Gas-Liquid Reaction Systems: A Heuristic Model and Its Steady Solutions

To identify conditions under which gas-liquid reaction systems exhibit natural oscillations, a model is formulated in which the time scales of the elementary processes play a leading role. The steady solutions of the model problem are investigated, with the finding that at most one solution may lie in each of five temperature ranges, each range corresponding to a dominant physicochemical process.

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SCOPE

We propose a model of gas-liquid chemical reaction systems. In so doing we observe that the order of importance of the elementary physicochemical processes depends on the reactor temperature. This leads to a sequence of physically based approximations at successive temperature intervals.

Even in the simplest idealization of such a system we must suppose that a liquid containing reactant *B* is fed to a reactor, that it encounters there a gas containing soluble reactant *A* and that dissolved *A* and *B* react in the liquid phase. The processes of interest, then, are mass transfer from the gas bubbles to the gas-liquid interface (assumed here to be fast), reaction-enhanced mass transfer from the interface to the bulk liquid, and chemical reaction in the bulk liquid phase.

The model of Hoffman et al. (1975) is a good starting point. Therein chemically enhanced absorption is represented via a reaction factor, but the estimation of this factor is tied to the estimation of the bulk composition of *A*, with the result that it is not evident how the roles of the elementary processes can be isolated and under what conditions each is more or less important. Simplifications of this model have been proposed that permit analysis to be carried out: uniform and excess *B*, fast reaction, and others. Indeed if it is also assumed that the concentration of *B* is constant at its feed value, the model reduces to the single-phase continuous stirred-tank reactor (CSTR) model but an important part of the problem is lost.

As an alternative we use the enhancement factor, ϕ, to represent the chemically enhanced rate of absorption. This leads to a liquid-side model that is simple and more complete. First, the enhancement factor itself is simple in the physical limits of slow, fast, and instantaneous reaction and these limiting regimes can be identified with three temperature intervals covering the required temperature range. This in turn leads to the identification of five temperature intervals in which the reactor model itself, at least under steady state conditions, takes a simple form in terms of the expressions for the dominant elementary processes. Second, the use of the enhancement factor permits us to make an important addition. Indeed it is the interfacial temperature that controls the solubility and this must exceed the bulk temperature whenever an exothermic reaction takes place close to the interface, as occurs under fast reaction conditions. We take this temperature rise into account; its estimate is tied to the estimate of the enhancement factor.

The model then takes the following form: Three equations that establish the state of the bulk liquid, containing terms depending on the state of the interface, and three equations that establish the enhancement factor, the fraction absorbed that is transferred to the bulk, and the interfacial temperature, for assigned bulk conditions. We identify six time constants: the bulk and interfacial reaction times, τ_{rb} and τ_{ri}, the bulk and interfacial contact times, τ and τ_i, the mass transfer time, τ_m, and the heat transfer time, τ_h. We use these to identify five temperature intervals wherein simple approximations obtain, reflecting the dominant elementary processes.

CONCLUSIONS AND SIGNIFICANCE

In gas-liquid reaction systems the bulk and interfacial reactions take place in distinct temperature ranges. This is fundamental and it holds under ordinary conditions because $\tau \gg \tau_i$. It leads to the identification of two main operating domains: a low-temperature or bulk domain where output via flow and bulk reaction are the slow processes, and a high-temperature or surface domain where input via mass transfer is the slow process. The first domain consists of two temperature intervals corresponding to slow and fast bulk reaction; the second domain consists of three temperature intervals corresponding to slow, fast, and instantaneous interfacial reaction. A steady performance problem, then, may have one or three or five solutions, but at most one in each such interval. Indeed the data of Ding et al. (1974) correspond to operation in the first three intervals and this implies that the absorption step is at most weakly enhanced and that the temperature rise is slight.

We note that the simple approximations defined for each temperature interval must be used carefully. Indeed a simple model may exhibit more than one solution, but at most one (and possibly none) can be physically meaningful inasmuch as the full model exhibits at most one solution at each temperature interval. For instance, only solutions to the fast reaction model that lie in the fast reaction region can be meaningful, and the full model has at most one solution there. We add the caveat that the fast reaction region is defined in terms of a temperature range that can only be deduced from the full model and that this diminishes the usefulness of simple models.

The liquid phase reactant plays a complicated role even though its bulk concentration, C_B, ordinarily exceeds the concentration of the absorbing gas phase reactant by orders of magnitude. This in itself does not produce a useful simplification unless C_B is small, i.e., unless the holding time is large. For then the pseudo-first-order expression for the enhancement factor can be used to account for the surface reaction in all regions. Otherwise, for small holding times and large values of C_B, large temperature rises are likely. Indeed the transition to instantaneous reaction depends strongly on the value of C_B, the transition temperature falling as C_B increases. This transition is dominated by the liquid phase reactant, and to predict it the pseudo-first-order enhancement factor must be corrected to account for the transport of B to the interface. We note that under conditions of large temperature rise, more than one value of the interfacial temperature, T_i, may correspond to assigned bulk conditions, C_B and T. This multiplicity does not add solutions to a reactor problem but it does change the conventional interpretation of the slope condition.

The Problem and Its Background

If a reactor could control its feed, varying it in time, there would be a physical basis for anticipating a natural oscillation in the reactor's performance. The elementary fact that reaction rates and absorption rates are countervariant with temperature suggests that gas-liquid reactors, where one reactant is fed as a gas and the other as a liquid and where the reaction takes place in the liquid phase, should exhibit natural oscillations. This conjecture is unsupported by experiment, but the experiments of Ding et al. (1974) show that gas-liquid reactors are physically interesting processes. We construct a simple model that provides direction in the search for periodic states.

The problem is this: A nonvolatile liquid containing reactant B is fed to a well-mixed reactor where it encounters a gas containing the soluble reactant A. Excess gas is bubbled through the liquid, the reaction of dissolved A and B takes place in the liquid phase, and the nonvolatile products flow out along with unreacted B and unreacted dissolved A. Under such conditions, which are not unlike conditions found in typical chlorinations, hydrogenations, etc., the gas phase is of secondary importance, excerising its influence via the dependence of the interfacial area on the gas phase flow rate and the dependence of the reactant solubility on the reactant partial pressure.

The early work of Schmitz and Amundson (1963) on two-phase reaction systems is not relevant to absorption-reaction oscillations, being limited in the way in which the heat release can modify the rates of adsorption and chemical reaction. The pioneering study is that of Hoffman et al. (1975). There it is proposed that the experimental findings of Ding et al. (1974) can be understood in terms of chemically enhanced gas absorption, which is represented via the use of a reaction factor: the rate of absorption is written $E^* k_L^o a C_{Ai} V$. (Without compromising Hoffman's model in the least, we show that the absorption in Ding's experiments is not chemically enhanced.)

