Measuring Simultaneous Mixing and Reaction in Batch Reactors by Dilatometry

A dilatometric technique is reported for studying simultaneous mixing and reaction as a function of time in batch systems. Volume-averaged fractional conversion is determined from small volume changes without sampling or flow disturbances.

Data are obtained for very fast and intermediate speed reactions in a turbulent, unbaffled, stirred laboratory reactor.

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SCOPE

Simultaneous mixing and chemical reaction with nonpremixed feed is poorly understood when the rates of mixing and chemical reaction are comparable. Some progress has been made in the rational design and scale-up of single reactions in tubular flow reactors as a result of the work of Toor and his coworkers (Vassilatos and Toor, 1965; Ajmera, 1969; Mao and Toor, 1971; Singh, 1973). Paul and Teybal (1971), and more recently Bourne et al. (1977) have made some progress in studying the more subtle and important question of selectivity in multiple reactions in semibatch and continuous flow reactors.

In this study, dilatometry is adapted to determine fractional conversion continuously as a function of time. The effects are studied of varying the ratio of reactants in batch systems with nonpremixed feed. Experiments are performed with two classes of irreversible, single-pathway, second-order reactions: very rapid (acid-base neutralization) and intermediate speed (ester saponification). The reactor is a 1,680 mL turbulent, quasiadiabatic, unbaffled, magnetically-stirred vessel at a Reynolds number of 10^4. The time scale of the experiments ranged from 4 to 20 s. The reactor consists of two cylindrical cells separated by a stretched rubber membrane. The reactants are fed separately to each cell; mixing and reaction begin when the membrane is ruptured. The volume change caused by chemical reaction is measured in a capillary tube affixed to the reactor. Tracer experiments are performed to characterize the flow field of the vessel. Fractional conversion is obtained as a function of time at reactant ratios of 1, 2, and 4 for both classes of reactions.

CONCLUSIONS AND SIGNIFICANCE

Simultaneous mixing and chemical reaction conversion data as a function of time are obtained in a batch reactor with nonpremixed feed. A very rapid reaction (acid-base neutralization) and an ester saponification reaction with a reaction rate comparable to the mixing rate are studied at three different reactant ratios in a quasiadiabatic, turbulent, unbaffled, stirred batch reactor. The flow field is very nonhomogeneous. The conversion data for both reaction systems display a strong dependency on reactant ratio.

The experimental technique, based on dilatometry, measures the volume change caused by chemical reaction. The volume change is approximately linearly dependent on chemical conversion for the dilute reactants used. Dilatometry is shown to be a simple and convenient experimental technique that bypasses the complications of sampling and flow disturbance associated with probes and other traditional measurement devices. Dilatometry yields volume-averaged results regardless of the degree of heterogeneity of the fluid, and is accurate.

The data obtained in this study may be useful in discriminating among existing mathematical models, and may contribute to the development of more reliable scale-up and design methodologies for batch systems.

BACKGROUND

A frequently encountered design problem is the prediction of reactor performance with nonpremixed reactants when the hydrodynamics, or mixing field of the reactor, and the kinetics of the reaction are known. Limiting cases when mixing is rapid compared to chemical reaction or vice-versa have reasonably well-developed methodologies for laboratory experimentation, mathematical

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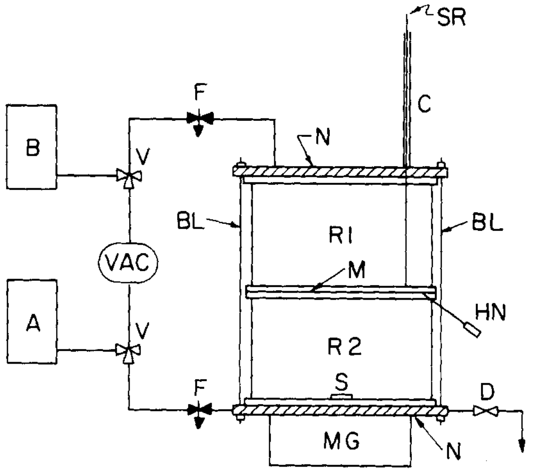

Figure 1. Experimental apparatus.

A,B	**Reactants**	**MG**	**Magnetic drive**
BL	**Bolts (tie rods)**	**N**	**Nylon lid and bottom**
C	**Capillary tubing**	**R1,R2**	**Reaction chambers**
D	**Drain valve**	**S**	**Stirring bar**
F	**Fine metering valve**	**SR**	**Steel rod (for puncturing membrane)**
HN	**Hypodermic needle**	**V**	**Three-way valves**
M	**Membrane**	**VAC**	**Vacuum source**

modeling, scale-up, and design. But when the rates of mixing and chemical reaction are comparable, the situation is not well understood.

Only a few experimental studies have been reported in the literature in which mixing and chemical reaction have comparable speed, because experiments are difficult to perform. Sampling a heterogeneous fluid field at multiple points in space and time presents problems. Even if *in situ* probes measuring composition are available, there are difficulties with speed of response, sample size, number of samples, location of samples, and disturbance of the fluid motion by the probes. If samples are withdrawn, there is the additional problem of stopping the chemical reactions at the instant of sampling.

Thus far, most of the experiments reported have been limited to special types of continuous flow reactors. Toor and his coworkers (Vassilatos and Toor, 1965; Ajmera, 1969; Mao and Toor, 1971; Singh, 1973) did pioneering experiments with both multijet and coaxial tubular reactors. Fractional conversion was determined by measuring the adiabatic temperature rise caused by the reaction at several downstream points. Paul and Treybal (1971) studied selectivity in a semibatch reactor using ultraviolet adsorption to analyze the final product distribution. Truong and Methot (1976) studied the saponification of ethylene glycol diacetate in a continuous stirred tank reactor, using titration and chromatography. More recently, Bourne et al. (1977) studied selectivity in semibatch and continuous reactors using gas chromatography to analyze the composition of the final mixture. The methods of analysis used in the above studies are not well suited to batch systems where composition is a function of time and is also heterogeneous in position.

Dilatometry—a technique used fruitfully in polymer and thermodynamic studies with fluids homogeneous in composition and temperature (reviewed by Ghodsizadeh, 1978)—is adapted in this study to measure transient volume changes caused by chemical reactions in mixing-reaction batch systems. Small volume changes primarily due to the difference in density between reactants and products are detected in a capillary tube attached to the reactor. Sampling and averaging are avoided, even though the fluid field is heterogeneous in composition and temperature.

