and since Squires has shown that to a better approximation V_B is proportional to V_{s_0} one can write

$$D_B \sim \frac{V_{s_0}^2}{(4.03)^2} \qquad (3)$$

so that

$$\frac{dU}{dy} \sim \frac{1}{V_{s_0}} \text{ and } \left(\frac{dU}{dy}\right)^2 \sim \left(\frac{1}{V_{s_0}}\right)^2 \qquad (4)$$

The dispersive grain pressure measurements of Bagnold have as a correlant the square of velocity gradient which is thus proportional to $1/V_{s_0}^2$.

The theoretical stable bubble sizes calculated by Squires can now be compared with the magnitude of the velocity gradient, or rather the dispersive pressure. A high velocity gradient corresponds to a high dispersive pressure and certainly a high dispersive pressure coupled with a small theoretically stable bubble size would lead to bubble disappearance or at any rate small probability of bubble formation ever fully occurring.

From correlations (*10*) of V_{s_0} it is possible to calculate relative values of the gradient $(dU/dy)^2$ within the bubble as a function of particle diameter. The results of such calculations are shown in Figure 2 for a few typical systems. Since Bagnold showed dispersive pressure to be directly proportional to velocity gradient, the ordinate of Figure 2 could be relabelled P_G; however, Bagnold showed that dispersive pressure is also a function of voidage. Since the loosest static bed density of powders is a function of particle size (finer powders exhibiting high bulk voidages), the curves of Figure 2 can be corrected for voidage. In making this correction it is assumed that the curves of Figure 2 are based on 40% voids for all particle sizes and that the actual voidage is a function of particle size as given in several sources (*11*). This voidage correction to Figure 2 bends the curves downward to a greater and greater extent as particle diameter decreases and effectively flattens them to the results shown in Figure 3 in which the ordinate is now labelled P_G. The degree of displacement due to the voidage correction is illustrated for the clay-water system in Figure 3 by the dashed curve, which is taken from Figure 2. Unfortunately, there is no direct quantitative means for matching the P_G scale to the abscissa. Quantitatively the coordinates of Figure 3 are reasonable and probably near the proper magnitude since Bagnold's measurements went up to 2 lb./sq. ft. at a voidage of 40%.

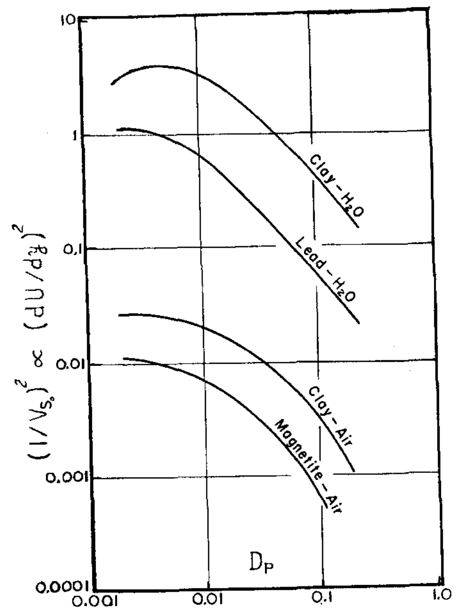

Fig. 2. Velocity gradients or dispersive pressures for various fluid-particle systems.

The ordinate of Figure 3 is a measure of the force tending to dilate the solids making up the bottom surface of the largest calculable stable bubble in a fluidized bed of particles of the size given in the abscissa. Since the gradient and, hence, dispersive, pressure is related to a calculated maximum bubble size, it is not to be implied that bubbles will or do exist under all conditions, but merely that if they did exist they would have a dis-

(*Continued on page 573*)

Kinetics of Ethane Pyrolysis

JOHN R. BARTLIT and HARDING BLISS
Yale University, New Haven, Connecticut

In the course of the development of a flow reactor for the study of pyrolysis reactions some interesting observations about the method and results with ethane have been determined. The essence of this method is the rapid mixing of ethane with very hot nitrogen at a temperature below that required for pyrolysis in an attempt to reduce the large axial temperature gradients usually experienced in a flow reactor. During the course of this work others (*1*) have arrived at a related idea and have developed the scheme with considerable success. The nature of the data and the treatment thereof vary considerably in the two cases.

Ethane was pyrolyzed at 696 to 826°C. and one atmosphere for contact times of 0.21 to 2.2 sec. with 9 to 72% decomposition. The ethane content of the mixed stream varied from 7 to 22%.

EXPERIMENTAL

Apparatus

The preheater-reactor (see Figure 1) was a Vitreosil quartz tube 7 mm. O.D. x 5 mm. I.D., in the shape of a tee with a cross near one end of the horizontal. The horizontal member was 31¼ in. long and the vertical 18 in. The vertical member was used for preheating ethane. The first 18 in. of the horizontal member was used for preheating nitrogen, the next 8¼ in. for the reaction zone proper, and the last 5 in. (which were outside the insulating box) for the admission of a thermocouple. The outlet cross was made of two 1 in. lengths of the same tubing to admit cold nitrogen as a quench and to discharge the products. In normal operation, the quench and discharge were through these short 2 in. lengths and the straight section of the quartz tube was plugged with a rubber *policeman*. When a gas temperature traverse was made, the straight section was unplugged and the gases allowed to flow out of this straight section.

The ethane leg was heated by means of 30 ft. of B & S 20 g. Nichrome wire on 15¾ in. (four units) of Norton Alundum grooved cores (No. 9099) and embedded in Norton RA 1162 cement. The nitrogen leg was heated by means of 24 ft. of 0.032 in. diameter Baker No. 1 platinum wire, similarly wound. The reaction zone was heated by means of 17¼ ft. of B & S 20 g. Kanthal A-1 resistance wire wound into a tight coil on a mandrel and stretched to allow about 1/16 in. between turns. This heater was held in place on the reaction tube with the same Alundum cement. The other heaters were, of course, removable. Certain thermocouples were immersed in this cement. Each of the three heaters was con-

(*Continued on following page*)

John R. Bartlit is at the University of California, Los Alamos, Scientific Laboratory, Los Alamos, New Mexico.

