

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

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

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

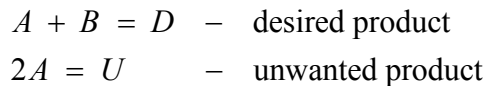
$$-\frac{dC_A}{dt} = k C_A^\alpha \quad - \int_{C_{A0}}^{C_{A0}/2} \frac{dC_A}{C_A^\alpha} = kt_{1/2} \quad (68)$$

$$t_{1/2} = \frac{2^{\alpha-1} - 1}{k(\alpha-1)} C_{A0}^{1-\alpha} \quad (69)$$

$$\underbrace{\log t_{1/2}}_y = \log \left\{ \frac{2^{\alpha-1} - 1}{k(\alpha-1)} \right\} + (1-\alpha) \underbrace{\log C_{A0}}_x \quad (70)$$

Starting with different C_{A0} 's and measuring the time that it takes for C_{A0} to drop to $C_{A0}/2$ and by plotting $t_{1/2}$ vs. C_{A0} on a log-log plot one can determine overall order α 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} , α , α_2 , β , γ , δ 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:

$$C_A = C_{A_0} - \xi_1 - 2\xi_2 \quad C_D = C_{D_0} + \xi_1$$

$$C_B = C_{B_0} - \xi_1 \quad C_U = C_{U_0} + \xi_2$$

Eliminating the extents ξ_1 , ξ_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 $C_{B_0} \gg C_D$

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

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

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

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 β 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 α_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 α_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.

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:

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

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

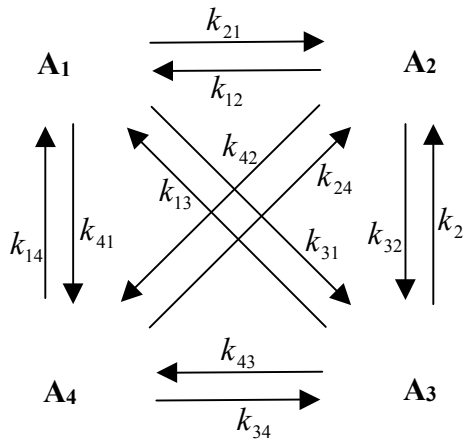
$$\frac{dC_s}{dt} = k_{s1} C_1 + k_{s2} C_2 + k_{s3} C_3 + \dots + \left(- \sum_{\substack{j=1 \\ j \neq s}}^S k_{sj} \right) C_s \quad (89c)$$

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:



$$k_{11} = - (k_{21} + k_{31} + k_{41})$$

$$k_{22} = - (k_{12} + k_{32} + k_{42})$$

$$k_{33} = - (k_{13} + k_{23} + k_{43})$$

$$k_{44} = - (k_{14} + k_{24} + k_{34})$$

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:

$$\frac{d\underline{C}}{dt} = \underline{K} \underline{C}; \quad t = 0 \quad \underline{C} = \underline{C}_o \tag{90}$$

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.

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

The problem is as follows:

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

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 $\underline{\underline{K}}$ 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:

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

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

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

Thus the matrix $\underline{\underline{K}}$ maps every eigenvector \underline{x}_m onto itself augmented by a "stretching" factor λ_m . Eigenvectors \underline{x}_m establish the characteristic directions for the matrix $\underline{\underline{K}}$, eigenvalues λ_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

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

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 λ_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 λ_m .

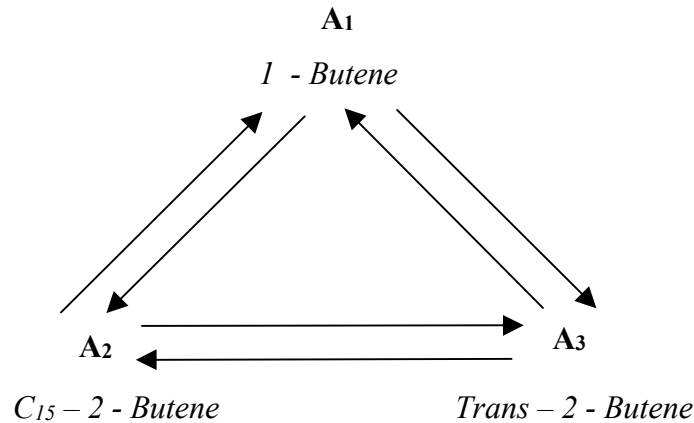
$$\ln \frac{b_1}{b_{10}} = -\lambda_1 t \quad (107)$$

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

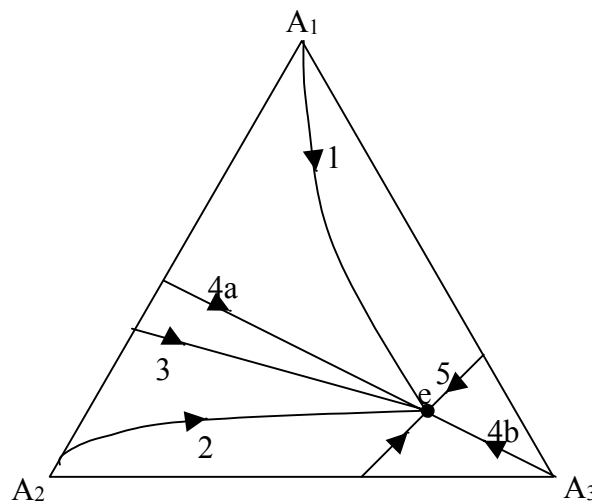
From the eigenvalues λ_m , by simple matrix manipulation, k_{ji} are determined.

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 λ_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 λ_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 λ '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 Δt . Then

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

or in matrix notation

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

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

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

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 known 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 terms 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

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

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 valued 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.