veloped to analytically account for the effect of temperature variation. With this technique, one may analyze the data and obtain specific Arrhenius constants (pre-exponential factor and activation energy) corresponding to the inlet temperature Analysis of non-isothermal incineration data is facilitated by use of this technique because simple linear arithmetic and graphical techniques can be used in place of more complex non-linear methods. It should also be noted that this technique can be used with other than first order reactions, since we are adjusting only for temperature effects.

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NOTATION

A = pre-exponential factor (s^{-1})
E = activation energy (kcal/gmol)
$\mathscr{E}$ = dimensionless activation energy
F_i = transformation factor for the ith increment of reactor distance
F_x = transformation factor, equal to F_i for $X = i\Delta X$
f_i = mole fraction at the ith increment of reactor distance
f_x = mole fraction, equal to f_i for $X = i\Delta X$
$\mathscr{F}$ = dimensionless fractional temperature drop across the entire reactor
i = index for number of distance increments
k = first-order reaction rate constant (s^{-1})
$\bar{k}_i$ = average value of rate constant over ith increment of reactor distance (s^{-1})
k_o = first order rate constant at the inlet temperature, T_o (s^{-1})
L = overall reactor length (m)
R = gas constant (0.001987 kcal/gmol°K)
T = absolute temperature (°K)
T_o = absolute temperature at reactor inlet (°K)
$\overline{T}_x$ = average temperature over ith reactor increment located at $X = i\Delta X$
t = time (s)
t' = transformed time (s)
U = linear velocity in the reactor (m/s)
$\overline{U}_i$ = average velocity in the ith increment of the reactor (m/s)
X = axial distance (m)
Z = dimensionless axial distance
Δt, $\Delta t'$ = incremental time, increment transformed time (s)
ΔX = incremental reactor distance (m)

LITERATURE CITED

Hemsath, K. H. and P. E. Susey, "Fume Incineration Kinetics and Its Applications," *AIChE Symp. Ser.*, **70**, No. 137, 439 (1974).

Lee, K. C., J. L. Hansen, and D. C. Macauley, "Predictive Model of the Time-Temperature Requirements for Thermal Destruction of Dilute Organic Vapors," 72nd Annual Meeting of the Air Pollution Control Association, Paper No. 79-10.1, Cincinnati, OH (June 24-29, 1979).

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Estimation of Kinetic Parameters—Initial Guess Generation Method

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Estimates of chemical kinetic equation parameters are obtained from calculation procedures which utilize the experimental data and consist of minimization of a suitable criterion function. A number of methods with criteria of various forms, using different calculation techniques, have been described (Froment, 1975; Himmelblau et al., 1967; Pexidr, 1974; Seinfeld, 1970; Van den Bosch and Hellinckx, 1974). In most cases the above problem is solved by means of an iterative procedure. The convergence of the algorithm depends on the goodness of the initial guesses. The importance of this aspect of calculations is emphasized in all papers dealing with estimation of parameters in the sets of both algebraic and differential equations. Various ways and preparation methods of initial estimations are discussed and illustrated by Kittrell et al. (1965). An independent algorithm for generation of preliminary parameter values is proposed apart from the accurate parameter determination algorithm (Seinfeld and Gavalas, 1970). This provides considerable economy of calculation time. This paper discusses the calculation technique for estimating initial parameters for the set of non-linear first-order ordinary differential equations.