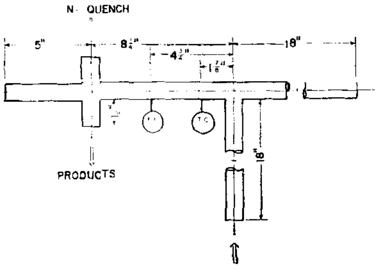

Fig. 1. Plan for quartz preheater-reactor assembly.

nected through a fuse to a manually operated *powerstat* for control.

The preheater-reactor was mounted horizontally on firebricks, and the entire assembly (except the quench cross and thermocouple port) was contained in a metal box that conformed roughly in plan to the preheater-reactor. The cross section of this box was about 11 in. in width and 12½ in. in height. The box was lined on the inside with aluminum sheet and was filled with firebricks. The space immediately above the quartz tube was filled with Johns-Manville Sil-O-Cel, coarse grade, and other void spaces around the bricks with ground firebrick. There is considerable heat loss at the joint of the tee of the quartz tube, since no heater could be extended quite to this point. An attempt was made to minimize this by adding one more heater, 20 ft. of B & S 20 g. Kanthal A-1 wound on an asbestos board about 3½ in. above the joint.

Nitrogen and ethane were introduced to the preheater-reactor via ⅜ in. O.D. x ¼ in. I.D. aluminum tubing connected with glyptal-sealed rubber couplings. Each gas was dried with Linde 5A molecular sieves placed in the annular space of a *vacuum trap* and cooled to ice temperature. These were frequently reactivated by heating. Flow rates were measured with Brooks Tru-Taper rotameters with spherical Pyrex floats. These rotameters with dry gases exhibited erratic behavior due to electrostatic charges. This problem was solved by wiping the outside of the tubes and the floats with Anstac M, made by Chemical Development Corporation.

The effluent gases were quenched with a metered stream of cold dry nitrogen. When sufficiently cooled, the combined gases were sampled with a hypodermic syringe, the needle of which pierced a serum stopper in the leg of an appropriate glass tee. Usually these gases were then vented to a stack, but sometimes they were sent to a gas collection system to permit volume measurement and a check of the flow rates.

An especially critical matter is the measurement of temperature. Four chromel-alumel thermocouples (B & S 30 g.) in 1/16 in. O.D. Inconel sheaths were used. The first was cemented to the outside tube wall 1¼ in. before the downstream end of the ethane preheater; the second was ½ in. from the tee joint. The third was embedded in alundum cement 1⅞ in. along the reaction zone proper and the fourth similarly embedded 4¾ in. along the reaction zone. A platinum-platinum 10% rhodium thermocouple of

(Continued on following page)

(Continued from page 386)

The book closes with an excellent set of appendices of tables of Laplace transforms, Z transforms, and signal flow diagram transformations. The tables of nomenclature, subject index, and author index are also well done.

This book is therefore highly recommended to the engineer who wishes to study process control on his own or who wishes an elementary reference text on the subject.

THEODORE J. WILLIAMS
MONSANTO COMPANY

Chemical Reactor Theory, Kenneth Denbigh, Cambridge University Press, London (1965), 184 pages, $6.50.

To anyone who has read one of his previous volumes, the appearance of a new book by Professor Denbigh is a noteworthy event. The readers of the present book will not be disappointed, since the very readable and lucid style is again apparent.

In such a short book, one would naturally not expect to find all the detailed information necessary for the design of a chemical reactor. The intent is rather to provide a survey of the entire field so as to enable the reader to get an overall view without getting too involved in details. This is not to say that there are no numerical examples, but usually they emphasize the problem statement and the interpretation of results rather than computational aspects. This makes the book especially valuable as a starting place for those not very familiar with modern reactor design methods. Also, in contradiction to Professor Denbigh's Preface, the reviewer feels that the audience that may find the book most useful is the busy practicing engineer who wants to find out about this important field. As one of the pioneers in chemical reaction engineering, Professor Denbigh is particularly qualified to discuss the many developments and their meaning in the field.

The topics covered are concerned almost entirely with chemical reactor performance rather than chemical kinetics. The first group of chapters covers the types of reactors commonly used with basic design methods for the plug flow and perfectly mixed cases. The emphasis is on the meaning and limitations of these models as illustrated by a few basic examples. The reasons for choosing one type over the other for the often crucial problem of selectivity with complex reactions completes the section.

The final two chapters discuss the more complicated topics of optimal design and temperature stability problems. The first topic is covered by using logical arguments rather than the extremely complicated formal mathematical apparatus of modern optimization techniques. The most important general principles are brought out in this way and sufficient references are given for the reader interested in further details. The same technique is used in the final chapter where the available published results are organized and discussed as to their practical meaning.

Thus, in summary, the book is a very readable introduction encompassing the vast area of chemical reaction engineering, and should be extremely useful for those who want a good general idea of the current status of the field.

KENNETH B. BISCHOFF
UNIVERSITY OF TEXAS

INFORMATION RETRIEVAL*

The prediction of the viscosity of multicomponent, nonpolar gaseous mixtures at atmospheric pressure, Strunk, Mailand R., and Gary D. Fehsenfeld, **A.I.Ch.E. Journal, 11,** No. 3, p. 389 (May, 1965).

Key Words: Components-6, Composition-6, Temperature-6, Viscosity-7, Nonpolar-0, Multicomponent-0, Gases-8, Predicting-0, Viscosity-9, Lennard-Jones-0, Characteristic-0, Mixture-0, Force Constants-10.

Abstract: The method for predicting the viscosity of binary nonpolar gaseous mixtures from pure component Lennard-Jones force parameters and composition has been extended to multicomponent mixtures. The 136 mixtures examined contained from three to seven components from sixteen different gases in the temperature range from 5° to 1,014°C. The predicted gaseous viscosities should fall between —0.3 and —6.7% of the actual viscosities 95% of the time. With a slight modification of the constant in the viscosity expression, the viscosity can be predicted to within ± 3.2% of the experimental viscosity 95% of the time for mixtures containing three or more components.

Stagnation in a fluid interface: properties of the stagnant film, Merson, R. L., and J. A. Quinn, **A.I.Ch.E. Journal, 11,** No. 3, p. 391 (May, 1965).

