cency matrix A, the augmented matrix $C^{(n)}$, and finally the reachability matrix after permutation. In order to make it easier to follow the intermediate steps, the original entries are denoted by "x", and "1", "2", "3", etc. are used to denote the successive arc augmentation in $C^{(i)}$. In actual implementation the storage of only one matrix will be required.

Methods based on reachability matrix computation have not been previously favored in partitioning process flow sheets and equations because they are generally slower than the alternative algorithms using path tracing and list processing (Sargent and Westerberg, 1964; Steward, 1965; Billingsley, 1967). For instance, comparison of computing times reported by Ledet and Himmelblau (1970) indicates that the "Boolean powers" method (Method 3) is slower than either Steward's algorithm or Billingsley's algorithm by a factor of up to 3. The disparity is greatest for the largest problem tested which contains 126 equations. It is interesting that the maximum computing time ratio is almost the same as $\frac{1}{2}\log_2(126)$ which is the approximate ratio of operation counts for the "Boolean powers" method and the arc-augmentation algorithm.*

NOTATION

$:=$ replaced by

LITERATURE CITED

Billingsley, D. S., *Chem. Eng. Sci.*, **22**, 719 (1967).

Himmelblau, D. M., "Decomposition of Large Scale Systems—I. Systems Composed of Lumped Parameter Elements," *ibid.*, **21**, 425 (1966).

Ledet, W. P., and D. M. Himmelblau, "Decomposition Procedures for the Solving of Large Scale Systems," *Adv. Chem. Eng.*, **8**, p. 185, Academic Press, N. Y. (1970).

Norman, R. L., "A Matrix Method for Location of Cycles of a Directed Graph," *AIChE J.*, **11**, 450 (1965).

Sargent, R. W. H., and A. W. Westerberg," 'SPEED-UP' in Chemical Engineering Design," *Trans. Instn. Chem. Engrs.*, **42**, T190 (1964).

Steward, D. V., "On an Approach to Techniques for the Analysis of the Structure of Large Systems of Equations," *SIAM Review*, **4**, 321 (1962).

———., "Partitioning and Tearing Systems of Equations," *J. SIAM Numer. Anal., Ser. B*, **2**, 345 (1965).

Kevorkian, A. K., and J. Snoek, "Decomposition in Large Scale Systems. Theory and Applications of Structural Analysis in Partitioning, Disjointing and Constructing Hierarchical Systems," in *Decomposition of Large Scale Problems*, D. M. Himmelblau (ed.), North Holland, Amsterdam (1973).

Manuscript received May 20, 1974; revision received and accepted July 25, 1974.

---

* The author is indebted to the referee for pointing out a partitioning method due to Kevorkian and Snoek (1973), who arrived at a similar result based on a formula for computing the successors (and predecessors) of each node. In this instance, path tracing and arc augmentation appear to lead to the same result through different intermediate steps. Instead of tracing the successors of each node, the constructive algorithm augments all the paths associated with the neighbors of each node in turn.

Experimental Almost Isothermal Reactor

JENN-MING STEPHEN HUANG and ALLEN J. BARDUHN

Department of Chemical Engineering and Materials Science
Syracuse University, Syracuse, New York 13210

In those cases where laboratory or pilot plant determination of chemical reaction rate data are taken in a tubular flow reactor, the equipment may consist of a long tube immersed in a bath of water, molten lead, or molten salt at some fixed temperature. Due to the difficulty of measuring the actual reaction temperatures except at the inlet and outlet of such a reactor, the conditions are usually so chosen that the reaction and bath temperatures may be assumed equal and the reaction thus isothermal. Isothermal rate data are much simpler to interpret and correlate and they minimize the question of how much the accuracy of the results depend on the method of treating the data. Towell and Martin (1961) present a method for analysis of data from a nonisothermal plug flow reactor, but it requires measuring the complete axial temperature profile and thus both the measurements and the analysis are complicated.