CALCULATION FORMULAS

Let us consider a set of differential equations with the preset initial condition:

$$\frac{dx}{dt} = f(t, x, k); \quad x(0) = x_o \tag{1}$$

Equation 1 may be solved by one of the known differential-difference methods (Lapidus and Seinfeld, 1971). The differential-difference method generating equation may be written, by using first derivatives, as follows:

$$x_{n+1} = \sum_{i=0}^{p} a_i x_{n-i} + h \sum_{i=-1}^{p} b_i x'_{n-i} \tag{2}$$

where $h = (t_{n+1} - t_n)$ is the integration step and $p + 1$ is the number of previous x values required for calculation of $x_{n+1} = x(t_{n+1})$. Depending on the numerical values of coefficients a_i, b_i and the values of p, Eq. 2 has different accuracies. The remainder may be expressed by the equation:

$$T_n = ch^{q+1} \frac{d^{q+1}}{dt^{q+1}} x(\eta); \quad t_n < \eta < t_{n+1} \tag{3}$$

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where c is a constant and q is the order of formula accuracy.

In specific cases, Eq. 2 yields the following formulas:

$$x_{n+1} = x_n + \frac{1}{2} h(x'_{n+1} + x'_n); \quad q = 2 \qquad (2a)$$

$$x_{n+1} = \frac{1}{8} (9x_n - x_{n-2}) + \frac{3}{8} h(x'_{n+1} + 2x'_n - x'_{n-1}); \quad q = 4 \qquad (2b)$$

Both methods are stable over a broad range of h values. Their remainders are:

$$-\frac{1}{12} h^3 \frac{d^3}{dt^3} x(\eta) \text{ and } -\frac{1}{40} h^5 \frac{d^5}{dt^5} x(\eta)$$

respectively.

One can consider other differential-difference formulas, apart from Eq. 2. They may contain higher order derivatives, for instance formula:

$$x_{n+1} = x_n + \frac{1}{2} h(x'_{n+1} + x'_n) + \frac{1}{12} h^2(-x''_{n+1} + x''_n); \quad q = 4 \qquad (4)$$

with the remainder of

$$T_n = \frac{1}{720} h^5 \frac{d^5}{dt^5} x(\eta)$$

One can also use the following relationship between the successive derivatives of the function desired:

$$\frac{d^m}{dt^m} x_{n+1} = \frac{d^m}{dt^m} x_n + \frac{1}{2} h\left(\frac{d^{m+1}}{dt^{m+1}} x_{n+1} + \frac{d^{m+1}}{dt^{m+1}} x_n\right) \qquad (5)$$

This is an $m + 2$ order formula. One can easily note that at $m = 0$ it is reduced to Eq. 2a.

Equations 2-5 can be used for initial estimates of parameters in differential Eq. 1. If state variables x are available at various values of t, these formulas are reduced to an algebraic equations. In a general case, with any form of function, Eq. 1 requires an iterative method of calculation. If, however, the right-hand side of Eq. 1 is linear with respect to parameters then the corresponding algebraic equations (generated by Eq. 2) are linear with respect to unknown quantities k. Therefore, their solution should not be very difficult even for a set of many equations. This property of Eq. 2 may be used for evaluation of rate constants in chemical kinetic equations.

EVALUATION OF RATE CONSTANTS IN THE KINETIC MODEL

For estimation of parameters the experimental values of a state variable (known function of the state variable) are compared with those calculated according to the process equation assumed. The calculation procedure consists usually of a suitable criterion minimization algorithm in the form of function of differences in the magnitudes to be compared.

Let us assume that the values of state variable measured at various times are available. We are not going to construct a criterion enabling us to minimize the measuring error. This error will be neglected for preliminary evaluation of parameters.

If the process Eq. 1 is replaced by a type (2) equation and the values of state variables taken from a preset set of not very "remote" experimental points $x(t_r)$, $r = 1, 2, \ldots, R$ are substituted, then from Eq. 2a we obtain:

$$x(t_r) = x(t_{r-1}) + \frac{1}{2} (t_r - t_{r-1}) (f(t_r, x(t_r), k) + f(t_{r-1}, x(t_{r-1}), k)) \qquad (6)$$

Relationships of a similar nature will be obtained on applying other formulas. The set of Eqs. 6 solved for successive time intervals renders it possible to obtain R values of k parameters. Each value will include an error resulting from assumptions adopted. If the approximation error is of the same order for all time intervals, then an arithmetic mean of the values determined in particular intervals may be considered an initial guess of k.