Key Words: A. Stagnation-8, 7, Interface-9, Fluids-9, Water-9, Channel-9, Horizontal-0, Compressible-0, Incompressible-0, Stearic Acid-6, Oleic-6, 9, Dodecyltrimethylammonium Chloride-6, 9, Film-8, Contaminants-6, Monolayers-9, Surface Active Agents-6, 9, Concentration-6, Surface Equation of State-8, Acids (Carboxylic)-6, 9, Fatty Acids-6, 9.

Abstract: The mechanism whereby surface-active agents cause stagnation in a fluid interface was studied for water flowing in a horizontal channel. Known surface active contaminants exhibiting varied surface behavior were added to the water. Distinctly different phenomena were observed with compressible and incompressible films.

Longitudinal dispersion in pulsed perforated-plate columns, Miyauchi, Terukatsu, and Haruhiko Oya, **A.I.Ch.E. Journal, 11,** No. 3, p. 395 (May, 1965).

Key Words: A. Dispersion Coefficient-8, 7, 9, Dispersion-8, 7, Size-7, Droplets-9, Holdup-7, Measurement-8, Columns-9, Geometry-6, Perforated Plates-10, Operating Conditions-6, Viscosity-6, Pulsations-10, Dispersers-10, Water-1, Extraction-8, Ketones-2, Methyl Isobutyl Ketone-2.

Abstract: Experimental measurements have been performed for pulsed perforated-plate columns of different column geometry, to determine longitudinal dispersion coefficient for each phase, droplet size, and droplet holdup. These quantities are correlated with operating conditions and column geometry, including those published by different authors.

(*Continued on page 566*)

---

* For details on the use of these Key Words and the A.I.Ch.E. Information Retrieval Program, see **Chem. Eng. Progr.,** Vol. 60, No. 8, p. 88 (August, 1964). A free copy of this article may be obtained by sending a post card, with the words "Key Word Article" and your name and address (please print) to Publications Department, A.I.Ch.E., 345 East 47 St., N.Y. N.Y., 10017. Price quotations for volume quantities on request. Free tear sheets of the information retrieval entries may be obtained by writing to the New York office.

(*Continued from preceding page*)

the same size and sheathing noted above was connected to the wall of the nitrogen preheater tube 1-11/16 in. before the downstream end of the preheater. The chromel-alumel couples had lead wires of the same material, but copper leads were used for the other. Movable thermocouples were built as the first four described above. Two of these could be moved along the ethane and nitrogen preheater legs between the grooved cores and the tube. The third movable couple (18 in. long) could be moved inside the reaction zone proper throughout its whole length and into the nitrogen preheater for a distance of 3¾ in. The temperature profiles measured with this thermocouple were of major importance. All thermocouples and their circuits were calibrated before and after use at the freezing point of aluminum according to NBS procedures (2). In all cases agreement within 5°C. was obtained. Thermocouple voltages were measured with a Leeds and Northrup Type K-1 potentiometer.

Some runs were made with an Inconel tube in place of quartz. This tube was ¼ in. O.D. with 1/20 in. wall, and differed only in a few details given by Bartlit (3) from that described here. The results obtained with Inconel will be mentioned but not stressed below, because catalytic effects were observed.

Analyses

Gas analyses were done with a Perkin-Elmer Vapor Fractometer, Model 154B, equipped with a Leeds & Northrup recorder Model G, provided with a Disc integrator. The column was two meters of silica gel, operated at 50°C. and 10 lb./sq. in. gauge helium pressure. Good resolutions of hydrogen, nitrogen, methane, ethylene, and ethane were obtained. The chromatograph was calibrated with known volumes of the pure components.

Materials

The gases used for calibration and the runs proper were as follows: ethane, Matheson C. P. (99%); ethylene, Matheson C. P. (99.72%); acetylene, Matheson purified (99.66%); hydrogen, Matheson special dry (99.8%); methane, Phillips Petroleum Co. research grade (99.56%); and nitrogen, Air Reduction Co., water pumped grade.

Procedure

The heaters were used to bring the preheater-reactor up to temperature very slowly, five or six hours being required to reach 750°C. Once heated, the assembly was not allowed to cool except for major changes. A run was begun by starting the flows of nitrogen and ethane. Some time was required for the attainment of steady state, as judged by relative constancy of the readings of the thermocouples and reproducibility of the exit gas analysis. When this was attained, the readings of the gas thermocouple were recorded for each 1-in. increment along the reaction zone length. Flow rates were checked by comparing the sum of the flows of the three rotameters (nitrogen, ethane, and nitrogen quench) with the total flow rate of exit gases as measured by water displacement. Agreement here was always

(*Continued on following page*)

(Continued from preceding page)

within 6%. A gas sample was then taken for final analysis, and during the analysis all fixed thermocouples and manometers were read.

DATA AND INTERPRETATION

Basic Data

Ten runs were made in both the quartz preheater-reactor and in the Inconel one. The basic data recorded were nitrogen and ethane feed rates, temperature and pressure of the room, gas temperature according to the movable thermocouple at the various lengths specified, and the gas analysis. Full details of these data are reported by Bartlit. Many problems arise in reducing these data to rate constants.

Mixing

The first of these problems is the rapidity of mixing of the hot nitrogen and relatively cold ethane. With the theoretical model of G. I. Taylor (*4*) for laminar flow (the highest Reynolds number used here was 50) it was shown that an original temperature difference of 200°C. would be reduced to 4°C. in about 0.015 sec., which was less than 6% of the shortest reaction time used. A thermal diffusivity of 12.5×10^{-4} sq.ft./sec. was used for this calculation. A similar calculation with a molecular diffusivity of 0.83×10^{-3} sq.ft./sec. indicated that the nitrogen stream should have undergone 98% of its ultimate dilution in 0.012 sec. The latter calculation may also be checked by the method of Klinkenberg, Krajenbrink, and Lauwerier (*5*) who considered eddy as well as molecular diffusion. With this method and a Peclet number of 10, it was shown that essentially complete mixing should have been attained within three tube radii, or about 0.3 in. It thus seems reasonably sure that thermal and concentration equalizations should have been fast enough to permit the neglect of this problem. This conclusion is strengthened by the fact that the reaction proceeds very slowly at the start of the reaction zone proper because of the relatively low temperature there.