No tubular flow reactor is truly isothermal since the heat of reaction changes the temperature of the reaction mixture and some temperature difference is necessary to carry away or supply the heat to bring the mixture back to the bath temperature. The isothermal condition can be approached to any degree necessary, however, by making the reactants adequately dilute in the feed stream (adding inert gas or solvent), by increasing the heat transfer area per unit volume of reactor (using a small diameter tube), by conducting the reaction at temperatures where the rate is low, or by improving the rate of heat transfer between the tube wall and reacting mixture (for example, using high velocities). Some of these remedies may not be desired, convenient, or possible, however, and thus the reactor may not operate isothermally to the degree necessary for assuming the observed reaction rate to be truly for the assumed temperature.

It is the purpose of this note (1) to present a simple method for predicting whether the reaction is adequately isothermal and (2) to provide a simple relation for correcting the rate constants to the assumed isothermal temperature when it is not. The method does not require measurement of the temperatures except at the reactor entrance, but it does require that the actual reaction temperature be typically no more than a few tens of degrees different from the initial temperature, that is, that the reaction be almost isothermal.

ANALYSIS

The system envisioned consists of a plug flow tubular reactor immersed in a bath which maintains the tube wall temperature at T_w. The reacting mixture enters the reactor at T_w and the composition is known at the entrance and exit of the tube. For small tubes the effect of axial disper-

---

Correspondence concerning this note should be addressed to A. J. Barduhn.

TABLE 1. DEFINITION OF PARAMETERS IN EQUATION (6)

Type of reaction	Rate equation	α	β	$f(x)$
Gaseous 1st order	$r = kPy_0\,(1-x)$	$\dfrac{-\Delta H y_0}{C_p T_w}\cdot\dfrac{E}{RT_w}$	$\dfrac{4h}{C_p D P k_w}$	$(1-x)$
Gaseous 2nd order	$r = kP^2y_0^2\,(1-x)^2$	Same	$\dfrac{4h}{C_p D P^2 y_0 k_w}$	$(1-x)^2$
Liquid 1st order	$r = kC_{A0}\,(1-x)$	Same	$\dfrac{4h\,y_0}{C_p D C_{A0} k_w}$	$(1-x)$
Liquid 2nd order	$r = kC_{A0}^2\,(1-x)^2$	Same	$\dfrac{4h\,y_0}{C_p D C_{A0}^2 k_w}$	$(1-x)^2$

sion is normally negligible when the tube is long enough to give any reasonable conversion. Even in laminar flow the radial dispersion is often rapid enough to give effective plug-flow-plus-axial-dispersion behavior which again may be a close approximation to plug flow conditions for long tubes.

Considering an exothermic reaction, the mean temperature of the solution rises at first with increasing distance from the entrance of the reactor since the amount of heat generated by chemical reaction exceeds the amount of heat transferred to the surrounding medium through the wall of reactor. At a certain distance, these two quantities become equal and the solution temperature attains a maximum at the hot spot. Thereafter, the reaction rate and solution temperature decrease due to the consumption of the reactant and the mixture reaches the wall temperature if the reaction goes to completion. The reaction rate constant, however, is calculated on the assumption that the reaction is isothermal and at T_w throughout the length of the reactor. We now proceed to find a correction factor g by which to multiply the calculated rate constant and get the true rate constant at T_w.

Consider a steady state tubular plug flow reactor with heat transfer to the tube wall. The energy balance yields

$$\frac{dT}{dz} = \frac{r(-\Delta H)\,A_c}{F\,C_p} - \frac{h\pi D(T-T_w)}{F\,C_p} \tag{1}$$

One could alternately use the overall heat transfer coefficient and the bath temperature instead of h and T_w as above. A material balance gives

$$\frac{dx}{dz} = \frac{rA_c}{F_{A0}} \tag{2}$$

Also dividing Equation (1) by Equation (2) and letting $F_{A0}/F = y_0$

$$\frac{dT}{dx} = \frac{(-\Delta H)\,y_0}{C_p} - \frac{4\,h(T-T_w)y_0}{C_p\,D\,r} \tag{3}$$

