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Steady State Multiplicity of Adiabatic Gas-Liquid Reactors:

I. The Single Reaction Case

A model of an adiabatic continuously stirred-tank reactor in which a single exothermic second order-gas liquid reaction occurs has been developed. The interactions between the rate of the chemical reaction, the diffusional resistances, and the solubility may cause the occurrence of up to five steady state solutions, even though no more than three solutions can be attained when the same reaction is carried out in a single phase CSTR. A parametric study is used to examine the sensitivity of the model to the value of several parameters. Topological arguments are used to obtain a simple instability criterion.

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SCOPE

Many important gas-liquid reactions such as chlorination, oxidation, and hydrogenation are carried out in a CSTR (continuously stirred-tank reactor). The interactions among the various physical and chemical rate processes in these reactors may cause the occurrence of steady state multiplicity as observed by Ding et al. (1974) and of unusual dynamic phenomena such as sustained periodic oscillation (Hancock and Kenney, 1972).

Theoretical analyses of the steady state multiplicity and stability of a two-phase CSTR have been presented by Schmitz and Amundson (1963a,b,c,d) and Luss and Amundson (1967) using mathematical models which assume that the chemical reaction and the interphase mass transfer are two independent noninteracting processes. However, this description does not properly account for the actual rate of reaction (or absorption) of gaseous reactant species except when the mass transfer resistance is negligible. For example, this formulation fails to account for the enhancement of the mass transfer coefficient by the chemical reaction when the mass transfer rate is the controlling resistance. Recent experiments carried out in our laboratory indicate that these simplified models are often capable of predicting many of the qualitative features of gas-liquid reactors. However, they are inadequate for a quantitative simulation of the behavior of a CSTR over a wide range of temperatures in which a continuous shift from chemical to mass transfer control occurs.

The main goal of this work is to apply a model, which accounts for the interactions between the chemical reaction and mass transfer, for a study of the steady state behavioral features of an adiabatic CSTR in which a single exothermic second order gas-liquid reaction is carried out. Specifically, we examine the maximal number of possible steady state solutions, explore the influence of various parameters on the occurrence of steady state multiplicity, and obtain an instability criterion which has a simple physical meaning.

CONCLUSIONS AND SIGNIFICANCE

A model of an adiabatic CSTR, in which a single exothermic second-order gas-liquid reaction is carried out, has been developed using a reaction factor to express the total rate of gas absorption [Equation (12)]. The technique of Van Krevelen and Hoftijzer (1948) as modified by Teramoto, et al. (1969) is used to compute this reaction factor from the solution of three implicit relations [Equations (22), (24), (25)]. The steady state solutions are determined from the intersections of the heat generation and heat removal curves (Figure 1). An efficient iterative numerical procedure for computing the heat generation curve as a function of the temperature is presented.

The interaction between the rate of the chemical reaction, the diffusional resistances, and the solubility cause the shape of the heat generation curve to be such that up to five steady state solutions can exist for certain operating conditions. This is a unique and interesting feature of gas-liquid reactions since no more than three solutions can be attained if the same reaction is carried out in a single-phase CSTR.

The reaction factor can be used only to express the gaseous reactant absorption rate under steady state conditions. Therefore, a rigorous dynamical model requires the solution of a coupled set of parabolic equations to determine the reactant flux through the interface under transient conditions. The complexity of the resulting model prevents derivation of explicit necessary and sufficient conditions for stability of the form which can be attained when the dynamic model consists of a set of ordinary differential equations. The dynamic model may be simplified by assuming that the reaction factor under transient conditions may be computed from the steady state relations [(22), (24), (25)]. In this case, topological arguments can be used to prove that any steady state which does not satisfy the slope condition [Equation (30)] is unstable.

A parametric study was conducted to examine the sensitivity of the model to the values of various parameters. Studies of this form are most useful for determining what information (and at what level of accuracy) is required for design and scale-up purposes. It was found that when multiple steady states exist, the high temperature branch is, in general, more influenced by variations in the parameters than is the low temperature branch. Similarly, the residence time corresponding to ignition is much more sensitive to parametric changes than is the residence time at which extinction occurs. The results suggest that the steady state multiplicity phenomenon can serve as an excellent tool for discriminating among rival models and assumptions and for estimation of the numerical values of some parameters of these models.

DEVELOPMENT OF STEADY STATE MODEL

We will consider a single irreversible second-order gas liquid reaction

$$A(\text{gas}) + B(\text{liq}) \rightarrow R(\text{liq}) + L(\text{gas}) \qquad (1)$$

occurring in an adiabatic CSTR. Second-order kinetics were chosen as they adequately represent the rate of many gas-liquid reactions. The mathematical model will be based on the following assumptions:

1. The liquid phase consists of nonvolatile components so that there are no material or energy losses due to evaporation. Clearly, this assumption restricts the model to operating conditions for which the temperature is well below the boiling point of the liquid.

2. The physical properties of the gas and liquid, the liquid mass transfer coefficient, and the volumetric flow rate of the liquid leaving the reactor (F_l) are independent of temperature and conversion.

3. The diffusion coefficients D_A and D_B are the same and are unaffected by changes in the temperature or composition of the liquid phase.

4. The heat capacities of the pure liquid and gas C_{pl} and C_{pg} as well as the heat of solution $(-\Delta H_s)$ are independent of temperature and composition.

5. The solubility of the reactant A in the liquid phase is independent of conversion and its temperature dependence can be expressed as

$$\log(x_A/P_A) = D_1/T - D_2 \qquad (2)$$

where x_A is the mole fraction of the dissolved gaseous reactant and $P_A = y_A P$ is the corresponding gas pressure. Moreover, the solubility of the product L in the liquid phase is negligible, and L is stripped from the liquid upon formation.

