

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.

5.1 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).

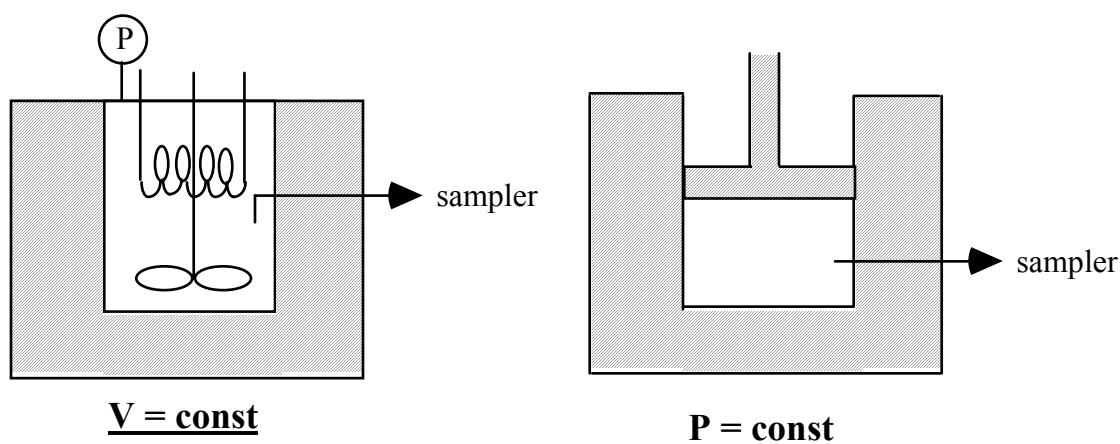
Non-isothermal experimental conditions are achieved:

- either when a temperature program with respect to time or position in the reactor is established
- 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.

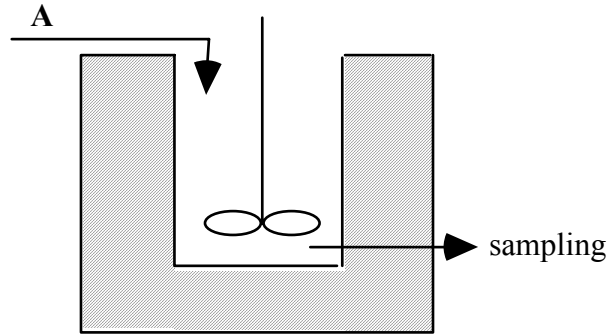
The typical reactor types in which experiments are performed are:

BATCH REACTOR:

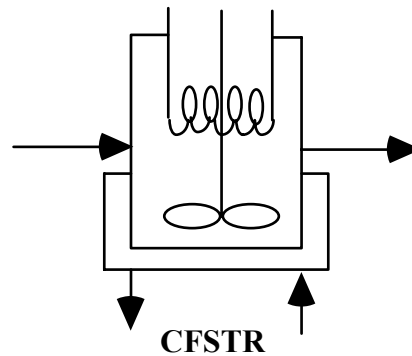
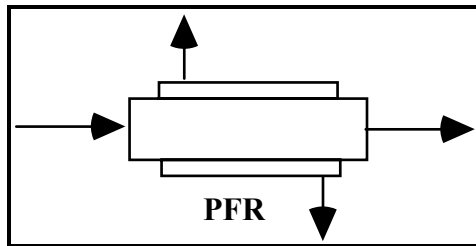


A typical batch reactor ($V = \text{const}$) is a vessel of constant volume (i.e., a flask, autoclave, etc.) into which the reactants are charged at the beginning of the run. The reactor is equipped either with a cooling/heating coil or jacket, or is well insulated, and can be run isothermally (or close 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).

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.

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).

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_t (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.

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 $P = const$, 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.