EXPERIMENTAL

Equipment

The reaction vessel (1,690 mL total volume) consists of two identical, unbaffled, Pyrex cylinders with ground joints, 10.5 cm I.D. and 9.7 cm high. A sketch of the reactor is shown in Figure 1. The cells are vacuum-sealed by means of two 2.5 cm thick nylon lids secured on the top and bottom of the reactor at four points with nuts and bolts. Seals are standard rubber O-rings. A thin (0.1 mm) stretched rubber membrane (latex dental dam) supported on an embroidery ring separates the two cells. A capillary precision bore tube (3.29 mm I.D. for very rapid and 2.58 mm I.D. for intermediate speed reactions) is affixed at the top to display the volume change. The liquid level rises about 12 cm in the capillary tube for both reaction systems at 100% conversion. A thin, sharpened steel rod 0.794 mm in diameter passing through the capillary tube is used to rupture the rubber membrane to initiate mixing and reaction. A hypodermic needle passed through the O-ring between the two cells and under the rubber membrane allows venting of any trapped gases in the lower cell. The capillary tube serves as a vent for the upper cell. Mixing is achieved by an octagonal Teflon-coated magnetic stirring bar, 3.80 cm long and 0.80 cm wide, driven at 450 rpm. This speed corresponds to an agitator Reynolds number ($d^2N\rho/\mu$) of 10,000. The stirring bar rests on the bottom nylon plate and is centered. Stirrer speed is measured by a stroboscope. The magnetic stirrer is powered by a constant voltage regulator to insure constant operating speed. Each reactant is fed separately through Tygon tubing T, a three-way valve V, and a needle valve F. The three-way valve V also connects the two chambers to vacuum. The two chambers, $R1$ and $R2$, are filled to within 5 mL of each other, despite the flexing of the rubber membrane. A movie camera (Canon 1014, Super 8 mm, 18 frames per second) is used to record continuously the position of the meniscus in the capillary tube. A digital clock displaying tenths of seconds is incorporated in the movies to monitor the reaction time. A scale with alternate 1 mm black and white bands is placed behind the capillary tube to facilitate measuring the meniscus height. All experiments are carried out in a 20 ± 1°C constant temperature room.

Reaction Systems

Two reaction systems are chosen such that the reaction rate is (a) much faster, and (b) comparable to, the speed of mixing. The reaction systems used are given in Table 1. The concentration of the limiting reactant is 0.05 gmol/L in all cases. The hydrochloric acid and sodium hydroxide used are standard solutions supplied by Fisher Scientific Co., and have an accuracy of ±0.0002 gmol/L. The methyl formate solutions are prepared by diluting a concentrated solution, and have an accuracy of ±0.0004 gmol/L. Both systems are run at stoichiometric ratios of 1, 2, and 4. Sodium hydroxide

TABLE 1. REACTION SYSTEMS

Class	Reactants	Reaction Rate Constant $k_r\left(\frac{1}{\text{gmol}\cdot\text{s}}\right)$ at 20°C	Heat of Reaction $\Delta h_r\left(\frac{\text{Kcal}}{\text{gmol}}\right)$	Reference
Very Rapid	HCl–NaOH	1.4×10^{11}	−13.29	Eigen et al. (1963)
Intermediate	$HCOOCH_3$–NaOH	27	−13.71	Leimu et al. (1946)

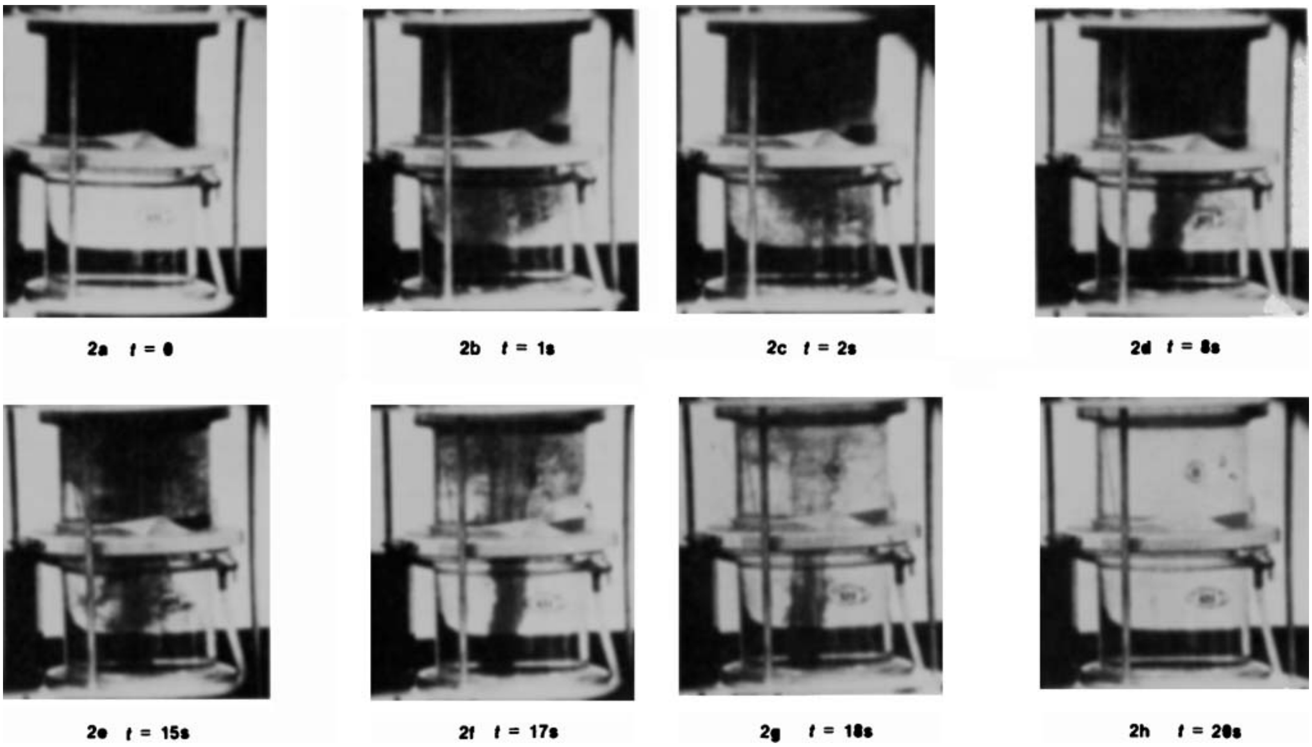
2a $t = 0$ 2b $t = 1s$ 2c $t = 2s$ 2d $t = 8s$
2e $t = 15s$ 2f $t = 17s$ 2g $t = 18s$ 2h $t = 20s$

Figure 2. Flow pattern in batch vessel.

is the excess reactant and is always placed in the upper cell together with phenolphthalein in order to facilitate reading the position of the meniscus in the capillary, and to aid in visualizing the flow field in the reactor.

Experimental Procedure

Two classes of experiments are carried out. One class involves chemical reaction, the other involves mixing with no reaction (dilution).

In the reaction experiments, the reaction chambers are initially put under vacuum through the three-way valves. The reactants are then fed separately to each cell and maintained unmixed by means of the stretched rubber membrane. Trapped gases are vented through the hypodermic needle and capillary tube. The needle valves are used to obtain the desired charges and initial setting of the meniscus in the capillary tube. The magnetic stirrer, digital clock, and the movie camera are turned on. Mixing and reaction are initiated by rupturing the rubber membrane with the steel rod.

In the dilution experiments, the same procedure is followed, except that one chamber is filled with a reactant and the other chamber filled with water.

