z_i = charge on ion i

Λ_i = equivalent conductivity of species i, sq.cm./equiv., ohm

τ = time lag, Equation (27)

Superscripts

0 = evaluated at $x = 0$

L = evaluated at $x = L$

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An Experimental Study of Steady State Multiplicity and Stability in an Adiabatic Stirred Reactor

S. A. VEJTASA and R. A. SCHMITZ

University of Illinois, Urbana, Illinois

Steady state and transient characteristics of an adiabatic, continuous flow, stirred reactor were studied in experiments employing the exothermic reaction between sodium thiosulfate and hydrogen peroxide in aqueous solution. Results illustrate the multiplicity of steady states in this system over a range of residence times. Temperatures of unstable states were attained experimentally by observing the effect of perturbations from stable temperatures. The observed steady states of the reactor under various mixing conditions are shown to be in good agreement with the predictions of a mathematical model which is based on the assumptions that mixing is perfect and that a single independent chemical reaction occurs. Less exact quantitative agreement between theoretical and experimental unsteady performance is accounted for in terms of the sensitivity of the unsteady state to small errors in the system parameters and the existence of appreciable extraneous heat capacities of the experimental equipment.

Continuous flow chemical reactors involving exothermic reactions are often operated autothermally; that is, the operating temperature is sustained entirely by the heat generated by reaction. Van Heerden (*1, 2*) studied the characteristics of such processes and showed that they may possess multiple steady states and that some steady states are unstable to small perturbations. A number of theoretical studies treating control and start-up problems as well as the general nature of steady and unsteady behavior in various reactor models followed Van Heerden's work. The majority of these were focused on the continuous flow, stirred tank reactor (CSTR) for reasons of mathematical tractability. We refer particularly to papers by Bilous and Amundson (*3*) and Aris and Amundson (*4*). Additional treatments and references may be found in some recent textbooks (*5* to *9*).

Multiple steady states are common in combustion processes as evidenced by the fact that a flowing combustible mixture may be either burning or almost completely nonreacting, depending on whether or not it has been ignited. Several experimental studies with continuous flow, mixed combustion chambers involving combustible gas mixtures have been reported. These date back to a publication by Longwell and Weiss (*10*) in 1955; further bibliography and discussion are available in reference *11*. Generally such studies have been concerned primarily with extinction phenomena and in effect utilized the notion of multiple steady states to interpret and correlate observations.

At the outset of the present study, there was not available in the literature, to our knowledge, any experimental or actual plant data showing the existence of multiple steady states in a CSTR that did not involve a combustion reaction, a surprising observation in view of the fact that numerous theoretical studies have been devoted to

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S. A. Vejtasa is presently with Shell Development Company, Emeryville, California.

such systems for nearly two decades. Near the completion of our work there appeared in the Japanese literature (*12*) a report of experiments showing multiplicity in a CSTR in which the liquid-phase hydration of propylene oxide was carried out. In that paper, experimental data, presented in a phase plane plot, clearly illustrated the existence of two stable states. Multiplicity was shown, however, for only one set of operating conditions. Unstable steady states and mixing effects were not pursued.

It has been generally acknowledged that multiple states and stability problems are encountered in industrial reactors, but apparently proprietary considerations have prevented the disclosure of data and of specific reactions.

In the present study, the exothermic reaction between sodium thiosulfate and hydrogen peroxide in aqueous solution was employed in experiments with an adiabatic CSTR to demonstrate the existence of multiple states; to examine in detail the steady state picture, including unstable states over a range of flow rates and mixing conditions; and to test the capability of the usual perfect mixing model for describing unsteady and steady characteristics. Recent experiments by Root and Schmitz (*13*, *14*) with an adiabatic loop reactor used this same reaction and demonstrated the existence of multiple states and of some unstable situations in that system.

THE THIOSULFATE-PEROXIDE REACTION

Calculations of the essential theoretical steady and unsteady characteristics of a perfectly mixed adiabatic CSTR will be shown in the next section to require nothing more in the line of kinetic information than the batch data of temperature vs. time reported and described previously (*13*) and the assumption that in effect a single-step chemical reaction occurs. Stated differently, this assumption requires that all concentration changes can be related to a single variable, the extent of reaction, at all times.

Studies of the kinetics of the thiosulfate-peroxide (TP) reaction have been reported (*15* to *20*). (Additional references to research into the basic chemistry, reaction mechanisms, and catalysts for the reaction may be found in references *15* to *17*.) These studies have shown that the reaction mechanism and the distribution of products are complicated and depend on the reaction conditions. They indicate, in particular, that under the conditions involved in the experiments of Root and Schmitz (*13*, *14*) (initial mixture of 0.8M $Na_2S_2O_3$ and 1.2M H_2O_2 at 0°C.), involved as well throughout the present work, the principal products of the uncatalyzed oxidation reaction are probably sodium sulfate, sodium trithionate, and water. They further show that the stoichiometric proportions are about 2 moles of peroxide/mole of thiosulfate and that the reaction is irreversible and apparently obeys the following stoichiometric equation:

$$2\,Na_2S_2O_3 + 4\,H_2O_2 \rightarrow Na_2S_3O_6 + Na_2SO_4 + 4H_2O$$

In some of the studies cited above (*18* to *20*), overall kinetic expressions based on a single-step irreversible model have been reported, and the experiments of Root and Schmitz strongly indicate that the assumption of a single-step model is valid, at least under the conditions of those experiments.

No reaction mechanism or rate expression is proposed in this paper. The expression given in the work of Spencer (*18*) did not predict the batch data of Root and Schmitz with suitable accuracy, probably because the experimental conditions differed somewhat. Further discussions and comparisons pertaining to this matter are available elsewhere (*21*).

We might mention that in addition to an investigation of the kinetics of the TP system, the thesis of Griegel (*20*) included a study of the possibility of multiple states in a CSTR with this reaction and presented a detailed design of a reactor including a multivariable control network for, experimentally studying the reactor and its control. No experiments were reported, however.

THEORY OF THE PERFECTLY-MIXED REACTOR

Basic Equations and Assumptions

Under conditions of perfect mixing and adiabatic operation, the equations describing the performance of a CSTR in which a single chemical reaction involving n chemical species is occurring may be written in the following familiar form:

$$V\rho \frac{dx_j}{d\theta} = w_f(x_{jf} - x_j) - a_j M_j V\, r(\rho, x_1, \ldots, x_n, T) \qquad (j = 1, 2, \ldots n) \qquad (1)$$

$$V\rho C_p \frac{dT}{d\theta} = w_f C_p (T_f - T) + (-\Delta H) V\, r(\rho, x_1, \ldots, x_n, T) \qquad (2)$$

In Equation (1), the stoichiometric coefficient a_j has a positive value if the j^{th} species is a reactant and a negative value if it is a product.