Following the ideas of Chambré (1956) and Barkelew (1959), we introduce a dimensionless excess temperature

$$\theta = \frac{T-T_w}{T_w}\cdot\frac{E}{R\,T_w} \tag{4}$$

and assume that in the rate expression $r = kc'f(x)$,

$$k = k_w\,e^{\theta} \tag{5}$$

Equation (5) is equivalent to the Arrhenius relation whenever

$$\frac{T-T_w}{T_w} < \text{about } 0.1$$

which will be true for an almost isothermal reactor.

Substituting Equations (4) and (5) into (3) gives a dimensionless nonlinear differential equation relating the temperature of the reacting mixture θ to the fractional conversion x:

$$\frac{d\theta}{dx} = \alpha - \frac{\beta\theta e^{-\theta}}{f(x)} \tag{6}$$

where α, β, and $f(x)$ are given in Table 1. For the case where θ at the reactor entrance is 0, that is, the reaction mixture is at the wall temperature (as is assumed in this derivation), Equation (6) shows the initial slope of $\theta(x)$ to be α and the final slope at $x = 1$ to be $-\alpha/(\beta-1)$ as shown by Chambré.

The general design relationship for a plug flow reactor can be written as

$$\tau = C_{A0}\int_0^x \frac{dx}{r} \tag{7}$$

If we write $r = k\,c'\,f(x)$ and $k = k_w e^{\theta}$, then

$$k_w = \frac{1}{(\tau/C_{A0})\,c'}\int_0^x \frac{e^{-\theta(x)}}{f(x)}\,dx \tag{8}$$

However, the experimenter who intends to find the rate constant at T_w assumes that the chemical reaction is isothermal and obtains

$$k_e = \frac{1}{(\tau/C_{A0})\,c'}\int_0^x \frac{1}{f(x)}\,dx \tag{9}$$

The value of k thus obtained is considered to be the reaction rate constant at the wall temperature. But from Equations (8) and (9), we know that

$$\frac{k_w}{k_e} = \frac{\displaystyle\int_0^x \frac{e^{-\theta(x)}}{f(x)}\,dx}{\displaystyle\int_0^x \frac{1}{f(x)}\,dx} \equiv g = \text{a correction factor} \tag{10}$$

Note that to find the correction factor at a given x, we have to solve Equation (6) first and then perform the integrations in Equation (10). Also note that Equation (6) is nonlinear and no analytic solution has been found even for the case where $f(x) = 1 - x$, although a graphical method of solution has been presented by Chambré and many numerical solutions are presented by Barkelew and by Bilous and Amundson (1956). Certain simple cases are soluble such as for $\beta = 0$ which gives an adiabatic reaction and $\beta \to \infty$ which gives a truly isothermal reaction.

One way to achieve an approximate analytic expression for g as a function of α, β, and x for the initial value of $x = 0$ and $\theta(0) = 0$ is as follows:

Let $e^{-\theta} \cong 1$ and $f(x) = 1 - x$, that is, assume first-order reaction with zero energy of activation, in Equation (6), and obtain a solution for θ, namely,

$$\theta_a = \frac{\alpha}{\beta-1}\left[(1-x) - (1-x)^{\beta}\right] \tag{11}$$

This is the exact solution for the case where $E = 0$, that is, where the temperature does not affect the reaction rate and it gives a close approximation to the actual temperature vs. x function for the case where E is not zero as long as T does not rise excessively above T_w. Equation (11) predicts the same initial and final slopes to $\theta(x)$ as does the general differential Equation (6). Equation (11) predicts the hot spot to occur at

$$x\ (\text{hot spot}) = 1 - \beta^{1/(1-\beta)}$$

and the maximum temperature to be

$$\theta(\text{max.}) = \alpha\beta^{\,\beta/(1-\beta)} = \frac{\alpha}{\beta}\,(1 - x_{\text{hot spot}})$$

