The integrand can now be written as:

$$\frac{1}{\left( \frac{1}{4} - \frac{1}{K} \right) \left( C_p - \frac{2 C_{A_0}}{1 - \sqrt{\frac{4}{K}}} \right) \left( C_p - \frac{2 C_{A_0}}{1 + \sqrt{\frac{4}{K}}} \right)} = \frac{A}{C_p - \frac{2 C_{A_0}}{1 - \sqrt{\frac{4}{K}}}} + \frac{B}{C_p - \frac{2 C_{A_0}}{1 + \sqrt{\frac{4}{K}}}}$$

Using partial fractions and evaluating for  $A$  and  $B$  we get:

$$A = \frac{1}{C_{Ao} \sqrt{\frac{4}{K}}} = -B$$

Thus:

$$\int_0^{C_p} \frac{dC_p}{\left(\frac{1}{4} - \frac{1}{K}\right) C_p^2 - C_{Ao} C_p + C_{Ao}^2} = \frac{1}{C_{Ao} \sqrt{\frac{4}{K}}} \left\{ \int_0^{C_p} \frac{dC_p}{C_p - \frac{2 C_{Ao}}{1 - \sqrt{\frac{4}{K}}}} - \int_0^{C_p} \frac{dC_p}{C_p - \frac{2 C_{Ao}}{1 + \sqrt{\frac{4}{K}}}} \right\}$$

$$= \frac{1}{C_{Ao} \sqrt{\frac{4}{K}}} \ln \left\{ \frac{\left( C_p - \frac{2 C_{Ao}}{1 - \sqrt{\frac{4}{K}}} \right) \frac{1}{1 + \sqrt{\frac{4}{K}}}}{\left( C_p - \frac{2 C_{Ao}}{1 + \sqrt{\frac{4}{K}}} \right) \frac{1}{1 - \sqrt{\frac{4}{K}}}} \right\} = k_f t$$

After some reorganization we get:

$$\ln \left\{ \frac{(\sqrt{K} - 2) C_p - 2 \sqrt{K} C_{Ao}}{(\sqrt{K} + 2) C_p - 2 \sqrt{K} C_{Ao}} \right\} = \frac{2 k_f C_{Ao}}{\sqrt{K}} t$$

Using the previously established relationship

$$K = \frac{4 x_{Ae}^2}{(1 - x_{Ae})^2}$$

We can rewrite this in the form:

$$\ln \left[ \frac{x_{Ae} - (2 x_{Ae} - 1) x_A}{x_{Ae} - x_A} \right] = k_f C_{Ao} \frac{1 - x_{Ae}}{x_{Ae}} t$$

Using the already evaluated value of  $K$  and known  $C_{Ao}$  we should plot

$$\ln \left\{ \frac{0.232 C_p - 24.548}{4.232 C_p - 24.548} \right\} = 4.929 k_f t$$

i.e.  $y = \frac{0.232 C_p - 24.548}{4.232 C_p - 24.548}$  vs.  $t$  on a semi-log plot.

$t$	0	41	48	55	75	96	127	146	162
$y$	1	1.240	1.295	1.369	1.595	1.853	2.256	2.742	2.809
$y^1$	1	1.255	1.311	1.390	1.627	1.897	2.322	2.831	2.901

$t$	180	194	212	267	318	368	379	410
$y$	3.298	3.733	4.114	5.884	8.482	11.46	12.22	14.46
$y^1$	3.412	3.877	4.263	6.095	8.757	11.77	12.53	14.76

Suppose that we have assumed a first order reversible reaction:

$$\frac{dC_p}{dt} = k_f^1 C_A - k_b^1 C_p \qquad \frac{k_f^1}{k_b^1} = K^1 = \frac{C_{P_{eq}}}{C_{A_{eq}}} = \frac{2 x_{Ae}}{1 - x_{Ae}}$$

upon integration  $K^1 = 2.23$

$$\ln \left[ \frac{C_{A_0}}{C_{A_0} - \left( \frac{1}{2} + \frac{1}{K^1} \right) C_p} \right] = k_f^1 \left( \frac{1}{2} + \frac{1}{K^1} \right) t$$

$$\ln \left( \frac{1}{1 - 0.172 C_p} \right) = 0.948 k_f^1 t$$

or in alternative form:

$$\ln \left( \frac{x_{Ae}}{x_{Ae} - x_A} \right) = \frac{k_f^1}{2 x_{Ae}} t$$

Now if we expect this rate form to hold we should also get a straight line on a semi-log plot of

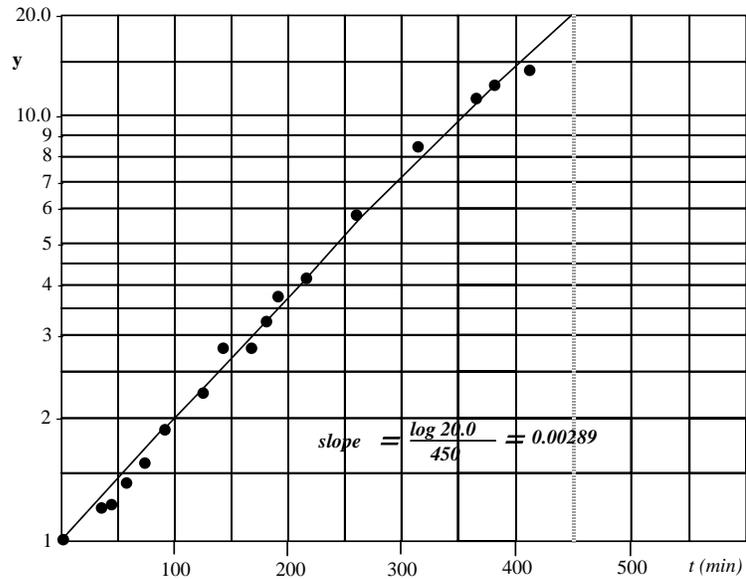
$y^1 = \frac{1}{1 - 0.172 C_p}$  vs.  $t$ . The values of  $y^1$  are also calculated in the table on the previous page.