6. The gas and liquid inside the reactor have the same temperature.

7. The total pressure of the gas bubbles is independent of position in the reactor.

8. The interfacial area and gas hold up are independent of temperature, conversion, and position within the reactor.

9. The resistance to mass transfer in the gas phase is negligible.

10. The liquid feed does not contain any dissolved gaseous reactant.

The above simplifying assumptions considerably reduce the number of parameters which characterize the reactor and are useful for focusing attention to the unique behavioral features of a gas-liquid adiabatic CSTR. Clearly, when a reactor is designed for a specific reacting system, it may be necessary to omit or modify some of the above assumptions.

The material and energy balances describing the CSTR are

$$q_{gf}y_{Af} - q_{g0}y_A - F_lA_l - R_AV_R = 0 \qquad (3)$$

$$q_{lf}x_{Bf} - q_{l0}x_B - R_B V_R = 0 \tag{4}$$

$$R_A V_R(-\Delta H_R) + F_l A_l(-\Delta H_s) + (q_{lf}C_{pl} + q_{gf}C_{pg})T_f - (q_{l0}C_{pl} + q_{g0}C_{pg})T_0 = 0 \tag{5}$$

where q_g and q_l are the liquid and gas molar flow rates, F_l is the constant liquid volumetric flow rate, A_l is the bulk concentration of the dissolved gas and the subscripts f and 0 refer to the feed and effluent streams. The assumption that the concentration of the dissolved gas in the effluent liquid stream is equal to the bulk concentration A_l is justified since in a CSTR the volume of the bulk liquid is much larger than that occupied by the mass transfer film. The molar flow rates of the gas and liquid satisfy the relations

$$q_{g0} = q_{gf} - F_l A_l \tag{6}$$

$$q_{l0} = q_{lf} + F_l A_l \tag{7}$$

The interfacial concentration of the reacting gas can be expressed as

$$A_i = x_A \tilde{\rho}_l \tag{8}$$

where $\tilde{\rho}_l$ — the molar density of the liquid phase is given by

$$\tilde{\rho}_l = \frac{q_{l0}}{F_l} = \frac{q_{lf} + F_l A_l}{F_l} \tag{9}$$

Substitution of (9) into (8) yields

$$A_i = \frac{x_A q_{lf}}{F_l(1 - x_A A_l/A_i)}$$

$$= \frac{P y_A 10^{\left(\frac{D_1}{T} - D_2\right)} q_{lf}}{F_l \left[1 - \frac{A_l P y_A}{A_i} 10^{\left(\frac{D_1}{T} - D_2\right)}\right]} \tag{10}$$

The model requires use of an expression which adequately describes the actual rate of gas absorption (or reaction) over a wide range of temperatures in which a continuous shift from chemical to mass transfer control occurs. It is customary to express the rate of gas absorption in a reacting liquid as

$$a_v V_R J_A = R_A V_R + F_l A_l = a_v V_R E_A k_l (A_i - A_l) \tag{11}$$

where E_A is defined as the enhancement factor. Many theoretical studies have been concerned with predicting the enhancement factor for various reaction networks and kinetics and a comprehensive review can be found in the monographs of Danckwerts (1970) and Astarita (1967). Unfortunately, most of the studies are concerned with cases of vanishing gas concentration in the bulk of the fluid, and their results are often nonapplicable to other cases.

When $A_l \neq 0$, as is often the case when a chemical reaction is carried out in a CSTR, use of (11) may require iterative computations as E_A and A_l affect each other. Thus, as noted by Kramers and Westerterp (1963), Bridgwater and Carberry (1967) and Teramoto et al. (1969), it may be preferable to express the rate of gas absorption as

$$a_v V_R J_A = R_A V_R + F_l A_l = a_v V_R E_A^* k_l A_i \tag{12}$$

where we define E_A^* as the reaction factor. Clearly, when $A_l = 0$ the reaction and enhancement factors are equal. It should be noted that, while the enhancement factor is always larger than unity, the reaction factor may be smaller than unity. This situation occurs when the actual rate of absorption in the reactive fluid is smaller than the maximal rate of gas absorption by a pure nonreactive fluid.

Several models can be used to compute the enhancement factor. However, the result is in general rather insensitive to the type of model used to describe the mass transfer (Danckwerts, 1970). The film model usually yields the easiest mathematical solution and was therefore used in this work to compute the reaction factor. It should be noted that use of the film theory to compute E_A^* does not imply that the same theory has to be used to compute k_l.

When a single irreversible second-order reaction between a dissolved gaseous species A and a nonvolatile solute B is carried out in a CSTR, the mathematical model describing the concentration profiles in the mass transfer film is

$$D_A \frac{d^2A}{dz^2} - k_1 AB = 0 \quad 0 \leq z \leq \delta \tag{13}$$

$$D_B \frac{d^2B}{dz^2} - k_1 AB = 0 \quad 0 \leq z \leq \delta \tag{14}$$

The corresponding boundary conditions are

$$A = A_i \quad z = 0 \tag{15}$$

$$\frac{dB}{dz} = 0 \quad z = 0 \tag{16}$$

$$B = B_l \quad z = \delta \tag{17}$$

$$-a_v D_A \frac{dA}{dz} = k_1 AB(\epsilon - a_v\delta) + \epsilon A/\tau \quad z = \delta \tag{18}$$

where δ is the thickness of the mass transfer film and τ is the liquid residence time in the reactor. The last boundary condition states that the rate of transfer of dissolved gas to the bulk liquid is equal to the amount consumed by reaction in the bulk plus that which leaves the reactor in the effluent stream.