The energy equation, as written above, involves the assumptions of a constant mixture heat capacity and negligible vessel and equipment heat capacities. The validity of the former has been substantiated for the TP system (*13*). The latter assumption is required only in considering the unsteady state and is probably well justified in liquid-phase systems in large volume processing equipment. In bench-scale processes, however, the soundness of that assumption may be open to doubt. Since it is of some concern in this study and could be important in scale-up considerations, the effect of such extraneous heat capacities will receive further attention later.

Changes in kinetic and potential energies and work effects, including the work input connected with mixing the reactor contents, are insignificant relative to reaction enthalpy effects in the present study.

The density is generally assumed to be constant in theoretical studies of the CSTR. In experiments with the TP system, Root and Schmitz (*13*) measured its change to be only about 5% through the course of a batch reaction in which the temperature rise was about 90°C. Nevertheless, since data are available from reference *13* and since no mathematical difficulties are introduced, the assumption of a constant density is not invoked here. Some results obtained with and without the assumption will be compared later.

Theoretical Steady State

Equating the right-hand sides of Equations (1) and (2) to zero leads to the following well-known relationship between the concentration of any species j and the temperature at steady state:

$$\varphi_j = \frac{(-\Delta H)}{C_p}(x_j - x_{jf}) - a_j M_j (T_f - T) = 0 \qquad (j = 1, 2, \ldots, n) \qquad (3)$$

This relationship is important because it allows one to express all concentrations in terms of feed conditions and the temperature at steady state. It follows that the density may also be expressed in terms of the steady state temperature and feed conditions, so that ascertaining the complete steady state of the system for a given feed state in principle requires determining only the steady state temperature.

Substitutions from Equation (3) may be introduced into the rate expression in Equation (2) to yield a single equation involving the steady state temperature as the only unknown variable. This equation may be written as

$$\frac{(T - T_f)}{\tau}\frac{\rho_f}{\rho} = \frac{(-\Delta H)r}{\rho C_p} \tag{4}$$

where τ is based on q_f and ρ and r are considered now to be functions of temperature and the feed state alone as a result of substitutions from Equation (3). In order to stress the elimination of the concentration variable, we shall use hereafter the symbols $R(T)$ and $G(T)$ to represent the left- and right-hand sides respectively, of Equation (4).

Traditionally in studies of the nonisothermal CSTR, it is pointed out that $G(T)$, or a similar function, represents the rate of heat generation by chemical reaction, while $R(T)$ gives the rate of heat removal. The character of the steady state is typically illustrated graphically by plotting both functions vs. temperature and by examining the intersections of the resulting curves. These notions and techniques were used in the pioneering study of Van Heerden (*1*) and have become familiar procedures through numerous subsequent publications. Some properties of $G(T)$ as well as the graphical solution of Equation (4) for the TP system will be taken up in the following section.

An important observation is that the steady state problem is reducible to a single equation involving only the temperature if, and only if, the assumption is made that the progress of reaction is describable in terms of a single rate expression, an assumption discussed earlier for the TP system.

The Generation Function and Predicted Multiplicity of States in the Thiosulfate-Peroxide System

For an adiabatic CSTR, the generation function $G(T)$ may be obtained directly through differentiation of the temperature vs. time curve from a batch experiment. Here we present a sketch of the arguments involved and of the procedures employed in obtaining that function in the present work.

A study of the usual differential equations describing the progress of a chemical reaction in a batch reactor shows readily that Equation (3) is valid throughout the course of the batch reaction, provided x_{jf} and T_f characterize the initial state of the batch. Furthermore, an energy balance on the batch reactor may be written as

$$\left(\frac{dT}{d\theta}\right)_{\text{batch}} = \frac{(-\Delta H)r}{\rho C_p} \tag{5}$$

As in Equation (4), r and ρ may be expressed as functions of temperature alone as a result of substitutions from Equation (3). Hence, according to Equation (5), the value of the generation function $G(T)$ at a particular temperature is simply the slope of the batch temperature-time curve at that temperature. We should emphasize, however, that because of the substitution from Equation (3), ρ and r involve x_{jf} and T_f, which characterize the feed state to the CSTR and the initial state of the batch.

In the present study $G(T)$ was obtained from the batch data reported previously (*13, 21*) for the TP system. The procedure for differentiating that data first involved fitting the temperature curve with a fifty-term Fourier cosine series, and then taking the time derivative of the resulting expression. Further details on this approach are available elsewhere (*22*). The resulting generation function for a feed state of 0.8M $Na_2S_2O_3$ and 1.2M H_2O_2 in aqueous solution at 0°C., the initial state in the batch experiments, is shown in Figure 1.

The geometry of the generation curve of Figure 1 is somewhat typical for exothermic reactions. In the early stages of the reaction, the rate of heat generation increases due to the sensitivity of the reaction rate to temperature, but eventually it decreases as a result of depletion of reactants and reaches zero at the adiabatic temperature of 88.5°C. when the limiting reagent (hydrogen peroxide in this case) has been entirely consumed. From the agreement between generation curves arrived at by similar treatment of the three separate batch runs reported in reference *21*, we estimate that the error in the curve of Figure 1, which is roughly the best fit of the three, does not exceed ± 0.1°C./sec. at any temperature.

Though a knowledge of the concentration distribution will not be required here, it might be noted that for every point on the generation curve, one could easily compute a set of concentrations using Equation (3) and the coefficients given earlier in the stoichiometric reaction equation. A value of $(-\Delta H)/(a_j M_j C_p)$ for use in Equation (3) of 2,420°C. was calculated from the adiabatic temperature rise with the assumption that ΔH is constant, an assumption compatible with the earlier one of a constant heat capacity.

We shall make use of the generation curve of Figure 1 throughout this paper to obtain predicted reactor performance; thus, the feed state will remain fixed at the concentrations and temperature given. The remaining parameter in the CSTR system is the mean residence time τ appearing in the heat removal function $R(T)$, given by the left-hand side of Equation (4). The effect of that parameter is illustrated in Figure 1. In particular, it is shown that for values of τ between 6.8 and 17.8 sec., three intersections of the removal and generation curves are obtained; hence, three steady state solutions exist. We shall refer to these states simply as high, intermediate, and low, according to their relative temperatures. It is clear that the adjectives high, intermediate, and low also describe the relative extents of chemical reaction for the three states.

For $\tau > 17.8$ sec., there exists a single high-temperature state in which chemical conversion is nearly complete, and for $\tau < 6.8$ sec. the unique steady state is one of low temperature and low chemical conversion. Interestingly, the effect of backmixing, usually a deleterious effect in isothermal reactions, is clearly an advantageous one in the TP system, as is often the case with exothermic reactions, in the sense that a high conversion state can be achieved at a relatively low residence time. As can be seen from the batch data in reference *13*, a residence time in excess of 50 sec. would be required for the attainment of a high conversion output from a plug flow tubular reactor with no backmixing. A disadvantage of backmixing, also clearly illustrated by the TP system, is the possibility of multiple states and unstable conditions.