Hoffman's model is logically sound but it presents certain practical problems insofar as most of the physical processes of interest are tied up in the estimation of the value of E^*. This is particularly true inasmuch as the film theory is used and the film is taken to be a physical, not a fictitious, entity. This implies that the values of E^* and C_A must be estimated simultaneously, with the result that it is not evident how the roles of the individual physiochemical processes can be identified and under what conditions each is more or less important.

Making a direct computational study of their model, Hoffman et al. draw interesting conclusions but cannot make general claims. Raghuram and Shah (1977) investigate the special case of Hoffman's model, corresponding to uniform and excess B, in the hope of identifying uniqueness conditions on the parameters of the problem. Their conclusions suppport, but are not unlike, Hoffman's inasmuch as the analysis of the model equations remain difficult, even if the reaction is assumed to be fast under all conditions. Huang and Varma (1981a) make one further approximation in the fast reaction model of Raghuram and Shah. By assuming that the concentration of B is constant at its feed value, they deduce results for the gas-liquid reactor that parallel in generality and completeness Poore's (1973) results for the corresponding single-phase problem. However, the model is now so simple that it is equivalent to the single-phase reactor model, whence all of the work of Uppal et al. (1974, 1976) becomes pertinent. (To establish this equivalence it is sufficient to identify one half the activation energy less the heat of solution as the apparent activation energy.) Thus, outside the uniqueness region, this model, like Raghuram and Shah's fast reaction model, predicts the existence of three solutions, two stable and one unstable.

The fast reaction approximation implies that $E^* = \sqrt{kC_BD/(k_L^o)^2}$, but this can be a reasonable estimate of E^* only over a certain range of k or T. If k goes to zero or infinity, the above implies that E^* goes to zero or infinity, but in fact E^* must be bounded below and above by the physical absorption and the instantaneous reaction limiting values. Now we cannot presume, without examination, that the solutions of a fast reaction model satisfy the fast reaction condition. To see if they do, we must investigate the parent model of Hoffman et al., but because of its form this information is difficult to extract. What we find is that in the nonuniqueness region all of the stable solutions of Huang and Varma (1981a) lie outside the fast reaction region; the only meaningful prediction is unstable. What accounts for the problem in the fast reaction model is that the fast reaction region is most easily identified with a certain temperature range, but temperature is not part of the specification of the problem, it is part of the solution. Subsequently, Huang and Varma (1981b), using the full model of Hoffman et al., reported extensive calculations that reveal a variety of remarkable multiplicity patterns.

In what follows we construct a model comparable in generality to that of Hoffman et al. In fact, we make an important addition. Although it is recognized that the reaction exercises an important influence on the absorption, what we do not overlook is that in the fast reaction region the reaction takes place close to the interface and releases its heat there. Thus, the interfacial temperature may be significantly higher than the bulk temperature and it is the interfacial temperature that controls the solubility.

It is difficult to extend Hoffman's model to account for this, but it is easy to account for this if we piece together simple limiting results and identify their regions of validity. We retain the accuracy of Hoffman's model, gain an understanding of the physics of the process, and avoid the problems besetting Huang and Varma (1981a). In particular, we identify five regions, find useful approximations in each, and show that in each region there can be at most one solution.

The Model

The reaction, $A + B \longrightarrow$ products, takes place in the liquid phase. Reactant A is nominally a gas, reactant B is the solvent, and the products are liquids. The gas stream, supplied in excess, is bubbled through the liquid phase, whereupon reactant A is adsorbed into the liquid; reactant B is fed directly. The liquid phase is spatially uniform outside regions of vanishingly small volume adjacent to the gas bubbles. The gas phase exercises its primary influence on the process through the pressure dependence of the solubility:

$$C_{Ai} = \frac{P_A}{H(T_i)}, \quad H(T_i) = H(T_f)e^{Q_s/R[(1/T_i)-(1/T_f)]}, \quad Q_s < 0 \qquad (1)$$

where P_A is assumed to be constant. The gas stream does not contribute to the cooling, its thermal capacity being small and the liquids being nonvolatile, but it does establish the value of a, the interfacial area per unit volume.

Under fairly general conditions then, the state of the liquid phase, defined by the values of C_A, C_B, and T, satisfies:

$$\frac{VdC_A}{dt} = -qC_A - kC_AC_BV + \phi k_L^o a(C_{Ai} - C_A)(1 - f_i)V \qquad (2)$$

$$\frac{VdC_B}{dt} = q(C_{Bf} - C_B) - kC_AC_BV - \phi k_L^o a(C_{Ai} - C_A)f_iV \qquad (3)$$

$$V\rho C_p\frac{dT}{dt} = q\rho C_p(T_f - T) - UA(T - T_c) - Q_rkC_AC_BV - Q_s\phi k_L^o a(C_{Ai} - C_A)V - Q_r\phi k_L^o a(C_{Ai} - C_A)f_iV \qquad (4)$$

where Eqs. 2, 3, and 4 are similar in form to the equations that correspond to the standard CSTR. In Eq. 2 only the third term is different. It accounts for the feed of reactant A. It expresses the net rate of absorption of A, that is, the rate of adsorption of A, chemically enhanced if $\phi > 1$, less the rate of reaction of A in the interfacial region giving rise to the chemical enhancement. Insofar as C_{Ai} depends on the state of the liquid phase, so also the feed of reactant A. It is in this manner that the reactor controls its feed.

To make the model equations concrete, we must establish the dependence of ϕ, f_i, and T_i on C_A, C_B, and T. We take the values of k_L^o and a to be assigned and estimate the enhancement of k_L^o by the chemical reaction. To do this we use the penetration model and assume that the contact time is randomly distributed about an average value τ_i that establishes the holding time in the interfacial region. (The film and penetration models make practically indistinguishable predictions of the chemical enhancement as long as the temperature rise is ignored, otherwise their predictions may differ; cf. White and Johns, 1985b.)

We assume the transport resistance to be on the liquid side and note that the rate of reaction is kC_AC_B where

$$k = k_oe^{-E/RT} \qquad (5)$$

Three special conditions satisfied in gas-liquid reactors allow the construction of a useful approximation to ϕ and thence to f_i and T_i:

$$\text{(i)} \quad \alpha \gg D \qquad (6)$$

$$\text{(ii)} \quad C_B \gg C_{Ai} \qquad (7)$$

$$\text{(iii)} \quad \tau_m \gg \tau_i \quad \text{(Astarita, 1967)} \qquad (8)$$

Condition (i) implies that absorption occurs at a uniform temperature T_i. Condition (ii) implies that absorption occurs at a uniform concentration of B. Condition (iii) implies that $C_A = 0$ whenever absorption is chemically enhanced and follows via a time scale argument. The time scales listed in Table 1 scale the elementary bulk and interfacial processes. The interfacial reaction is negligible until its time scale falls to the corresponding holding time τ_i. Before this happens $\phi = 1$, $f_i = 0$, $T_i = T$, and $\tau_{ri} = \tau_{rb}$. On decreasing τ_{ri}, the condition $\tau_{ri} = \tau_{rb} = \tau_i$ signals the onset of chemically enhanced absorption, and when this is satsified condition (iii), Eq. 8, implies that $\tau_m \gg \tau_{rb}$. This means that the bulk reaction of A is fast compared to the absorption of A and that we may set $C_A = 0$ in estimating the value of ϕ for $\phi > 1$. The result is

$$\phi = \sqrt{1 + \frac{\tau_i}{\tau_{ri}}} \tag{9}$$

and

$$f_i = \frac{\tau_i/\tau_{ri}}{1 + \tau_i/\tau_{ri}} \tag{10}$$

where T_i remains to be found.