Effective Length

The next problem is the matter of the effective length of the reaction zone. The actual length was 8 in. between the tee and the outlet cross. The first ¼ in. must be assigned to mixing, and a consideration of the axial temperature gradient (discussed below) shows that the last 2¾ in. may be discarded simply because the temperature is reduced so much by heat loss at the end that only negligible reaction can occur. Thus, 5 in. was selected as the reactor length. The soundness of this selection will be defended later.

(Continued on following page)

INFORMATION RETRIEVAL

(*Continued from page 564*)

Films of non-Newtonian fluids adhering to flat plates, Gutfinger, Chaim, and John A. Tallmadge, **A.I.Ch.E. Journal, 11,** No. 3, p. 403 (May, 1965).

Key Words: A. Flux-8, Thickness-8, Film-9, Thin-0, Profile-8, Velocity-9, Drainage-9, Withdrawal-9, Fluids-9, Non-Newtonian-0, Plates-9, Flat-0, Equation-8, Flow-9, Comparison-8, Newtonian-0, Ellis Model Fluid-9, Power Law Fluid-9, Carbopol-9, CMC-9, Rheology-8, Theoretical-0, Experimental-0, Capillary Statics-8, Capillary Number-8.

Abstract: This paper presents a study of flux, film thickness, and velocity profiles in the drainage and withdrawal processes of non-Newtonian fluids on flat plates. The flow equations for the drainage from a vertical plate are solved for an Ellis model fluid. The withdrawal case is solved for the power law fluid.

Coalescence of liquid drops in two-component-two-phase systems: Part I. Effect of physical properties on the rate of coalescence. Part II. Theoretical analysis of coalescence rate, Jeffreys, G. V., and J. L. Hawksley, **A.I.Ch.E. Journal, 11,** No. 3, p. 413 (May, 1965).

Key Words: Coalescence-8, Single Drops-8, Plane Interface-8, First Step Coalescence-8, Overall Coalescence-8, Benzene-5, Iso-Octane-5, Normal Heptane-5, Liquid Paraffin-5, Interfacial Tension-6, Viscosity-6, Drop Size-6, Density-6, Descent Distance-6, Temperature-6, Coalescence Time-7, Coalescence Time Distribution-7, Mathematical Model-10, Correlation-10, High-Speed Photography-10.

Abstract: Experimental coalescence time and time distribution studies of a single drop at a plane interface are presented for four two-component–two-phase systems. The experimental results have been analyzed by dimensional and statistical analysis and a correlation of coalescence time and time distribution with physical properties presented. This is followed with the presentation of a theoretical model to estimate film drainage time and the pressure drop in the film which has shown that the film is thinnest at its periphery. High-speed photographic studies confirmed the theoretical model findings.

The mixed suspension, mixed product removal crystallizer as a concept in crystallizer design, Randolph, Alan D., **A.I.Ch.E. Journal, 11,** No. 3, p. 424 (May, 1965). 1965).

Key Words: A. Design-8, Crystallizers-9, 8, Crystallization-8, Kinetics-7, Crystal Size Distribution-7, Residence Time-6, Nucleation-7, 9, Alum-1, Growth Rate-7, 9, Ethanol-1, Water-1, Removal-6, Crystals-9, Classification-6, Concentration-6, Solids-9, Staged Vessels-6, Supersaturation-6, Size-7, Population Balance-8, Mass Balance-8, Alcohols-1.

Abstract: Simultaneous population and mass balances have been solved together with a generalized form of nucleation-growth kinetics to obtain the form of crystal size distribution for several idealized modes of crystallizer operation including seed crystal removal, product classification, arbitrary solids concentration, and staged vessels. The effect of holding time and feed supersaturation on crystal size was also studied.

Bounded and patched solutions for boundary value problems, Churchill, Stuart W., **A.I.Ch.E. Journal, 11,** No. 3, p. 431 (May, 1965).

Key Words: A. Mathematical Model-8, Approximate Solutions-8, Bounding-10, 8, 9, Patching-10, 8, 9, Multiphase Media-4, Reliability-8, Pseudo Solutions-10. B. Bounding-10, Conduction-9, Convection-9, Solution-8, Analytical-0. C. Patching-10, Conduction-9, Solution-8, Analytical-0, Freezing-9.

Abstract: The technique of bounding, that is of constructing general solutions for all ranges of the variables and parameters from solutions for a few limiting and special cases, is outlined and illustrated for problems in conduction and convection. The technique of patching, that is of constructing approximate solutions for multiphase media by the combination of pseudo solutions for the different regions, is also outlined and illustrated for problems in conduction and freezing. The shortcomings and possible inaccuracies of these two techniques are indicated as well.

(*Continued on page 568*)

(*Continued from preceding page*)

Flow Regime

The third problem is that of the laminar flow regime, which ordinarily requires rather special treatment. It has been shown by Cleland and Wilhelm (*6*), however, that the plug flow assumption is valid for a first-order reaction when

$$\frac{Dt_o}{R_o^2} > 1.0$$

With the shortest times used here this ratio was 2.1. Thus, the plug flow assumption was made. It should be noted also that this problem does not ordinarily become severe until high conversions are reached; the conversions found here were low to moderate.

Temperatures

The next (and undoubtedly the most important) problem is that of temperature. A typical measured axial temperature distribution is shown in Figure 2. The range of temperatures shown there is of the same order as that shown by Crocco et al. (*1*). The range of temperature is considerably less than that of Towell and Martin (*20*), but it should be noted that their ingenious interpretation method does not require a small range. We must note that the ideal of bringing the ethane quickly to a constant temperature is not realized. Heat losses that could be overcome only rather unevenly in this apparatus play a major part in this matter. Thus, gradients are less than in a conventional flow reactor but they are certainly not eliminated.

There is ample evidence reported by Bartlit (3) that the gas temperature is very near that of the wall, measured on the outside with several fixed and moving couples. Certainly the gas temperature thermocouple reading was not influenced by rotation on its axis, by gas velocity, or by the provision of a highly reflective tip shield. The gas temperature was influenced only by its axial position.