The physical location of the hot spot occurs at

$$\frac{r_0\, z\ (\text{hot spot})}{G\, y_0} = \frac{\ln\beta}{\beta - 1}$$

where r_0 is the initial reaction rate (at T_w and $x = 0$). For any nonisothermal reactor the above relation for $\theta(\text{max})$ is lower than the true hot spot temperature, but the following relation, which is determined from the intersection of the tangents of $\theta(x)$ at $x = 0$ and $x = 1$, predicts a $\theta(\text{max})$ which is greater than the true value for the almost isothermal reactor.

$$\theta(\text{max}) = \alpha/\beta$$

The true $\theta(\text{max})$ will thus lie between these two estimates of $\theta(\text{max})$, but this method is not useful when the reaction temperature is much greater than T_w or when the reaction is not first order. The hot spot usually falls at an x between 0 and 0.3 and approaches the reactor entrance as the reaction becomes more isothermal.

Now if we approximate $e^{-\theta} \cong (1 - \theta)$ in Equation (10), use Equation (11) for θ, and perform the integrations, we find

$$\frac{k_w}{k_e} = g \cong g_a = \frac{\displaystyle\int_0^x \frac{1-\theta}{1-x}\,dx}{\displaystyle\int_0^x \frac{1}{1-x}\,dx} = 1 - \frac{\dfrac{\alpha}{\beta - 1}\left[\dfrac{(1-x)^\beta}{\beta} - (1-x)\right] + \dfrac{\alpha}{\beta}}{\ln\left(\dfrac{1}{1-x}\right)} \qquad (12)$$

Equation (12) is the required formula for the correction factor derived for first-order reactions. The values of g_a are always less than or equal to 1 as expected for an exothermic reaction. Note that for $f(x) = (1 - x)^2$ the same approximating procedure does not yield an analytic expression for g_a. It turns out, however, that under certain mild limitations Equation (12) is useful for correcting experimental data from both first and second-order reactions, and an analysis of its applicability is made below.

For rate expressions different from those used here, for example, as in the Langmuir-Hinshelwood type expressions which yield

$$r = kc'f(x, \theta),$$

the general ideas used above can still be applied to correct experimental values of k, but to solve for the correction factor will generally require a numerical solution. For the type of rate expressions considered here one needs however only a simple algebraic calculation to make the corrections. No solution of differential equations by numerical technique is required.

COMPARISON WITH NUMERICAL RESULTS

In order to know the applicability of Equation (12), we have solved Equation (6) by a Runge-Kutta fourth-order scheme for both first- and second-order reactions. Sufficiently small increments of Δx were used so that further subdivision did not change the results. This gives θ as a function of x with α and β as parameters. Equation (10) is then integrated numerically to yield the true correction factor g. Also from Equation (12) the approximate correction factor g_a is obtained for the corresponding set of x, α, and β. The relative percentage error of the approximation ($= 100|g_a - g|/g$), which is also the error in calculating k_w, is also computed. Table 2 shows one typical set of the computational results for $\alpha = 4$ and $\beta = 8$, for which values the reaction is rather far from isothermal, and it is remarkable that Equation (12) is useful under such conditions. In this particular case, the maximum θ is greater than 0.5 and for a value of $E/RT = 5$ this would mean that the reaction temperature could depart from the wall temperature as much as 30° to 60°C.

From the results of the computation ($\beta/\alpha = 1$ to 100), it is concluded that for $\beta/\alpha > 40$, the assumption of the truly isothermal reactor is valid and g or $g_a > 0.98$ and no correction is necessary. For $\beta/\alpha > 20$, it is valid for g or $g_a > 0.95$. Note that specifying β/α is a much better way of deciding whether the temperature is adequately constant than specifying the temperature departure itself

Table 2. Comparison of Equation (12) with Numerical Solutions for g
$\alpha = 4 \qquad \beta = 8$