Both forms are plotted on semi-log paper on the next page and both yield a reasonable straight line!?! Apparently from the experimental data given we are unable to distinguish between a reversible 2nd order reaction in both directions and a reversible first order reaction in both directions. If we consider again the two integrated forms written in terms of conversion we can readily see that when  $x_{Ae} = 0.5$  the two forms become identical and indistinguishable from each other. Since under the conditions of the experiment equilibrium conversion was  $x_{Ae} = 0.527$ , which is close to 0.5, due to experimental scatter we cannot distinguish between the two forms.

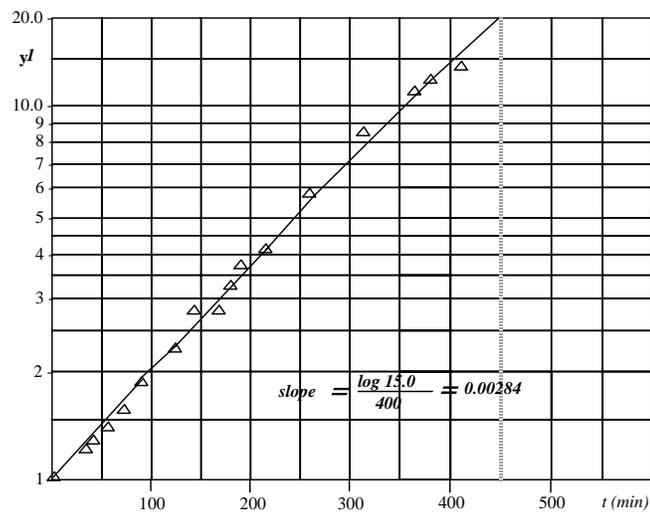
If we performed the experiments at different  $T$  so that  $x_{Ae}$  is far from 0.5; or if we used nonstoichiometric ratio of reactants, we would find that the rate indeed is 2nd order in each direction. It is important to determine the proper order since when designing a larger reactor we may be operating at

conditions when  $x_{Ae} \gg 0.5$  and the predictions of the reactor size for a desired production rate will differ vastly based on the rate form.

**Plot for 2nd order reversible:**



**Plot for 1st order reversible:**



From the slope for the 2nd order rate form we get the value of the rate constant  $k_f$ .

$$\frac{4.929}{2.3026} k_f = \text{slope} = 0.00289$$

$$k_f = \frac{0.00289 \times 2.3026}{4.929} = 1.35 \times 10^{-3} \left( \frac{\text{lit}}{\text{mol min}} \right)$$

Then  $\frac{k_f}{k_b} = K$

$$k_b = \frac{k_f}{K} = \frac{1.35 \times 10^{-3}}{4.98} = 2.71 \times 10^{-3} \left( \frac{\text{lit}}{\text{mol min}} \right)$$

The rate in ( $\text{mol/lit min}$ ) is given by the above expression at  $T = 22.9^\circ\text{C}$ . The temperature dependence of the constants would have to be found by performing experiments at different temperatures.

**Caution:** A note of caution is here in order. The integrated expression that we used for a reversible 2nd order reaction of the type  $A + B = 2P$  was:

$$\ln \left[ \frac{x_{Ae} - (2x_{Ae} - 1)x_A}{x_{Ae} - x_A} \right] = k_f \frac{1 - x_{Ae}}{x_{Ae}} C_{A0} t$$

**Note 1:** This expression is only valid when the experiment is performed with stoichiometric ratio of  $A$  and  $B$ . It is not valid when  $C_{A0} \neq C_{B0}$ .

**Note 2:** The expression for the same reaction type is reported by Levenspiel (page 63, equation 56) and it looks almost exactly the same as the one above except that it has an extra factor of 2 on the right hand side.

**Question:** Is there a mistake? Note that  $k_f$  and  $k_1$  in the book (which are rate constants for the reaction forward) will differ by a factor of two!!?

**Answer:** There is no mistake but  $k_f$  is based on production of  $P$  while  $k_1$  is based on disappearance of  $A$ . Since due to stoichiometry  $\frac{-r_A}{1} = \frac{r_P}{2}$  this implies  $k_1 = \frac{k_f}{2}$   
 $k_f = 2k_1$  which indeed is the case.

**Potential Trouble:**

The choice of the subscript  $f$  or 1 etc. does not indicate on which component the rate constant is based. Thus, if one has only an integrated form to work with, one has no way of knowing whether  $k_1$  is based on reactant or product, etc. Clarify that whenever possible.

**Note 3:** Since the above mentioned ambiguity about rate constants always exists try to:

- use integrated forms only when you know what the  $k$ 's are based on;
- develop your own integrated forms by the help of integral tables.

This last choice after all is not that difficult. In the problem that we just solved we had to integrate

$$\int_0^{C_p} \frac{dC_p}{\left(C_{Ao} - \frac{C_p}{2}\right)^2 - \frac{1}{K} C_p^2} = \int_0^{C_p} \frac{dC_p}{\left(\frac{1}{4} - \frac{1}{K}\right) C_p^2 - C_{Ao} C_p + C_{Ao}^2} = k_f t$$

A quick look in the CRC Mathematical Tables shows that we have a problem of the type

$$\int \frac{dx}{y} \quad \text{where } x = C_p$$

$$y = a + bx + cx^2$$

$$a = C_{Ao}^2$$

$$b = -C_{Ao}$$

$$c = \frac{1}{4} - \frac{1}{K}$$

**The answer is:**

$$\int \frac{dx}{y} = \frac{1}{\sqrt{-q}} \ln \frac{2cx + b - \sqrt{-q}}{2cx + b + \sqrt{-q}}$$

where  $q = 4ac - b^2$

Thus in our case  $q = -\frac{4 C_{Ao}^2}{K}$ .