An analytical solution of the above equations is not possible except for two limiting cases. The first is when the reaction rate is so low that the concentration of B is practically uniform throughout the film yielding pseudo first-order kinetics. Here (Kramers and Westerterp, 1963)

$$E_A^* = M \frac{M^2(\alpha - 1) + 1/\theta + M \tanh M}{(M^2(\alpha - 1) + 1/\theta)\tanh M + M} \tag{19}$$

where

$$M = \sqrt{k_1 D_A B_l}/k_l; \quad \alpha = \epsilon/a_v\delta \tag{20}$$

$$\theta = k_l a_v \tau/\epsilon$$

The second limiting case occurs when the reaction is essentially instantaneous for which the film theory predicts that (Astarita, 1967; Danckwerts, 1970)

$$E_A^* = E_i = 1 + \frac{D_B B_l}{D_A A_i} \tag{21}$$

where E_i is the instantaneous enhancement factor. In the general case, the reaction factor can be computed from the following approximate expression which was derived by Van Krevelen and Hoftijzer (1948):

$$E_A^* = M\sqrt{b_i} \frac{M^2(\alpha - 1) + 1/\theta + M\sqrt{b_i} \tanh M\sqrt{b_i}}{(M^2(\alpha - 1) + 1/\theta) \tanh (M\sqrt{b_i}) + M\sqrt{b_i}} \tag{22}$$

where

$$b_i = \frac{B_i}{B_l} = \frac{E_i - E_A^*}{E_i - 1} \tag{23}$$

and E_i and E_A^* are computed by Equations (21) and (22), respectively. The above approximation was derived assuming that in the bulk fluid $A_l = 0$, and $E_A^* > 1$. However, when D_A/k_l^2 the characteristic time for mass transfer is very small compared to $1/k_1B_l$ the characteristic time of the chemical reaction (small value of M), the bulk concentration of A is not negligible and the reaction factor may be less than unity. For such cases Equation (23) predicts that $b_i > 1$, which is of course impossible. Teramoto et al. (1969) have shown that the Van Krevelen-Hoftijzer approximation can be modified to treat cases for which $A_l > 0$ if b_i is computed from the equation

$$b_i = \frac{B_i}{B_l} = \frac{E_i - E_A^* - A_l/A_i}{E_i - 1} \tag{24}$$

where

$$\frac{A_l}{A_i} = \frac{M\sqrt{b_i}}{M\sqrt{b_i}\cosh(M\sqrt{b_i}) + (M^2(\alpha - 1) + 1/\theta)\sinh(M\sqrt{b_i})} \tag{25}$$

Thus, E_A^* can be computed by an iterative solution of (22), (24), and (25). The approximation converges to the analytical solutions for the two limiting cases.

Numerical computation by Brian et al. (1961) indicate that the error obtained by use of the Van Krevelen and Hoftijzer approximation is usually very small and about several percents at most. These comparisons were restricted to cases for which $E_A^* > 1$. We computed numerically the reaction factor for many cases using parameters for which E_A^* was both smaller and larger than unity (Hoffman, 1974). It was found that the deviations between the exact values and those computed by the approximation technique of Teramoto, et al. (1969) were always very small, the maximal value being less than 4%. The values computed by the Van Krevelen and Hoftijzer technique yielded a very good approximation when $A_l = 0$. Surprisingly, this technique yielded very good approximation of E_A^* even when its value was substantially less than unity under conditions for which (23) predicted the conceptually wrong result of $b_i > 1$.

In this work the approximation of Teramoto et al. (1969) was used for computing the rate of gas absorption due to its superior ability to predict E_A^*.

STEADY STATE DETERMINATION

We will present here a numerical technique of determining all the possible steady state solutions. Combination of (3) and (4) and use of the fact that $R_A = R_B$ yields

$$x_B = (q_{lf}x_{Bf} + q_{g0}y_A - q_{gf}y_{Af} + F_lA_l)/q_{l0} \tag{26}$$

This relation enables us to express x_B as a simple function of A_l and y_A. The heat capacities of the gas and liquid as well as the heat of solution are assumed to be independent of temperature and concentration. Therefore, (5) can be rewritten as

$$Q_I \equiv T - T^* = \frac{(-\Delta H_R)R_AV_R + F_lA_l(-\Delta H_s)}{q_{lf}C_{pl} + q_{gf}C_{pg}} \equiv Q_{II} \tag{27}$$

where

$$T^* = (q_{lf}C_{pl}T_{lf} + q_{gf}C_{pg}T_{gf})/(q_{lf}C_{pl} + q_{gf}C_{pg}) \tag{28}$$

When the Q_I and Q_{II} curves are drawn as a function of the temperature, every intersection between these two graphs represents a steady state solution. The determination of the heat generation curve Q_{II} as a function of temperature requires some iterative calculations due to the implicit nature of the equation describing the dependence of A_l and B_l on the temperature.

The following numerical procedure was used for computing Q_{II} at any prescribed temperature. We first computed the molar and volumetric flow rates of the feed streams for the prescribed residence time and liquid hold-up. Then values of y_A and A_l/A_i were assumed and used to compute q_{l0} and q_{g0} by (6-7) and A_i from (10). The value of x_B and $\tilde{\rho}_l$ were then computed from (26) and (9) and used to determine $B_l = x_B\tilde{\rho}_L$. The parameters θ and M and the instantaneous enhancement factor were then computed from (20) and (21). Then Equations (22) and (24) and (25) were solved by Wegstein's iterative method for E_A^* and A_l/A_i.

The gaseous reactant material balance, Equation (3), can be written as

$$y_A = (q_{gf}y_{Af} - a_vV_Rk_lA_iE_A)/q_{g0} \tag{29}$$

When this computed value of y_A or that of A_l/A_i did not agree with the assumed values, the calculations were repeated using a modified Wegstein technique, described by Hoffman (1974), to select new assumed values. The convergence was usually rather rapid. Typical numerical results will be presented later.

STABILITY CONSIDERATIONS

Every steady state has to be obtained as a result of a start-up procedure. Thus, it is of practical importance to carry out a stability analysis to determine which of the steady states can be realized (stable) and which are unstable (any infinitesimal disturbance will move the reactor away from such a steady state).