	Numerical (exact) solutions							
	First order		Second order		Equation (11)	Equation (12)	% error in g_a	
x	θ	$g = k_w/k_e$	θ	$g = k_w/k_e$	θ_a	$g_a = k_w/k_e$	1st order	2nd order
0.05	0.167	0.916	0.166	0.915	0.164	0.912	0.4	0.4
0.10	0.288	0.853	0.282	0.853	0.268	0.844	1.1	1.1
0.15	0.379	0.805	0.359	0.805	0.330	0.792	1.5	1.6
0.20	0.446	0.766	0.405	0.768	0.361	0.754	1.5	1.8
0.25	0.494	0.734	0.422	0.741	0.371	0.727	1.0	1.9
0.30	0.525	0.708	0.412	0.723	0.367	0.708	0.0	2.0
0.35	0.539	0.687	0.378	0.712	0.353	0.696	1.3	2.3
0.40	0.538	0.671	0.324	0.711	0.333	0.690	2.9	2.9
0.45	0.521	0.659	0.260	0.718	0.310	0.688	4.5	4.1
0.50	0.488	0.651	0.197	0.732	0.283	0.690	6.0	5.7
0.55	0.442	0.648	0.144	0.753	0.256	0.696	7.4	7.6
0.60	0.384	0.650	0.104	0.777	0.228	0.704	8.3	9.4
0.65	0.320	0.657	0.074	0.804	0.200	0.714	8.8	11.2
0.70	0.255	0.669	0.052	0.832	0.171	0.727	8.7	12.6
0.75	0.195	0.686	0.035	0.860	0.143	0.742	8.2	13.7

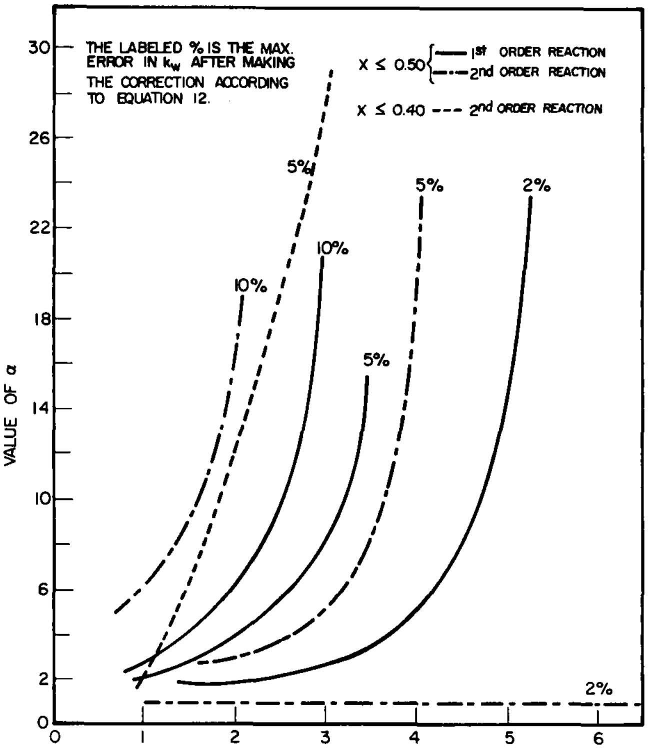

Fig. 1. Range of applicability of Equation (12).

since β/α measures not only the temperature departure but also the effect of temperature on the rate constant. When E is small the temperature may change more without affecting the observed rate constants. If E is 0 there is no need to control the temperature at all since k is independent of T.

When the reactor is inadequately isothermal, Equation (12) may be used to correct the observed result. A topographical map is plotted on Figure 1, which gives a clear picture of the limits of application of Equation (12). On Figure 1 if a coordinate point $(\beta/\alpha, \alpha)$ lies on the right-hand side of a curve, the percentage error involved in obtaining the rate constant due to the use of Equation (12) will be less than the number marked on the curve; and vice versa. For example, when $\alpha = 10$ and $\beta/\alpha = 4$, the error in k_w using g_a as the correction factor is less than 5% but more than 2%, for either first- or second-order reactions, while if the reactor were assumed isothermal and no correction were made the error would be about 20%. Also shown by a dotted line on the figure, is the 5% curve for a second-order reaction when $x \leqq 0.40$.