Another aspect of the temperature problem is that of assigning an appropriate mean value for a particular run. This was done first by determin-

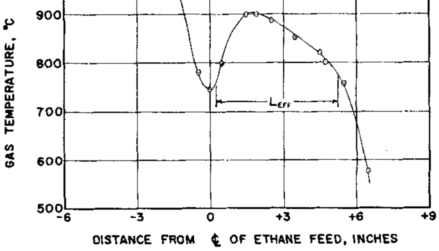

Fig. 2. Typical temperature traverse.

(*Continued on following page*)

(Continued from preceding page)

ing a simple graphical average, denoted by T_{Avg}. This was adequate for preliminary and semiquantitative interpretation of the data. The final interpretation depended, however, on a more carefully defined mean, T_m, defined by

$$e^{-\frac{E}{RT_m}} L_{eff} = \int^{L_{eff}} e^{-\frac{E}{RT(L)}} dL \quad (1)$$

The indicated integration requires, of course, the measured gradient $T(L)_a$ and the unknown activation energy. A trial and error procedure was thus involved in all the data. It should be noted that the change of gas density with temperature is neglected in T_m. A few calculations showed this neglect to be warranted. Since the average temperature T_{Avg} could be calculated only after a run was completed, because the mean temperature T_m could be calculated only after the whole array of runs was completed, and since changes in atmospheric conditions affected the temperature traverses, the repetition of runs at the same T_{Avg} or T_m was essentially impossible. The best that could be done was replicate runs within a few degrees of each other.

Contact Time

The above problems are brought together in the calculation of contact time which is computed with the equation

$$t = \frac{sL_{eff}P}{1/2(n_o + n_1)RT_{Avg}} \quad (2)$$

The term $1/2\ (n_o + n_1)$ is merely an average of the inlet and outlet flow rates. In this equation L_{eff} of 5 in. was used. The assumption of plug flow is retained.

Product Distribution

The analyses of hydrogen and the hydrocarbons permitted the calculation of the product distribution as a function of the contact time, calculated with T_{Avg}. It should be noted that no C_3H_8 or propane was ever found. These calculations involved the as-

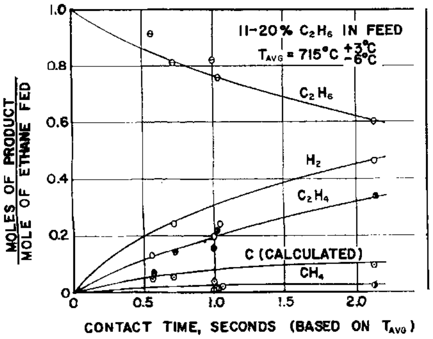

Fig. 3. Product distribution—ethane decomposition in quartz.

(Continued on following page)

INFORMATION RETRIEVAL

(*Continued from page 566*)

Significance of pressure gradients in porous materials: Part I. Diffusion and flow in fine capillaries, Wakao, Noriaki, Seiya Otani, and J. M. Smith, **A.I.Ch.E. Journal, 11,** No. 3, p. 435 (May, 1965).

Key Words: A. Flow-8, 7, 2, Diffusion-8, 7, 2, Capillaries-9, Pressure Gradient-6, Gases-9, Binary System-9, Knudsen Flow-9, Poiseuille Flow-9, Equations-8, 10, Carbon Dioxide-9, Nitrogen-9, Permeability-8, Calculation-8, Experimental-0, Mathematical-0.

Abstract: Equations are derived for the effect of a total pressure gradient on flow and diffusion of a binary gas system in a fine capillary. The results apply over the pressure and pore radius regimes from Knudsen flow to Poiseuille flow. Application of the equations to a pure component leads to an expression for the permeability which predicts the observed minimum flow in the slip-flow region. The predicted results agrees well with experimental results for carbon dioxide and nitrogen.

Significance of pressure gradients in porous materials: Part II. Diffusion and flow in porous catalysts, Otani, Seiya, Noriaki Wakao, and J. M. Smith, **A.I.Ch.E. Journal, 11,** No. 3, p. 439 (May, 1965).

Key Words: A. Flow-8, 9, Rate-8, 7, 2, Diffusion-8, 7, 9, 2, Pressure Gradient-6, Alumina-9, Vycor-9, Catalysts-9, Porous-0, Prediction-8, Equations-10, Pore Size-6, Voids-6, Permeability-7, 8, 9, Comparison-8, Theoretical-0, Experimental-0, Knudsen Flow-9, Poiseuille Flow-9, Geometry-6, Boehmite-9, Transport Rate-7, 8, 9, 2, Binary Systems-9, Calculation-8.

Abstract: Diffusion and flow rates through porous catalysts were measured under the conditions of finite pressure gradients for single- and two-component systems. Alumina pellets and Vycor were used in the studies. The calculated and experimental results were compared.

Significance of pressure gradients in porous materials: Part III. Effect of pressure gradients on the effectiveness of porous catalysts, Otani, Seiya, Noriaki Wakao, and J. M. Smith, **A.I.Ch.E. Journal, 11,** No. 3, p. 446 (May, 1965).

Key Words: Effectiveness Factor-7, Bulk Diffusion-9, Knudsen Diffusion-9, Moles-6, Pressure Gradient-6, Diffusion-9, Reactant-9, Catalyst-9, 10, Porous-0, Capillary-9, Reaction-9, 6, Calculation-8, Alumina-9, Concentration Profile-2.

Abstract: The effect of a change in moles, due to reaction, on the effectiveness of a catalytic reaction is analyzed by calculating the concentration profile along a capillary whose wall surface acts as a catalyst and within a spherical, porous, catalyst pellet. The influence on the effectiveness factor is studied for different types of diffusion.

A matrix method for location of cycles of a directed graph, Norman, R. L., **A.I.Ch.E. Journal, 11,** No. 3, p. 450 (May, 1965).

Key Words: A. Determination-8, 10, Nests-9, Cycles-9, Graph-9, Directed-0, Matrices-10, Program-8, Computer-10, Heat Balances-10, 8, 9, Material Balances-10, 8, 9, Recycling -10, 8, 9.

Abstract: A matrix method is given for determining the nests of cycles of a directed graph. This has been applied to determining the recycle loops of a chemical process flow diagram.