A dynamic model of gas-liquid reactors consists of a set of coupled ordinary and partial parabolic differential equations even though the steady state is obtained as a solution of a set of algebraic equations. The reason for this is that the transient concentrations of the various species in the mass transfer film and the instantaneous fluxes through it have to be obtained as a solution of partial differential equations. Thus, a linearized stability analysis requires determination of the eigenvalues of a coupled set of algebraic and second-order ordinary differential equations. A necessary and sufficient condition for asymptotic stability is that the real part of all the eigenvalues of this set of equations is negative. The existence of at least one eigenvalue with a positive real part is sufficient for instability.

One major purpose of a stability analysis is to obtain some general stability or instability criteria which are based on the structure of the steady state solutions or at least some which can be expressed explicitly in terms of the various parameters appearing in the model. Unfortunately, the complex nature of the linearized equations requires a numerical computation of the eigenvalues and does not enable derivation of explicit necessary and sufficient conditions for stability.

One may obtain approximate stability criteria by simplifying the dynamic model so that it consists only of ordinary differential equations. One possibility is to apply a pseudo steady state approximation and to compute the reaction factor under transient conditions from the steady state relations (22), (24), (25). The small volume of the mass transfer film as compared to that of the bulk liquid phase tends to make this simplifying assumption reasonable. However, the assumption reduces the validity of the analysis due to the reduction in the degrees of freedom of the disturbances and to the change in the form of the mathematical model. A somewhat similar assumption is made sometimes in the stability analysis of packed bed reactors using a steady state expression to compute the instantaneous effectiveness factor.

We shall use this pseudo steady state approximation and topological arguments (Krasnoselski, 1964; Gavalas, 1968) to prove that a necessary condition for stability is that

$$\frac{dQ_I}{dT} > \frac{dQ_{II}}{dT} \tag{30}$$

Consequently, when $2m + 1$ solutions exist, m of them do not satisfy the above slope condition and are unstable. The equation describing the simplified dynamic model can be written as

$$\frac{d\mathbf{u}}{dt} = \mathbf{f}(\mathbf{u}) \tag{31}$$

where $\mathbf{u}$ is a vector representing the N dependent variables. In our model $N = 3$. However, as the same arguments can be used for any N we will not specify its value. Every steady state solution can be characterized by an index which is defined as

$$\gamma_i = \text{sgn}\{\det \mathbf{A}\} \tag{32}$$

where $\mathbf{A}$ is the Jacobian matrix obtained by linearization of the rhs of (31). Thus, if the index is equal to $(-1)^{N+1}$, the linearized equations

$$\frac{d\boldsymbol{\eta}}{dt} = \mathbf{A}\boldsymbol{\eta} \tag{33}$$

have an odd number of real positive eigenvalues and the solution is unstable.

When the steady states are described as a function of the liquid residence time, the solutions can be divided into branches, which emanate or coalesce at bifurcation or branching points. For example, the branching points in Figures 1 to 9 are those at which $dT/d\tau = \pm\infty$.

Topological arguments indicate that all the solutions belonging to the same branch have the same index. Moreover, the sum of the indexes of two branches, which emanate from the same bifurcation point, is zero. Thus, one of the two branches of solutions, which emanate from the same bifurcation point, consists of solutions with an index of $(-1)^{N+1}$.

Gavalas (1968) has proven that for a very small residence time a unique low temperature solution is obtained whose index is $(-1)^N$. This implies that the index of all the solutions belonging to the low temperature branch is $(-1)^N$. Using this information and the fact that the sum of the indexes of two branches which emanate from the same bifurcation point is zero, we can show that all the branches, which are marked by dashed curves in Figures 1 to 9 have an index of $(-1)^{N+1}$, and are therefore unstable. These arguments imply that all the solutions, which do not satisfy the slope condition, are unstable.

Unfortunately, topological arguments yield no conclusive information regarding the stability of the steady states whose index is $(-1)^N$. In fact, not all the solutions belonging to a branch with an index of $(-1)^N$ need have the same stability characteristics, and it is not uncommon that some of the solutions, belonging to a branch with an index of $(-1)^N$, are stable while others are unstable.

A stability analysis of the solutions with an index of $(-1)^N$ requires examination of the sign of the real part of all the eigenvalues of the Jacobian matrix. The reaction factor can not be expressed as an explicit function of the dependent variables y_A, x_B, and T but has to be computed from the implicit relation (22), (24), (25). Thus, when implicit differentiation is used for obtaining the partial derivatives of the reaction factor, the resulting stability criteria contain rather unwieldly complex algebraic expressions, which yield no insight into the behavior of the system. A detailed analysis of the validity of the stability criteria derived from the approximate model and of the dynamic behavior of the system will be the subject of a future publication.

NUMERICAL RESULTS AND DISCUSSION

A numerical example was used to investigate the behavioral features of the model and its sensitivity to the values of the various parameters. The values of the parameters for the base case were selected such as to be similar to those representing the chlorination of n-decane, which is a typical gas-liquid reaction. A discussion justifying the choice of these values is presented by Hoffman (1974). The values used for the base case are:

$k_1 = 0.05$ cc/mole-s at (50°C)
$x_A = y_A\, 10^{(1010/T\text{-}4.16)}$
$D_A = 6 \times 10^{-5}$ cm²/s
$C_{pg} = 6.5$ cal/mole-°K
$-\Delta H_R = 25000$ cal/mole
$\epsilon = 0.9$

$E_1 = 30000$ cal/mole
$k_l = 0.04$ cm/s
$a_v = 2.0$ cm^{-1}
$C_{pl} = 70.0$ cal/mole-°K
$-\Delta H_s = 5000$ cal/mole

The properties of the feed streams were chosen as

$$T_{gf} = T_{lf} = 25°\text{C}$$
$$y_{Af} = x_{Bf} = 1.0$$
$$\rho_{lf} = 0.725 \text{ g/cc}$$
$$\rho_{gf} = 0.00298 \text{ g/cc}$$
$$M_{wB} = 142 \text{ g/g mole}$$
$$M_{wA} = 71 \text{ g/g mole}$$