For small values of τ_{ri} absorption cannot occur at a uniform concentration of B, even though condition (ii) is ordinarily satisfied. Indeed for instantaneous reaction the diffusion of B to the interface places a bound on ϕ such that for $\tau_{ri} \rightarrow 0$

$$\phi = \phi_\infty \equiv 1 + \frac{C_B}{C_{Ai}} \tag{11}$$

$$f_i \rightarrow 1 \tag{12}$$

The argument of van Krevelen and Hoftijzer (1948), which estimates the interfacial concentration of B, leads to a formula:

$$\phi = \frac{1}{2}\frac{\tau_i/\tau_{ri}}{(\phi_\infty - 1)}\left[\sqrt{1 + \frac{4\phi_\infty(\phi_\infty - 1)}{\tau_i/\tau_{ri}} + \frac{4(\phi_\infty - 1)^2}{(\tau_i/\tau_{ri})^2}} - 1\right] \tag{13}$$

that turns out to be accurate for all τ_{ri}, reducing to Eq. 9 for large τ_{ri}, and to Eq. 11 for small τ_{ri}. Indeed the three limiting expressions corresponding to slow, fast, and instantaneous reactions

$$\begin{aligned} &\phi = 1 && \tau_i/\tau_{ri} < 1 \\ &\phi = \sqrt{\tau_i/\tau_{ri}} && 1 < \tau_i/\tau_{ri} < \phi_\infty^2 - 1 \\ &\phi = \phi_\infty && \phi_\infty^2 - 1 < \tau_i/\tau_{ri} \end{aligned} \tag{14}$$

give a reasonable representation of ϕ, and the transition values of τ/τ_{ri} turn out to be important in reactor modeling.

Table 1. Characteristic Times

Bulk Liquid-Phase Model	
Bulk holding time	$\tau = V/q$
Bulk reaction time	$\tau_{rb} = 1/k(T_b)C_{Bb}$
Absorption time	$\tau_m = 1/k_L^\circ a$
Heat transfer time	$\tau_h = \rho C_p V/UA$
Interfacial Model	
Interfacial holding time	$\tau_i = D_A/(k_L^\circ)^2$
Interfacial reaction time	$\tau_{ri} = 1/k(T_i)C_{Bb}$

Assuming, as condition (i), Eq. 6, implies, that the heat generated is released at the interface, we use the heat balance condition to estimate T_i, whence there obtains

$$T_i - T = \frac{-Q_s - Q_r f_i}{\rho C_p}\sqrt{\frac{D}{\alpha}}\,\phi C_{Ai} \tag{15}$$

Equations 10, 13, and 15 constitute the interfacial model, predicting f_i, ϕ, and T_i for assigned values of C_B and T, where we note that $C_A = 0$, else $f_i = 0$, $\phi = 1$, and $T_i = T$. Thus, Eqs. 1, 2, 3, 4, 10, 13, and 15 constitute the model problem. We investigate its steady solutions in the next section.

The Steady Solutions: Qualitative Study of the Model Problem

Under steady conditions x_A, x_B, and θ, defining the state of the liquid phase, satisfy

$$0 = -x_A - \frac{\tau}{\tau_{rb}}x_A + \frac{\tau}{\tau_m}\phi(1 - f_i)(x_{Ai} - x_A) \tag{16}$$

$$0 = 1 - x_B - \frac{\tau}{\tau_{rb}}S_f x_A - \frac{\tau}{\tau_m}\phi S_f f_i(x_{Ai} - x_A) \tag{17}$$

and

$$\begin{aligned} 0 = -\theta - \frac{\tau}{\tau_h}(\theta - \theta_c) + \frac{\tau}{\tau_{rb}}B_r x_A \\ + \frac{\tau}{\tau_m}\phi(B_s + B_r f_i)(x_{Ai} - x_A) \end{aligned} \tag{18}$$

where

$$x_{Ai} = e^{-\gamma_s\theta_i/1+\theta_i} \tag{19}$$

$$\frac{1}{\tau_{\mathrm{rb}}} = \frac{1}{\tau_{rf}}e^{\gamma_r\theta/1+\theta}x_B \tag{20}$$

and

$$\frac{1}{\tau_{\mathrm{ri}}} = \frac{1}{\tau_{rf}}e^{\gamma_r\theta_i/1+\theta_i}x_B \tag{21}$$

and where θ_i, the interfacial temperature, satisfies

$$\theta_i = \theta + \sqrt{\frac{D}{\alpha}}(B_s + B_r f_i)\phi x_{Ai} \tag{22}$$

The constants γ_s, B_s, γ_r, B_r, S_f, and $1/\tau_{rf}$ define the chemistry; the time constants τ, τ_m, τ_i, and τ_h define the operating conditions.

Equation 16 implies

$$x_A = \frac{\dfrac{\tau}{\tau_m}\phi(1 - f_i)}{1 + \dfrac{\tau}{\tau_{rb}} + \dfrac{\tau}{\tau_m}\phi(1 - f_i)}x_{Ai} \tag{23}$$

and, if $B_s \simeq 0$, Eqs. 17 and 18 imply

$$x_B = 1 - \frac{S_f}{B_r}\left(\theta + \frac{\tau}{\tau_h}(\theta - \theta_c)\right) \tag{24}$$

so that Eq. 18 establishes the steady solutions of the model problem. It is important therefore to determine how the heat generation, the nonlinear terms in Eq. 18, depends on the temperature; to do this we determine how the absorption of reactant A depends on temperature.

Scaling the rate of absorption by qC_{Ai} (Sherwood et al., 1975), we introduce the relative rate of absorption:

$$r \equiv \frac{Vak_L^\circ \phi (C_{Ai} - C_A)}{qC_{Ai}} = \frac{\tau}{\tau_m}\phi\left(1 - \frac{x_A}{x_{Ai}}\right)$$

and find, using Eq. 23, that

$$r = \frac{\dfrac{\tau}{\tau_m}\phi\left(1 + \dfrac{\tau}{\tau_{rb}}\right)}{\left(1 + \dfrac{\tau}{\tau_{rb}}\right) + \dfrac{\tau}{\tau_m}\phi(1 - f_i)}$$

whence $1/r = 1/r_{\text{out}} + 1/r_{in}$ where $r_{\text{out}} = [1 + (\tau/\tau_{rb})][1 + (\tau_i/\tau_{ri})]$ and $r_{\text{in}} = (\tau/\tau_m)\phi$.

