Equivalent Isothermal Temperatures for Nonisothermal Reactors

JOHN B. MALLOY and HERMAN S. SEELIG, Standard Oil Company (Indiana), Whiting, Indiana

A simple procedure has been developed for evaluating the equivalent isothermal temperature for nonisothermal reactors. Reaction-rate constants determined from a kinetic study are averaged by a simplified integration method; the average rate constant defines the equivalent isothermal temperature. Use of this equivalent temperature permits direct comparison of experiments carried out in reactors having widely different temperature profiles.

Temperature so strongly influences the rate of chemical reaction that in any reaction study temperature must be accurately known. Ideally such studies are carried out in isothermal systems where the reaction temperature is known without question. When the reaction absorbs or evolves much heat, however, isothermal operation at practical conversion levels is almost impossible. Different parts of the reacting system are at widely different temperatures, and determining average reaction temperature becomes a real problem.

Endothermic reactions, for example, are often carried out commercially in a number of adiabatic reactors in series. A large variation in temperature exists in each reactor. Figure 1 shows a temperature profile typical of such a system. Pilot-plant studies attempt to duplicate the commercial operation and therefore operate with the same type of temperature profile. In smaller scale reactors it is extremely difficult to carry out reactions with large heat effects either adiabatically or isothermally. Small-scale reactors operate with quasiisothermal profiles such as the profile shown in Figure 2. In this example temperature drops rapidly in the inlet end of the bed because the reaction absorbs heat faster than it can be supplied through the reactor walls. This situation is reversed as the reaction slows down, and temperature rises in the exit end of the bed. Changes in feed composition, reaction conditions, size and location of reactor heaters, and dilution of the catalyst bed with inert material obviously make a wide variety of temperature profiles possible.

Researchers are thus confronted with the problem of comparing experiments performed in reactors that have widely different temperature profiles. Direct comparison is possible only if each temperature profile can be expressed by a single equivalent temperature—the equivalent isothermal temperature. This important concept of equivalent temperature has been recognized but rarely used. Previous authors(*1, 2*) developed algebraic solutions for the equivalent temperature for cases in which temperature can be related algebraically to reaction time or to distance through the catalyst bed. However, these solutions are complex. Calculating equivalent temperature for anything more than a handful of experiments is so time consuming that the concept has been little used. This paper presents a simple method for calculating equivalent temperatures that can be readily applied to a large number of experiments.

EQUIVALENT ISOTHERMAL TEMPERATURE

A reaction-rate equation can usually be expressed in the following form:

$$\frac{dn_A}{d\theta} = k\,\phi\,(p_A, p_B, \ldots) \qquad (1)$$

where the effect of temperature on reaction rate is contained in the rate constant k. Conversion is obtained by integrating Equation (1):

$$\int \frac{dn_A}{\phi\,(p_A, p_B, \ldots)} = \int k d\theta = k_{avg} \int d\theta \qquad (2)$$

For any nonisothermal reactor, Equation (2) shows that the effect of temperature is given by the average rate constant. The equivalent isothermal temperature is the temperature that corresponds to this average rate constant; it is the temperature at which an equivalent isothermal reactor would give the same conversion as the nonisothermal reactor.

To average rate constants the relation between temperature and rate constant must first be determined by a kinetic study. This relation is usually expressed by the Arhennius equation

$$k = Ae^{-\Delta E/RT} \qquad (3)$$

If radial temperature gradients are ignored, the average rate constant in the catalyst bed is

$$k_{avg.} = \int_0^1 kds \qquad (4)$$

where s is the fractional distance through the bed. Equivalent isothermal temperature is obtained by substituting k_{avg} into Equation (3). To determine the equivalent temperature for the profile shown in Figure 2, for example, the profile is replotted in terms of rate constant and fractional bed length, as shown in Figure 3. The average rate constant is obtained by integration and is equal to the area under the curve. Equivalent temperature is obtained from the average rate constant and Equation (3).