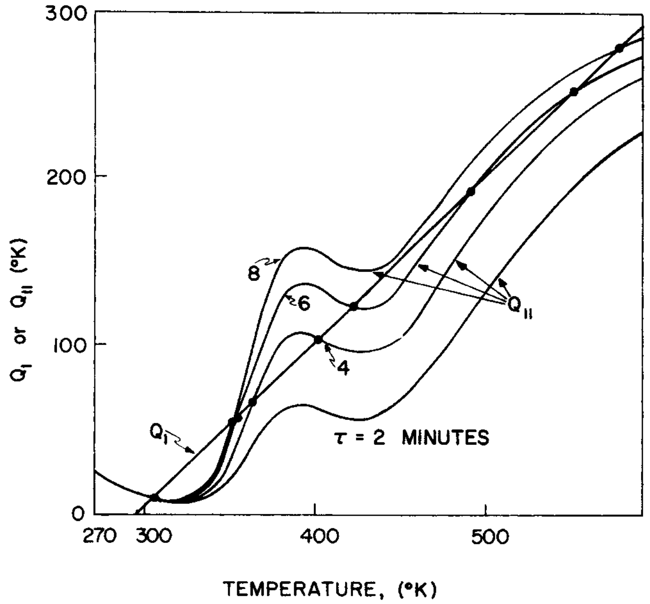

Fig. 1. Q_I and Q_{II} as a function of temperature and liquid residence time.

In all the simulations the molar gas and liquid feed rates were assumed to be equal. When the influence of a certain parameter was investigated, the values of all the other parameters were set equal to those of the base case. The base case is described by the curves labeled *B* in Figures 1 to 9.

When a single second-order homogeneous chemical reaction is carried out in a CSTR, the heat generation curve has a sigmoidal shape such that no more than three steady state solutions exist. However, when a single second-order reaction is carried out in a gas liquid CSTR, the shape of the heat generation curve Q_{II} is such that under certain conditions five steady state solutions exist. This unique feature of a gas liquid reacting system is shown in Figure 1, which describes the effect of residence time distribution on the shape of the Q_{II} graph. It is seen that for this example a unique steady state exists for residence times of either 2 or 8 min., three steady states for $\tau = 4$ min., and five steady states for $\tau = 6$ min. This special shape of the heat generation curve is due to the conflicting influences of the temperature on the enhancement factor and on the solubility of the gas.

When the temperature is low (in this case $T < 330°K$), the reaction rate is very low and the rate of absorption is about equal to the amount needed to saturate the effluent liquid stream, and the heat of solution is the main cause for heat generation. As the heat of solution is positive and the solubility is a decreasing function of temperature, the heat generation curve Q_{II} is a decreasing function of the temperature in this low temperature range.

When the temperature is further increased, the fraction of the absorbed gaseous reactant which is dissolved in the effluent stream becomes very small and the chemical reaction becomes the major cause for the heat generation. The temperature dependence of Q_{II} is influenced by the increase of the reaction factor and the decrease of the solubility with temperature. In the example shown here Q_{II} is an increasing function of the temperature in the ranges $330 < T < 390°K$ and $T > 430°K$ and a decreasing function of temperature elsewhere. It should be noted again that the validity of the present model and of the corresponding heat generation curve becomes questionable at very high temperatures at which the vapor pressure of the liquid becomes appreciable and is definitely not valid for temperatures which are either close to or exceed the boiling temperature of the liquid phase.

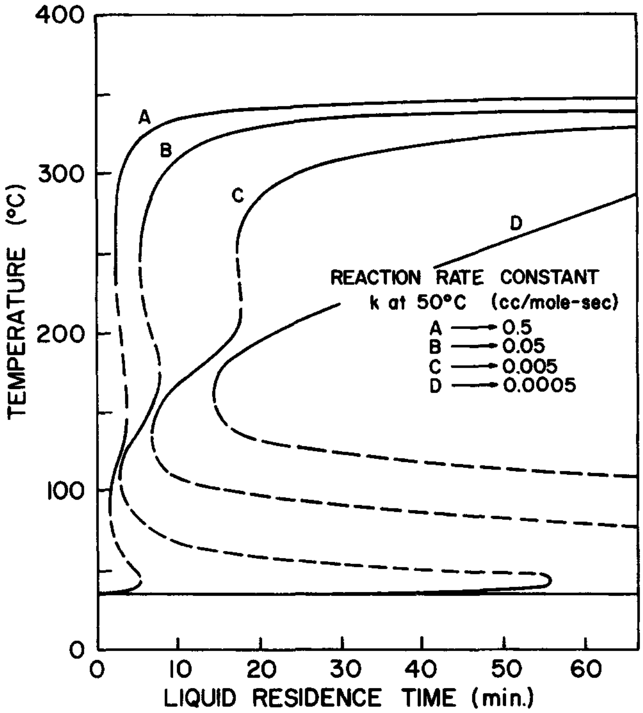

Fig. 2. The influence of the reaction rate constant and the liquid residence time on the steady state temperature.

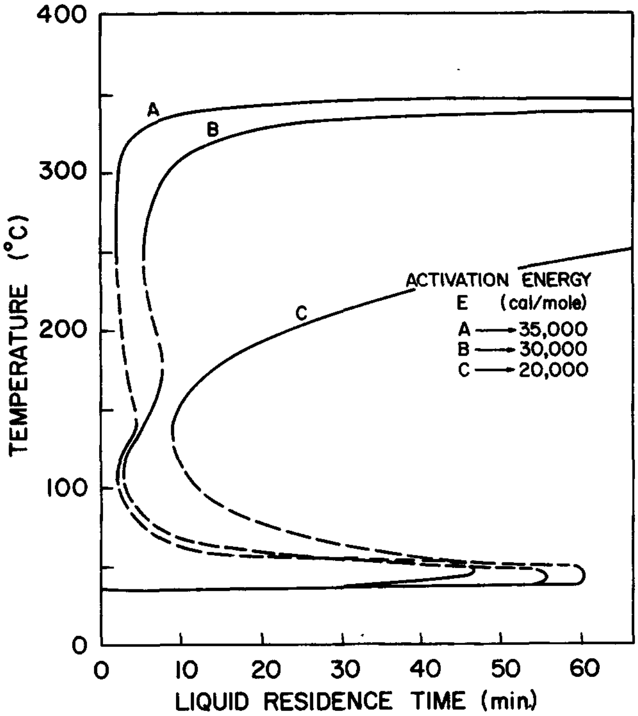

Fig. 3. Influence of the activation energy and the liquid residence time on the steady state temperature.