TABLE 1. INITIAL VALUES OF RATE CONSTANTS k_1 AND k_2 DETERMINED BY MEANS OF FORMULA 6.

$t \cdot 10^4$	y_1	y_2	k_1	k_2
0.0	0.0	0.0		
			350.924	491.247
5.63	0.828	0.0737		
			354.581	408.804
11.32	0.704	0.113		
			343.924	377.416
16.97	0.622	0.1322		
			338.445	424.042
22.62	0.565	0.14		
			335.112	399.001
34.0	0.499	0.1468		
			327.988	377.589
39.7	0.482	0.1477		
			334.749	431.423
45.2	0.470	0.1477		
			82.091	107.535
169.7	0.433	0.1476		

EXAMPLE

In paper (Seinfeld and Gavalas, 1970) the estimated results of reaction rate constants describing the pyrolysis of benzene are presented and discussed. In the above mentioned paper, the quasilinearization method for minimization of the criterion function was used. This method has an iterative nature and requires fairly good values of initial parameters to be known. These magnitudes will be determined below from Eq. 6.

The process in question is described by stoichiometric equations:

$$2A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B + C \qquad (7)$$

$$A + B \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} D + C$$

The kinetic model equations are as follows:

$$\frac{dx_1}{dt} = -k_1x_1^2 + k_{-1}x_2x_3 - k_2x_1x_2 + k_{-2}x_3x_4; \quad x_1(0) = 1$$

$$\frac{dx_2}{dt} = \frac{1}{2} k_1x_1^2 - \frac{1}{2} k_{-1}x_2x_3 - k_2x_1x_2 + k_{-2}x_3x_4; \quad x_2(0) = 0 \qquad (8)$$

$$\frac{dx_3}{dt} = \frac{1}{2} k_1x_1^2 - \frac{1}{2} k_{-1}x_2x_3 + k_2x_1x_2 - k_{-2}x_3x_4; \quad x_3(0) = 0$$

$$\frac{dx_4}{dt} = k_2x_1x_2 - k_{-2}x_3x_4; \quad x_4(0) = 0$$

where x_1, x_2, x_3, x_4—molar fractions of the A, B, C, D components. For calculations the experimental results of molar fractions (y_1, y_2) and the values of equilibrium constants ($K_1 = 0.242$; $K_2 = 0.428$) quoted in paper (Seinfeld and Gavalas, 1970) were used. The results of calculations are summarized in Table 1.

The values of k_1 and k_2 calculated for the last time interval, in which system approaches the chemical equilibrium, differ considerably from other values. It is not surprising because the kinetic model equations, near of the chemical equilibrium, are not in form (Eq. 8). Mean values of the rate constants given in Table 1, calculated without taking into account of k_1 and k_2 for the last time interval, are: $\bar{k}_1 = 340.8$; $\bar{k}_2 = 415.6$. Most favourable estimators of the rate constants determined by Seinfeld and Gavalas (1970) by the quasilinearization method and equal to: $k_{1,opt} = 347$; $k_{2,opt} = 403$, respectively, differ from the values $\bar{k}_1$ and $\bar{k}_2$ by 2 and 3%, respectively. Thus, the values obtained by means of algebraic Eq. 6 should be considered good initial guesses of parameters.

If it is justified to assume that the measuring error is low then, at a suitably small step h and by applying an approximating formula of high accuracy, the resulting values of rate constants may be considered accurate. For many applications such an approximation may be fairly sufficient. It should be merely remembered that formulas 2 of an order higher than 2 require a constant step.

Because of its simplicity, the suggested method for calculation of the approximate values of model parameters or time dependences of state variables may be of substantial assistance for initial selection of models and for evaluation of the experimental conditions.