Flow Pattern

Amberlite AXO-8 ion-exchange resin beads (Rohm and Haas) (approximately 1 mm dia, 1.05 g/mL wet density) were added to water in order to observe the flow pattern at the same Reynolds number used in the reaction experiments. The fluid properties of this dilute dispersion are essentially unchanged from water. The tangential velocity component is very high relative to the radial and axial components. Two distinct flow regions are observed: an inner core with a predominantly tangential flow, and an outer core where a secondary (axial and radial) flow exists in addition to the smaller tangential flow. In another experiment, the mixing in the vessel is filmed during a very rapid reaction at stoichiometric ratio of reactants, with the pink sodium hydroxide solution placed in the upper cell. A few representative frames from this film are reproduced in Figure 2 to illustrate the flow pattern. The inner core, swirling like a solid cylinder, (pink, with a diameter roughly one-half of the magnetic stirrer diameter) is distinguishable about 7 s after rupture of the membrane, Figure 2d. The pink color of the inner core indicates that its contents are supplied primarily from the upper cell. After about 18 s, the color in the outer core disappears, Figure 2g. The color in the inner core persists for an additional 2 s, Figure 2h, indicating poor intermixing between the two regions. These observations are in general agreement with studies by Nagata et al. (1959) of the flow pattern in agitated, unbaffled vessels. The circulation time, estimated from the method of Holmes et al. (1964), is about 1.2 s. Visual observation and conversion data indicate appreciable momentum penetration from the lower to upper cell occurs during the first second after rupture of the membrane, Figure 2b.

Clearly the unbaffled batch vessel used in this study has a very heterogeneous flow field. This is in sharp contrast to the other reactor geometry where similar conversion data are available—the multijet flow reactor (Mao and Toor, 1971), where a fairly isotropic mixing field is attained a short distance downstream of the entrance.

Batch Blend Time

The batch blend time of the system, obtained from the stoichiometric very rapid reaction data, is roughly 20 s. A direct comparison with batch blend times reported in the literature is not possible because the agitator variables (shape and position) of this study are different. Typical blending times for a fully baffled, similar geometry with a six-blade, disk-type turbine positioned in the center of tank, with an agitator-to-tank-diameter ratio of 0.36, are about 5 s (Khang and Levenspiel, 1976).

THEORY

Overview

The height h of the meniscus in the capillary tube is a state function of the conversion F, the spatial distribution of the reactant and product species, the pressure P, the fluid temperature T_f, and the reactor wall temperature T_w. Therefore, to obtain conversion from meniscus height data, a model relating meniscus height to the above state variables is needed.

The model used in this study to approximate the situation at time t ($0 \leq t \leq \infty$) is shown in Figure 3. There are four regions of different composition. The regions at the top and bottom marked A and B are unmixed reactants at their initial concentration. The region marked $A + B$ consists of equal volumes of homogeneously

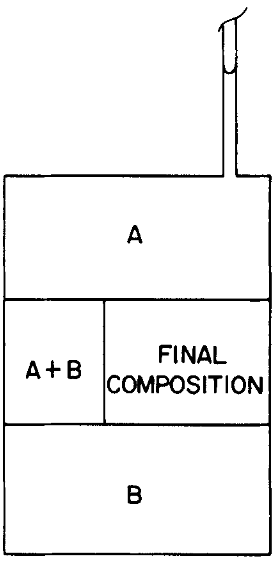

Figure 3. Model representation of dilatometer at time *t*.

mixed but unreacted reactants. The region marked *Final Composition* has the composition which results when all mixing and reaction have been completed ($t \rightarrow \infty$). The fraction of the total volume in the two regions marked $A + B$ and *Final Composition* is denoted by ω. Also of importance, but not shown explicitly in Figure 3, are the average temperature of the fluid, T_f, and the average temperature of the reactor wall, T_w.

The virtue of this model is that it represents the system exactly at time zero (when all of the volume is A and B) and at infinite time (when all of the volume is *Final Composition*). At intermediate time $0 < t < \infty$, the model differs from reality in the spatial distribution of species. The effect of this approximate representation on the accuracy of the meniscus height-conversion relationship can be estimated by studying a variety of more sophisticated mixing models. Based on simulations with a 500-cell Monte Carlo mixing model, and a model approximating the maximum mixedness model, the error in the conversion vs. time results has been estimated. The inaccuracy is greatest for the highest reactant ratio ($\beta = 4$); about 2%, (two standard deviations) for very rapid reactions, and about 3.5% for intermediate speed reactions, as discussed in detail in Appendix 1.

State Representation

The algorithm for determining the conversion from the meniscus height data is based on the notion that the meniscus height change with time is a function of state:

$$h[\omega(t),F(t),P(t),T_f(t),T_w(t)] - h[\omega(o),F(o),P(o),T_f(o),T_w(o)]$$

where $0 < t < \infty$. Since h is a function of state, arbitrary paths may be used to calculate $h(t) - h(o)$. For convenience the pathway shown in Figure 4 is chosen.

State 1 is the initial condition at $t = 0$, i.e., the reactants are separated by the rubber membrane. The path from state 1 to state 2 allows some mixing of reactants characterized by $\omega(t) - \omega(o)$ to occur. Therefore, state 2 consists of three separate regions: unmixed A, unmixed B, and the mixed zone $A + B$ containing equal volumes of A and B blended homogeneously.

The path from state 2 to state 3 allows some chemical reaction characterized by $F(t) - F(o)$ to occur. Therefore, state 3 consists