The existence of five steady state solutions for a single second-order exothermic gas liquid reaction in a CSTR is a unique and interesting feature of this reacting system. This phenomenon is due to the coupling between the rate of the chemical reaction, the diffusional resistance, and the solubility, and has not yet been reported in the literature.

We have used dashed lines to represent in Figures 1 to 9 all the steady state solutions whose index is $(-1)^{N+1}$ and which are therefore unstable. Obviously, these steady states can not be realized unless we apply a control scheme to keep the reactor at or close to these steady states. As mentioned in the previous section some of the steady state solutions whose index is $(-1)^N$ (those which satisfy the slope condition) may be unstable.

The effect of changes in the rate constant on the steady state temperature is shown in Figure 2. The base case labeled as curve B has five steady states for residence times in the range of 5 to 7 min. Due to the special shape of the Q_{II} curve, an increase in the residence time ignites the low temperature steady state and shifts the reactor to a high temperature steady state. However, when the residence time is decreased, the extinction occurs by a shift of the high temperature steady state to the intermediate temperature branch. Upon a further decrease of the residence time, a second extinction occurs due to a shift from the intermediate to the low temperature branch.

The graphs indicate that the intermediate temperature steady state solutions are most sensitive to variations in the rate constants. The low temperature solutions are rather insensitive to these changes. In general, a decrease of the reaction rate constant causes an increase in the ignition as well as the extinction time.

The influence of the activation energy on the steady states is shown in Figure 3. It is seen that decreasing the activation energy increased the extinction residence time and decreased the ignition residence time. This particular influence is caused by the assumption that all reaction rate constants are equal at 50°C. The steady state temperature corresponding to ignition is above 50°C. Therefore, at the low temperature branch an increase of the activation energy corresponds to a decrease in the reaction rate. The inverse is of course true for the high temperature solutions. The low temperature branch solutions are rather insensitive to variations in the activation energy since the major cause for heat generation is the physical absorption of the gas and not the chemical reaction.

Variations in the solubility of the gas had a marked influence on the range of residence times for which multiple steady states exist (Figure 4). An increase in the solubility (increase in the value of D_1) caused a

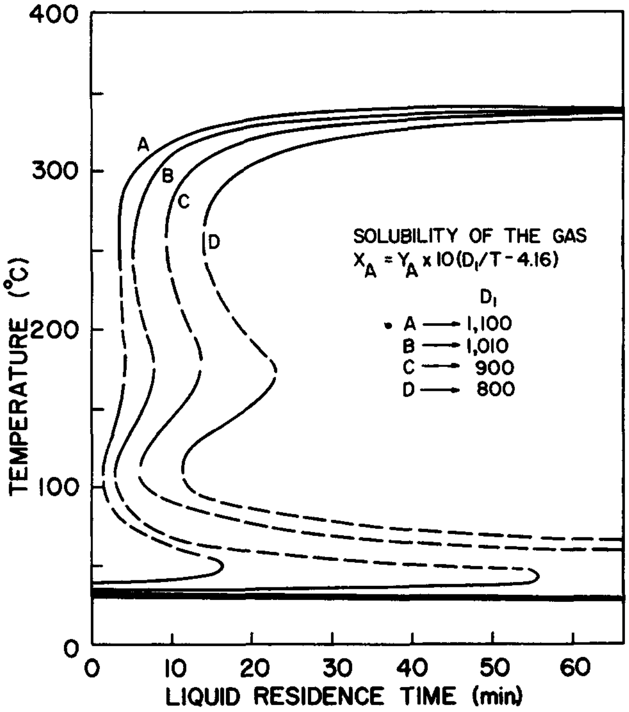

Fig. 4. The influence of the solubility of the gas and the liquid residence time on the steady state temperature.

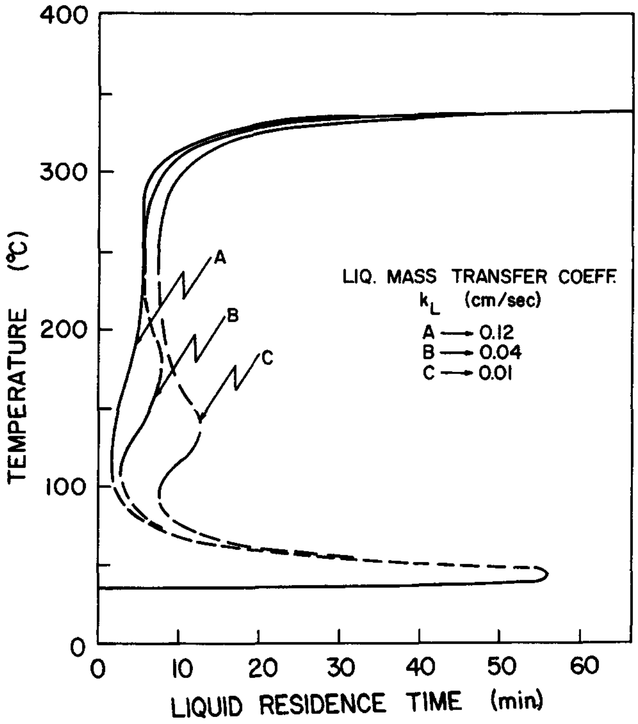

Fig. 5. The influence of liquid mass transfer coefficient and residence time on the steady state temperature.