Evidently then the relative resistance to absorption is the sum of two resistances, the first deriving from the output processes, flow and chemical reaction, the second deriving from the input process, mass transport. From this point of view mass transport is in series with the resultant of flow and chemical reaction, where the flow and chemical reaction are in parallel.

It follows that r must be less than the lesser of r_{out} and r_{in}. To see what this means we fix the values of θ and x_B and investigate r_{out} and r_{in} as the chemical reactivity, $1/\tau_{rf}$, increases. We hold τ, τ_m, and τ_i constant, such that $\tau > \tau_m \gg \tau_i$. The values $\tau = 200$ s, $\tau_m = 8.3$ s, and $\tau_i = 0.0375$ s deduced from Ding et al. (1974) are representative values for gas-liquid systems and are used in Figure 1 to illustrate the variation of the relative absorption rate on increasing chemical reactivity. We note that increasing chemical reactivity may be caused by increasing k_o or T_f or C_{Bf}. For bulk reaction the slow to fast transition can be identified by $\tau_{rb} \simeq \tau$. Whereas for interfacial reaction the corresponding transition point is $\tau_{ri} \simeq \tau_i$.

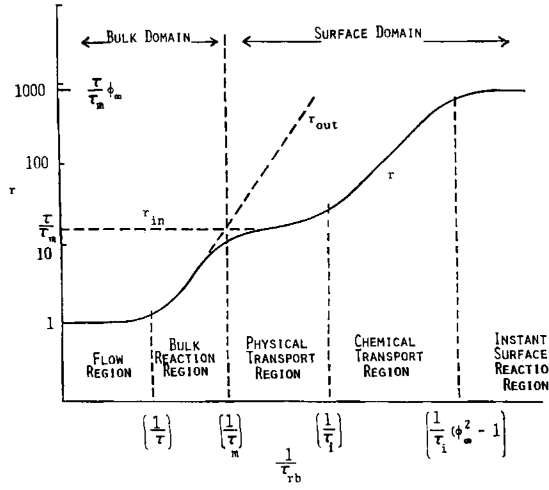

Figure 1. Relative rate of absorption vs. chemical reactivity.

We sketch r_{out} and r_{in} in Figure 1 using a logarithmic scale to underscore the order-of-magnitude nature of the argument. The corresponding variation of r is also shown. Because $1/\tau$ is ordinarily several orders of magnitude less than $1/\tau_i$, it separates naturally into five distinct regions, three plateau regions separated by two regions of monotonic increase. Bulk processes control in the first two regions, the flow and bulk reaction regions; interfacial processes control in the last three regions, the physical transport, chemical transport, and instantaneous reaction regions. In the second and fourth regions r is proportional to $1/\tau_{rb}$ and $\sqrt{1/\tau_{ri}}$; otherwise it is independent of $1/\tau_{rb}$ and $1/\tau_{ri}$. In the first region both bulk and interfacial reaction are slow; in the third region bulk reaction is complete and interfacial reaction is slow; in the fifth region interfacial reaction is complete. We summarize Figure 1 in Table 2.

We rewrite Eqs. 18 and 24 to make the role of r explicit:

$$\theta + \frac{\tau}{\tau_h}(\theta - \theta_c) = rx_{Ai}(B_s + B_r f) \tag{25}$$

$$x_B = 1 - rx_{Ai}S_f f$$

where

$$f = f_i + f_b(1 - f_i) \text{ and } f_b = \frac{\tau/\tau_{rb}}{1 + \tau/\tau_{rb}} \tag{26}$$

and where f is the fraction of the absorbed solute that undergoes reaction. The righthand side of Eq. 25 is the heat generation; the lefthand side is the heat removal, it is linear in temperature and its intersections with the heat generation establish the steady solutions of the problem. To understand how the heat generation depends on the temperature we must account for the dependence of r, x_{Ai}, and $(B_s + B_r f)$ on θ. Now the basic structure of the heat generation is established by the double-S structure of r shown in Figure 1. We conclude, therefore, that the steady state problem may possess as many as five solutions, but not more than five, and that there can be at most one solution in each region identified in Figure 1. To see that this is so we first

Table 2. Operating Regions

Region	Relative Absorption Rate	Transition Point
Flow	1	
Bulk reaction	$\frac{\tau}{\tau_{rb}}$	$\frac{1}{\tau_{rb}} \simeq \frac{1}{\tau}$
Physical transport	$\frac{\tau}{\tau_m}$	$\frac{1}{\tau_{rb}} \simeq \frac{1}{\tau_m}$
Chemical transport	$\frac{\tau}{\tau_m}\sqrt{\frac{\tau_i}{\tau_{ri}}}$	$\frac{1}{\tau_{rb}} = \frac{1}{\tau_{ri}} \simeq \frac{1}{\tau_i}$
Instantaneous reaction	$\frac{\tau}{\tau_m}\phi_\infty$	$\frac{1}{\tau_{ri}} \simeq \frac{1}{\tau_i}(\phi_\infty^2 - 1)$

observe that Figure 1 gives an accurate qualitative picture of how r depends on θ if we modify it to take into account:

1. The fact that $\phi_\infty = 1 + x_B/(S_f x_{Ai})$ depends on θ via x_{Ai}, Eq. 19, so that the plateau in the fifth region of Figure 1 becomes a region of increasing r on increasing θ.
2. The fact that x_B, assumed to be constant in Figure 1 on increasing $1/\tau_{rf}$, is decreasing on increasing θ, cf. Eq. 26.

Because S_f is small, the variation of x_B is small (this is true unless the coefficient of S_f in Eq. 24 is large) and its most important contribution to our picture is in translating the transition values of $1/\tau_{rb}$ and $1/\tau_{ri}$ in Table 2 into the corresponding transition values of θ and θ_i.

Second, we observe that the variation of $(B_s + B_r f)$ and of x_{Ai} do not contradict the main conclusion. Because $(B_s + B_r f)$ is a monotonic increasing, S-shaped function on increasing θ and because it executes this variation on the first S-shaped segment of r, it does not introduce features into the heat generation that cannot be inferred from r itself.

