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INFORMATION RETRIEVAL*

Key Words: A. Kinetics-8, Correlation-2, Computers-10, Differential Equations-1, Concentrations-2, Integration-10. B. Kinetics-8, Ethylene Oxide-1, Ammonia-1, Ethanolamines-2, Benzene-1, Chlorine-1, Chlorobenzene-2, Methanol-1, Propylene-1, Proplyene Oxide-1, Correlation-1, Computers-10, Rate Constants-2, Concentrations-1, Least Squares-4.

Abstract: A new method of obtaining an approximate integral solution of a set of differential rate equations is described. The method is used to correlate experimental data on systems whose stoichiometry would indicate a consecutive competitive mechanism. The estimates of the rate constants, found by fitting the approximate solution to the data, are within experimental error of the values obtained by other methods.

Reference: Friedman, M. H., and R. R. White, **A.I.Ch.E. Journal, 8,** No. 5, p. 581 (November, 1962).

* For details on the use of these key words and the A.I.Ch.E. Information Retrieval Program, see **Chem. Eng. Progr., 57,** No. 5, p. 55 (May, 1961), No. 6, p. 73 (June, 1961); **58,** No. 7, p. 9 (July, 1962).

(Continued on page 705)

ERRATUM

It has been called to the attention of R. E. Emmert and R. L. Pigford by Professor P. V. Danckwerts that some data which they extracted from a paper by Bates and Pinching* were misinterpreted in "Gas Absorption Accompanied by Chemical Reaction," which appeared in the May, 1962, issue of the *A.I.Ch.E. Journal.* As a consequence, Emmert and Pigford's analysis of the relative effects of competing reactions based on previous workers' data must be modified. This change does not in any way alter their own data or their interpretation. This erratum describes the changes needed to account for this misinterpretation. All changes are in the section labeled "Reaction Mechanism."

In order to determine the concentrations of hydroxyl ion and free amine

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* Bates, R. G., and G. D. Pinching, *J. Research Natl. Bur. Standards,* 46, 349 (1951).

TABLE 1. CONCENTRATIONS OF OH^- AND FREE MONOETHANOLAMINE IN SOLUTIONS OF VARIOUS STRENGTHS OF TOTAL AMINE BASED ON DATA OF BATES AND PINCHING

B_o	(B)	(OH^-)	$(B)/(OH^-)$
0.01	0.00945	0.00055	17.3
0.1	0.0982	0.00178	55.1
0.5	0.496	0.00397	125
1.0	0.9944	0.0056	177
2.0	1.9926	0.00744	268

in solutions of various total amine strengths Emmert and Pigford used the basic dissociation constant for this reaction as reported by Bates and Pinching. In the original Bates and Pinching paper, the basic dissociation constant was defined as being equal to K_w, "the ionization constant of water," divided by K_{bh}, the dissociation constant of ethanol ammonium ion. Actually Bates and Pinching intended that K_w be the ion product of water, which is equal to 10^{-14}, instead of the dissociation constant of water which is equal to 1.8×10^{-16}. The consequence is that the equations shown in Column 1, page 173, of Emmert and Pigford's article should read

$$K_b = \frac{(BH^+)(OH^-)}{(B)} \cdot \frac{\gamma BH^+ \gamma OH^-}{\gamma B} = 3.18 \times 10^{-5}\ (25°C.)$$

and

$$\frac{(BH^+)(OH^-)}{(B)} = 3.18 \times 10^{-5}\ (25°C.)$$

Tables 1 and 2 must then be revised to the following:

TABLE 2. RELATIVE INFLUENCE OF PARALLEL, FAST-REACTION BATHS IN CONSUMING CARBON DIOXIDE (BASED ON INITIAL RATES) Per Cent of Carbon Dioxide Consumed by *Rx*

B_o	1	2	3	Moles amine consumed/mole CO_2 reaction, ν
0.01	91.6	8.1	0.3	1.08
0.1	97.2	2.7	0.1	1.03
0.5	98.6	1.2	0.2	1.01
1.0	98.8	0.9	0.3	1.01
2.0	99.0	0.6	0.4	1.01

So the average stoichiometric factor is estimated theoretically to lie between 1.0 and 1.1, as contrasted with the experimentally observed value of 1.78.