The curves representing $R(T)$ in Figure 1 are slightly concave upward, owing to the change in density with temperature. The curvature is so slight, however, that it causes a maximum of 1°C. difference in steady state temperatures from constant density predictions, and it decreases the range of τ on which multiple states exist by only 0.2 sec.

In the actual computation of steady states in this study, the function $G(T)$ was tabulated, along with ρ, on a digital computer. Predicted reactor performance in the form of temperature vs. residence time was obtained by choosing various values of T and by using the tabulated functions to compute the corresponding value of τ from Equation (4).

We might discuss briefly at this point the advantages and limitations associated with prediction of nonisothermal CSTR behavior directly from batch data as described above. The notable advantage is that the usual labor and difficulties involved in the intermediate step of obtaining a kinetic rate expression from batch data are eliminated. Thus, uncertainties in kinetic constants are removed as a possible cause of discrepancies between observed and predicted reactor performance. One limitation is that the approach is not easily extended to nonadiabatic systems. In addition, a study of various feed states requires obtaining a different generation function, hence carrying out a separate batch experiment, for each different set of feed states. Though studies cited in an earlier section have shown that the assumption of a single-step kinetic mechanism is valid in the TP system, that assumption nevertheless renders the approach as described here inapplicable in many important reaction processes. Other limitations pertaining to the prediction of unsteady behavior by using $G(T)$ from Figure 1 will be recognized in the next section.

Theoretical Transient State

The focus in this section is on the unsteady state of a CSTR which is perturbed from initially steady operation by means of disturbances only in the feed flow rate. We are especially interested in this type of disturbance because a particularly simple form of the mathematical description of the unsteady state results, as will be shown, which readily yields information concerning stability of a steady state and which allows the theoretical transient state to be computed through use of the $G(T)$ curve of Figure 1 without requiring additional reaction kinetic information. Furthermore, this type of disturbance can be introduced conveniently in experimentation.

From Equations (1) and (2) it may be shown that if the feed state is held constant at all times, any change in φ_j, defined in Equation (3), during the time w_f is transient and thereafter is governed by

$$V\rho \frac{d\varphi_j}{d\theta} + w_f(\theta)\, \varphi_j = 0 \quad (j = 1, 2, \ldots, n) \qquad (6)$$

But since the initial value (that is, the steady state value) of φ_j is zero, it follows that Equation (6) has only the trivial solution $\varphi_j = 0$ at all times. Obviously, the same result is obtained if the initial state is equal to the feed state, since then also the initial value of φ_j is zero. It follows that if the only significant disturbances are those in the feed flow rate, the transient state of the reactor will lie at all times on the curve given by Equation (3) in the $(n + 1)$ dimensional phase space. The curve extends from the feed state to the completely reacted state of the system and passes through all possible steady states. Thus, with the limitation that the only disturbance variable is w_f, we may substitute for all x_j in Equation (2) in terms of T from Equation (3) and arrive at the following equation for the unsteady temperature in terms of temperature alone:

$$\frac{dT}{d\theta} = G(T) - R(T) \qquad (7)$$

All of the theoretical unsteady reactor behavior to be shown later in this paper were obtained by numerical integration of Equation (7) with $G(T)$ taken from Figure 1. The method involved standard procedures on a digital computer and is described elsewhere (*22*). It should be emphasized, however, that the results are limited to transients for which $\varphi_j = 0$ at all times.

Using Equation (7) one can argue, as follows, that an intermediate steady state is unstable. At any temperature between the low and intermediate steady states, the right-hand side of Equation (7), and hence the time derivative of the temperature, is negative, while for temperatures between the intermediate and high states, it is positive, as can be seen from the geometry of the curves in Figure 1. It follows that perturbations to the left of the intermediate state will grow in that direction and lead to the low state, and those to the right will lead eventually to the high state. Similar reasoning leads to the conclusions that any unique state is globally stable and that high and low states are stable so long as disturbances in w_f do not cause a temperature excursion beyond the temperature of the intermediate state. This, in essence, is the result of the classical stability argument used by Van Heerden (*1*, *2*). It is rigorous only for an adiabatic reactor, as analyses of more general mathematical descriptions have shown (*5*, *6*, *9*, *23*), and, in addition, the latter part of the conclusion relies on the assumption that φ_j is infinitesimally small. Generally, the magnitude of temperature perturbations that can be tolerated from the high and low states must depend on the magnitude of the perturbation in φ_j. Through an inspection of Equations (6) and (7), however, one can ascertain that the part of the conclusion pertaining to unique states is valid even for $\varphi_j \neq 0$ in an adiabatic reactor.

The preceding considerations suggest a convenient experimental approach for locating the intermediate state, an approach which in fact was employed in the experimental part of this work. The method consists simply of creating successively larger perturbations from a stable high or low state by appropriate manipulation of the feed flow rate. The experimental intermediate temperature is that temperature limiting the maximum temperature perturbation which decays to the original state and the minimum perturbation which grows to the other stable state.

It was stated earlier that one of the assumptions involved in Equation (2) was that equipment heat capacities were negligible relative to the heat capacity of the reacting fluid. The assumption is implicated only in the transient state. At this point we wish to examine briefly the possible effects of extraneous heat capacities in order to provide a basis for later discussion of experimental observations. Consider first an instance in which the rate of heat transfer between the reacting fluid and the vessel, baffles, stirrer, and any other incidental equipment is very rapid, and where the thermal conductivity of the equipment is large so that the equipment and fluid temperatures can be considered equal throughout the unsteady state. Then the only modification necessary in the mathematical description is the replacement of C_p on the left-hand side of Equation (2) by an effective heat capacity for the entire system. It can be established without difficulty by means of a standard linear stability analysis that the nature of the transient response to small perturbations will be unaffected by the larger effective heat capacity. However, Equation (6), and hence Equation (7), is no longer valid; the value of φ_j does not remain at zero in response to disturbances in w_f, and the technique prescribed above for locating the intermediate state is not rigorous. Clearly one arrives at the same conclusions in considering a finite rate of heat exchange between the reactor contents and the equipment or a finite thermal conductivity of the solid material, since modification of the describing equations would then necessitate in the first case appending a term accounting for the rate of exchange on the right-hand side of Equation (2) and in either case formulating an additional differential heat balance on the equipment.

It is worth mentioning that besides those cases in which the equipment capacity is negligible, earlier analysis and arguments in this section are also meaningful if processes in the fluid phase are very rapid relative to heat exchange rates between the fluid and solid. Such may be the case if the solid material has a very low thermal conductivity or if the solid-fluid heat transfer coefficient is very small. In the limit as either of these quantities approaches zero, the fluid phase reacting system reaches its steady state (actually a pseudo steady state) following a perturbation before any appreciable change in the solid temperature is realized. Eventually, the effect of the solid capacity would show up, but it would not mask the intrinsic transient nature of the reacting fluid phase.