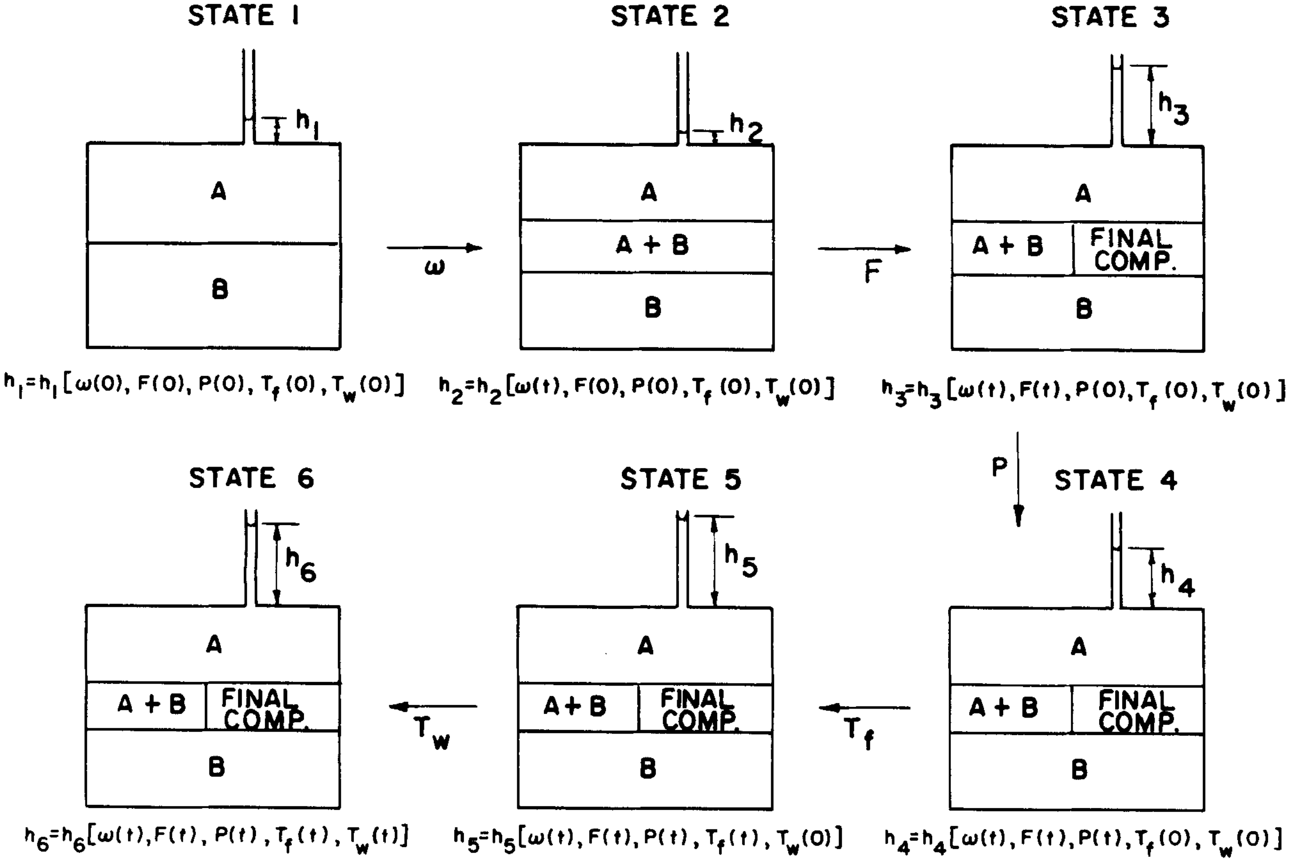

Figure 4. State representation of meniscus height change in capillary tube.

TABLE 2. DILATOMETER RESPONSE CHARACTERISTICS

Initial volume of each reactant 840 mL
Initial concentration of each reactant 0.05 gmol/L

Variable	Intermediate Speed Reaction	Very Rapid Reaction
t_r, reaction time, s*	148	10^{-7}
$t_{r,1/2}$, reaction half life, s*	1.5	10^{-9}
t_b, batch blend time, s	20	20
$t_{b,1/2}$, blend time half life, s	3	3
Δh_r, heat of reaction, kcal/gmol‡	13.71	13.29
Q, heat generated, kcal‡	0.58	0.56
ΔT, adiabatic temperature rise of fluid,** °C	0.34	0.33
$(\Delta V)_r$, volume change due to reaction, mL	*** (0.52)†	0.99
$(\Delta V)_T$, volume change due to temperature rise, mL	0.14	0.13
$(\Delta V)_w$, volume change due to wall expansion during reaction time, mL	−0.02	−0.01
$(\Delta V)_h$, volume change due to hydrostatic effect, mL	−0.001	−0.001
$(\Delta V)_d$, volume change due to dilution, mL	−0.01	−0.01
$(\Delta V)_{hd}$, volume change due to heat of dilution, mL	0.001	0.001
$(\Delta V)_{\text{theo}}$, theoretical total volume change, mL	***	1.10
$(\Delta V)_{\text{exp}}$, experimental total volume change, mL	0.63	1.03

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* For 99% conversion of homogeneous reaction, i.e., assuming very rapid mixing.

** Assuming no heat loss from reactor.

*** Theoretical estimates not possible because density data for methyl formate and sodium formate solutions not available.

† Order of magnitude value back-calculated from experimental total volume change.

‡ S.I. conversion: kJ = kcal × 4.19.

of four separate zones: unmixed A, unmixed B, mixed zone $A + B$, and the final composition zone consisting of product species and excess reactant.

State 4 is identical to state 3 except that the pressure is changed to account for the hydrostatic pressure increase caused by the rise in the meniscus level in the capillary tube due to the mixing and reaction steps above. State 5 is identical to state 4 except that the temperature of the fluid is changed to account for the temperature

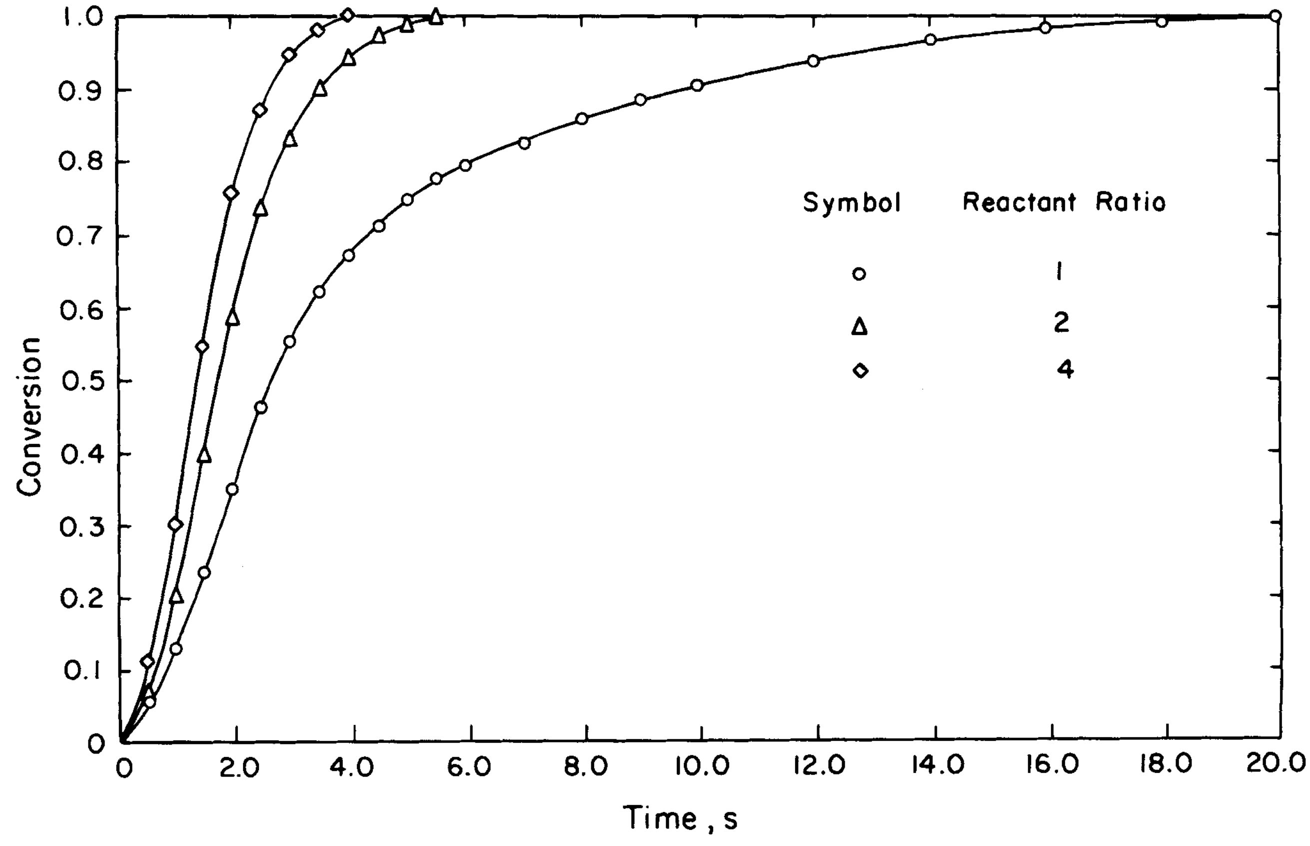

Figure 5. Very rapid reaction.

rise caused by chemical reaction. State 6 is identical to state 5 except that the temperature of the reactor wall is changed to account for the temperature rise caused by heat transfer from the fluid.