5.2 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



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:

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

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

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

↑ evaluated at t

By definition

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

Then

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

(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:

$$N_{A0} - N_A(t) - a \int_0^t \int_V r(T, C_j) dV dt = 0 \quad (8)$$

Similarly an energy balance gives:

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

$$\begin{aligned} (\rho C_v VT)_0 - (\rho C_v VT)_t + a \int_0^t \int_V (-\Delta U)_r r(T, C_j) dV dt \\ - \int_0^t UA_h (T - T_c) dt = 0 \end{aligned} \quad (9a)$$

- ρ - density of the reaction mixture (kg/m^3)
- C_v - specific heat of the reaction mixture ($\text{J}/\text{kg} \cdot \text{C}$)
- V - reaction mixture volume (m^3)
- ΔU_r - heat of reaction (J/mol)
- U - overall heat transfer coefficient ($\text{J}/\text{m}^2 \cdot \text{s} \cdot \text{C}$)
- 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.

$$N_{A0} - N_A(t) - aV \int_0^t r(T_c, C_j) dt = 0 \quad (10)$$

Differentiating eq. (10) we get

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

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

$$-r_A (C_j, T_c)$$

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

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

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

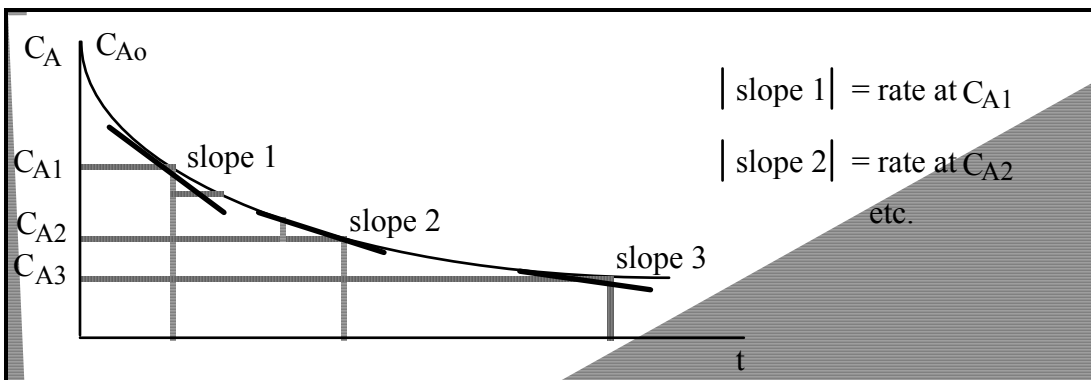
$$\text{If } V = \text{const } \tan t \xi = \frac{X}{V} = \frac{C_{Ao} - C_A}{a} \quad (14)$$

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

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

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

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 $N_{B_0}/N_{A_0} \gg 1$ 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

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

$$\begin{array}{c} F_{A_0} \\ \left(\frac{\text{mol}}{\text{hr}} \right) \end{array} - \begin{array}{c} F_A \\ \left(\frac{\text{mol}}{\text{hr}} \right) \end{array} - a \int_V r(C_A, T_c) dV = 0 \quad (18a)$$

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

In terms of conversion:

$$F_A = F_{A_0} (1 - x_A) \quad (19)$$

$$F_{A_0} x_A - a \int_V r(C_A, T_c) dV = 0 \quad (20)$$

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):

$$-r_A(C_A, T_c) = \frac{F_{A_0} x_A}{V} = \frac{C_{A_0} q_o - C_A q}{V} \quad (21)$$

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

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.

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

C_{Am} – mean value of concentration $C_{Aexit} < C_{Am} < C_{A_o}$. 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.

5.3 EVALUATIONS OF RATE FORMS USING BATCH REACTORS (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

$$\frac{N_{A_o} - N_A}{a} = \frac{N_{B_o} - N_B}{b} = \frac{N_D - N_{D_o}}{d} = \frac{N_G - N_{G_o}}{g} = X \quad (2)$$

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

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

can be extended by dividing it by V and since $\frac{N_{A_o}}{V} = C_{A_o}$, $\frac{N_A}{V} = C_A$ etc., while

$\xi = \frac{X}{V}$ is the extent per unit volume we get

$$\frac{C_{A_o} - C_A}{a} = \frac{C_{B_o} - C_B}{b} = \frac{C_D - C_{D_o}}{d} = \frac{C_G - C_{G_o}}{g} = \xi \quad (23)$$

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

Let us that suppose we have charged the reactor with N_{A0} , N_{B0} 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 $V = \text{const}$ 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 α , β , γ , δ .

