Use of Computers in Kinetic Calculations

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The present writer has read the paper by Gee, Linton, Maier, and Raines(*1*) with a great deal of interest. He wishes, however, to make a few comments on two of the four differential equations which the authors developed in order to describe the chemical and physical processes occurring in their tubular reactor. The writer will show that both the kinetic equation [Equation (1), Table 1] and the equation for the pressure drop through the reactor [Equation (2), Table 1] may be somewhat simplified without any loss in rigor.

In the mathematical developments which follow, the writer has adopted the nomenclature of reference *1*.

Kinetic Equation

The kinetic equation [Equation (1), Table 1 (*1*)] was developed by use of concentration units. It should be written

$$\frac{\partial z}{\partial L} = \frac{\pi K\,(1-z)}{4x_o} \cdot \frac{(r-z)}{(r+1-z)^2} \left[\frac{pD}{R\,(273+t)}\right]^2 \qquad (1)$$

Incidentally, there seems to be a typographical error in this equation in reference (*1*), as the factor π in the numerator has been omitted.

The reaction-rate constant K in Equation (1) may, according to Figure 2 in reference *1*, be written

$$K = e^{\left[a - \frac{b}{(273+t)}\right]} \qquad (2)$$

where

K has the units cu.ft./(mole) (hr.)
a and b are constants

However, if in deriving the kinetic equation one uses activities instead of concentration units, the following equation is obtained

$$\frac{\partial z}{\partial L} = \frac{\pi k\,(1-z)}{4x_o}\,\frac{(r-z)}{(r+1-z)^2}\,(pD)^2 \qquad (3)$$

where

k has the units moles/(cu.ft.) (hr.) (atm.^{2})

Equation (2) may be written in the Arrhenius form

$$\mathrm{K} = Ae^{-\frac{E}{RT}} \qquad (4)$$

where

K = reaction-rate constant
A = a collision factor (same units as K)
E = energy of activation (cal./mole)
R = gas constant (cal./(mole) (°K.)
T = absolute temperature (°K.)

Equation (4) is, however, not rigorous, as the collision factor A is proportional to the molecular velocity, which again, according to the kinetic theory of gases, is proportional to the square root of the absolute temperature. Consequently, one may write

$$\mathrm{K} = Z\sqrt{T}\,e^{-\frac{E}{RT}} \qquad (5)$$

where

Z = a constant

It may easily be shown that the error which is introduced by use of Equation (4) instead of Equation (5) for all practical purposes is negligible even when the temperature interval is of the order of magnitude of 300° to 400°C. As

$$k = \frac{\mathrm{K}}{(RT)^2} = \frac{Z}{R^2\,T^{1.5}}\,e^{-\frac{E}{RT}} \qquad (6)$$

it is apparent that the error in this case also is negligible. Equation (6) may consequently be written in a form identical with Equation (2), or

$$k = A_1 e^{-\frac{E}{RT}} = e^{\left[a_1 - \frac{b}{(273+t)}\right]} \qquad (7)$$

where

a_1 = a constant different from a in Equation (2)
b = the same constant as b in Equation (2)

It is thus seen that one may use Equation (3) instead of Equation (1) in the reactor calculations without any loss in rigor. To what extent this simplification will reduce the time or simplify the programming in the machine computation the present author does not know.

Pressure-drop Equation

The equation for the pressure drop through the reactor [Equation (2), Table 1 (*1*)] is developed from the basic differential equation

$$-\frac{dp}{dL} = \frac{2fG^2}{g_c\rho D} \qquad (8)$$

When the following substitutions are made,

$$G = \frac{(B_o+x)\,M_{av}}{\frac{\pi}{4}D^2} \qquad (9)$$

and

$$\rho = \frac{pM_{av}}{R\,(273+t)} \qquad (10)$$

and introducing the new variables $r = B_o/x_o$ and $z = 1 - (x/x_o)$ the authors arrive at their final form of the pressure-drop equation,

$$-\frac{\partial p}{\partial L} = \frac{2f\mathrm{M}_{av}R\,(273+t)\,[x_o\,(r+1-z)]^2}{g_c\left(\frac{\pi}{4}\right)^2 D^5\,p} \qquad (11)$$

When an average molecular weight and constant feed composition are assumed the pressure drop is thus a function of feed rate, conversion, reactor diameter, temperature, and pressure; or

$$-\frac{\partial p}{\partial L} = \psi\,(x_o, z, D, t, p) \qquad (12)$$

However, if instead of Equation (9) the following substitution is made,

$$G = \frac{W}{\frac{\pi}{4}D_2} \qquad (13)$$

where

W = total weight flow rate, lb./hr., Equation (11) reduces to the following expression

$$-\frac{\partial d}{\partial L} = \frac{2f\,R\,(273+t)\,W^2}{g_c\left(\frac{\pi}{4}\right)^2 M_{av}\,D^5p} \qquad (14)$$

Contrary to Equation (11), where the pressure drop is a function of five variables, Equation (14) gives the pressure drop in terms of only four variables, i.e., feed rate, reactor diameter, temperature, and pressure, or

$$-\frac{\partial p}{\partial L} = \psi(W, D, t, p) \quad (15)$$

It seems to the author that using Equation (14) instead of Equation (11) should simplify the programming of the problem and also reduce the time needed for the machine computation.