CONSIDERATION OF THE MIXING PROBLEM

Clearly, the condition of instantaneous and perfect mixing throughout the contents of a CSTR is an idealization that can never actually be attained in a real reactor. It should be realized that the assumption of perfect mixing as invoked in the preceding theoretical analysis implies not only thorough mixing of the reactor contents at the macroscopic level, as might be determined through studies of flow patterns, residence time distributions, or concentration and temperature profiles, but also complete uniformity at the *molecular* or microscopic level, the so-called *maximum-mixedness* state described by Zwietering (*24*). Some insight into the possible effect of deviations from perfect mixing on the multiplicity of steady states in a CSTR can be gained by considering the opposite extreme in mixing both from the macroscopic and microscopic viewpoints.

On the macroscopic level, the opposite of complete backmixing is plug or piston flow with no dispersion. This situation leads to a unique steady state in all cases; the output state is simply the state in a batch reactor after an equal residence time. Thus, in an actual CSTR where backmixing lies between these extremes, showing, no doubt, effects of a certain amount of short circuiting in the flow and some relatively stagnant regions, unique states could be found to exist in situations where the perfect mixing model predicts multiplicity.

Somewhat less obvious and more difficult to appraise are the effects of deficiencies in mixing on a microscopic scale, where the opposite of mixing is complete segregation. In considering the possible effects on multiplicity here, suppose that a premixed stream of reactants enters the CSTR as separate filaments or packets of fluid, as imagined by Zwietering in his description of the completely segregated state (*24*). If each packet retains its identity through its life in the reactor, exchanging neither heat nor mass with its neighbors, it is clear that the state of the reactor is unique, regardless of the extent of mixing at the macroscopic level, for each packet simply behaves as a batch reactor. Hence it is possible for multiplicity of states to be affected by microscopic mixing effects that are not made evident by flow patterns, residence time distributions, or profile sampling.

Aiming at an intermediate model of micromixing, Vejtasa (*25*) carried out a theoretical study of an adiabatic CSTR imagining that the fluid was completely segregated as far as material transfer was concerned but that the temperature was uniform throughout the reactor and the macroscopic mixing perfect. Such a model has some plausibility in a liquid system where the thermal diffusivity is typically greater by two orders of magnitude than the molecular diffusivity. Vejtasa's calculations, which were based on Spencer's (*18*) kinetic model of the TP reaction with second-order kinetics, showed multiplicity of steady states with only modest quantitative deviations from the maximum mixedness results.

Still other deliberations are required if the reactant streams enter the reactor separately, an unmixed feed condition. Here, if no mass is exchanged between imaginary filaments or packets, no reaction takes place. Thus the mechanism of establishing contact between the reactants is added to the overall mixing problem.

A comprehensive treatment of mixing phenomena in chemically reacting systems and other processes may be found in two volumes devoted to the subject of mixing (*26*, *27*). These also contain a number of references to studies of mixing models of chemical reactors, including the CSTR.

The derivation and testing of mathematical models of mixing were not within the scope of the present investigation. Our intention in the preceding discussion was to bring into view various considerations which compelled us to look into mixing effects in our experimental work. These effects were probed experimentally by observing and by comparing the reactor performance under various mixing conditions. Such conditions were created by varying the impeller speed and by feeding the thiosulfate and peroxide solutions to the CSTR in separate streams, an unmixed feed, in some experiments and by mixing them prior to their entry into the reactor in others.

EXPERIMENTAL APPARATUS AND PROCEDURE

Diagrams of the reactor and of the feed injection assemblies used in obtaining experimental data are shown in Figure 2.

The reactor itself was cylindrical in shape, and was constructed of type 304 stainless steel. The feed entered at the center of the bottom of the reactor, and the exit port was located near the wall in the top. During a run the reactor was slightly tilted so that the exit port was the highest point of the reactor. This protected against the possible trapping of air and other gases.

Stirring was accomplished with a 5-cm. diameter, three-blade, polyethylene marine type of impeller driven by a variable speed electric motor through a ⅛-in. diameter stainless steel shaft. The impeller was centrally located in the reactor 1 in. from the bottom. Three copper-constantan thermocouples, enclosed in stainless steel protection tubes, were immersed in the reacting fluid. These thermocouples, labeled t_1, t_2, and t_3, in Figure 2, were located as shown in that figure, with t_1 being movable vertically and t_2 horizontally.

The void volume of the reactor with baffles, thermocouples, and impeller assembly in place was measured to be 510 cc. Other dimensions and details including the baffle arrangement are given in Figure 2.

The mixing head shown in Figure 2 was used to obtain data with premixed reactants entering the CSTR. It was designed to insure intimate mixing of the thiosulfate and peroxide streams without allowing time during the mixing for any appreciable chemical reaction to occur. Machined from a type 316 stainless steel block, it followed a design similar to that employed in the loop reactor studies of Root and Schmitz (*13*). Pertinent dimensions and other details are given in Figure 2; the important feature is the tangential entrance of each feed stream into the main bore in opposing directions so as to promote swirling and mixing. The volume of the central bore was 1.22 cc., giving a residence time range of 0.01 to 0.05 sec. in the experiments conducted in this study. The central bore was tapered near its exit to provide high injection velocities (10 to 40 ft./sec.) at the reactor inlet so that back

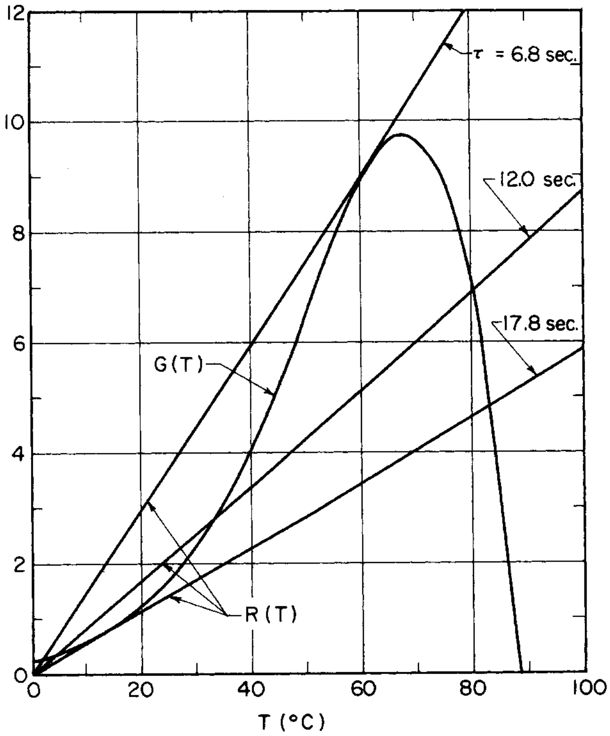

Fig. 1. Heat generation and removal functions for feed mixture of 0.8M $Na_2S_2O_3$ and 1.2M H_2O_2 at 0°C.

diffusion of heat and mass from the reactor into the mixing head was minimized. As evidence of negligible back diffusion and of negligible chemical reaction in the mixing head, the temperature measured by means of a thermocouple located ½ in. upstream of the exit of the main bore never exceeded 0.25°C. in any of the experiments.