Because x_{Ai} is a monotonic decreasing function on increasing θ, Eq. 19, regions one and three of constant r become regions of decreasing heat generation, whereas region five of increasing r becomes a region of constant heat generation. Regions two and four, where r is increasing, become regions of either increasing or decreasing heat generation depending on the increasing or decreasing behavior of

$$\frac{\tau}{\tau_{rb}} x_{Ai} = \frac{\tau}{\tau_{rf}} e^{(\gamma_r - \gamma_s)\theta/1+\theta}$$

and

$$\frac{\tau}{\tau_m}\sqrt{\frac{\tau_i}{\tau_{ri}}}\, x_{Ai} = \frac{\tau}{\tau_m}\sqrt{\frac{\tau_i}{\tau_{rf}}}\, e^{(1/2\gamma_r - \gamma_s)\theta_i/1+\theta_i}$$

It follows that if the variation of x_{Ai} is strong enough, the heat generation becomes a nonincreasing function of θ and there can be at most one solution to the problem. Thus, we conclude:

- There can be at most one solution (uniqueness) if $\gamma_r < \gamma_s$.
- There can be at most three solutions if $1/2\ \gamma_r < \gamma_s$, and if there are three one must lie in each of regions one and two.
- There can be at most five solutions if $1/2\ \gamma_r > \gamma_s$ where at most one solution lies in each region.

Because this time-scale picture of the absorption process is useful, we translate the information in Table 2 into heat generation terms and record it in Table 3.

Table 3. Heat Generation in Each Operating Region

Region	Heat Generation
Flow	$B_s x_{Ai}$
Bulk reaction	$\left(B_s + B_r \frac{\tau/\tau_{rb}}{1 + \tau/\tau_{rb}}\right)\frac{\tau}{\tau_{rb}} x_{Ai}$
Physical transport	$(B_s + B_r)\frac{\tau}{\tau_m} x_{Ai}$
Chemical transport	$(B_s + B_r)\frac{\tau}{\tau_m}\sqrt{\frac{\tau_i}{\tau_{ri}}}\, x_{Ai}$
Instantaneous reaction	$(B_s + B_r)\frac{\tau}{\tau_m}\left(1 + \frac{x_B}{S_f x_{Ai}}\right) x_{Ai}$

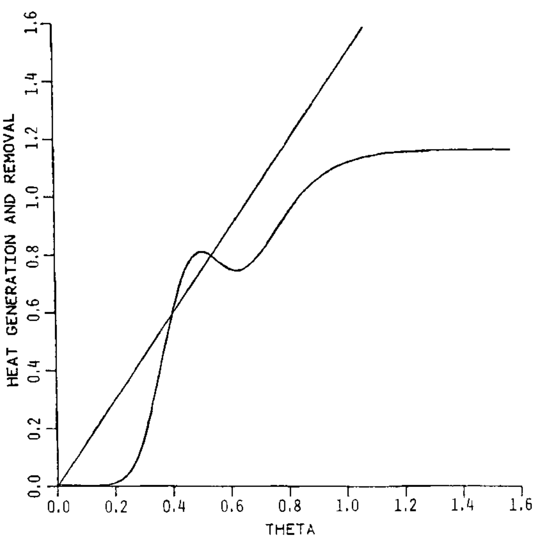

Figure 2. Heat generation and removal vs. temperature.
Data of Table 4, τ = 40 min.

We note that the apparent activation energy for the bulk reaction is $(E + Q_s)$, which is greater than the apparent activation energy for the interfacial reaction, $(1/2\,E + Q_s)$. Nonetheless it is because $\tau \gg \tau_i$ that the bulk reaction dominates at low temperatures, the interfacial reaction at high temperatures.

In Figure 2 we show a concrete heat generation function using the physical constants deduced from Ding et al. (1974) and recorded in Table 4. The double-S shape and the corresponding five regions are evident. For $\tau = 40$ min and the data of Table 4, we predict three solutions; for other values of τ we predict one low-temperature solution but never five solutions. This is what Ding et al. found. The three solutions lie in regions one, two, and three; it follows that absorption is not chemically enhanced under the conditions of Table 4. Nonetheless the values of τ_h and/or θ_c can be set so that Eq. 25 possesses five solutions, but not more than five and not more than one in each region.

The slope of the heat generation function less that of the heat removal function must alternate in algebraic sign over the naturally ordered solutions of Eq. 25 and it must be negative at the

Table 4. Data for the Chlorination of Decane*

k_o	=	2.1×10^{11}	m^3/mol · s	=	2.1×10^{17}	cm^3/mol · s
E	=	1.25×10^5	J/mol	=	30,000	cal/mol
Q_r	=	-1.05×10^5	J/mol	=	$-25{,}000$	cal/mol
$\rho = C_{Bf}$	=	5.1×10^3	mol/m^3	=	5.1×10^{-3}	mol/cm^3
C_p	=	3.6×10^2	J/mol · K	=	85	cal/mol · K
V	=	3.44×10^{-4}	m^3	=	344	cm^3
D	=	6.0×10^{-9}	m^2/s	=	6.0×10^{-5}	cm^2/s
α	=	7.7×10^{-8}	m^2/s	=	7.7×10^{-4}	cm^2/s
T_f	=	297 K				
T_c	=	298 K				
UA	=	1.26×10^{-1}	J/K · s	=	0.03	cal/K · s
P_A	=	1.0×10^5	Pa	=	1	atm
$H(T_f)$	=	5.46×10^2	Pa · m^3/mol	=	5,465	atm · cm^3/mol
Q_s	=	-1.9×10^4	J/mol	=	$-4{,}500$	cal/mol
k_L°	=	4.0×10^{-4}	m/s	=	0.04	cm/s
a	=	3.0×10^2	m^{-1}	=	3.0	cm^{-1}

*Ding et al. (1974), Hoffman et al. (1975), Sharma et al. (1976)

low-temperature solution. This sign is also that of the Jacobian determinant of Eqs. 16, 17, and 18, and if that determinant is positive, the solution is unstable. This then is the slope condition. It follows that every other solution must be unstable and, specifically, that solutions in regions two and four must be unstable, if not unique.

The condition that the slope of the heat generation function not exceed the slope of the heat removal function for all values of the temperature is necessary and sufficient for a unique solution. The time-scale picture shows that the slope of the heat generation function is nonpositive in regions one, three and five; thus, uniqueness conditions can be inferred from the simple expressions in Table 3 for the heat generation in regions two and four (White, 1982). The results generalize the conditions $\gamma_r < \gamma_s$, and $1/2\,\gamma_r < \gamma_s$.

This suggests that restricting the model problem to a certain region can produce useful results. However, if the model problem is so simplified, only the solutions that lie in the corresponding region are admissible and there can be at most one such solution because the full model problem admits at most one solution in each region. Thus, if a simplified model problem possesses more than one solution, at most one can satisfy the parent problem. Now Huang and Varma (1981a) propose a fast reaction model where $\phi = \sqrt{\tau_i/\tau_{ri}}$ for all θ, but this formula is correct only in region four. Aside from the approximations $x_B = 1$ and $\theta_i = \theta$, their solutions are not generally admissible. Thus, whenever three solutions are reported, the two stable solutions are not admissible and the only admissible solution is unstable. The formula $\phi = \sqrt{\tau_i/\tau_{ri}}$ does not respect the bounds $1 < \phi < \phi_\infty$, and what results is shown in Figure 3.