Algorithm

The algorithm for deriving conversion from the raw data $h(t) - h(o)$ and the magnitude of the contribution of each step in Figure 4 is discussed in this section. The dilatometer response characteristics are summarized in Table 2.

The first step in Figure 4 involves mixing equal volumes of reactant solutions to achieve a uniform concentration in the mixed zone marked $A + B$ in state 2. The dilution in reactant species causes a change in meniscus level $h_2 - h_1$. The magnitude of this dilution signal is obtained both experimentally and theoretically for each reactant. In the experimental method, the upper cell of the batch reactor is filled with original, nondiluted reactant, and the lower cell is filled with water. The experiments are then carried out according to the procedure outlined in the Experimental section above. In the theoretical approach, the dilution volume change is estimated from density-concentration or apparent molar volume-concentration data for each reactant, following the method of Hepler et al. (1965). The theoretical approach is outlined in detail in Appendix 1. The magnitude of the dilution effect is on the order of 1% of the total signal for the stoichimetric very rapid reaction system, and attains its largest value of about 10% of the total signal for the intermediate speed reaction system at a reactant ratio of 4.

Steps 2 through 4 in Figure 4—i.e., the chemical reaction, fluid temperature rise, and the hydrostatic pressure rise—produce linear changes in the meniscus level. Chemical reaction is the main contributor to the total height change signal (about 80%). The fluid temperature rise caused by the heat of reaction contributes about 20% to the total signal. The hydrostatic pressure effect is essentially negligible (about −0.1%).

The meniscus level change $h_6 - h_5$ in step 5 of Figure 4 is caused by expansion of the reactor due to the wall temperature rise. This contribution is small (less than 1% of the total signal) within the time scale of all the experiments except the stoichiometric intermediate speed reaction. This case is treated separately and discussed in detail in Appendix 2.

The increments in the meniscus height change can be combined as follows to yield the composite signal:

$$\begin{array}{rcl} h_2 - h_1 &=& h_2 - h_1 \\ h_3 - h_2 &=& K_1F \\ h_4 - h_3 &=& K_2\Delta P = K_3F \\ h_5 - h_4 &=& K_4\Delta T_f = K_5F \\ h_6 - h_5 &\cong& o \\ \hline h_6 - h_1 &=& h_2 - h_1 + KF \end{array} \qquad (1)$$

In the above summation, the dilution effect $h_2 - h_1$ is the only term that is not linearly dependent on conversion. From Eq. 1,

$$F = \frac{[h(t) - h_1(o)] - [h_2(t) - h_1(o)]}{[h(\infty) - h_1(o)] - [h_2(\infty) - h_1(o)]} \qquad (2)$$

where $h(t) = h_6(t)$. Equation 2 is used to calculate conversion for meniscus height change data. The reaction experiments provide

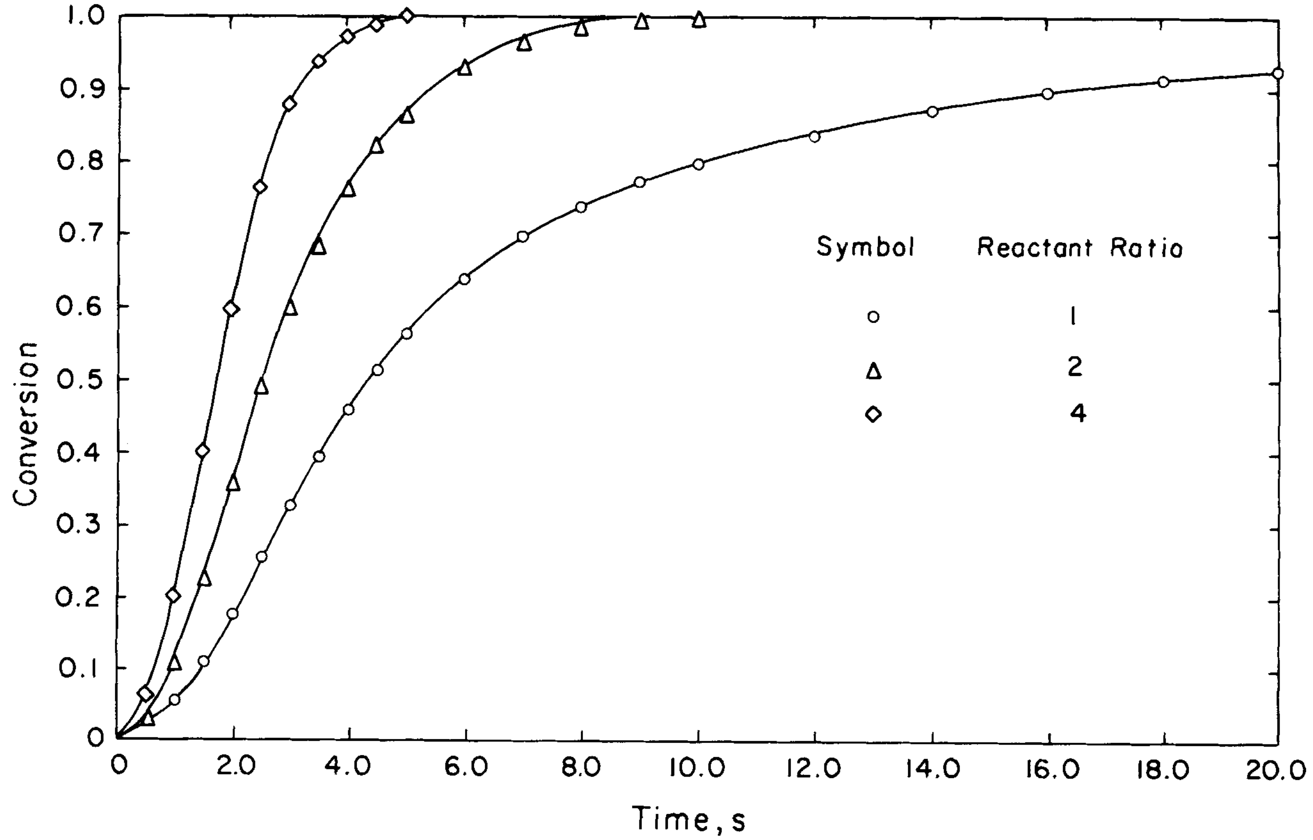

Figure 6. Intermediate speed reaction.

the $h(t)$ data, and the mixing without reaction (dilution) experiments provide the $h_2(t)$ data.