In experiments with unmixed feed streams, the thiosulfate and peroxide solutions were injected through separate ports, as shown in Figure 2, which were situated diametrically in the bottom of the reactor straddling the center point. The velocities through each of these ports varied from 9 to 35 ft./sec. in the experiments conducted.

The reactor and a section of the feed lines were enclosed in a Plexiglas cylinder which was evacuated during a run to about 20 mm. Hg to provide insulation. All feed lines not enclosed by the Plexiglas were insulated.

A quantity of some interest is the effective heat capacity of the system which we estimated to amount to about 1.13 times the heat capacity of 510 cc. of the reacting fluid. This estimate takes into account only the shell of the reaction vessel and the immersed materials; it does not include the mixing head, the flange at the top of the reactor, or other incidental attached equipment.

Sodium thiosulfate and hydrogen peroxide feed solutions of 1.60 and 2.40 molar, respectively, were prepared in deionized water, stored in separate 100 gal. polyethylene drums, and cooled to about −3°C. by a circulating brine coolant prior to each run. This storage capacity permitted run durations of up to 4 hr. Solution concentrations were always within ±0.015 moles/liter of the specified values which were determined by usual volumetric methods by using potassium iodate as the primary standard for the thiosulfate and potassium permanganate as the titrant for the peroxide. During a run, these solutions were fed in equal volumetric rates so as to produce a mixed feed concentration equal to that involved in Figure 1. (The experiments of Root and Schmitz showed that the volume change upon mixing the solutions at these conditions is negligible.) To achieve an inlet temperature of 0°C., each feed stream was passed through 24 ft. of ½-in. diameter coiled aluminum tubing immersed in an ice bath.

Each solution was pumped from its storage vessel during a run by means of centrifugal pumps through a rotameter and a flow control system. The rotameters were calibrated directly with the solutions at feed conditions; the maximum error in flow rate measurements was estimated at ±1.0% of reported values. This led to a maximum error in the determination of the mean residence time of about ±0.2 sec. The flow control system consisted of a Foxboro pneumatic differential pressure cell transmitter, a Foxboro pneumatic proportional plus reset controller, and a linear pneumatic control valve. Switch selection of either manual or automatic adjustment of the air pressure signal from the controller to the valve was provided on both controllers.

Materials with which reacting fluids came into contact between the storage vessels and the reactor exit included polyethylene, Teflon, glass, aluminum, and stainless steel (types 304 and 316). These materials were also involved in the experimental apparatus employed by Root and Schmitz.

The usual start-up procedure was to run deionized water at about 6°C. through the reactor system up to starting time in order to check out all recording instruments and the flow controls before switching to the thiosulfate and peroxide feeds.

The experimental procedure for obtaining stable steady states involved simply adjusting the set points on the feed flow controllers to correspond to the desired reactor residence time and allowing time for the .temperature recordings to become steady. The time required to reach steady operation following a change in flow rates was generally of the order of 4 min. Considerably longer times, up to 15 or 20 min., were required in those instances when the change caused a transition from a low state to a high one.

As was stressed earlier in the discussion of the theory, unsteady behavior of particular interest in this study concerns the response of the CSTR to disturbances in the total feed rate with the state of the feed maintained constant. Such disturbances were effected with initial operation at a low state by switching off the feed pumps for both reactant streams simultaneously and leaving them off until the temperature in the reactor increased to a desired perturbed value. Before the flows were stopped, the flow controllers were switched to the manual mode so that the control valve positions were undisturbed. They were switched back to the automatic mode once the pumps were restarted and flow rates were near their setpoint values. Generally less than 5 sec. were required for the flows to reach their desired values afted the pumps were restarted.

Perturbations from high temperature states were introduced by manually changing both feed flow rates in a step by step manner simultaneously to 2,700 ml./min. The flow rates were held steady at the disturbed rate until the reactor temperature decreased to a desired perturbed value, at which time they were reset again manually and simultaneously in a stepwise manner to their original values. It was found to be easier and faster to make these flow adjustments manually than to disturb the flows by stepwise changes in the controller setpoints. Furthermore, the reactor response was more consistent and reproducible. Generally about 10 sec. were required to

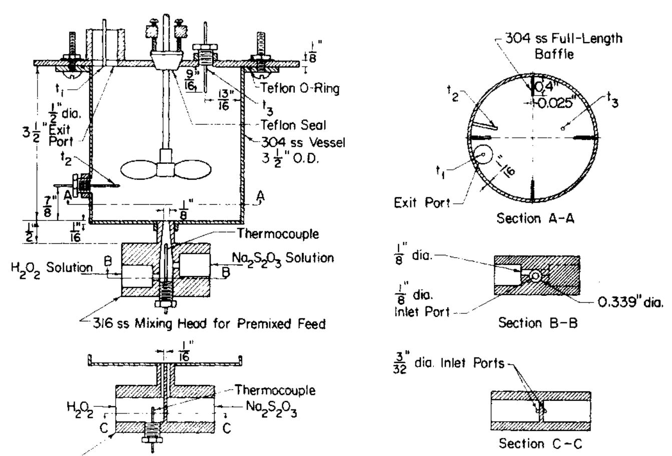

Fig. 2. Experimental CSTR and feed injection assemblies.

achieve steady flows when the rates were decreased from 2,700 ml./min. to their original values.

Thermocouple responses in the transient studies were recorded on a Sargent recorder capable of responding at a rate of 100°C./sec.

RESULTS

Well-Mixed Reactor Data

We present first the data taken from experiments in which deliberate steps were employed to insure a high degree of mixing. The peroxide and thiosulfate feed streams were premixed for these experiments in the mixing head described in the preceding section, and the impeller speeds ranged from 600 to 900 rev./min. The speed was chosen in any particular experiment to give the asymptotic reactor performance as made evident by the fact that an increase in the impeller speed had no effect on temperature recordings. Under these conditions the maximum spread in temperatures recorded from the three thermocouples was 0.5°C., except when t_2 was positioned directly in the path of the incoming feed. Because of noninstantaneous mixing, the temperature at this location fluctuated randomly, the amplitudes reaching 10°C. at high states even at the highest impeller speed.

The agreement attained between experimental and theoretical steady state temperatures for the CSTR system under these conditions is illustrated in Figure 3. For the stable steady states, the agreement is very good, the average absolute deviation for all high and low states being 0.9°C. As is evident in Figure 3, the results indeed verify the existence of multiple steady states in the CSTR.