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

$$\begin{aligned} C_B &= C_{B0} - \frac{b}{a} (C_{A0} - C_A) & \text{In General:} \\ C_D &= C_{D0} + \frac{d}{a} (C_{A0} - C_A) & C_j = C_{j0} + \frac{v_j}{v_1} (C_1 - C_{10}) \\ C_G &= C_{G0} + \frac{g}{a} (C_{A0} - C_A) \end{aligned} \quad (27)$$

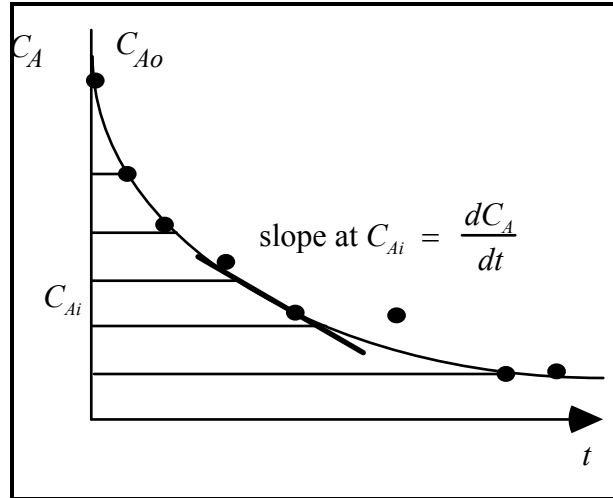
Thus we would have

$$a \left\{ k_f C_A^\alpha \left[C_{B0} - \frac{b}{a} (C_{A0} - C_A) \right]^\beta - k_b \frac{dg}{a^2} (C_{A0} - C_A)^{\gamma + \delta} \right\} = -\frac{dC_A}{dt} \quad (28)$$

This follows nice since
 $C_{D0} = C_{G0} = 0$ were assumed

$$\text{At } t = 0 \quad C_A = C_{A0} \quad (28a)$$

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: α , β , γ , δ , 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: α , β , 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

$$\frac{b}{a} x_A = \frac{b}{a} \frac{C_{Ao} - C_A}{C_{Ao}} \text{ in comparison to } \frac{C_{Bo}}{C_{Ao}}$$

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: α 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 β and k_{fo} , and then runs starting with only C and D can be performed to determine the reverse rate's parameters γ , δ , 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 α 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.

Differential Method:

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

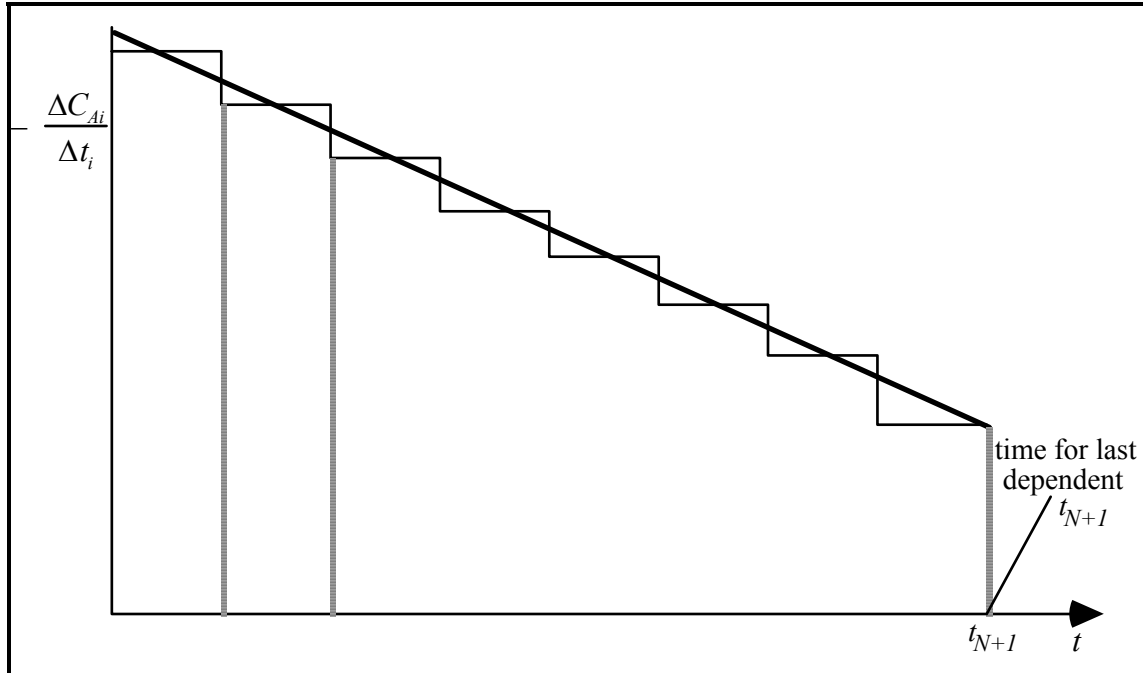
1. Tabulate the data and evaluate the differences $\Delta C_{Ai} = C_{Ai+1} - C_{Ai}$ and $\Delta t_i = t_{i+1} - t_i$.
2. Evaluate the approximation to the derivative $\frac{dC_A}{dt}$.