Literature Cited

1. Gee, R. E., W. H. Linton, Jr., R. E. Maier, and J. W. Raines, *Chem. Eng. Progr.*, 50, 497 (1954).

Adiabatic-temperature Change

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The following equation may be derived from thermodynamics and is applicable to all states of matter:

$$\left(\frac{\partial T}{\partial p}\right)_s = \frac{T\alpha}{C'_p\rho} = \frac{TV\alpha}{C'_p} \quad (1)$$

where

T = temperature, °K.
p = pressure, atm.
$\alpha = 1/V(\partial V/\partial T)_p$ = cubical coefficient of expansion, °K.$^{-1}$
ρ = density, g./ml.
V = specific volume, ml./g.
C'_p = specific heat, ml. (atm.)/(g.)(°K.) = 41.3 cal./,g.)(°K.) = 41.3C_p
S = entropy

Equation (1) may be written as

$$d\ln T = \frac{\alpha\, dp}{41.3\, C_p\, \rho} \quad (2)$$

For a liquid α, C_p, and ρ will not change greatly with pressure; therefore, integration of Equation (2) gives

$$\Delta T = T_1\left[{}_e\left(\frac{\alpha_{avg}\,\Delta p}{41.3\, C_{pA}\,\rho_A}\right)_{-1}\right] \quad (3)$$

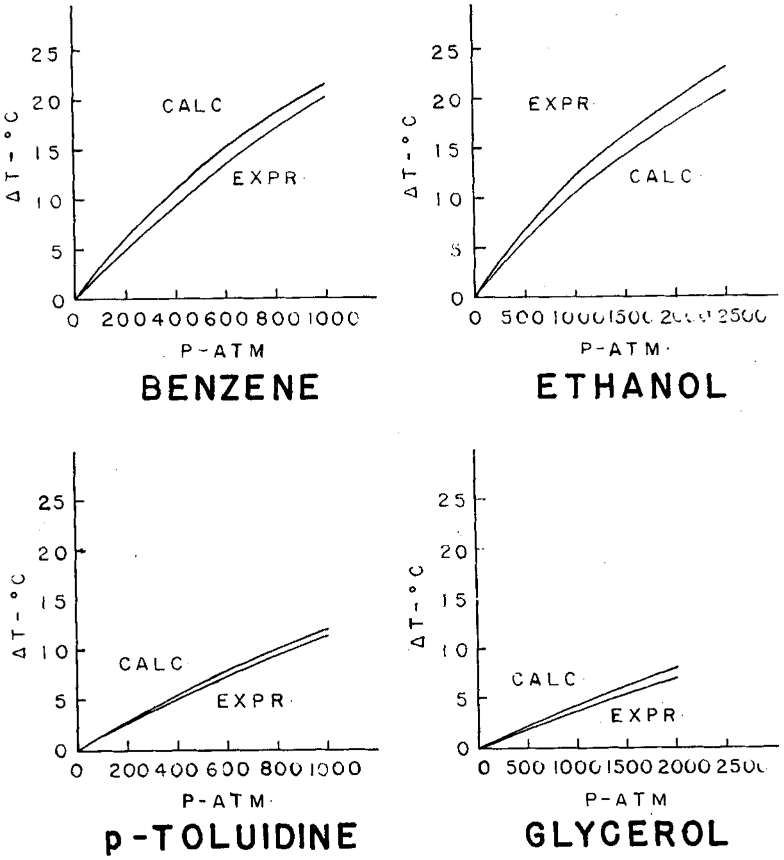
where the subscripts 1 and *avg* represent initial and average values respectively, and the subscript A represents values at atmospheric pressure.

A simpler relation between ΔT and Δp may be obtained by use of the following approximate form of Equation (1):

$$\Delta T = \frac{T_1\,\alpha_{avg}\,\Delta p}{C_{pA}\,\rho_A} \quad (4)$$

Thus it is possible to calculate the adiabatic-temperature change of a liquid produced from a given change in pressure by use of Equation (3) or (4). In most cases Equation (4) is sufficiently accurate.

This method of calculation is simple as long as α values are available as a function of pressure. Thus for water the calculated values of ΔT are in agreement with those calculated from experimental values of $(\partial T/\partial p)_s$ obtained from Dorsey(*2*). α values as a function of pressure are not available for most substances; however, values of the compressibility coefficient β as a function of pressure are known for many substances. The following discussion shows a useful relation between the cubical coefficient of expansion and the compressibility coefficient.



BENZENE

ETHANOL

p-TOLUIDINE

GLYCEROL

Fig. 1.

For the variables pressure, temperature, and volume, it has been shown mathematically that

$$\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial p}\right)_T\left(\frac{\partial T}{\partial V}\right)_p = -1 \quad (5)$$

Equation (5) may be written as

$$\alpha = \beta\left(\frac{\partial p}{\partial T}\right)_V \quad (6)$$

where

$\beta = -1/V(\partial V/\partial p)_T$ = compressibility coefficient, atm.$^{-1}$

When Equation (6) is differentiated, temperature constant