Substitute proper terms for  $q$ ,  $c$ ,  $a$ ,  $b$  and  $x$  in the above expression.

**Caution:** Do not forget to evaluate the above expression at the upper and lower limit of integration (expression at upper limit - expression of lower limit) since you started with a definite integral and CRC Tables gives you the answer for an indefinite one. You should get the expression used in the problem.

## 10.5 Precision of Kinetic Measurements

Random errors can never be completely avoided in kinetic measurements but we can often estimate the maximum possible error in our measurements of concentrations, temperature fluctuations, etc.

In general, if we are interested in obtaining values of a dependent variable  $f$  from values of independent variables  $x_i$ ,  $i = 1, 2, \dots$

where  $f = f(x_1, x_2, x_3, \dots)$

the relative error in  $f$  can be related to the relative errors in  $x_i$  by

$$\left(\frac{\Delta f}{f}\right)^2 = \sum_{j=1}^n \left(\frac{\partial \ln f}{\partial \ln x_j}\right)^2 \left(\frac{\Delta x_j}{x_j}\right)^2 \quad (57)$$

Suppose we are interested in the accuracy of the rate constant which we have obtained from the following expression:

$$k = \frac{-r_A}{C_A C_B} \quad (58)$$

$$\ln k = \ln(-r_A) - \ln C_A - \ln C_B \quad (59)$$

$$\frac{\partial \ln k}{\partial \ln(-r_A)} = 1 \quad \frac{\partial \ln k}{\partial \ln C_A} = -1 \quad \frac{\partial \ln k}{\partial \ln C_B} = -1 \quad (60)$$

$$\left(\frac{\Delta k}{k}\right)^2 = \left(\frac{\Delta(-r_A)}{(-r_A)}\right)^2 + \left(\frac{\Delta C_A}{C_A}\right)^2 + \left(\frac{\Delta C_B}{C_B}\right)^2 \quad (61)$$

If we measured each concentration with precision better than 2% and the precision of the rate measurements is 10% we get

$$\left(\frac{\Delta k}{k}\right)^2 = 0.1^2 + 0.02^2 + 0.02^2 = 0.0108 \quad (62)$$

$$\frac{\Delta k}{k} = 0.1039 \quad (63)$$

The error in  $k$  is 10.4%

From the Arrhenius relationship we see

$$\left(\frac{dk}{k}\right) = \frac{E}{RT} \left(\frac{dT}{T}\right) \quad (64)$$

The larger the error in  $T$  and the larger the activation energy,  $E$ , the larger the error in  $k$ .

We usually estimate  $E$  from

$$\frac{E}{R} = \frac{\ln(k_1/k_0)}{\frac{1}{T_0} - \frac{1}{T_1}} \quad (65)$$

$$\ln \frac{E}{R} = \ln [\ln(k_1/k_0)] - \ln \left(\frac{1}{T_0} - \frac{1}{T_1}\right) \quad (66)$$

$$\left(\frac{\Delta E}{E}\right)^2 = \left(\frac{1}{\ln k_1/k_0}\right)^2 \left[\left(\frac{\Delta k_0}{k_0}\right)^2 + \left(\frac{\Delta k_1}{k_1}\right)^2\right] + \left(\frac{T_1}{T_0 - T_1}\right)^2 + \left(\frac{T_0}{T_0 - T_1}\right)^2 \left(\frac{\Delta T_1}{T_1}\right)^2 \quad (67)$$

The larger the interval  $T_1 - T_0$  the smaller the error in  $E$  provided that classical Arrhenius form with  $E = \text{const}$  holds over such a temperature range.

Useful guidelines can be found in Benson, Foundations of Chemical Kinetics.

To obtain the rate constant with an error of  $\pm \varepsilon$  it is necessary:

1. To measure the concentration with an accuracy

$$\pm \frac{\text{Change in concentration}}{\text{Largest concentration}} \frac{\varepsilon}{1.4} \%$$

2. To measure time (or equivalent) with accuracy of

$$\pm \frac{\text{Time interval}}{\text{Largest time}} \frac{\varepsilon}{1.4} \%$$

3. To measure temperature with an accuracy of

$$\pm \frac{\varepsilon}{35} \% = \pm \frac{\varepsilon T}{3500} T \text{ in } K$$

## 5.6 Estimation of kinetic parameters in more complex reaction systems

So far we have dealt with single reactions only, yet an engineer will almost always encounter a problem involving multiple-mixed reactions. Nevertheless the methods described so far can often be utilized, if adequate amount of experimentation can be obtained, to estimate at least some of the kinetic parameters.

The method of half-time is often utilized to:

- a. **evaluate the overall order of reaction (single reaction) by using all reactants in stoichiometric ratio;**
- b. evaluate the order with respect to  $A$  when other reactants are used in excess.

The assumption is that the reaction is irreversible and follows n-th order behavior

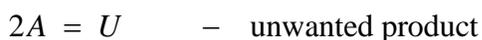
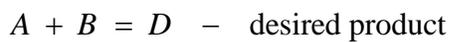
$$-\frac{dC_A}{dt} = k C_A^\alpha \quad - \int_{C_{Ao}}^{C_{Ao}/2} \frac{dC_A}{C_A^\alpha} = kt_{1/2} \quad (68)$$

$$t_{1/2} = \frac{2^{\alpha-1} - 1}{k(\alpha-1)} C_{Ao}^{1-\alpha} \quad (69)$$

$$\underbrace{\log t_{1/2}}_y = \log \left\{ \frac{2^{\alpha-1} - 1}{k(\alpha-1)} \right\} + (1-\alpha) \underbrace{\log C_{Ao}}_x \quad (70)$$

Starting with different  $C_{Ao}$ 's and measuring the time that it takes for  $C_{Ao}$  to drop to  $C_{Ao}/2$  and by plotting  $t_{1/2}$  vs.  $C_{Ao}$  on a log-log plot one can determine overall order  $\alpha$  and rate constant  $k$ .