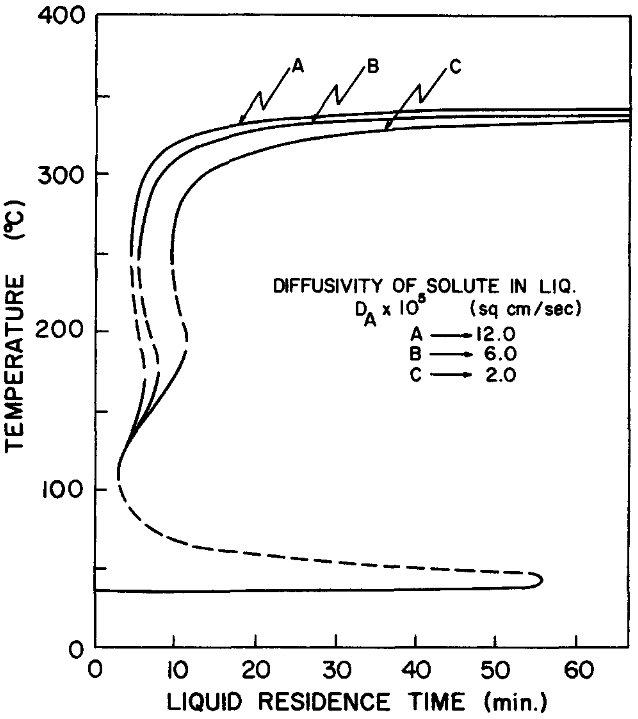

Fig. 6. The influence of the diffusivity of the solute and the liquid residence time on the steady state temperature.

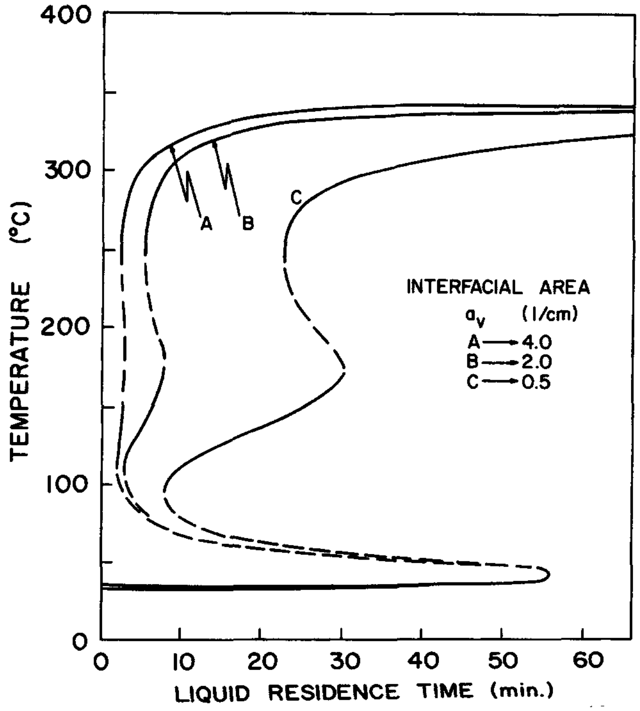

Fig. 7. The influence of the interfacial area and liquid residence time on the steady state temperature.

large decrease in the liquid residence time at which ignition occurred. Moreover, a decrease in the solubility increases the range of residence times for which five steady state solutions exist. The changes in the solubility have a rather weak influence on the high temperature steady states.

Figure 5 reveals that changes in the liquid mass transfer coefficient have only a minor impact on the low and high temperature steady states and on the ignition residence time. When the mass transfer coefficient was increased above 0.04 cm/s, it had a negligible influence on the high temperature steady state temperature or conversion. The reason for this interesting effect is that the mass transfer coefficient is inversely proportional to the modulus M. For the high temperature steady states $E_A^* \approx M$ and the rate of gas absorption, which is proportional to $k_l E_A^* \approx k_l M$, is not influenced by the changes in the mass transfer coefficient.

Changes in the diffusion coefficient affect in general the parameter M as well as the mass transfer coefficient. Figure 6 describes the influence of the diffusion coefficient on the steady state temperature assuming a fixed value of k_l. The graphs indicate that the diffusion coefficient has a negligible influence on the low temperature steady state and ignition but has a certain influence on the high temperature steady states.

The interfacial area had an important influence on the intermediate and high temperature steady states but negligible influence on the low temperature branch and the ignition. The graphs shown in Figure 7 indicate that decreasing the interfacial area increases by a large factor the range of residence times for which five steady state solutions exist.

The influence of the liquid heat capacity on the reactor is shown in Figure 8. A decrease in the heat capacity causes an increase in the adiabatic temperature rise and in the temperature of the high temperature steady states and a decrease in the residence time at which the low temperature steady state ignites. Moreover, the variation of the heat capacity from the base case value (curve B) reduces the region in which five steady state solutions can exist. For example, for the case represented by curve C, no more than three solutions exist for any residence time. Changes in the gas heat capacity have a similar influence. However, the impact of changing the gas heat capacity is much smaller since its heat capacity in this example is small compared to that of the liquid. The qualitative influence of changes in either the heat capacity or in the heat of reaction are similar. The reason for this is that the impact of these changes is via the adiabatic temperature rise.

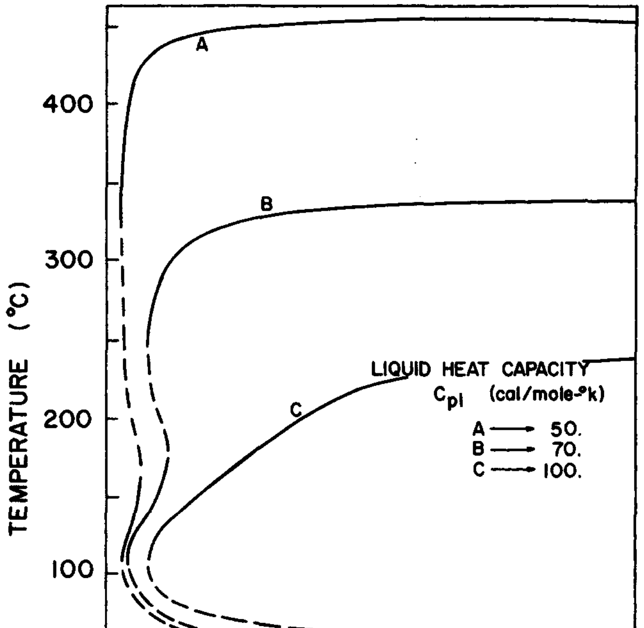

Fig. 8. The influence of liquid heat capacity and residence time on the steady state temperature.