Here the reactivity has been increased from that given in Table 4 so that solutions exist in the enhanced mass transfer regions. The full model exhibits five solutions, one in each region, but only the solution in region four is predicted by the fast reaction model. But we note that the solution in region five is fairly well approximated by a solution of the fast reaction model. We can establish conditions for this as follows: For chemically enhanced absorption the heat generation is approximately $(\tau/\tau_m)\,B_r\,\phi\,x_{Ai}$, where for fast reaction $\phi \simeq \sqrt{\tau_i/\tau_{ri}}$, and for instantaneous reaction $\phi = 1 + x_B/(S_f\,x_{Ai})$. Using $x_B = 1 - (\tau/\tau_m)\,S_f\,\phi\,x_{Ai}$, the corresponding high-temperature asymptotes of the heat generation are B_r/S_f and $(\tau/\tau_m/1 + \tau/\tau_m)\,(B_r/S_f)$. Thus, assuming the temperature rise is small, and we see later that $\tau/\tau_m \gg 1$ implies $\theta_i \simeq \theta$, we conclude that the simple pseudo-first-order expression for ϕ can be used in a reactor model for all values of θ if $\tau/\tau_m \gg 1$ and if the consistent value of x_B is used.

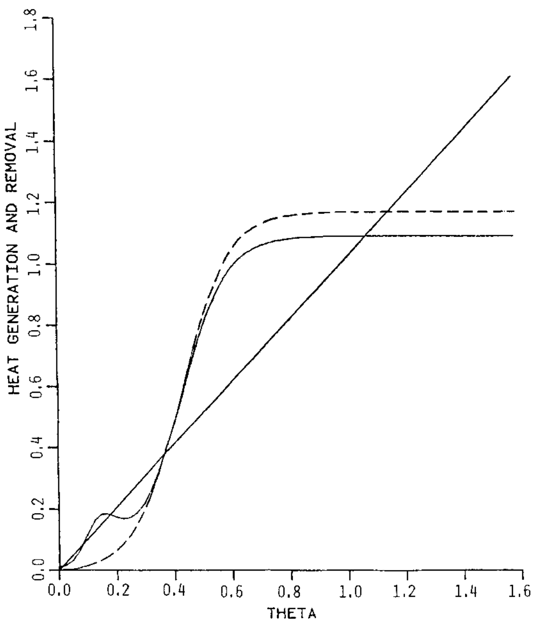

Figure 3. The fast reaction approximation.
Data of Table 4 except $1/\tau_{rf} = 9.0 \times 10^{-4}\ s^{-1}$, $\tau = 2$ min.
--- Fast reaction approximation
___ Full model

The Steady Solutions: Quantitative Study of the Model Problem

Using the values of the physical constants in Table 4, we illustrate the τ dependence of the solutions of the model problem in Figure 4. The predictions are reasonable estimates of the experimental results of Ding et al. (1974). Because the reactivity is low the problem possesses at most three solutions for each value of τ, i.e., only the first S of the heat generation function comes into play. The solutions exhibit a standard CSTR multiplicity pattern called an isola, although Ding's results do not confirm the isola. If we increase $1/\tau_{rf}$ by a factor of 100 we get an isola with an S-shaped boundary and hence we see intervals of one, three, five, three, and one solutions, Figure 5. We label the jump points I or E or I/E to signify ignition or extinction or indeterminate points. In Figure 6 we summarize the results of calculations based on the data of Table 4; we show the locus of the ignition (I), extinction (E), and indeterminate (I/E) points on a graph of $1/\tau_{rf}$ vs. τ.

The ignition and extinction loci enclose the region of multiple solutions, namely, three or five; the indeterminate locus encloses the region of five solutions. For each value of $1/\tau_{rf}$ the multiplicity pattern is revealed by the number of ignition and extinction points: one of each implies an S-shaped multiplicity pattern, two of each implies a mushroom, and two extinction points imply an isola. The results of an extensive set of calculations based on the full model equations of Hoffman et al. (1975) are given by Huang and Varma (1981b). The difference between the two models, i.e., the interfacial temperature rise, does not manifest itself in this example. For this reason we report only the main

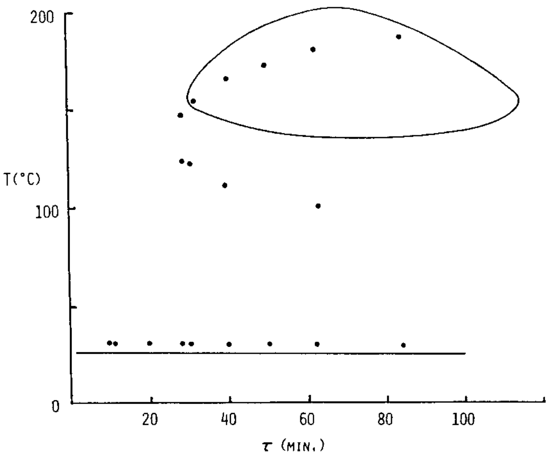

Figure 4. Steady state temperature vs. holding time.
Data of Table 4.
● Experimental values from Ding et al. (1974)

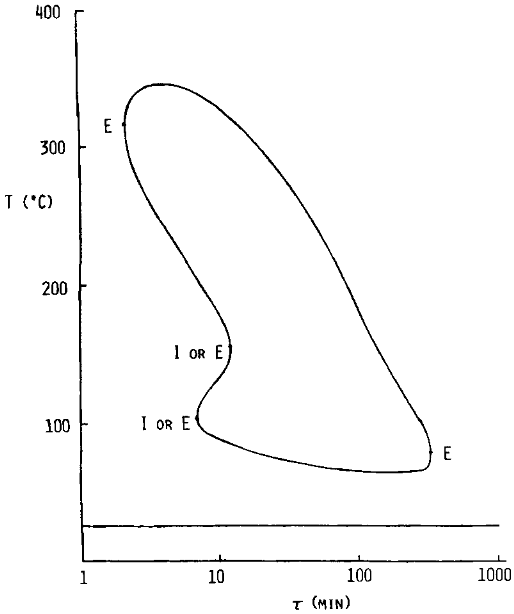

Figure 5. 1-3-5-3-1 multiplicity with an isola.
$1/\tau_{rf} = 9.0 \times 10^{-6}\ s^{-1}$
E, Extinction points; I, Ignition points

conclusion of our calculations. It is this: $1/\tau_{rb} < 1/\tau_i$ implies $x_B \simeq 1$ provided that $S_f(\tau/\tau_m)\,x_{Ai} \ll 1$ so that the holding time is not extraordinarily large, and $1/\tau_{rb} > 1/\tau_m$ implies $x_A \simeq 0$. Thus, the full three-state variable model reduces to two two-state variable models in overlapping domains, the first in regions one to three where $x_B = 1$, and the other in regions three to five where $x_A = 0$. This is true of the steady model problem; it remains to be seen if it is true of the dynamic model problem where it would be of much greater significance.