When investigating multiple reactions in batch systems of constant volume we have to monitor as many variables as there are independent reactions in the system. For example, if we are studying the rates in a system of the type



we could monitor  $C_A$  and  $C_D$  in time. If the experiments are performed in a constant volume batch system and if we assume n-th order rate forms we have to evaluate the parameters  $k_{1f}$ ,  $k_{1b}$ ,  $k_{2f}$ ,  $k_{2b}$ ,  $\alpha$ ,  $\alpha_2$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  which appear in the following description of the systems component mass balance:

$$-\frac{dC_A}{dt} = k_{1f} C_A^{\alpha_1} C_B^\beta - k_{1b} C_D^\delta + 2k_{2f} C_A^{\alpha_2} - k_{2b} C_U^\gamma \quad (71)$$

$$\frac{dC_D}{dt} = k_{1f} C_A^{\alpha_1} C_B^\beta - k_{1b} C_D^\delta \quad (72)$$

We could again perform the experiments at low conversions of A and B so as to measure the initial rates in the region where reverse rates can be neglected. Then:

$$-\frac{dC_A}{dt} = k_{1f} C_A^{\alpha_1} C_B^\beta + 2k_{2f} C_A^{\alpha_2} \quad (73)$$

$$\frac{dC_D}{dt} = k_{1f} C_A^{\alpha_1} C_B^\beta \quad (74)$$

By forming the expression for a point yield  $y \left( \frac{D}{A} \right)$  we get:

$$y \left( \frac{D}{A} \right) = \frac{dC_D}{-dC_A} = \frac{1}{1 + \frac{2k_{2f}}{k_{1f}} C_A^{\alpha_2 - \alpha_1} C_B^{-\beta}} \quad (75)$$

The stoichiometry of the reaction dictates:

$$\begin{aligned} C_A &= C_{A_0} - \xi_1 - 2\xi_2 & C_D &= C_{D_0} + \xi_1 \\ C_B &= C_{B_0} - \xi_1 & C_U &= C_{U_0} + \xi_2 \end{aligned}$$

Eliminating the extents  $\xi_1$ ,  $\xi_2$  in terms of measured concentrations we get:

$$\xi_1 = C_D - C_{D_0} = C_D \text{ since } C_{D_0} = 0 \text{ was selected}$$

$$\xi_2 = \frac{1}{2} (C_{A_0} - C_A - C_D)$$

Thus  $C_B = C_{B_0} - C_D$

$$\frac{dC_D}{-dC_A} = \frac{1}{1 + \frac{2k_{2f}}{k_{1f}} C_A^{\alpha_2 - \alpha_1} (C_{B_0} - C_D)^{-\beta}} \quad (76)$$

If in addition we perform the experiment with large excess of B, then  $C_{B_0} \gg C_D$

$$\frac{dC_D}{-dC_A} = \frac{1}{1 + \frac{2k_{2f} C_{B_0}^{-\beta}}{k_{1f}} C_A^{\alpha_2 - \alpha_1}} \quad (77)$$

$$\frac{dC_A}{-dC_D} - 1 = \frac{2k_{2f}}{k_{1f} C_{Bo}^\beta} C_A^{\alpha_2 - \alpha_1} \quad (78)$$

$$\log \left( -\frac{dC_A}{dC_D} - 1 \right) = \log \left( \frac{2k_{2f}}{k_{1f} C_{Bo}^\beta} \right) + (\alpha_2 - \alpha_1) \log C_A \quad (79)$$

From  $C_A$  vs.  $C_D$  data we can get estimates of  $-\frac{dC_A}{dC_D}$  as shown before, and by plotting the quantities indicated above on a semi-log plot we get a slope of  $\alpha_2 - \alpha_1$ .

Working now at moderate levels of  $C_{Bo}$  so that  $C_{Bo} - C_D \neq C_{Bo}$  we can plot for the new set of experiments

$$\log \underbrace{\left( \frac{-\frac{dC_A}{dC_D} - 1}{C_A^{\alpha_2 - \alpha_1}} \right)}_y = \log \left( \frac{2k_{2f}}{k_{1f}} \right) - \beta \log \underbrace{(C_{Bo} - C_D)}_x \quad (80)$$

From the slope one can get  $\beta$  and from all points an average for  $2k_{2f}/k_{1f}$ .

Now one can use  $C_D$  vs.  $t$  data  $C_A$  vs.  $t$

$$-\frac{dC_D}{dt} = k_{1f} C_A^{\alpha_1} C_B^\beta - k_{1f} C_A^{\alpha_1} (C_{Bo} - C_D)^\beta \quad (81)$$

$$\log \underbrace{\left( \frac{-\frac{dC_D}{dt} - 1}{(C_{Bo} - C_D)^\beta} \right)}_y = \log k_{1f} + \alpha_1 \log \underbrace{(C_A)}_x \quad (82)$$

From the slope  $\alpha_1$  is determined and from the data points an average value of  $k_{1f}$ . Now since  $\alpha_2 - \alpha_1$ , and  $\frac{k_{2f}}{k_{1f}}$  are already known, also  $k_{2f}$  and  $\alpha_2$  can be evaluated.

The above served to demonstrate that the differential method of analysis, as illustrated for single reactions, can also be used in more complex reaction schemes. In order to do so one needs to plan the experiments in a proper way and manipulate the data properly.