The start-up procedure described earlier invariably led to initial operation at a low state if the residence time was below 17.8 sec. Stable steady state data at low states were usually obtained at successively larger residence times, until a transition to a high state, or ignition of the reaction, occurred. Subsequent decrease of the residence time yielded high states, and, eventually, a transition back to the low state, an extinction of the reaction, was observed. Thus, a hysteresis loop was traversed experimentally.

Careful study of the transition points showed that the jump from low to high states occurred when a step change in τ was made from 17.8 to 18.0 sec. and from high to low states in response to a change from 7.0 to 6.6 sec. For comparison, the corresponding theoretical values of τ at the transitions are 17.8 and 6.8 sec. The experimental transition following the change from 17.8 to 18.0 sec. was very slow, requiring nearly forty-five residence times.

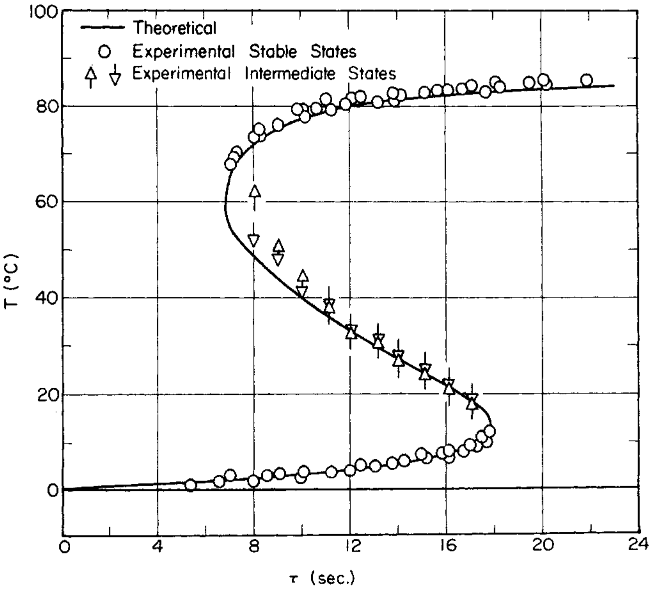

Fig. 3. Steady state results.

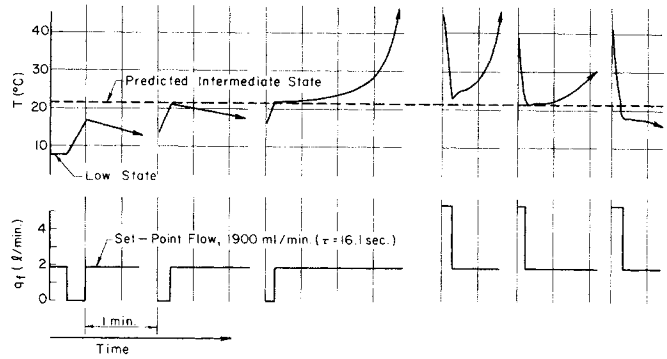

Fig. 4. Transient responses to perturbations from stable temperatures.

The temperatures indicated by the arrowheads in Figure 3 represent apparent intermediate states as observed by the perturbation approach described earlier. The arrows pointing upward on the graph indicate the apparent intermediate states as determined by perturbations from steady low states, while those pointing downward resulted from perturbations from high states. A sequence of recorded temperature perturbations and transient responses and a schematic of the flow disturbances leading to the arrows for a residence time of 16.1 sec. are shown in Figure 4. As the figure shows, transients were very slow near the intermediate state, the temperature holding nearly constant over a period of a couple of residence times.

As the data in Figure 3 indicate, the intermediate states arrived at through carefully executed disturbances from operation at low states and at high states were virtually identical and in excellent agreement with the predicted intermediate states for residence times greater than 10 sec. Furthermore, after some skill was acquired in the experimental technique, these results were very reproducible.

The apparent intermediate states for residence times of 10 sec. and less are not in such close agreement with the theoretical curve and show significant deviations between the two arrows for a given value of τ. This might at first be attributed to a breakdown in the model, say in the assumption concerning the reaction kinetics, but this seems unlikely since data at all other conditions agree so well with the predicted reactor performance. It seems more reasonable to explain these deviations as being the result of experimental difficulty in manipulating both feed flows identically, as is required to maintain φ_j at a zero value, through the duration of the disturbances with the higher flow rates involved in these cases. The time periods involved in resetting the individual feed rates (5 to 10 sec.) were about equivalent to a reactor residence time, so that any small difference in the instantaneous rates of the two streams would be more significant than at larger residence times. Furthermore, the increased sensitivity of the system at the higher intermediate temperatures made it difficult to zero in on the transition point and probably also caused small perturbations in φ_j to be more significant. Reproducibility of the data at residence times of 8 and 10 sec. was relatively poor.

The experimental results in Figure 3 also show clearly the need for a special start-up procedure if operation at a high state is desired and if the design residence time is less than 17.8 sec. Such states were accessible in the present experiments through temporary operation of the reactor at lower flow rates. Industrial reactors occasionally employ a preheater on the feed lines temporarily during start-up to ignite the reaction.

Some typical plots comparing the recorded unsteady reactor temperature with the results of computer simulations which utilized Equation (7) are shown in Figures 5 and 6. The first of these shows the response to a step change in residence time from 12.0 to 18.0 sec., the initial state being the low state at the former time. As shown, the reactor temperature rose very sharply at a maximum rate of about 5°C./sec. after a rather slow rise over a period of 8 min. One would expect small uncertainties in parameter values to have a significant effect on the exact time of this sudden temperature rise. Such an effect of residence time errors of 0.1 and 0.2 sec. is shown by the two computed curves of Figure 5. Since the experimental error in residence time determinations may be as large as ± 0.2 sec., a highly accurate simulation of so sensitive a transient would seem to be fortuitous. Attempts at reproducing such experimental curves yielded results showing roughly the degree of scatter one would predict judging from the sensitivity illustrated in Figure 5.

Figure 6 shows a recorded temperature transient and two simulated responses, curves (a) and (b), which attempt to show the possible effect of extraneous heat capacities. In the experimental situation, the reactor temperature was perturbed from the low state to a temperature just above the intermediate state at a residence time of 16.1 sec. Curve (a) of Figure 6, which accounts for equipment heat capacities, was obtained simply by dividing the right-hand side of Equation (7) by 1.13, a quantity explained earlier. This maneuver relies on the assumption that the reactor shell and contents are in instantaneous thermal equilibrium. Even with this assumption granted, the computed response is an approximation due to the fact that Equation (6) and hence the assumption that $\varphi_j = 0$ at all times and Equation (7) are valid only if equipment heat capacities are negligible. Nevertheless, a comparison of curves (a) and (b) gives some idea of the possible effect of these capacities and shows that these effects preclude, as do uncertainties in experimental parameters, the possibility of obtaining a consistently high degree of quantitative agreement between theoretical and experimental reactor transients under rapidly changing conditions. The possible effect of equipment heat capacities could obviously be important in design of control systems and large scale reactors when the design is based on experiments with small equipment. This applies especially to nonadiabatic reactors where oscillations, sustained or otherwise, are possible. Extraneous capacities, not negligible in small equipment, are certain to have a damping effect on oscillatory behavior.