RESULTS

Fractional conversion data for the very rapid and intermediate speed reactions, each run at reactant ratios of 1, 2, and 4 are shown in Figures 5 and 6, respectively. Each data point represents the average of three experiments run under similar conditions. All the original data (raw and processed) are given elsewhere (Ghodsizadeh, 1978). The theoretical precision of the conversion results (two standard deviations) for the very rapid reaction system is about 1, 1.5, and 2.5% for the $\beta = 1$, 2, and 4 cases, respectively. The corresponding values for the intermediate speed reaction are 1, 2, and 4%, respectively. The bulk of the error is caused by the inaccuracy in the species' spatial representation (in Figure 4), the reactant concentrations, and in reading the position of the meniscus in the capillary. The reproducibility of the data is ±3% (two standard deviations). The main source of uncertainty in duplicating identical runs is the exposed area of the ruptured rubber membrane, which has a baffling effect on the system. All experiments where the rubber area remaining after rupturing exceeded 5% of the vessel cross-sectional area were discarded. In addition, this effect gives rise to a small variation in stirrer speed which in turn affects the reproducibility of the data. The stirrer speed, monitored by a stroboscope, dropped from an initial value of 475 to a range of 445–450 rpm upon rupture of the rubber membrane. The drop in stirrer speed is attributed to the increased resistance caused by the additional mass of liquid in circulation.

The effect of the mixing currents caused by the sudden retraction of the rubber membrane upon rupture is determined by the following experiment. A stoichiometric very rapid reaction experiment is run with the stirrer not in use. The subsequent volume change after 1 and 20 s is roughly 15 and 10%, respectively, of the magnitude of the signal obtained when the stirrer is used. The above volume change is reasonably reproducible. Thus, although this effect enhances somewhat the mixing intensity due to the stirrer, it does not add any appreciable error to the conversion vs. time results.

The volume change caused by rupture of the rubber membrane is found to be zero by the following experiment. Water is placed in both cells, and the membrane is ruptured. The change in height of the liquid in the capillary tube corresponds exactly to the volume displacement caused by the increase in depth of the steel rod in the reactor (2.5 cm).

The conversion data for both reaction systems indicate a strong dependency on the reactant ratio. The effects of reactant ratio are studied in detail by testing various mathematical models against the data obtained in this study (Ghodsizadeh, 1978).

NOTATION

A = first reactant
B = second reactant
D = diameter of stirring bar, 3.80 cm
F = fractional conversion of limiting reactant, dimensionless
h = height of liquid meniscus in capillary tube, cm
K_1–K_5 = constants of proportionality defined preceding Eq. 1
K = $K_1 + K_3 + K_5$ = constant of proportionality defined in Eq. 1
N = stirring speed, rev/s
P = pressure
T_f = average temperature of fluid, °C
T_w = average temperature of wall, °C
t = time after membrane rupture, s

Greek Letters

β = stoichiometric ratio of excess reactant to limiting reactant, moles per mole, dimensionless
ω = fraction of reactor volume in the mixed region $A + B$ plus the reacted region *Final Composition* (Figure 4), dimensionless
ρ = density of fluid, 1.00 $g{\cdot}cm^{-3}$
μ = viscosity of fluid, $g{\cdot}cm^{-1}{\cdot}s^{-1}$

APPENDIX 1: DILUTION EFFECTS

In this appendix, the method used to compute the dilution effect on the meniscus height ($h_2 - h_1$ in Figure 4), and the associated errors are discussed.

Theory

When a volume ν of a relatively concentrated solution is mixed isothermally with a volume ν' of pure solvent, the final volume V in general will be different from $\nu + \nu'$. The volume change occuring in this dilution process $\Delta\nu$ is given by

$$\Delta\nu = V - (\nu + \nu') \tag{A1}$$

The apparent molar volume ϕ of a solute is defined by

$$\phi = (V - n_1\overline{V}_1^\circ)/n_2 \tag{A2}$$

where n_1 and n_2 are the number of moles of solvent and solute, respectively, in the volume V, and $\overline{V}_1^\circ$ is the molar volume of the solvent. Hepler et al. (1965) obtained the following exact equation relating $\Delta\nu$ to the apparent molar volume for a dilution process, by manipulating Eqs. A1 and A2:

$$\Delta\nu = n_2(\phi_f - \phi_i) \tag{A3}$$

where the subscripts f and i refer to the final and initial values, respectively.

The apparent molar volume increases roughly linearly with the square root of concentration in dilute solutions, and this simple relationship often extends to concentrated solutions (Masson, 1929).

$$\phi = a\sqrt{C_2} + b \tag{A4}$$

where $C_2 = n_2/V$ is the solute concentration, and a,b are constants. Substituting Eq. A4 in Eq. A3

$$\Delta\nu = an_2[\sqrt{C_{2,f}} - \sqrt{C_{2,i}}] \tag{A5}$$

Experimental data for ϕ as a function of concentration for several electrolytes and pertinent references are given by Harned and Owen (1958).

Estimates of $\Delta\nu$ for the reactants used in this study, obtained from apparent molar volume data, are found to be in good agreement with the experimental data, as shown in Table A1.

Dilution Volume Change as a Function of Time

In order to derive conversion from meniscus height change data (from Eq. 2), information on dilution volume change as a function of time is needed. Three models are tested. These models are based on (a) partial segregation, (b) linear dependence of concentration on mixing, and (c) linear dependence of volume on mixing. These approaches are applied to the dilution of 840 mL (corresponding

TABLE A1. MAGNITUDE OF DILUTION VOLUME CHANGE*

Reactant	Init. Conc. gmol/L	$\Delta\nu$, Dilution Volume Change (mL) Theory	Exper.	Apparent Molar Vol., Data Source
NaOH	0.2	−0.062	−0.068	Hepler et al. (1965)
NaOH	0.1	−0.022	−0.024	Hepler et al. (1965)
NaOH	0.05	−0.008	−0.008	Hepler et al. (1965)
HCl	0.05	−0.003	−0.008	Geffcken (1931)
$HCOOCH_3$	0.05	—	−0.010	—

* For dilution of 840 mL solution with 840 mL water.

to the volume of each chamber) of 0.2N gmol/L NaOH with 840 mL water to demonstrate the procedure and examine the difference in results.

(*a*) *Partial Segregation* (*Monte Carlo Coalescence and Redispersion*). The fluid is divided into 500 cells of equal size. Each cell is homogeneous in concentration at all times. Initial conditions correspond to the initial composition distribution in the cells. Randomly selected pairs of cells coalesce (mix perfectly) and immediately redisperse (split in half). Between steps of coalescence and redispersion, the volume of each cell is changed in accordance with the dilution volume change. Further details are given by Kattan and Adler (1967). The mixing characteristic describing the mixing within the reactor as a function of time is determined by Ghodsizadeh (1978) using stoichiometric very rapid reaction data.