Similarly for many practical reaction orders of interest the expression for the yield can be integrated and integral analysis can be applied. For example if we guess

$$\alpha_2 = 1 = \alpha_1 = 1 \quad \beta = 1$$

$$-\frac{dC_D}{dC_A} = \frac{1}{1 + \frac{2k_{2f}}{k_{1f}} C_B^{-1}} = \frac{1}{1 + \frac{2k_{2f}}{k_{1f}} (C_{Bo} - C_D)^{-1}} \quad (83)$$

$$\int_0^{C_D} \left[ 1 + \frac{2k_{2f}}{k_{1f}} (C_{Bo} - C_D)^{-1} \right] dC_D = - \int_{C_{Ao}}^{C_A} dC_A \quad (84)$$

$$C_D + \frac{2k_{2f}}{k_{1f}} \ln \left( \frac{C_{Bo}}{C_{Bo} - C_D} \right) = C_{Ao} - C_A \quad (85)$$

Thus, if the hypothesized orders  $\alpha_2 = \alpha_1 = 1 = \beta$  are correct, then a plot of

$$\underbrace{\ln \left( \frac{C_{Bo}}{C_{Bo} - C_D} \right)}_y = \frac{k_{1f}}{2k_{2f}} \underbrace{(C_{Ao} - C_A - C_D)}_x \quad (86)$$

should yield a straight line with a slope  $\frac{k_{1f}}{2k_{2f}}$ .

If we guessed  $\alpha_2 = 2, \alpha_1 = \beta = 1$  we would have to integrate:

$$- \frac{dC_D}{dC_A} = \frac{1}{1 + \frac{2k_{2f}}{k_{1f}} C_A (C_{Bo} - C_D)^{-1}} \quad (87)$$

which upon integration yields

$$\left[ \frac{C_{Bo} - C_D}{C_{Bo}} \right]^{-\frac{2k_{2f}}{k_{1f}}} = \frac{C_{Ao} - \frac{k_{1f}}{k_{1f} - 2k_{2f}} C_{Bo}}{C_A - \frac{k_{1f}}{k_{1f} - 2k_{2f}} (C_{Bo} - C_D)} \quad (88)$$

Now it is difficult to rewrite the result in a form which would yield a straight line plot in a properly selected coordinate system.

Clearly when dealing with multiple reactions a point is reached very fast when conventional methods of integral analysis become tedious and often impossible to use. In such a situation one must perform a sufficient number of experiments so that some statistical parameter estimation methods can be used. The initial estimates may frequently be obtained by differential analysis as presented above.

## 10.7. Parameters in systems of monomolecular reactions

In many complex reaction schemes there often is some indication that most or even all reactions can be considered to be first order. (The same assumption is frequently arbitrarily made, since this simplifies tremendously the treatment of the system, and this is to be avoided). For  $M$  independent first order reversible reactions between  $S$  species in a batch system of constant volume one can write:

$$\frac{dC_1}{dt} = \left( - \sum_{j=2}^S k_{j1} \right) C_1 + k_{12} C_2 + k_{13} C_3 + \dots + k_{1s} C_s \quad (89a)$$

$$\frac{dC_2}{dt} = k_{21} C_1 \left( - \sum_{\substack{j=1 \\ j \neq 2}}^S k_{j2} \right) C_2 + k_{23} C_3 + \dots + k_{2s} C_s \quad (89b)$$

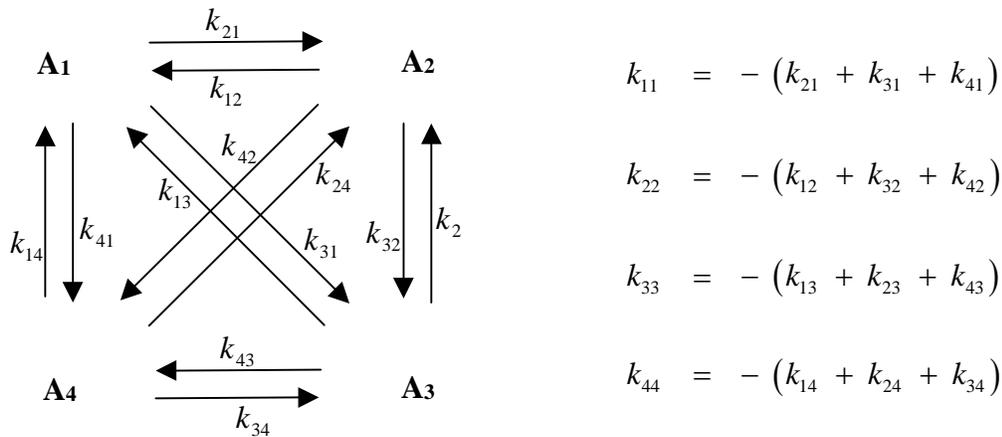
$$\frac{dC_s}{dt} = k_{s1} C_1 + k_{s2} C_2 + k_{s3} C_3 + \dots + \left( - \sum_{\substack{j=1 \\ j \neq s}}^S k_{sj} \right) C_s \quad (89c)$$

where  $k_{ji}$  is the rate constant for the rate for formation of component  $j$  in reaction  $A_i \rightarrow A_j$ . For example,  $k_{12}$  is the rate constant for the rate of formation of species 1 in reaction  $A_2 \rightarrow A_1$ . The reversible rate is viewed for each species as rate of formation - rate of disappearance. Thus, to obtain the accumulation of say species 1,  $\frac{dC_1}{dt}$ , we have to sum over the rates of formation of 1 in all reactions

where 1 appears. Then  $\sum_{j=2}^S k_{j1}$  is the sum of the rate constants for rates of formation of species  $j$  from species 1 summed up over all species  $j$ . This properly appears with the negative sign since it is equal to disappearance of species 1. We could arbitrarily define  $k_{11} = - \sum_{j=2}^S k_{j1}$  or in general

$$k_{ii} = - \sum_{\substack{j=1 \\ j \neq i}}^S k_{ji}.$$

The above scheme considers the possibility that every species in the system can produce all the others or be produced from them. For example:



Naturally the above form is the most general one and in specific situations many constants can be a priori set to be zero.