Having introduced the interfacial temperature rise into gas-liquid reactor modeling, we are interested in establishing conditions under which it is important. For the experiments of Ding et al. (1974) an instantaneous reaction calculation based on the feed leads to an estimated 100 K temperature rise. Notwithstanding this, the actual temperature rise is slight inasmuch as the absorption step turns out not to be chemically enhanced under the conditions of the experiments. Higher values of the chemical reactivity result in solutions in which the absorption step is enhanced, but the temperature rise remains small. The reason is this: For the data of Table 4, x_B is small in the enhanced transport regions so that the corresponding values of ϕ cannot be large. Now x_B is bounded below by its large θ asymptote; indeed in the instantaneous reaction region we find that

$$x_B = \frac{1 - \dfrac{\tau}{\tau_m} S_f\, x_{Ai}(\theta_i)}{1 + \dfrac{\tau}{\tau_m}} \le \frac{1}{1 + \dfrac{\tau}{\tau_m}}$$

Evidently small values of τ/τ_m imply large values of x_B, which in turn encourage large values of ϕ and hence $\theta_i - \theta$. In fact the temperature rise in the instantaneous reaction region, where it achieves its maximal value, is

$$\theta_i - \theta = \sqrt{\frac{D}{\alpha}}\,(B_s + B_r)\left(x_{Ai}(\theta_i) + \frac{x_B}{S_f}\right)$$

$$= \sqrt{\frac{D}{\alpha}}\,(B_s + B_r)\,\frac{1}{S_f}\,\frac{(1 + S_f\, x_{Ai})}{1 + \dfrac{\tau}{\tau_m}}$$

so that the smaller τ/τ_m, the larger $\theta_i - \theta$.

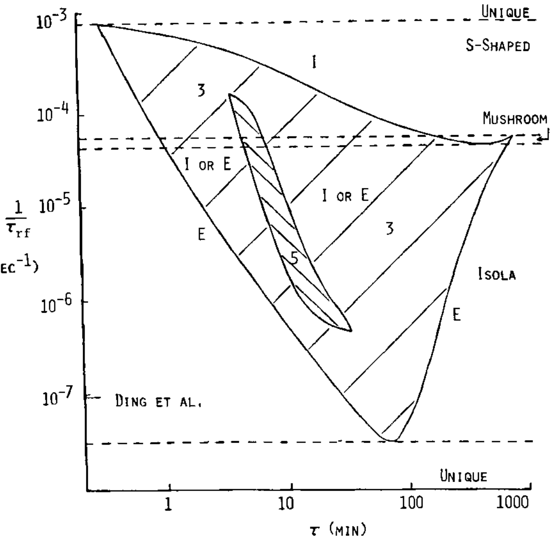

Figure 6. Multiplicity regions and patterns.
Parallel lining shows regions of three and five solutions.

In Figure 7 we illustrate the influence of the interfacial temperature rise on the solutions of a reactor problem. For a certain small value of τ/τ_m, we show two graphs of the heat generation function vs. the bulk temperature, one based on Eq. 22, one based on $\theta_i = \theta$. Evidently including the temperature rise increases the likelihood of solutions in regions four and five. For the heat removal line shown, the corresponding temperature rises are 90 and 155 K. Now the large θ asymptote of the heat generation is independent of the temperature rise inasmuch as $\phi\, x_{Ai} \rightarrow (x_{Ai}(\theta_i) + 1/S_f)/(1 + \tau/\tau_m)$. Thus, the temperature rise does not have much bearing on solutions well into the instantaneous reaction region, although the temperature rise may be very large there. It exercises its major influence in the fast reaction region in driving the heat generation to its asymptote quickly on increasing θ as θ_i runs ahead of θ. Its importance then is this: a larger temperature rise establishes instantaneous reaction conditions at a smaller value of θ.

It is worth noting that the foregoing illustrates the value of simple approximate models defined within restricted temperature intervals. In this connection we see that conditions that favor a large temperature rise do not favor extension of the fast reaction model and vice versa.

An interesting variation of Figure 7 obtains when Eq. 22 defines three values of θ_i for each value of θ at some interval. White and Johns (1985a) estimate the bulk temperature interval in which this takes place. Surprisingly, the multiplicity of Eq. 22 does not increase the multiplicity of a reactor problem. To see this (for which credit is due Ashutosh Sharma, 1984) we observe that whenever $x_A = 0$ (otherwise $f_i = 0$ and hence $\theta_i = \theta$) Eqs. 18 and 22 imply that

$$\frac{\theta_i - \theta}{\sqrt{D/\alpha}} = \frac{\theta + \dfrac{\tau}{\tau_h}(\theta - \theta_c)}{\tau/\tau_m}$$

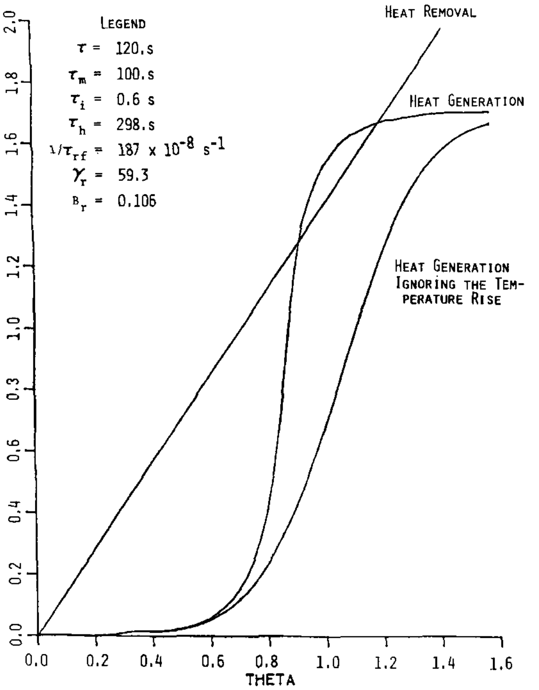

Figure 7. An example in which temperature rise is crucial.

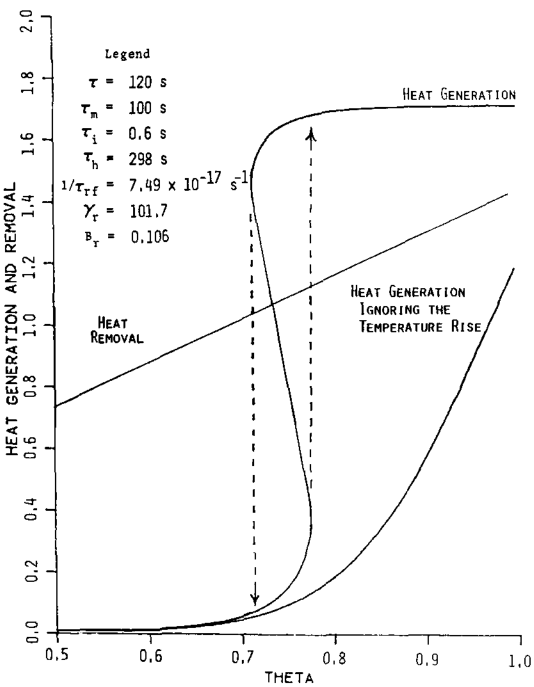

Figure 8. A multiple-valued heat generation function.