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 Δt_i are uneven and large and ΔC_{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} .

$$\begin{array}{c} \text{Means } -\frac{dC_A}{dt} \\ \text{Evaluated at } t_i \end{array}$$

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

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

$\begin{array}{ccc} y & a & x \end{array}$

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 α . 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 α and the kinetic constant k are then extracted by the method. The main weakness of the method is poor accuracy.

Integral Method:

Objective: given a set of data C_A vs. t , i.e. C_{Ai} vs. t_i , determine α 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 α , i.e. $\alpha = 1$, or $\alpha = \frac{1}{2}$ or $\alpha = 2$, etc.
3. Integrate the batch mass balance.

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A^\alpha} = k \int_0^t dt \quad (37)$$

$F(C_A, C_{A0}) = kt$

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

Assuming ideal gases

$$C_{A_0} = \frac{P_{A_0}}{RT} \quad C_{B_0} = \frac{P_{B_0}}{RT} \quad (41)$$

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

$$C_{A_0} + C_{B_0} = \frac{P_{A_0} + P_{B_0}}{RT} = C_{T_0} = \frac{P_{T_0}}{RT} \quad (42)$$

Concentrations are related to extent per unit volume ξ , as shown below:

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

$$\begin{aligned} C_T &= (C_A + C_B + C_D + C_G) = \frac{(P_A + P_B + P_D + P_G)}{RT} = \frac{P_T}{RT} = C_{T_0} + (\Delta n)\xi \\ C_T &= \frac{P_T}{RT} = \frac{P_{T_0}}{RT} + (\Delta n)\xi \Rightarrow \xi = \frac{P_T - P_{T_0}}{(\Delta n) RT} \end{aligned}$$

or in general

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

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

$$\begin{aligned} -\frac{dC_A}{dt} &= k C_A^\alpha C_B^\beta \\ -\frac{1}{RT} \frac{dP_A}{dt} &= k P_A^\alpha P_B^\beta \frac{1}{(RT)^{\alpha+\beta}} \end{aligned} \quad (45)$$

$$-\frac{dP_A}{dt} = [k_p (RT)]^{1-(\alpha+\beta)} P_A^\alpha P_B^\beta \quad (46)$$

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

$$P_{A_0} = y_{A_0} P_{T_0} \quad (48)$$

↑ Mole fraction of A initially

$$\frac{dP_A}{dt} = -\frac{a}{\Delta n} \frac{dP_T}{dt} \quad (49)$$

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

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

This equation relates now the change of total pressure P_T with time and from the P_T (t_i) vs. t_i data α , β , 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)

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

y x

Integral method (n-th order reaction)

$$F(C_{A1}) = F(C_{A_0}) + kt f(n) \quad (53)$$

$$\frac{1}{C_A^{n+1}} = \frac{1}{C_{A_0}^{n+1}} + k(n+1)t \quad (53a)$$

y x

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:

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

y
x
y
x

Integral Analysis:

$$\left(\frac{\ln \frac{C_{A0}}{C_A}}{C_{A0} - C_A} \right) = \frac{k}{K} \left(\frac{t}{C_{A0} - C_A} \right) - \frac{1}{K} \quad (56)$$

y
x

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