A comparison of curves (b) and (c) in Figure 6 indicates the effect of a variable density on the predicted transient response. Curve (c) was computed by taking ρ_f/ρ to be unity in $R(T)$. The large effect of the variable density is surprising in view of the fact that its effect on steady performance is negligible.

As a final remark concerning Figures 5 and 6, we point out that both figures show an experimental temperature curve along which the temperature rise subsides noticeably as the high state is approached, while the theoretical curves show a more rapid and abrupt approach to the steady state. This tailing off in the experimental case is probably due to conductive resistances of solid materials, particularly of attached equipment other than the shell, causing a temperature lag.

It is not surprising that on the one hand theoretical and experimental steady states are in excellent agreement, while on the other such good quantitative agreement is not exhibited by unsteady states. Steady states, particularly the stable ones, are very insensitive to small parameter changes as compared with the sensitivity of the unsteady state illustrated in Figures 5 and 6. Furthermore, as was mentioned earlier, extraneous heat capacities have no effect on the steady state. The excellent agreement obtained in most cases for the intermediate states indicates that the equipment heat capacities, which enter the picture for those states since they were obtained from unsteady data, have little influence in determining whether a perturbation grows or decays. The influence apparently is mainly in determining the rate of growth or decay. That is to say that these capacities seem to have little effect on the region of asymptotic stability of the stable states in the TP system studied.

In concluding this section, we make mention of the fact that in none of the experiments in this study with the adiabatic CSTR has any oscillatory behavior been observed. This is as expected for a perfectly mixed adiabatic reactor (23). Furthermore, in the experiments described in this paper in which φ_j was deliberately held constant at zero, there was no temperature overshoot of the steady state values. This also is expected for this particular type of perturbation as one can readily conclude by examining

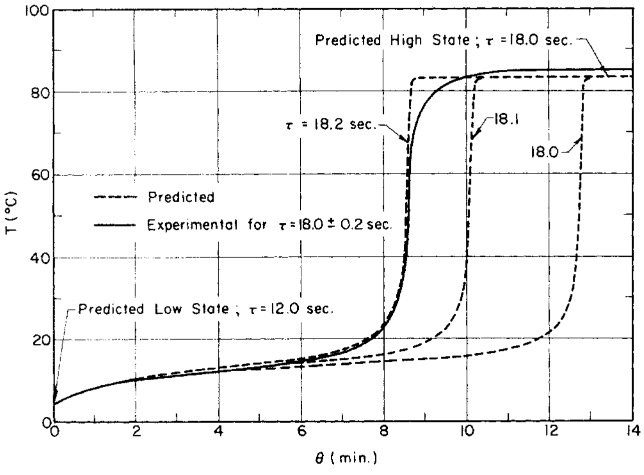

Fig. 5. Theoretical and experimental responses to step change in residence time.

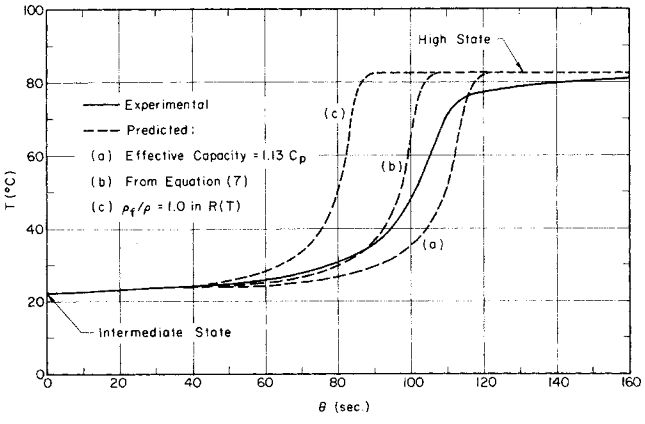

Fig. 6. Comparison of theoretical and experimental transient temperatures; $\tau = 16.1$ sec.

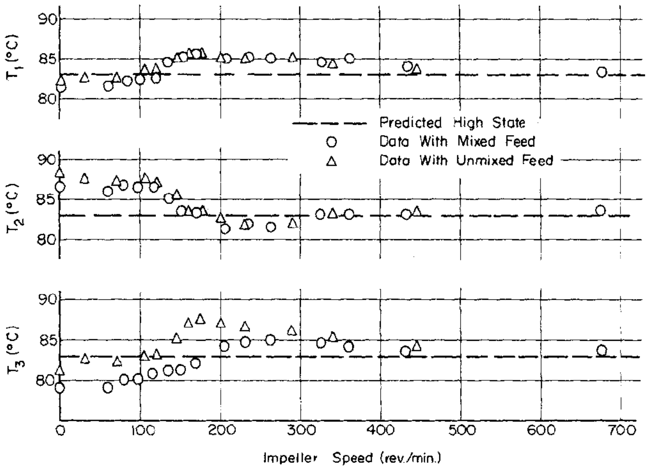

Fig. 7. Effect of the impeller speed on the steady state for τ = 16.1 sec.

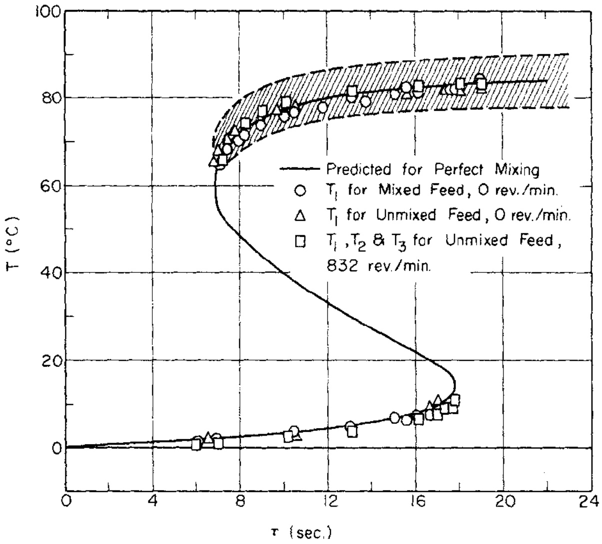

Fig. 8. Effect of mixing on steady state temperatures.

Equation (7). In other cases not illustrated here, usually involving start-up, where no attempt was made to hold φ_j constant, some temperature overshoot was observed.