(*Continued on page 570*)

(*Continued from preceding page*)

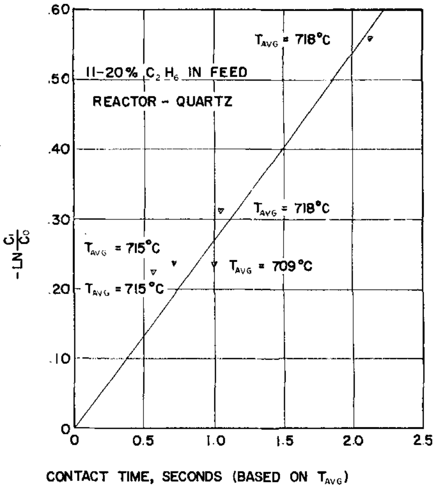

Fig. 4. First-order rate correlation for ethane.

sumption that all hydrogen in the feed appeared in the gaseous products as analyzed and that all carbon in the feed appeared in gaseous products or in elemental carbon. Certainly carbon formation was observed, and no tarry substances that would invalidate the above assumption were observed. The product distributions thus calculated for a few runs are shown in Figure 3 in which the moles of product per mole of ethane feed vs. contact time are shown. It should be noted that the values of T_{Avg} were not exactly the same for these points. Nonetheless, the behavior is orderly, and the ethane curve appears to exhibit approximately first order behavior.

RESULTS AND DISCUSSION

Order and Rate Constants

Calculation of rate constants from the data involves, of course, consideration of order and of possible changes in the number of moles due to reaction. Due to the presence of diluent nitrogen, the change in number of moles was very small (below 2% in most cases); thus, this effect was neglected, and the batch form of kinetic equations was used. This form has the advantage that the complete stoichiometry of the reactions involved is not required. Concentrations of ethane were calculated thus

$$C_0 = \left(\frac{n_{C_2H_6}}{n_{C_2H_6} + n_{N_2}} \right)_0 \frac{P}{RT_{Avg}}$$

$$C_1 = \left(\frac{n_{C_2H_6}}{n_{Prod} + n_{N_2}} \right)_1 \frac{P}{RT_{Avg}}$$

One may question the use of T_{Avg} and assert that T_0 and T_1 should have been used. However, T_0 and T_1 were about the same and therefore they or T_{Avg} vanish in the ratio $\frac{C_1}{C_0}$, which is appropriate for the first-order behavior

(*Continued on following page*)

(Continued from preceding page)

found. A plot of $\ln \frac{C_1}{C_0}$ vs. contact time is shown in Figure 4. The behavior is reasonably linear, particularly when one realizes that a certain unavoidable temperature variation is present. This confirms the previous observations (see below) that this reaction is first order. It should be noted that the ethane content of the feed varied from 11 to 20%, strengthening an assumption basic to the whole work that the diluent does not affect the conversion (7, 8). There should be no simple dilution effect with a first-order reaction.

Activation Energy

The values of the rate constants based on contact time, which were, in turn, based on T_{Avg}, were correlated in the usual way with T_{Avg} and a linear relation resulted

$$\log_{10} k = 14.19 - \frac{66{,}500}{RT_{Avg}} \quad (3)$$

This must be considered only an approximation.

The values were then refined by computing T_m with Equation (1), recomputing contact time with Equation (2) using T_m, recomputing k with this new contact time, and correlating this k with T_m. The resulting refined relation for the temperature dependence is

$$\log_{10} k = 13.50 - \frac{64{,}100}{2.3RT_m} \quad (4)$$

This is shown in Figure 5. It should be noted that T_m and T_{Avg} differed by only about 1.5%, and that the refined and preliminary values of activation energy are nearly the same. Equation (4) fits the measured k values with an average deviation of 16% and an extreme deviation of 31% over a 48-fold range of k values.

Comparisons with Literature Values

The results here reported must be considered only another link in the chain of knowledge of ethane pyrolysis. Most of the other workers found

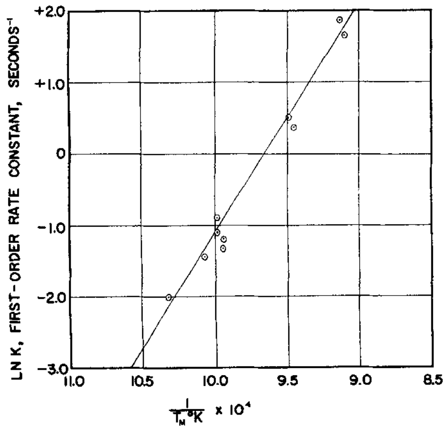

Fig. 5. Arrhenius plot of ethane data.

(Continued on following page)

INFORMATION RETRIEVAL

(*Continued from page 568*)

The effect of concentration on diffusion coefficient in polymer solutions, Secor, Robert M., **A.I.Ch.E. Journal, 11,** No. 3, p. 452 (May, 1965).

Key Words: A. Concentration (Composition)-6, Diffusion Coefficient-7, 8, Solutions-9, Polymers-9, Dimethyl Formamide-9, Polyacrylonitrile-9, Theoretical-0, Experimental-0, Mass Transfer-8, Diffusion-8, Microinterferometer-10, Mixtures-9, Acrylic Resins-9, Plastics-9, Addition Resins-9, Synthetic Resins-9, Thermo Plastic Resins-9, Amides-9, Vinyl Resins-9, Measuring Instruments-10, Optical Instruments-10.

Abstract: A microinterferometric method was used to measure the diffusion coefficient as a function of concentration in the system dimethylformamide-polyacrylonitrile. The diffusion coefficient obtained experimentally was consistent with the theoretical value.

Vapor-liquid equilibria in hydrogen-benzene and hydrogen-cyclohexane mixtures, *Thompson, Richard E., and Wayne C. Edmister,* **A.I.Ch.E. Journal, 11, No. 3,** p. 457 (May, 1965).

Key Words: A. Vapor-Liquid Equilibrium-8, 9, Binary Mixtures-9, Hydrogen-9, Benzene-9, 5, Experimental-0, Solubility-8, Consistency Tests-8, Thermodynamic-0, High Pressure-0, Equilibrium-8, 9, Mixtures-9, Aromatic Compounds-9, 5, Hydrocarbons-9, 5, Physical Properties-8. B. Equilibrium-8, 9, Mixtures-9, Hydrocarbons-9, 5, Allyl Cyclic Compounds-9, 5, Physical Properties-8, Vapor-Liquid Equilibrium-8, 9, Binary Mixtures-9, Hydrogen-9, Cyclohexane-9, 5, Experimental-0, Solubility-8, Consistency Tests-8, Thermodynamic-0, High Pressure-0.