Equivalent temperatures have seldom been used because of the labor and time involved in this integration. In its place a simple arithmetic average temperature, or some other arbitrary temperature—such as that of the inlet, outlet, or an intermediate point in the bed or reactor wall—is often used. Such temperatures are usually poor substitutes for the true equivalent temperature. They lead to inconsistent correlations, particularly when changes in conversion, space velocity, pressure, feed stock, etc., cause changes in the temperature profile.

SIMPLIFIED INTEGRATION METHOD

Integrating rate-constant profiles is greatly simplified by a technique devised by Gauss(*3*). The method integrates exactly a polynomial of degree 2*n*-1 from *n* predetermined ordinates in the interval of integration. To apply the method to averaging reaction-rate constants, it is necessary only to determine how high the degree of the polynomial must be to describe with fair accuracy the relation between rate constant and bed length. For temperature profiles of the type shown in Figure 2, a seventh-degree polynomial is adequate, and a four-point integration applies:

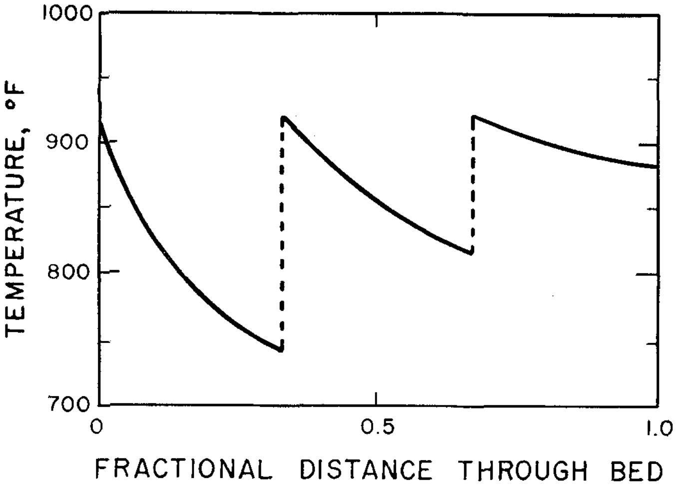

Fig. 1. Temperature profile in a multireactor system.

$$k_{avg} = 0.174\, k_{0.07L} + 0.326\, k_{0.33L} + 0.326\, k_{0.67L} + 0.174\, k_{0.93L} \qquad (5)$$

where $k_{0.07L}$ is the value of k at a point 7% of the distance through the bed, etc.

The constants of the polynomial need not be evaluated; it is necessary only to ensure that the degree is high enough to represent adequately the relation between k and position in the bed. This requirement is easily checked by progressively increasing the number of points used in the method until the result agrees with a careful graphical integration.

Calculation of equivalent isothermal temperature by this simple procedure is illustrated by an example from the Ultraforming process. The average activation energy for the predominant reactions has been established in kinetic studies as 96,000 B.t.u./mole. This value fixes the relation between temperature and reaction-rate constant. To calculate the equivalent isothermal temperature for the temperature profile shown in Figure 2, the k's are determined at the four points required by Equation (5). Substituting these k's into Equation (5) gives an equivalent isothermal temperature of 915°F., which agrees exactly with a careful graphical integration. A two- and a three-point integration of this profile would have given temperatures of 920° and 917°F. respectively. If the four-point integration had not agreed with the graphical integration, one could either use more points or divide the catalyst bed into two sections and apply Gauss's method to each section.

When a large number of equivalent temperatures are to be calculated, the procedure can be simplified even further by a nomographic solution of Equation (5). The nomograph is graduated directly in temperature rather than k. With such a nomograph, equivalent isothermal temperature can be calculated on a routine basis in about a minute.