The problem in matrix form is:

$$\frac{d\underline{C}}{dt} = \underline{K} \underline{C}; \quad t = 0 \quad \underline{C} = \underline{C}_0 \quad (90)$$

where

$$\underline{C} = \begin{bmatrix} C_1 \\ C_2 \\ \cdot \\ \cdot \\ C_s \end{bmatrix} \quad \underline{K} = \begin{bmatrix} k_{11} & k_{12} \dots & k_{1s} \\ k_{21} & k_{22} \dots & k_{2s} \\ \dots & \dots & \dots \\ k_{s1} & k_{s2} \dots & k_{ss} \end{bmatrix}$$

with  $k_{ii} = - \sum_{\substack{j=1 \\ j \neq i}}^s k_{ji}$

Most often in order to deal with unit vectors every row is divided by  $C_{TOT}$ , total molar concentration, and the equations are written in terms of mole fractions:

$$y_j = \frac{C_j}{C_{TOT}} \quad (91)$$

$K$  is ( $s \times s$ ) matrix of rate constants.

$$\frac{d\underline{y}}{dt} = \underline{K} \underline{y}; \quad t = 0 \quad \underline{y} = \underline{y}_o \quad (92)$$

The problem is as follows:

From a continuous record of  $\underline{y}$  vs.  $t$  (or from a set of  $N$  discrete measurements of  $\underline{y}$  at  $t_l, l = 1, 2, \dots, N$  where  $N \gg S$ ) determine the constants comprising the matrix  $\underline{K}$ .

An elegant and useful theory of monomolecular reactions of this type was developed by Wei and Prater [Advances in Catalysis 13, 203-392 (1962)] and is also presented in abbreviated form by Boudart, M. "Kinetics of Chemical Processes", Chapter 10, p. 210, Prentice Hall, N.J., 1968.

Basically the theory states that since  $\underline{K}$  is an ( $s \times s$ ) positive definite matrix it must have  $S$  real eigenvalues  $\lambda_m, m = 0, 1, 2, \dots, s - 1$ . To each eigenvalue corresponds a particular eigenvector  $\underline{x}_m$  so that the following matrix equation is satisfied:

$$\underline{K} \underline{X} = \underline{X} \underline{\Lambda} \quad \text{or} \quad \underline{K} \underline{x}_m = - \underline{x}_m \quad (93)$$

where  $\underline{X} = [\underline{x}_0 \ \underline{x}_1 \ \underline{x}_2 \ \dots \ \underline{x}_{s-1}] = \begin{bmatrix} x_{01} & x_{11} & x_{s-1, 1} \\ x_{02} & x_{12} & x_{s-1, 2} \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ x_{0s} & x_{1s} & x_{s-1, s} \end{bmatrix} \quad (94)$

$$- \underline{\Lambda} = \begin{bmatrix} \lambda_0 & 0 & 0 & \cdot & \cdot & 0 \\ 0 & \lambda_1 & 0 & \cdot & \cdot & 0 \\ 0 & 0 & \lambda_2 & \cdot & \cdot & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & \cdot & \cdot & \lambda_{s-1} \end{bmatrix} = \text{diagonal matrix} \quad (95)$$

Thus the matrix  $\underline{\underline{K}}$  maps every eigenvector  $\underline{x}_m$  onto itself augmented by a "stretching" factor  $\lambda_m$ . Eigenvectors  $\underline{x}_m$  establish the characteristic directions for the matrix  $\underline{\underline{K}}$ , eigenvalues  $\lambda_m$  give the scale factors in these directions.

If one selects now

$$\underline{y} = \underline{\underline{X}} \underline{b} \quad \underline{b} = \begin{bmatrix} -b_0 \\ b_1 \\ b_{s-1} \end{bmatrix} \quad (96)$$

$$\frac{d\underline{y}}{dt} = \underline{\underline{X}} \frac{d\underline{b}}{dt} = \underline{\underline{K}} \underline{y} = \underline{\underline{K}} \underline{\underline{X}} \underline{b} \quad (97)$$

Premultiplying both sides with  $\underline{\underline{X}}^{-1}$

$$\underline{\underline{X}}^{-1} \underline{\underline{X}} \frac{d\underline{b}}{dt} = \underline{\underline{X}}^{-1} \underline{\underline{K}} \underline{\underline{X}} \underline{b} \quad (98)$$

and remembering

$$\underline{\underline{X}}^{-1} \underline{\underline{X}} = \underline{\underline{I}} \quad \text{Identity matrix} \quad (99)$$

$$\underline{\underline{K}} \underline{\underline{X}} = \underline{\underline{X}} \underline{\underline{\Lambda}} \quad (100)$$

we get

$$\frac{d\underline{b}}{dt} = \underline{\underline{\Lambda}} \underline{b} \quad t=0 \quad \underline{b} = \underline{b}_0 = \underline{\underline{X}}^{-1} \underline{y}_0 \quad (101)$$

This is a decoupled matrix equation

$$\begin{aligned} \frac{db_0}{dt} &= -\lambda_0 b_0 & b_0 &= b_{00} e^{-\lambda_0 t} \\ \frac{db_1}{dt} &= -\lambda_1 b_1 & b_1 &= b_{10} e^{-\lambda_1 t} \\ \frac{db_{s-1}}{dt} &= -\lambda_{s-1} b_{s-1} & b_{s-1} &= b_{s-10} e^{-\lambda_{s-1} t} \end{aligned} \quad (102)$$