Abstract: Vapor-liquid equilibrium data were determined experimentally for the binary mixtures of hydrogen-benzene and hydrogen-cyclohexane at temperatures of 150 and 250°F. and pressure up to 10,000 lb./sq.in.abs. Thermodynamic consistency tests were applied to the data. Solubilities of hydrogen in benzene and in cyclohexane were also obtained.

An analysis of fully developed laminar flow in an eccentric annulus, Snyder, William T., and Gerald A. Goldstein, **A.I.Ch.E. Journal, 11,** No. 3, p. 462 (May, 1965).

Key Words: Fluid Flow-8, Laminar-0, Annulus-9, Eccentric-0, Fluid-9, Velocity Distribution-8, Shear Stress-8, 7, Friction Factor-8, 7, Eccentricity-6, Ratio-6, Radius-9.

Abstract: An analysis is presented of fully developed laminar flow in an eccentric annulus. An exact solution for the velocity distribution is presented. From this solution may be obtained expressions for local shear stress on the inner and outer surfaces of the annulus, friction factors based on the inner and outer surfaces, and the overall friction factor. Curves of these data are presented covering a range of eccentricity values and radius ratio values.

Normal stress and viscosity measurements for polymer solutions in steady cone-and-plate shear, *Williams, Michael, C.,* **A.I.Ch.E. Journal, 11,** No. 3, p. 467 (May, 1965).

Key Words: A. Viscosity-8, 9, 7, Non-Newtonian-0, Stress-8, 9, 7, Shear Strain-8, 9, 7, Elastic Modulus-8, 9, 7, Measurement-8, Cone-and-Plate Instruments-10, Temperature-6, Concentration-6, Molecular Weight-6, Chemical Structure-6, Ferry Reduced Variables-10, Liquids-9, Viscoelastic-0, Polymers-9, Solutions-9, Rheology-8, Polyethylene Oxide-9, Hydroxyethyl Cellulose-9, Polyvinyl Alcohol-9, Physical Properties-8, 9, 7.

Abstract: Normal stress and viscometric measurements were made on nine polymer solutions with cone-and-plate instruments. Temperature, concentration, molecular weight, and chemical structure were varied. Zero-shear viscosities, obtained by extrapolation of falling-sphere data, ranged from 0.7 to 380 poise. Non-Newtonian viscosity, normal stress, recoverable shear strain, and elastic modulus are resented in terms of modified Ferry reduced variables.

(*Continued on page 572*)

(*Continued from preceding page*)

this reaction to be first order with the rate constant expressible as

$$k = Ae^{-E/RT}$$

Values of $\log_{10} A$ and E are compared in the following table:

	$\log_{10}A$	E, cal./g. mole
Marek and McCluer (*9*)	16.06	77,700
Sachsse (*10*)	14.1	69,800
Kuchler and Thiele (*1*)	15.33	77,000
Steacie and Shane (*12*)	14.02	69,700
Hepp, Spessard, and Randal (*13*)	14.02	69,700
Kinney and Crowley (*14*)	15.66	74,010
Schutt (*15*)	14.19	70,200
Skinner and Ball (*16*)	14.7	79,300
This work	13.5	64,100

The activation energy here recorded is the lowest yet reported and agrees very well with that theoretically predicted with the Rice-Herzfeld mechanism (*17*). This figure, using the values of Brooks et al. (*18*) of activation energies for the elemental steps involved is 65,500. This original mechanism was based on an initiation step of methyl radical formation from ethane; propagation reactions of methyl radical with ethane to yield methane (see reported product distribution) and ethyl radical, decomposition of ethyl radical, and reaction of hydrogen atoms with ethane; and termination reactions between ethyl radicals and hydrogen atoms.

Verifications of Methods Used

Any method used to interpret data must pass the test of reproducing the data. This was done by calculating the conversion for each ½ in. increment along the length of the reactor proper. The temperature for each increment was the arithmetic average of those at the start and at the end of the increment, as read on a temperature vs. length curve (see Figure 2). In a typical run 22% conversion was calculated, while 18.7% was measured—a reasonable agreement. More interesting is the observation that only 0.3 absolute percent of the 22% conversion calculated occurred outside the selected 5 in. *effective* reaction zone.

Results in Inconel Reactor

Comparable data observed in an Inconel reactor, interpreted in the same way, showed that Inconel certainly affects the reaction. Rates below 990°K. are higher in Inconel than in quartz. The activation energy is reduced to about 48,000 cal./g.-mole. Such an effect has been interpreted by

(*Continued on following page*)

(Continued from preceding page)

Laidler (19) as an indication of a heterogeneous surface reaction.

It should be noted that the Inconel sheath on the movable gas thermocouple should not have affected the results in quartz, because this thermocouple was present in the gas stream only for the measurement of temperature and not during the main parts of the runs when gas samples were taken.

CONCLUSIONS

It may be concluded that this method is generally satisfactory for observing the rates of pyrolysis reactions, although the temperature profiles must be improved. Current work shows that great improvements can be attained.

That ethane pyrolysis is a first-order reaction is confirmed, and the activation energy is shown to be 64,100 cal./g.-mole, in excellent agreement with the Rice-Herzfeld mechanism.

ACKNOWLEDGMENT

The fellowship assistance of Continental Oil Company and of U. S. Industrial Chemicals Corporation is gratefully acknowledged.

NOTATION

A = pre-exponential factor
C = concentration, moles/cc.
D = diffusivity, sq.cm./sec.

(Continued on following page)

INFORMATION RETRIEVAL

(*Continued from page 570*)

The stability of nonlinear systems in the region of linear dominance: Parts I and II, Gura, I. A., and D. D. Perlmutter, **A.I.Ch.E. Journal, 11,** No. 3, p. 474 (May, 1965).