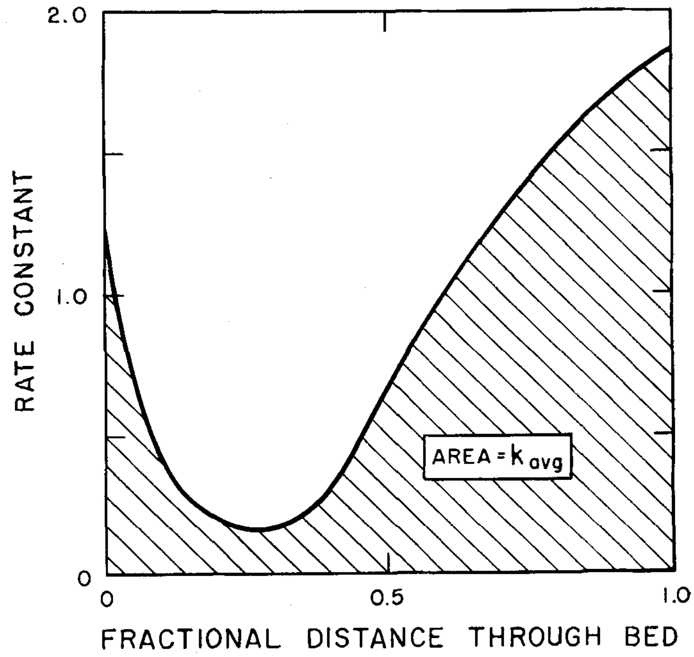

Fig. 3. Rate constant profile in a quasiisothermal reactor.

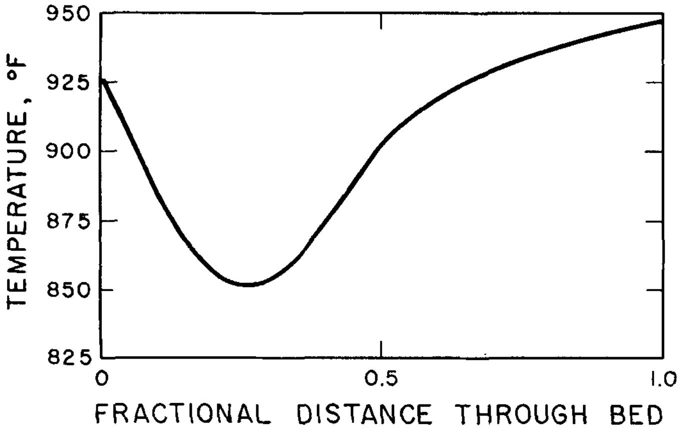

Fig. 2. Temperature profile in a quasiisothermal reactor.

APPLICATION TO COMPLEX SYSTEMS

In systems involving simultaneous reactions an exact definition of equivalent isothermal temperature is not generally possible because the individual reactions have different activation energies. For these systems equivalent temperature is an approximation of the influence of temperature on the several reactions. The degree to which equivalent temperature measures the temperature effect depends on the number of major reactions, and the difference between their activation energies. By suitable choice of ΔE, the equivalent temperature can be made to approximate quite closely the over-all temperature effect.

Although the number of simultaneous reactions involved in a given system may be large, it will almost always be true that only one or two control conversion, yield, or product quality. This is particularly true if conversion is high. By using the average ΔE of the controlling reactions, the equivalent temperature becomes a close measure of the over-all temperature effect.

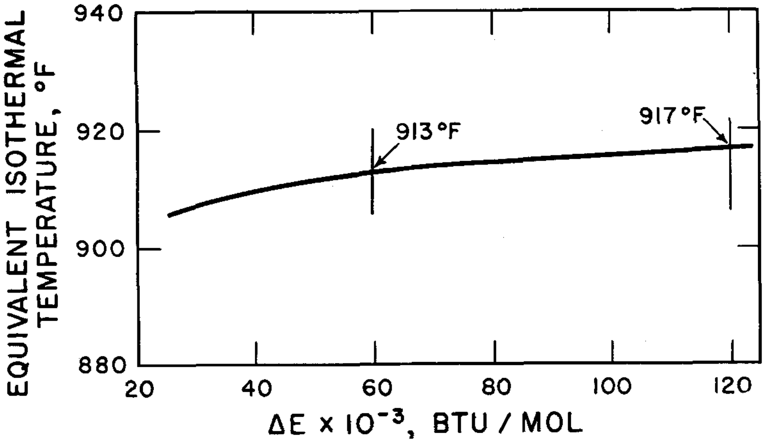

Fig. 4. Effect of activation energy on equivalent isothermal temperature.