The above matrix manipulation shows that in principle one can find a set of  $S$  fictitious components  $\underline{B}$  so that the equations for quantities of  $\underline{B}$ ,  $\underline{b}$ , are uncoupled and can be solved one by one. Furthermore at equilibrium:

$$\frac{d\underline{y}_{eq}}{dt} = \underline{0} = \underline{\underline{K}} \underline{y}_{eq} \quad (103)$$

$$\text{Remember } -\lambda_m \underline{x}_m = \underline{\underline{K}} \underline{x}_m, \quad m = 0, 1, 2, \dots, s-1 \quad (104)$$

Thus the first eigenvector can be selected as the equilibrium composition:

$$\underline{x}_0 = \underline{y}_{eq} \quad \text{and} \quad b_0 = b_{00} = \text{const} = 1 \quad (105)$$

and the first eigenvalue is zero  $\lambda_0 = 0$

Thus

$$\begin{aligned} \underline{y} &= \underline{x} \underline{b} = b_0 \underline{x}_0 + b_1 \underline{x}_1 + b_2 \underline{x}_2 + b_3 \underline{x}_3 \dots \\ \underline{y} - \underline{y}_{eq} &= b_1 \underline{x}_1 + b_2 \underline{x}_2 + b_3 \underline{x}_3 \dots + b_{s-1} \underline{x}_{s-1} \\ &= b_{10} e^{-\lambda_1 t} \underline{x}_1 + b_{20} e^{-\lambda_2 t} \underline{x}_2 + \dots + b_{s-1} e^{-\lambda_{s-1} t} \underline{x}_{s-1} \end{aligned} \quad (106)$$

This describes the decay of deviations from equilibrium. Each eigenvector  $\underline{x}_m$  is a direction in space, and the right hand side of the equation represents all contributions that make up the reaction paths.

A good choice of initial compositions  $\underline{y}_0$ , so that say  $b_{10} \neq 0$  but  $b_{20} = b_{30} = b_{40} = \dots = 0$ , would yield a straight line reaction path in the direction of  $\underline{x}_1$ .

Thus when one knows the rate constants  $k_{ji}$  one can compute all  $\lambda_m$ 's and corresponding  $\underline{x}_m$ 's, find the  $\underline{b}$  vector and determine all the straight line reactions paths.

However, this theory is helpful even when  $k_{ji}$  are not known and are sought since it provides the guidelines for searching for straight line reaction paths. Once these are experimentally established semi log plots of  $\frac{b_i}{b_{i0}}$  vs.  $t$  give all the eigenvalues  $\lambda_m$ .

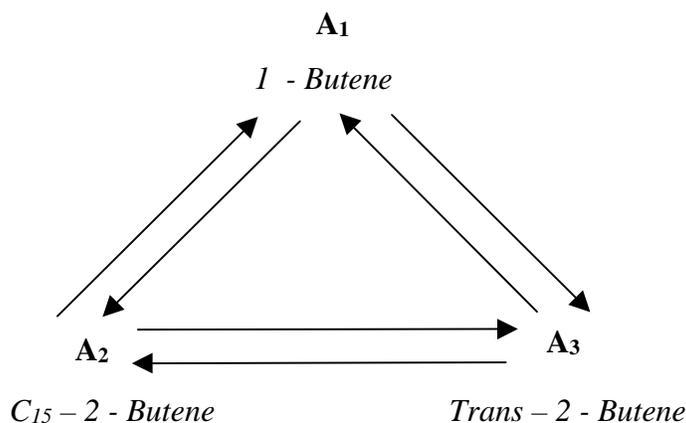
$$\ln \frac{b_1}{b_{10}} = -\lambda_1 t \quad (107)$$

$$\ln \frac{b_2}{b_{20}} = -\lambda_2 t \quad (108)$$

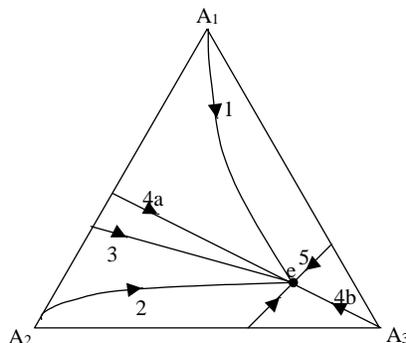
From the eigenvalues  $\lambda_m$ , by simple matrix manipulation,  $k_{ji}$  are determined.

Since  $y_m$ ,  $m = 1, 2, \dots, s$  are measured as a function of time and  $b_m$ ,  $m = 0, 1, 2, \dots, s - 1$ , are obtainable from  $y_m$ 's only if  $k_{ji}$ 's are known, which they are not, this means that one has to use a trial and error method and search for suitable combinations of  $y_{i0}$ 's giving the desired straight line reaction paths from which  $\lambda_n$  and  $b_i$ 's can be determined leading to evaluation of  $k_{ji}$ 's.

One of the best examples is the classical analysis of the isomerization of butane on alumina which was studied extensively by Haag & Pines and Lago & Haag and was used by Wei & Prater to illustrate the power of their method.



Let us describe now a set of experiments and the use of Wei-Prater technique. We will follow the reaction path for every experiment on the triangular composition diagram. In the first experiment (path 1) start with pure  $A_1$  and let the system reach equilibrium. The equilibrium composition of point  $e$  establishes the zeroth eigenvector  $\underline{x}_0$  for  $\lambda_0 = 0$ . Since path 1 is not straight we know that pure  $A_1$  is not a component of  $\underline{b}$ .