These corrections do not alter Emmert and Pigford's previous conclusions in comparing stoichiometric coefficients extracted from their absorption data with those predicted from mechanism data. The disagreement which previously existed is even greater now. They still have no explanation for this disagreement.

TABLE 3. RATE CONSTANTS FOR REACTION $HOC_2H_4NHCOOH + H_2O$ $HOC_2H_4NH_4CO_3$ CALCULATED FROM DATA OF FAURHOLT (18°C.) (CARBAMATE + H_2O CARBONATE)

B_o	$k_{forward}$, sec.$^{-1}$	$k_{reverse}$, sec.$^{-1}$
1.0	1.2×10^{-6}	1.5×10^{-6}
0.1	1.6×10^{-5}	0.44×10^{-5}
0.01	1.3×10^{-4}	0.12×10^{-4}

The rate constants for the carbamate-to-carbonate reaction calculated from the rate expression of Faurholt, et al. (employing dissociation constants from Bates and Pinching) must also be revised, although little change results. Agreement with the writers' rate measurements for a 0.1N amine solution still remains good. Based on an estimated activation energy Emmert and Pigford's measurement (corrected to 18°C.) gives $k_{forward}$ of 2×10^{-5} sec.$^{-1}$ compared with the calculated value of 1.6×10^{-5} sec.$^{-1}$. Table 3 shows revised values. However the values for the reverse reaction rate constant (which Emmert and Pigford did not employ in interpreting their data) are changed significantly.

COMMUNICATIONS TO THE EDITOR

Equations for Transient Heat Transfer in Packed Beds

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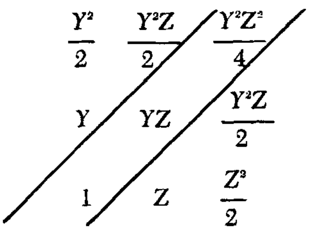
Readers interested in transient heat and mass transfer in packed beds [theories developed since 1926 by Anzelius (*1*), Schumann (*2*), Furnas (*3*), Nusselt (*4*), Thomas (*5*), and many others, see a 1954 survey (*6*)] may have use for the following table, an array of terms from some frequently met infinite double-power series [see (*5*) and (*6*)], higher terms than those of second degree in *Y* and *Z* having been omitted only for the sake of simplicity in reproduction:



Starting from unity, in the left-hand bottom corner, each term is derived either from the one below it by an integration with respect to *Y* or from the one to the left by an integration with respect to *Z*.

By combining groups of terms with equal degree, one sees that the sum is e^{Y+Z}.

By moving one step in the 45-deg. direction this sum is seen to be a solution of $\frac{\partial^2 \phi}{\partial Y \partial Z} = \phi$.

If one divides the table by lines in the 45-deg. direction, as shown, the same differential equation holds true for each part of the table, the boundary conditions varying from case to case because in each section separately all terms are converted into others of the same section by the $\frac{\partial^2}{\partial Y \partial Z}$ operation.

Now if T_1 and T_2 are the solutions of the well-known heat transfer problem

$$\frac{\partial T_2}{\partial Z} = -\frac{\partial T_1}{\partial Y} = T_1 - T_2$$

with

$$Z = 0; \quad T_2 = 0$$
$$Y = 0; \quad T_1 = 1$$

where T_1 and T_2 represent the gas and solid temperatures at place *Y* and time (corrected for position) *Z*, the three sections of the table represent (from left to right) see for instance (*6*):

$$e^{Y+Z}(1 - T_1) = e^Y \int_0^Y e^{-u} I_0\ (2\sqrt{uZ})\ du = \phi(Y, Z)$$

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