The true excess temperature θ obtained from numerical solutions cannot be approximated by θ_a computed from Equation (11) for the inadequately isothermal case, as can be seen from Table 2. More serious deviation of θ from θ_a occurs for the combination of lower values of β/α and higher values of α. However, the approximate correction factor g_a based on the expression for θ_a gives surprisingly good results even in these cases.

Note that although we do not compute the case of a second order reaction with nonstoichiometric feed or that of a first-order variable volume reaction, the suggested correction factor may also be applicable for these cases. The two conditions we considered, namely, $r = kC_{A0}(1 - x)$ and $r = kC_{A0}^2(1 - x)^2$, are two extremes for the general second-order reaction. A second-order reaction in which one reactant is in excess will behave in a manner somewhere between the first- and second-order reactions studied here; in fact if an adequately large excess is used, the reaction will exhibit pure first-order behavior.

To evaluate the correction factor it is first necessary to know α and β, which contain the unknown parameters E, the activation energy, and k_w, the rate constant at the wall temperature. All the other quantities in α and β can normally be predicted or are known. It is thus necessary to use an iterative scheme to yield the correct values of the required rate constants. After collecting experimental data and calculating the uncorrected rate constants from Equation (9) or its equivalent at various temperatures, one can find estimated values of E and k_w for the reaction or reassure oneself that no corrections are needed. Based on the uncorrected k's and the estimated E, the parameters α and β can be calculated, and the correction factors can be obtained from Equation (12). From these correction factors an improved set of k's will be obtained, which could be used to improve the results iteratively.

NOTATION

A_c = cross-sectional area of reactor = $\pi D^2/4$
c' = proportionality constant in $r = k\,c'\,f(x)$
C_{A0} = initial concentration of reactant
C_p = heat capacity of reacting mixture
D = diameter of reactor
E = activation energy of reaction (Arrhenius)
F = total feed rate, mass or moles/time
F_{A0} = reactant feed rate, mass or moles of A/time
$f(x)$ = functions defined in Table 1
G = F/A_c
g = exact correction factor = k_w/k_e
g_a = approximate correction factor
ΔH = enthalpy change for reaction
k = rate constant for first- or second-order reactions with either concentrations or partial pressures as driving forces. See Table 1 for determining units.
k_e = experimental rate constant (without correction)
k_w = true rate constant at T_w
P = total pressure
R = gas constant
r = rate of reaction moles or mass of reactant/(time)(vol.)
T = absolute temperature
T_w = wall temperature
h = heat transfer coefficient, tube wall to reacting mixture
x = fractional conversion of limiting reactant
y_0 = mole or mass fraction of limiting reactant in feed
z = distance from entrance of reactor

Greek Letters

α = dimensionless parameter describing the heat release in the system, Table 1
β = dimensionless parameter controlling the heat transfer, Table 1
θ = dimensionless excess temperature Equation (4)
θ_a = approximate solution for θ, Equation (11)
τ = nominal residence time

LITERATURE CITED

Barkelew, C. H., "Stability of Chemical Reactors," *Chem. Eng. Progr. Symp. Ser. No. 25*, **55**, 37 (1959).

Bilous, Olegh, and Neal R. Amundson, "Chemical Reactor Stability and Sensitivity, Part II," *AIChE J.*, **2**, 117 (1956).

Chambre, Paul L., "On the Characteristics of a Non-isothermal Chemical Reactor," *Chem. Eng. Sci.*, **5**, 209 (1956).

Towell, Gordon D., and Joseph J. Martin, "Kinetic Data from Non-isothermal Experiments: Thermal Decomposition of Ethane, Ethylene, and Acetylene," *AIChE J.*, **7**, 693 (1961).

Manuscript received May 13, 1974; revision received and accepted June 18, 1974.