An exact equation for the dilution volume change incurred upon mixing two solutions of different concentrations is developed as follows. Let V' and V'' be the volumes of two solutions containing n_2' and n_2'' moles of solute, and n_1' and n_1'' moles of solvent, respectively, and denote the apparent molar volume at the prevailing concentrations by ϕ_v' and ϕ_v'', respectively. Then

$$V' = n_1'\bar{V}_1^o + n_2'\phi_v' \tag{A6}$$

$$V'' = n_1''\bar{V}_1^o + n_2''\phi_v'' \tag{A7}$$

Let ϕ_v^f represent the apparent molar volume of the mixed solution, then the dilution volume change $\Delta\nu$ is given by

$$\Delta\nu = (n_2' + n_2'')\phi_v^f - n_2'\phi_v' - n_2''\phi_v'' \tag{A8}$$

Note that the above equation reduces to Hepler et al.'s equation for $n_2'' = o$.

The apparent molar volume quantities ϕ_v^f, ϕ_v', and ϕ_v'' for sodium hydroxide are determined from the following equation (Hepler et al., 1965):

$$\phi_v = 2.8\sqrt{C_2} - 5.25 \tag{A9}$$

The Monte Carlo simulation is carried out on an HP-3000 digital computer.

(*b*) *Linear Dependency of Concentration on Degree of Mixing.* The density distribution function characterizing concentration is approximated by a space-averaged concentration $\tilde{C}_2$, such that $\tilde{C}_2$ is linearly dependent on the degree of mixing achieved between the solution and diluent. Thus

$$\tilde{C}_2(t) = \omega(t)[C_{2,f} - C_{2,i}] + C_{2,i} \tag{A10}$$

where $\omega(t)$ is the degree of homogeneity of the fluid (defined more precisely in the paper) and is given by the stoichiometric very rapid reaction data, (Toor, 1969). The dilution volume change is then determined as a function of time from Eqs. A5 and A10. This model approximates the maximum mixedness case.

(*c*) *Linear Dependence of Volume on Degree of Mixing.* The dilution volume change is linearly related to the degree of homogeneity of the fluid. Thus

$$\Delta\nu(t) = \omega(t)\Delta\nu \tag{A11}$$

This model uses the experimental magnitude of dilution volume change $\Delta\nu$, and the stoichiometric very rapid reaction data for $\omega(t)$. This simple model has the virtue of not requiring any data on the reactants density or the apparent molar volume.

Simulation Results

The predictions of the three models are given in Figure A1, and compared to the experimental data. The precision of the experimental data is only ±5% (two standard deviations) owing to the small magnitude of the dilution volume change.

The Monte Carlo partial segregation model provides excellent predictions over the entire range. The second model, based on linear dependency of concentration on mixing, tends to underestimate the experimental data by as much as 25%. The third model, based on linear dependency of volume on mixing, fits the experimental data to within 10% accuracy.

Owing to its extreme simplicity, the latter model is employed to estimate the $\Delta\nu(t)$ data required for deriving conversion data.

The dilution volume change ($h_2 - h_1$ in Figure 4) is found to be negligible in all cases except when NaOH is used at a concentration of 0.2 gmol/L, corresponding to a reactant ratio of 4. For this case, the dilution volume change is roughly 5 and 10% of the very rapid and intermediate speed reaction overall signals, respectively. Since the maximum difference between the three model predictions and the experimental data is 25%, the error in the conversion results (two standard deviations) due to the assumption on the species' spatial distribution, is no more than 2 and 3.5% for the very rapid and intermediate speed reactions, respectively (for $\beta = 4$).

During the course of a reaction, some dilution of the product species occurs. However, since the average concentration of the product species is only one-half of the limiting reactant concentration (0.025 gmol/L for this study), dilution of such small concentrations is of secondary importance and can be disregarded.

NOTATION FOR APPENDIX 1

a,b = constants
C = concentration, gmol/mL
n = number of moles
t = time, s
V = total volume, mL
$\bar{V}_1^o$ = molar volume of solvent, mL

Greek Letters

ν = volume of relatively concentrated solution, mL
ν' = volume of pure solvent, mL
$\Delta\nu$ = volume change in dilution process, mL

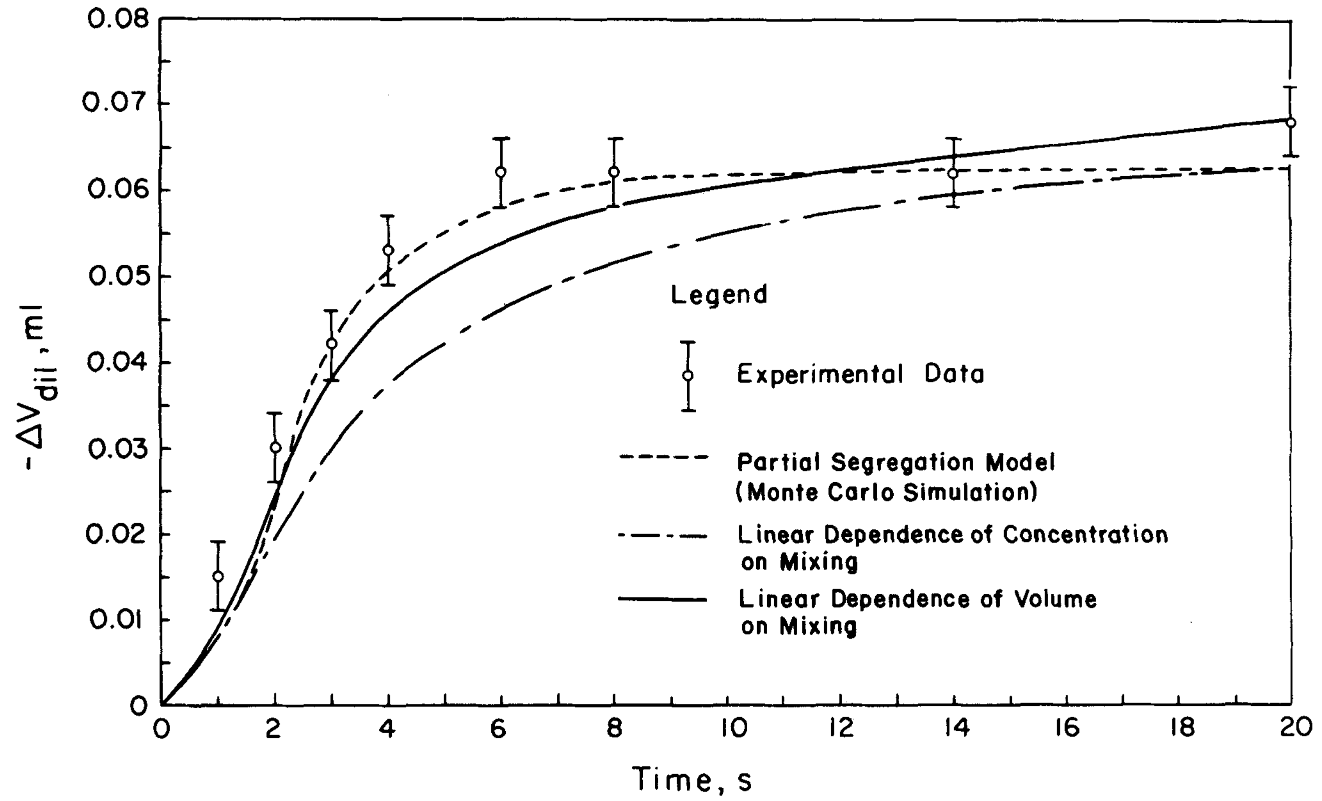

Figure A1. Dilution volume change, 840 mL 0.2N NaOH mixed with 840 mL H_2O.