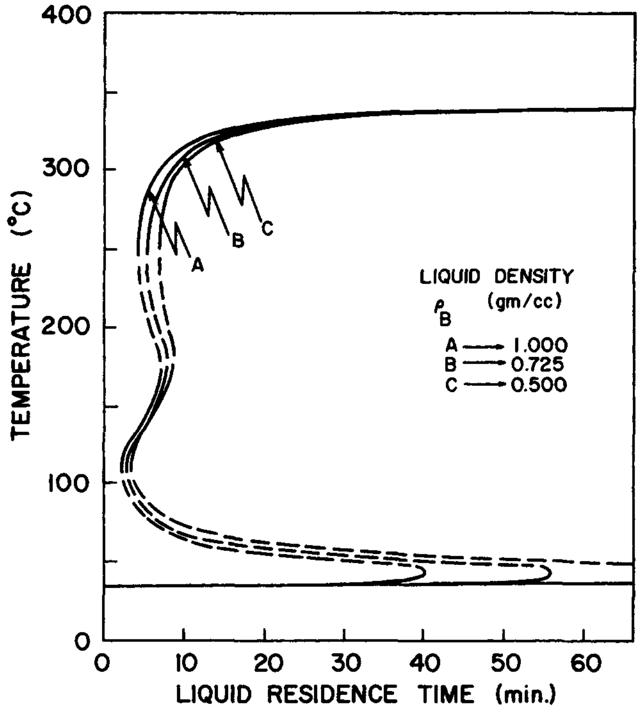

Fig. 9. The influence of change in the liquid density and residence time on the steady state temperature.

Changes in the liquid density increase the concentration of the liquid reactant but do not affect the adiabatic temperature rise. The parametric study shown in Figure 9 indicates that changes in the liquid density affected mainly the residence time at which ignition occurred but had a rather small influence on the high temperature steady states.

The parametric study indicates that for the example studied here the lower branch was most sensitive to solubility of the gas and the activation energy of the system. The intermediate branch was most influenced by variations in the reaction rate and to a lesser extent by changes in the interfacial area. The high temperature steady states were sensitive mainly to the liquid heat capacity and heat of the reaction. All steady states were rather insensitive to changes in the liquid mass transfer coefficient and diffusivity. The upper temperature branch was usually more sensitive to variations in the parameters than was the lower branch. The ignition residence time was much more sensitive than the extinction residence time to variations in the parameters.

Parametric studies of this type are most useful for determination of the sensitivity of design models to the value of various physical and chemical parameters and to various simplifying assumptions. This information is needed for the design of experimental laboratory and pilot plant studies.

CONCLUDING REMARKS

A major difference between the model used in this work and the series resistances model, used in previous analyses of steady state multiplicity in gas-liquid reactors, is the application of the reaction factor to account for the interactions between the chemical reaction rate and the diffusional resistances. Experimental data, which will be reported in the follow-up paper, indicates that the inclusion of the enhancement factor is essential in developing a model capable of a quantitative prediction of the behavior of the reactor in the region of steady state multiplicity.

One of the most interesting predictions of the model is the possible existence of five steady state solutions for a second-order gas-liquid reaction in an adiabatic CSTR. Such a multiplicity cannot be attained when the same reaction is carried out in a single-phase adiabatic CSTR. This unique feature of gas-liquid reactions is caused by the interaction between the enhancement factor which increases with temperature and the solubility which decreases with temperature. It would be of interest to experimentally verify this prediction.

The modeling of adiabatic gas-liquid reactors requires quantitative information about a large number of interacting chemical and physical rate processes, including their dependence on the operating conditions. Unfortunately, this information is usually not available. Thus, the design is usually based on a simplified model which does not account for all the rate processes or all the interactions among them. The validity of this design model is usually examined by comparing its predictions with laboratory or pilot plant experimental data. The existence of steady state multiplicity can serve as an excellent test for the predictive capabilities of any model and as a means of discriminating among rival models and assumptions.

NOTATION

A = concentration of species A
a_v = interfacial area per unit volume
B = concentration of species B
b_i = dimensionless interface concentration, defined by Equation (23)
C_p = heat capacity
E_A = enhancement factor
$E_A{}^*$ = reaction factor
E_i = instantaneous enhancement factor, defined by Equation (21)
F_l = liquid volumetric flow rate
H = enthalpy
$-\Delta H_R$ = heat of reaction
$-\Delta H_s$ = heat of solution
J = molar rate of absorption per unit surface area per unit time
k_1 = reaction rate constant
k_l = liquid mass transfer coefficient
M = modulus defined by Equation (20)
M_w = molecular weight
N = number of dependent variables in transient model
P = total gas pressure
P_A = partial pressure of species A
q = molar flow rate
R = reaction rate
t = time
T = temperature
T^* = temperature, defined by Equation (28)
V_R = volume of reactor
x = mole fraction in liquid phase
y = mole fraction in gaseous phase
z = length coordinate normal to interface

Greek Letters

α = ratio of film to bulk volume, defined by Equation (20)
δ = thickness of mass transfer film
ϵ = liquid holdup
θ = dimensionless residence time, defined by Equation (20)
τ = liquid residence time

Subscripts

A = of species A
B = of species B
f = feed stream
g = gas phase
i = at interface
l = liquid phase
0 = effluent stream

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