Key Words: A. Stability-8, Asymptotic-0, Nonlinear Systems-9, Reversible-0, Chemical Reactions-9, Irreversible-0, Stirred-0, Reactor-10, Region of Linear Dominance-9.

Abstract: A technique has been developed for finding quantitative regions of asymptotic stability for nonlinear systems by using a known proof of the theorem which substantiates the linearization. The practical problems of both reversible and irreversible chemical reactions occurring in a continuous flow stirred vessel have been analyzed.

Local rates of mass transfer from spheres in ordered arrays, Rhodes, John M., and Fred N. Peebles, **A.I.Ch.E. Journal, 11,** No. 3, p. 481 (May, 1965).

Key Words: Mass Transfer-8, 9, Local-0, Beds-9, 5, Packed-0, Spheres-9, Fluids-9, Heat Transfer-8, Rate-8, 6, Benzoic Acid-9, Water-9, 5, Sherwood Number-8, 7, Packing-6, Reynolds Number-6, Flow-9, 6, Carboxylic Acids-9.

Abstract: The local mass transfer rates from a sphere in a regular packing array have been determined by measuring the local radius change of a benzoic acid test sphere having been immersed in a water stream. Results in the form of typical local Sherwood number profiles are reported for single spheres and for spheres in simple cubic packing and rhombohedral packing.

Pressure drop studies in a plate heat exchanger, Smith, Vernon C., and Ralph A. Troupe, **A.I.Ch.E. Journal, 11,** No. 3, p. 487 (May, 1965).

Key Words: A. Pressure Drop-8, 7, Plate Heat Exchangers-9, Heat Exchangers-9, Design-8, 4, Velocity-6, Water-9, Fluid-9, Chester-Jensen Exchanger-9, Entrance-9, Exit-9, Crossover-9, Ribs-9.

Abstract: This paper presents the results of experimental studies to obtain pressure drop relationships useful in plate heater design. A plastic prototype of a commercial model (Chester-Jensen) exchanger was fabricated and used to obtain entrance, exit, crossover, ribbed section, and overall pressure drops as a function of velocity with water as the fluid. These individual losses were combined into an expression for overall pressure drop for a series plastic plate pack having any number of plates and employing any fluid.

Calorimetric determination of the isothermal pressure effect on the enthalpy of the propane-benzene system, Yarborough, Lyman, and Wayne C. Edmister, **A.I.Ch.E. Journal, 11,** No. 3, p. 492 (May, 1965).

Key Words: A. Pressure-6, Enthalpy-7, 8, 9, Isothermal-0, Propane-9, Benzene-9, Mixtures-9, Calorimeter-10, Liquid Phase-0, Vapor Phase-0, Comparisons-8, Calculation-9, Experiments-9, Virial Equation of State-10, Alkanes-9, Benedict-Webb-Rubin Equation-10, Equations of State-10, Aliphatic Compounds-9, Hydrocarbons-9, Aromatic Compounds-9.

Abstract: Isothermal effects of pressure on the enthalpy of propane, benzene, and three mixtures were measured in the liquid and vapor regions with a new calorimeter. Comparisons of measured values were made with enthalpy values calculated from equations of state.

(*Continued on page 574*)

(*Continued from preceding page*)

E = activation energy, cal./g.-mole

k = first-order rate constant, sec.$^{-1}$

L = general length of reactor, in.

L_{eff} = effective length of this reactor, 5 in.

n = number of g.-moles

P = pressure, atm.

R = gas constant

R_o = radius of tube, cm.

s = cross section of tube, sq.cm.

t = general contact time, sec.

t_o = contact time of center streamline, sec.

T = temperature, °K. or °C.

T_{Avg} = average temperature determined by simple graphical integration, °K.

T_m = mean temperature [see Equation (1)], °K.

Subscripts

o = entrance of reactor

1 = exit of reactor

Prod = sum of gaseous products excluding nitrogen

LITERATURE CITED

1. Crocco, L., I. Glassman, and I. E. Smith, *J. Chem. Phys.*, **31**, 506 (1959).
2. National Bureau of Standards Circular 561.
3. Bartlit, John R., D. Eng. dissertation, Yale School of Engineering (1962).
4. Taylor, G. I., *Proc. Roy. Soc.* (*London*), **A219**, 186-191 (1953).
5. Klinkenberg, A., H. J. Krajenbrink, and H. A. Lauwerier, *Ind. Eng. Chem.*, **45**, 1202-1208 (1953).
6. Cleland, F. A., and R. H. Wilhelm, *A.I.Ch.E. Journal*, **2**, 489-497 (1956).
7. Germain, J. E., and C. Vaniscotte, *Bull. Soc. Chim. France*, 319-323 (1958).
8. Wheeler, R. V., and W. L. Wood, *Fuel*, **7**, 535-539 (1928); *ibid.*, **9**, 567-574 (1930).
9. Marek, L. F., and W. B. McCluer, *Ind. Eng. Chem.*, **23**, 878-881 (1931).
10. Sachsse, H., *Z. Phys. Chem.*, **B31**, 79-104 (1935).
11. Kuchler, L., and H. Thiele, *ibid.*, **B42**, 359-379 (1939).
12. Steacie, E. W. R., and G. Shane, *Can. J. Res.*, **B18**, 203-216 (1940).
13. Hepp, H. J., F. P. Spessard, and J. H. Randall, *Ind. Eng. Chem.*, **41**, 2531-2535 (1949).
14. Kinney, R. E., and D. J. Crowley, *ibid.*, **46**, No. 1, 258-264 (1954).
15. Schutt, H. C., *Chem. Eng. Progr.*, **55**, No. 1, 68-74 (1959).
16. Skinner, G. B., and W. E. Ball, *J. Phys. Chem.*, **64**, 1025-1028 (1960).
17. Rice, F. O., and K. F. Herzfeld, *J. Am. Chem. Soc.*, **56**, 284-289 (1934).
18. Brooks, B. T., C. E. Boord, S. S. Kurtz, and L. Schmerling, "The Chemistry of Petroleum Hydrocarbons," Vol. II, Reinhold, New York (1955).
19. Laidler, K. J., "Chemical Kinetics," McGraw-Hill, New York (1950).
20. Towell, G. D., and J. J. Martin, *A.I.Ch.E. Journal*, **7**, 693-698 (1961).