We can now perform an experiment starting with pure  $A_2$  (path 2). Since this does not yield a straight line we know that pure  $A_2$  is not a component of  $\underline{b}$  vector. However, Wei and Prater method shows how to use the data from path 2 close to equilibrium in order to extrapolate to the side of the triangle and select a new starting composition for run 3. Run 3 (path 3) does not give a straight line but with one more correction leads to starting point for run 4. Path 4a is a straight line, thus, the composition on the side of the triangle determines  $b_{10}$  and  $\lambda_1$  can be found from  $\ln \frac{b_1}{b_{10}} = -\lambda_1 t$ . However, a run 4b from

pure  $A_3$  to verify the straight line path is necessary. Then matrix algebra allows the prediction of the last straight line, path 5, and calculation of all  $\lambda$ 's and  $b_i$ 's and  $k_{ij}$ 's by matrix manipulation as shown in Boudart's book. Straight reaction path 5 can naturally be verified by experiments.

Certainly a powerful method to cut down on experimental work but restricted to first order reactions.

Cheng, Fitzgerald and park [Ind. Eng. Chem. Process Design and Development Vol. 19, No. 1, 59, 1977] proposed to following method for determining  $k_{ij}$ 's in a system of unimolecular reactions.

Let  $\bar{C} = [C_1, C_2, C_3 \dots C_N]$  be a row vector of concentration of all the species and let these concentrations be determined at equal time increments  $\Delta t$ . Then

$$\begin{aligned} \bar{C}(\Delta t) &= \bar{C}(0) e^{\underline{K} \Delta t} \\ \bar{C}(2\Delta t) &= \bar{C}(\Delta t) e^{\underline{K} \Delta t} = \bar{C}(0) e^{2\underline{K} \Delta t} \\ \bar{C}(m \Delta t) &= \bar{C}((m-1) \Delta t) e^{2\underline{K} \Delta t} \end{aligned} \quad (109)$$

or in matrix notation

$$\begin{bmatrix} C(\Delta t) \\ C(2 \Delta t) \\ C(m \Delta t) \end{bmatrix} = \begin{bmatrix} C(0) \\ C(\Delta t) \\ C((m-1) \Delta t) \end{bmatrix} \left[ e^{\underline{K} \Delta t} \right] \quad (110)$$

$$\left[ e^{\underline{K} \Delta t} \right] = \begin{bmatrix} C(0) \\ C(\Delta t) \\ C((m-1) \Delta t) \end{bmatrix} \begin{bmatrix} C(\Delta t) \\ C(2 \Delta t) \\ C(m \Delta t) \end{bmatrix} \quad (111)$$

$$\underline{\underline{K}} = \frac{1}{\Delta t} \ln \left\{ \begin{bmatrix} C(0) \\ C(\Delta t) \\ C((m-1) \Delta t) \end{bmatrix}^{-1} \begin{bmatrix} C(\Delta t) \\ C(2 \Delta t) \\ C(m \Delta t) \end{bmatrix} \right\} \quad (112)$$

All of the above computations (matrix inversion, logarithm of a matrix etc.) are readily programmable or available on modern computers. Thus the above computations yield the matrix of rate constants directly.

### n-th order reactions:

A more general procedure valid for a set of n-th order reactions of known order (or even for complex know rate forms) was developed by Himmelbaum, Jones & Bischoff [Ind. Eng. Chem. Fundamentals Vol. 6, No. 4, 539 (1967)] for evaluation of the rate constants. In a batch constant volume system the equations for materials balance for all components can be cast in the following form:

$$\frac{dC_j}{dt} = \sum_{i=1}^M k_i r_{ji} (\underline{C}); \quad j = 1, 2, \dots, S \quad (113)$$

$S$  – total number of components

$M$  – total number of reactions i.e. number of tems in the rate expressions

$r_{ji}$  – concentration dependent term in rate of production (if  $> 0$ ) or depletion (if with negative sign) of component  $j$  in reaction path  $i$

$k_i$  – rate constant for path  $i$

$\underline{C}$  – vector of  $S$  concentrations

The derivatives  $\frac{dC_j}{dt}$  cannot be measured directly but the differences in concentrations at various times can. By integrating the above equations one gets:

$$\underbrace{C_j(t_n) - C_j(t_o)}_{\text{directly from measured data}} = \sum_{i=1}^M k_i \underbrace{\int_{t_o}^{t_n} r_{ji}(\underline{C}(t)) dt}_{\text{by integration (since concentration dependence of the rates is known) of measured data}} \quad (114)$$

$$C_j(t_n) - C_j(t_o) = \sum_{i=1}^M k_i X_{nji} \quad (115)$$

The standard least squares method can now be used to minimize the following expression

$$S = \sum_{n=1}^N \sum_{j=1}^S \left[ w_{nj} (y_{nj} - \hat{y}_{nj}) \right]^2 \quad (116)$$

$n$  – indicates n-th data point at  $t_n$

$N$  – total number of data points

$S$  – total number of species

$y_{nj} = C_j(t_n) - C_j(t_o)$  experimentally measured concentration difference of component  $j$  at time  $t_n$  and at time  $t_o \Rightarrow$  dependent variable

$\hat{y}_{nj} = \sum_{i=1}^M k_i X_{nji}$  - predicted value of the dependent variable  $y_{nj}$  at point  $n$  where  $X_{nji}$  are calculated from experimental data and  $k_i$  are to be found.

$w_{nj}$  - any desired weighing function

These weights can be picked all to be 1 leading to the usual least square fits, or they can be selected to be proportional to the inverse of measured concentration difference, or to be inversely proportional to the  $\sqrt{\text{variance}}$  of concentration values for each species  $j$ .

Setting then

$$\frac{\partial S}{\partial k_i} = 0 \text{ for all } i = 1, 2, \dots, M \quad (117)$$

leads to a set of linear equations from which  $k_i$  can be promptly determined.

The above method although quite powerful in many situations also leads in general only to rough estimates of reaction constants.