NOTATION

a, b = coefficients in formula 2
f = vector of rate of change of concentration
h = integration step size
k = vector of parameters
K = equilibrium constant
m = differential index
n = integration step index
N = number of state variables
R = number of values of t at which data are taken
t = time variable
q = order of formula accuracy
x = state vector
y = observation vector
η = value of t in error formula

LITERATURE CITED

Froment, G. F., "Model Discrimination and Parameter Estimation in Heterogeneous Catalysis," *AIChE J.*, **21**, 1041 (1975).

Himmelblau, D. M., C. R. Jones, and K. B. Bischoff, "Determination of Rate Constants for Complex Kinetics Models," *Ind. Eng. Chem. Fundamentals*, **6**, 539 (1967).

Kittrell, J. R., R. Mezaki, and C. C. Watson, "Estimation of Parameters for Nonlinear Least Squares Analysis," *Ind. Eng. Chem.*, **57**, 18 (1965).

Lapidus, L. and J. H. Seinfeld, *Numerical Solution of Ordinary Differential Equations*, Academic Press, New York (1971).

Pexidr, V., "Evaluation of Nonlinear—Regression Kinetic Data. III. Evaluation of Integral Kinetic Data," *Chem. Prum.*, **24**, 354 (1974).

Seinfeld, J. H., "Nonlinear Estimation Theory," *Ind. Eng. Chem.*, **62**, 32 (1970).

Seinfeld, J. H. and G. R. Gavalas, "Analysis of Kinetic Parameters from Batch and Integral Reaction Experiments," *AIChE J.*, **16**, 644 (1970).

Van den Bosch, B. and L. Hellinckx, "A New Method for the Estimation of Parameters in Differential Equations," *AIChE J.*, **20**, 250 (1974).

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An Explicit Equation for Particle Settling Velocities in Solid-Liquid Systems

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Zanker (1980) has recently presented nomographs for determining particle settling velocities in solid-liquid systems. These nomographs were based on the general correlations developed by Barnea and Mizrahi (1973) and Barnea and Mednick (1975),

$$C_{D_\phi} = \left(0.63 + \frac{4.8}{\sqrt{\mathrm{Re}_\phi}}\right)^2 \qquad (1)$$

where

$$C_{D_\phi} = \left(\frac{4d(\rho_d - \rho_c)g}{3\rho_c U_\phi^2}\right)\left(\frac{1-\phi}{1+\phi^{1/3}}\right) \qquad (2)$$

and

$$\sqrt{\mathrm{Re}_\phi} = \left(\frac{U_\phi d \rho_c}{\mu_c \exp\left[5\phi/3(1-\phi)\right]}\right)^{1/2} \qquad (3)$$

Setting ϕ equal to zero yields the equations for single particle settling.

In order to avoid an implicit solution for the settling velocity, U_ϕ, from Eqs. 1-3, Zanker presented his nomographs. However, it is shown below that Eqs. 1-3 can be combined to yield an explicit solution for U_ϕ; thus, eliminating the need for either an iterative solution or Zanker's nomographs.

Substitution of Eq. 3 into Eq. 1 and combining the result with Eq. 2 yields

$$U_\phi = a - b\sqrt{U_\phi} \qquad (4)$$

where

$$a = \frac{2}{0.63\sqrt{3}}\left[\frac{(\rho_d - \rho_c)gd(1-\phi)}{\rho_c(1-\phi^{1/3})}\right]^{1/2}$$

and

$$b = \frac{4.8}{0.63}\left[\frac{\mu_c \exp\left[5\phi/3(1-\phi)\right]}{\rho_c d}\right]^{1/2}$$

Equation 4 for U_ϕ can be rewritten in the form of the quadratic

$$U_\phi^2 - (2a + b^2)U_\phi + a^2 = 0 \qquad (5)$$

and easily solved to yield the desired result for the settling velocity.

$$U_\phi = c - \sqrt{c^2 - a^2} \qquad (6)$$

where

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