Mixing Effects

A typical illustration of the effect of impeller speed on the reactor performance at a high steady state is shown in Figure 7 for both mixed and unmixed feed cases at a mean residence time of 16.1 sec. (T_1, T_2, and T_3 in Figure 7 refer to temperatures measured by thermocouples t_1, t_2, and t_3, respectively.) Results, qualitatively similar to these, for other residence times may be found elsewhere (22). For these measurements, thermocouple t_1 was positioned flush with the top of the reactor and t_2, ¾ in. from the side wall. Among the noteworthy observations to be made in connection with Figure 7 is that the temperature measured by the thermocouple t_1, which is at the reactor exit, shows little effect of the impeller speed or of the state of mixing of the feed and is in close agreement with the prediction of the perfect mixing model. This was found to be the case at all residence times studied, in spite of the fact that the other two temperatures differed from each other by as much as 9°C. in some instances.

For decreasing impeller speeds between 600 and 200 rev./min., the curves in Figure 7 show a moderate but definite trend. The temperature T_3 increases while T_2 decreases, indicating on the macroscopic picture that in these experiments the fluid surrounding thermocouple t_3 was relatively stagnant and that high chemical conversion took place locally. On the other hand, as the impeller speed was decreased, t_2 became influenced more and more by the noninstantaneous mixing of the incoming cold feed. The dominating factor in determining the flow pattern in the reactor under these conditions was probably the downward pumping action of the impeller.

Between impeller speeds of 100 and 200 rev./min., a transition in the basic flow pattern is indicated in Figure 7 by all three temperature measurements. In particular, T_3 is shown to shift to temperatures below and T_2 to temperatures above that predicted by the perfect mixing model. Over the same range T_1 moves from temperatures slightly above the theoretical one to temperatures slightly below. Apparently below impeller speeds of 100 rev./min. in these experiments, the downward pumping action of the impeller was nullified by the velocity of the incoming feed streams which act as mixing jets. As a result, t_2 was in a relatively stagnant region of the reactor, and t_3 was affected somewhat by the lack of complete backmixing. Such a transition in the mixing pattern must occur generally in flow through stirred vessels. The location of the transition as well as the quantitative effects of the mixing on either side of it depend on many factors including geometry and design of the vessel and impeller, the properties of the fluid mixture, the location of inlet and exit ports, the velocity of the incoming feed, and the chemical reaction rate.

As the data in Figure 7 indicate, mixing effects, whether they are due to macroscopic or microscopic phenomena or both, are observable under experimental conditions in this study, but the assumption of perfect mixing under all conditions is not gross, particularly in predicting the reactor output. It might be noted also that the data in Figure 7 show little effect of whether the feed is premixed or injected in separate streams. The differences that are noticeable may be due to segregation effects or to a small effect of the means of injection on the flow pattern in the CSTR. Thus, contacting the two reactants in the CSTR even with an impeller speed of zero is apparently accomplished with only minor overall effects.

It should be stated that the temperature recordings were frequently found to fluctuate randomly at impeller speeds below 300 rev./min. The fluctuations generally spanned about 2° to 4°C. and were most pronounced for thermocouple t_3 with unmixed feed and with impeller speeds between 100 and 200 rev./min., the apparent transition region. For these cases, the data points in Figure 7 represent temperatures midway between the extremes.

Results of all studies of mixing effects are summarized in Figure 8. In essence they show very good qualitative and even quite good quantitative agreement with the predictions of the perfect mixing model. The boundary of the shaded area in Figure 8 encloses all high steady state data points obtained from all three thermocouples with t_1 flush with the top of the reactor and t_2 positioned ¾ in. from the side. Temperatures measured by t_2 with unmixed feed and by t_3 with premixed feed, both at an impeller speed of zero, form the upper and lower boundaries of the area, respectively. The former extends about 1.5°C. above the adiabatic reaction temperature at the longer residence times. Shown also in Figure 8 are the reactor output data, taken from thermocouple t_1, in experiments with an impeller speed of zero and mixed and unmixed feeds and with an impeller speed of 832 rev./min. and unmixed feed. In all cases the outlet temperatures and the regions of multiplicity agree very well with those predicted by the perfect mixing model, and in the latter case all three thermocouples gave nearly identical temperature readings. Also in this case intermediate states for residence times of 13.0 and 16.0 sec. were located by means of perturbations from high and low states and agreed almost perfectly with the predicted intermediate states. It should be added that the spread in the temperatures from the three thermocouples at low states was never greater than 2°C.

The results presented in this section clearly show that while mixing was not perfect under all conditions studied, any deviations from perfect mixing either at the macroscopic or microscopic level had little effect on the principal characteristics of the reactor behavior. This, of course, is not to be construed as a general conclusion concerning the role of mixing effects in reacting system, since many parameters, most of which were not studied here, are involved. Certainly an important factor which influenced the mixing in this study was the high velocity of the injected feed streams in all experiments.

CONCLUDING REMARKS

Principally, this work has provided experimental verification of steady state multiplicity in a stirred reactor involving an exothermic liquid-phase reaction and has given a general impression of the accuracy with which steady and transient reactor characteristics can be predicted on the basis of a simple mathematical model. The results of the experiments show that very good agreement between the predictions of the perfect mixing model and observed performance can be attained if care is taken to insure a high degree of mixing of the reactant feed streams and of the reactor contents. They show further that the model is meaningful, in a quantitative as well as qualitative sense, over a range of mixing conditions.

Another important result of this work is that, along with earlier studies (*13*, *14*), it has demonstrated the general suitability of the reaction between sodium thiosulfate and hydrogen peroxide for use in experimental investigations into steady state multiplicity and stability in chemical reactors involving homogeneous reactions. The phenomena of interest are exhibited with this reaction at atmospheric pressure and on a convenient temperature range. Experiments can be coupled conveniently to theoretical results because the assumptions of a single chemical reaction and of constant mixture properties, both usually invoked for mathematical convenience, are valid, at least under the experimental conditions reported here. Furthermore, the reacting system is apparently not sensitive to small amounts of impurities; it neither attacks nor is attacked or catalyzed by a variety of common materials to any noticeable extent under these conditions.

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NOTATION

a_j = molar stoichiometric coefficient for species j
C_p = heat capacity
$G(T)$ = heat generation function defined as the right-hand side of Equation (4)
ΔH = heat of reaction
M_j = molecular weight of species j
n = number of chemical species involved in the overall reaction
q_f = total volumetric flow rate of feed
r = intrinsic molar reaction rate
$R(T)$ = heat removal function defined as the left-hand side of Equation (4)
t = thermocouple
T = temperature
V = reactor volume
w_f = total mass flow rate of feed
x_j = mass fraction of species j
θ = time
ρ = density
τ = mean reactor residence time based on feed conditions
φ_j = function defined in Equation (3)

Subscripts

1,2,3 = thermocouples designated in Figure 2
f = feed

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