If different reactions control in different operating ranges, one should use the appropriate ΔE in each range. Equivalent temperature is not sensitive to ΔE, however, and unless the controlling reactions have widely different ΔE's use of a single value over the whole range is justified. Figure 4 shows the small change for the profile shown in Figure 2 as ΔE varies from 30,000 to 120,000 B.t.u./mole. Between 60,000 and 120,000 B.t.u./mole, equivalent temperature changed only 0.7°F. 10,000 B.t.u./mole change in ΔE. The solution for equivalent temperature involves raising $e^{-1/RT}$ for each increment of the bed to the ΔE power and taking the ΔE root of the sum. Raising the individuals to the ΔE power and extracting the same power from the sum causes equivalent temperature to be insensitive to ΔE. Hence, even in the absence of accurate kinetic data, reliable equivalent temperatures can still be calculated from approximate values of ΔE.

The only problem radial gradients introduce is determining k at the points along the axis of the reactor required by Equation (5). For a cylindrical reactor of radius R in which the radial gradient is symmetrical, k_{avg} for an element of catalyst perpendicular to the axis of the reactor is

$$k_{avg} = \frac{\int k dV}{\int dV} = 2 \int_0^1 k \left(\frac{r}{R}\right) d\left(\frac{r}{R}\right) \qquad (6)$$

where r is the distance along the radius. Gauss's method may also be used for this integration. The value of the group kr/R is needed at n points along the radius. Again, the number of points needed depends on the complexity of the radial gradient. Values of k_{avg} are determined for the positions in the bed required by Equation (5). The average rate constant for the entire bed is then calculated as before.

When a reaction is carried out in a series of catalyst beds, discontinuities in the temperature profile occur and the relation between rate constant and position in the bed cannot be represented by a single polynomial. The three-bed profile of Figure 1 is an example. In this case an average k must be computed for each bed. Equivalent temperature corresponds to an average of the k's for the individual beds, weighted according to the amount of catalyst in each bed.

TEST OF THE METHOD

Different reactors give the same product when they are operated under the same reaction conditions. If reactors having different temperature profiles are made to yield the same product under otherwise identical conditions, then their equivalent isothermal temperatures must be equal. This fact serves as a test of the method. Ultraforming reactors with temperature profiles shown in Figures 1 and 2 have been operated with aliquots of the same catalyst to give identical products. The equivalent isothermal temperatures calculated for two such tests are

	Adiabatic multibed	Quasi-isothermal one bed
Test A	912°F.	911°F.
Test B	912°F.	908°F.

The good agreement between the calculated temperatures shows that equivalent isothermal temperature is a valid measure for comparing catalyst beds having widely different temperature profiles. Furthermore, because the Ultraforming process involves a number of simultaneous reactions, these tests also demonstrate that the concept of equivalent temperature can be useful in complex reaction systems.

NOTATION

A = constant
ΔE = activation energy
L = length of catalyst bed
R = gas law constant, radius of catalyst bed
T = absolute temperature
V = volume
k = reaction-rate constant
n_A = moles of component A
r = distance along radius from axis of reactor
s = fractional distance through catalyst bed
θ = reaction time
$\phi(p_A, p_B \ldots)$ = function of partial pressures of components A, B, . .

LITERATURE CITED

1. Otake, T., E. Kunugida, and H. Kobayashi, *Chem. Eng. (Japan)*, 18, 413 (1954).
2. Sherman, J., *Ind. Eng. Chem.*, 28, 1026 (1936).
3. Sherwood, T. K., and C. E. Reed, "Applied Mathematics in Chemical Engineering," p. 272, New York, McGraw-Hill Book Company, Inc., New York (1939).

(Presented at A.I.Ch.E. New York meeting)