This can be used in place of Eq. 22 so that the multiplicity of a reactor problem remains that predicted by graphs of heat removal and heat generation vs. bulk temperature. What happens when Eq. 22 has multiple solutions is that the heat generation function takes a heretofore unanticipated shape. We illustrate this in Figure 8, where it becomes obvious that multiple solutions of Eq. 22 cannot increase the multiplicity of the problem itself. The heat generation now exhibits a hysteresis; for values of θ such that three values of θ_i exist, the heat generation is a multiple-valued function of θ. For such a multiple-valued heat generation function the slope of the difference, heat removal less heat generation, need not alternate in sign over successive solutions.

Conclusion

In gas-liquid reactors, bulk and interfacial reactions take place in distinct temperature ranges, low temperatures favoring bulk reaction. This is implied by the condition $\tau \gg \tau_i$ and leads to a double-S shaped heat generation function, the first S lying in the temperature range where $\tau_{rb} \cong \tau$, the second in the range where $\tau_{ri} \cong \tau_i$. Thus we may identify five temperature intervals in each of which a certain elementary process is dominant, and this invites the construction of simple approximations. The simple models so constructed may exhibit more than one solution, but at most one can be physically meaningful as the full model exhibits at most one solution in each interval. This decomposition leads to a preliminary conclusion that sustained oscillations are not likely to be a high-temperature phenomenon. Indeed, in the instantaneous reaction region, the rate of adsorption is independent of temperature, as increasing enhancement just offsets decreasing solubility.

Notation

a = interfacial area per unit volume
B_r, B_s = dimensionless heat of reaction and solution, $-Q_rC_{Aif}/\rho C_pT_f$, $-Q_sC_{Aif}/\rho C_pT_f$
C = concentration in the liquid phase
C_p = heat capacity of the liquid
D = diffusivity
E = activation energy
f_i = fraction of gas absorbed that reacts near the interface
H = Henry's law coefficient
k = second-order rate constant
k_L, k_L° = mass transfer coefficient with and without reaction
P_A = partial pressure of gas A
Q_r, Q_s = heat of reaction and solution
q = volumetric flow rate of the liquid
S_f = ratio of the concentration of A to B at feed conditions, C_{Aif}/C_{Bf}
T = temperature
UA = overall heat transfer coefficient
V = volume of the liquid phase
x_A, x_B = dimensionless concentration of A and B, C_A/C_{Aif}, C_B/C_{Bf}

Greek letters

α = thermal diffusivity
γ_r, γ_s = dimensionless activation energy for reaction and solubility, E/RT_f, $-Q_s/RT_f$
ρ = liquid density
θ = dimensionless temperature, $(T - T_f)/T_f$
τ, τ_i = holding time for the bulk and the interface
τ_h, τ_m = characteristic times for heat transfer, mass transfer
$\tau_{rf}, \tau_{rb}, \tau_{ri}$ = characteristic times for reaction at feed, bulk, and interfacial conditions, $1/k(T_f)C_{Bf}$, $1/k(T)C_B$, $1/k(T_i)C_B$
ϕ = enhancement factor

Subscripts

A = gas phase reactant
B = liquid phase reactant
b = bulk

c = cooling water
f = feed
i = interfacial

Literature Cited

Astarita, G., *Mass Transfer with Chemical Reaction*, Eslevier, Amsterdam, Ch. 3 (1967).

Ding, J. S. Y., S. Sharma, and D. Luss, "Steady State Multiplicity and Control of the Chlorination of Liquid *n*-Decane in an Adiabatic Continuously Stirred Tank Reactor," *Ind. Eng. Chem. Fund.*, **13**(1), 76 (1974).

Hoffman, L. A., S. Sharma, and D. Luss, "Steady State Multiplicity of Adiabatic Gas-Liquid Reactors. I: The Single Reaction Case," *AIChE J.*, **21**, 318 (1975).

Huang, D. T.-J., and A. Varma, "Steady State and Dynamic Behavior of Fast Gas-Liquid Reactions in Nonadiabatic Continuous Stirred Tank Reactors," *Chem. Eng. J.*, **21**, 47 (1981a).

———, "Steady State Uniqueness and Multiplicity of Nonadiabatic Gas-Liquid CSTRs, I and II," *AIChE J.*, **27**, 481 (1981b).

Poore, A. B., "A Model Equation Arising from Chemical Reactor Theory," *Archive for Rat. Mech.*, **52**, 358 (1973).

Raghuram, S., and Y. T. Shah, "Criteria for Unique and Multiple Steady States for a Gas-Liquid Reaction in an Adiabatic CSTR," *Chem. Eng. J.*, **13**, 81 (1977).

Schmitz, R. A., and N. R. Amundson, "An Analysis of Chemical Reactor Stability and Control," *Chem. Eng. Sci.*, **18**, 265, 391, 415, 447 (1963).

Sharma, A., "Gas-Liquid Reactors," M.S. Thesis, The Pennsylvania State Univ., University Park (1984).

Sharma, S., L. A. Hoffman, and D. Luss, "Steady State Multiplicity of Adiabatic Gas-Liquid Reactors. II: The Two Consecutive Reactions Case," *AIChE J.*, **22**, 324 (1976).

Sherwood, T. K., R. L. Pigford, and C. R. Wilke, *Mass Transfer*, McGraw-Hill, New York, Ch. 8 (1975).

Uppal, A., W. H. Ray, and A. B. Poore, "On the Dynamic Behavior of Continuous Stirred Tank Reactors," *Chem. Eng. Sci.*, **29**, 967 (1974).

———, "The Classification of the Dynamic Behavior of Continuous Stirred Tank Reactors—Influence of Reactor Residence Time," ibid., **31**, 205 (1976).

Van Krevelen, D. W., and P. J. Hoftijzer, "Kinetics of Gas-Liquid Reaction: General Theory," *Rec. Chim. Pays-Bas*, **67**, 563 (1948).

White, Daniel, Jr., "Gas-Liquid Reactors," Ph.D. Diss., Univ. Florida, Gainesville (1982).

White, D., Jr. and L. E. Johns, "The Diffusional Limitation on the Temperature Rise in the Adsorption of Chemically Reactive Gases," accepted by *Chem. Eng. Comm.* (1985a).

———, "Temperature Rise Multiplicity in the Absorption of Chemically Reactive Gases," *Chem. Eng. Sci.*, **40**(8), 1,598 (1985b).

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