ϕ = apparent molar volume, mL/gmol
ω = degree of homogeneity of fluid

Subscripts

f = final value
i = initial value
1 = index referring to solvent
2 = index referring to solute

Superscripts

$\sim$ = space-averaged quantity
$-$ = partial molar quantity
$'$ = index referring to first solution
$''$ = index referring to second solution

APPENDIX 2: HEAT EFFECTS

Thermal Characteristics of Dilatometer

The heat liberated by chemical reaction of 840 mL of each reactant is 580 calories (2.43 kJ) in the intermediate speed case, and the adiabatic temperature rise of the fluid is 0.34°C (the heat of dilution of reactants is negligible in comparison, see Table 2). Comparable information on the very rapid reaction system is given in Table 2. The temperature rise has a negligible effect on the reaction rate constant and the physical properties of the fluids. The major effect of the temperature rise is to expand the volume of the fluid linearly with conversion. The heat loss to the surroundings in 4 min, estimated by assuming the outside heat transfer coefficient controls, is about 10 calories (41.9 J) or about 2% of the heat released by the reaction. Since the maximum time of experiments is less than a few minutes, the system can be considered essentially adiabatic even without the use of insulation.

The heat released by chemical reaction is absorbed mainly by the fluid, and to a lesser extent by the nylon top and bottom, and the glass wall. At thermal equilibrium the fluid, nylon, and glass absorb 83, 13, and 4%, respectively, of the heat generated. The time required for thermal equilibrium between the fluid and (a) the glass, and (b) the nylon, estimated from an unsteady-state heat balance assuming uniform fluid temperature and no heat loss to the surroundings, is about 50 and 500 s, respectively. An upper bound estimate of the volume change caused by thermal wall expansion is 0.01 mL over a period of 20 s and 0.02 mL at infinite time. When compared to the magnitude of the volume change signals and time scales of the reactions studied, the thermal wall expansion effect is found to be negligible for all experiments except the stoichiometric intermediate speed case. The special treatment used for this case is explained next.

Stoichiometric Intermediate Speed Reaction

The stoichiometric intermediate speed reaction is the only case where the reaction time exceeds 20 s, and the heat effects and subsequent wall expansion become appreciable. This effect obscures the detection of the final stages of height change in the capillary tube. The following procedure is used to determine the magnitude of the total height change. The homogeneous conversion curve is calculated by assuming very rapid mixing (effectively for premixed feed). When the reaction takes place with nonpremixed feed, the reactants become thoroughly mixed after about 20 s, and chemical reaction then becomes the rate-controlling step. Therefore, the experimental and homogeneous conversion curves approach the same asymptote at about 95% conversion, corresponding to a reaction time of 27 s. This concept is verified by studying Mao and Toor's (1971) Figures 4 and 5 for tubular flow reactors. Thus

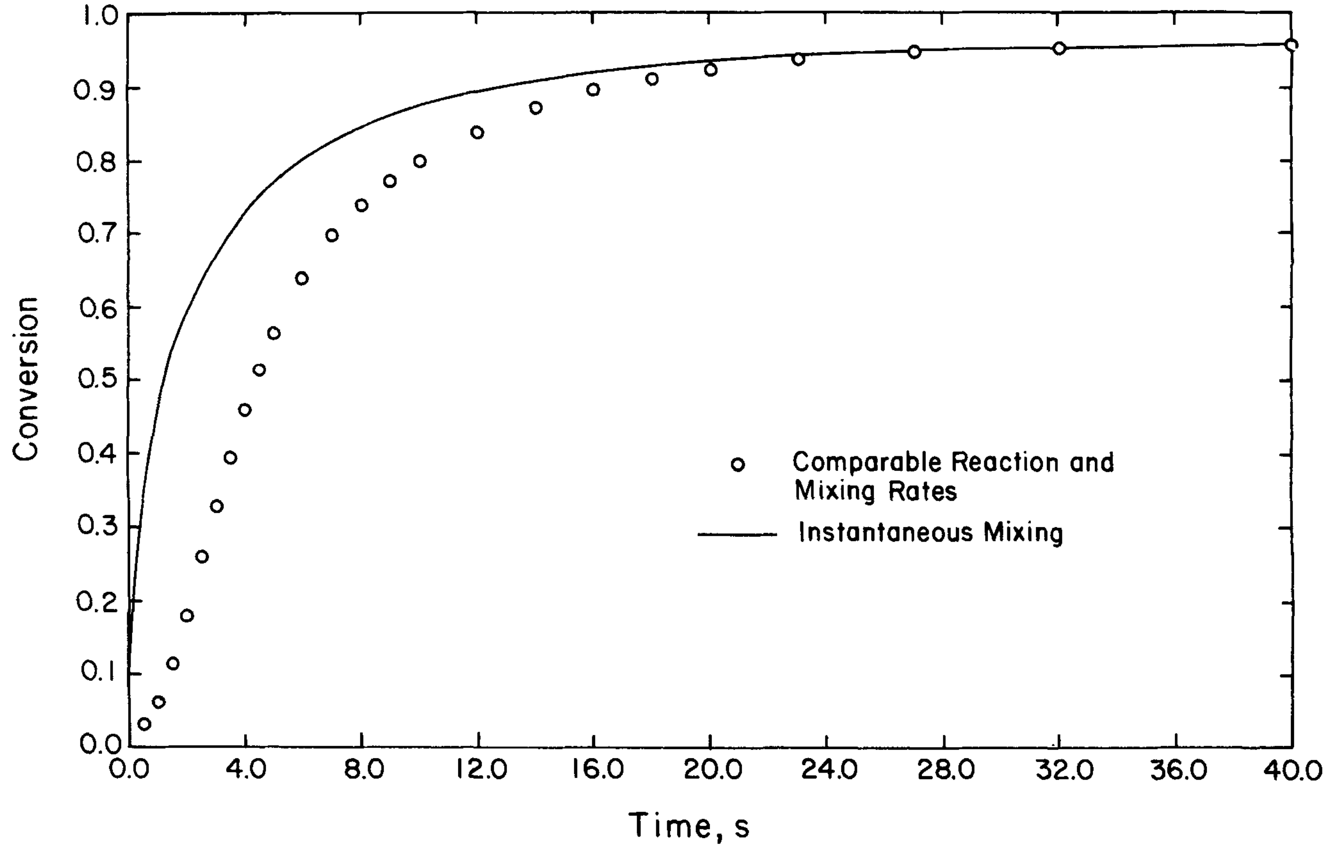

Figure A2. Stoichiometric, intermediate speed reaction.

the height change signal for 100% conversion is calculated by dividing the magnitude of the experimental height change signal obtained at 27 s reaction time by 0.95. This value of the total height change is then used to determine the fractional conversion. The corrected intermediate-speed conversion data is compared to the homogeneous conversion curve in Figure A2.

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