$$N_{St} = C_T(N_{Re}N_{Sc})^{\frac{(p+1)\,(rp+2r-1)}{p+2}}\,(x^+)^{\frac{rp+2r-1}{p+2}} \tag{38}$$

where

$$C_T = C_L[2]^{\frac{-p(rp+2r-1)}{p+2}}$$

$$N_{Re} = \frac{2V_\infty R}{\nu}$$

$$N_{Sc} = \left(\frac{\nu}{D}\right)$$

$$x^+ = \frac{x}{2R}$$

This equation has little meaning for mass transfer since there are few fluids with very low Schmidt Numbers ($\simeq 0.001$) such that the boundary layer will penetrate the turbulent core in the entrance region. However, it is useful to note that this correlation predicts that the Stanton Number should depend upon the product of the Reynolds Number and the Schmidt Number. This level of dependency was found for the analogous heat transfer problem with liquid metals [see Bird, et al. (1960)]. For liquid metals no simple power law rule as suggested by Eq. 38 could be found.

In summary, a simple integral boundary layer analysis suggests various dependencies for the Stanton number as a function of Schmidt Number, Reynolds Number, and dimensionless entry length for the case of power law velocity profiles and wall boundary concentrations.

NOTATION

C_T, C_L, C', C'' = constants
C = concentration
C_o = concentration at transfer surface
C_∞ = concentration far from transfer surface
D = diffusivity
f = dimensionless velocity profile
g = dimensionless concentration function of x
h = dimensionless concentration function of y
k, k_1, k_2 = constants
K = local mass transfer coefficient
N_{Re} = Reynolds Number
N_{Sc} = Schmidt Number
N_{St} = Stanton Number
p = power of velocity power law
r = power law for wall concentration dependency
R = radius of tube
v_x, v_y = x and y components of fluid velocity
V_c = characteristic velocity
V^* = friction velocity
x = coordinate in direction of flow
x^+, x^* = dimensionless distance in direction of flow
y = coordinate perpendicular to flow
y^* = dimensionless distance perpendicular to flow

Greek Symbols

γ = dimensionless local mass transfer rate (Stanton number)
Γ = dimensionless concentration
δ_B = boundary layer thickness
δ^* = dimensionless boundary layer thickness
η = similarity variable
ν = fluid kinematic viscosity
ϵ = integration variable

LITERATURE CITED

Bird, R. B., W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, J. Wiley and Sons, 1960.

Chapman, D. R., and M. W. Rubesin, "Temperature and Velocity Profiles in the Laminar Boundary with Arbitrary Distribution of Surface Temperature," *J. of Aero. Sci.*, **16**, 547 (1949).

Levy, S., "Free Stream Velocity and Wall Temperature Variation," *J. of Aero. Sci.*, **19**, 341 (1952).

Mixon, F. O. and J. J. Carberry, "Diffusion within a Developing Boundary Layer—A Mathematical Solution for Arbitrary Velocity Distribution," *Chem. Eng. Sci.*, **13**, 30 (1960).

Nagendra, H. R. and M. A. Tirunarayanan, "Laminar Film Condensation from Non-isothermal Vertical Flat Plates," *Chem. Eng. Sci.*, **25**, 1073 (1970).

Shaw, D. A. and T. J. Hanratty, "Turbulent Mass Transfer Rates to a Wall for Large Schmidt Numbers," *AIChE J.*, **23**, 28 (1977).

Son, J. S. and T. J. Hanratty, "Limiting Relation for Eddy Diffusivity Coefficient Close to a Wall," *AIChE J.*, **13**, 689 (1967).

Sparrow, E. M. and J. L. Gregg, "Similar Solutions for Free Convection From a Non-isothermal Vertical Plate," *Transactions of ASME*, **80**, 379 (1958).

Verhoff, F. H. and M. K. Choi, Effects of Sulfuric Acid Condensation On Stack Gas Equipment, Preprints of Petroleum Division ACS, p. 562, presented at ACS meeting, Honolulu, Hawaii, April 1979.

Manuscript received October 1, 1979; revision received June 5 and accepted June 19, 1980.

On the Possible Existence of Concentration Stability Effects within a Continuous Well-Mixed Reactor When a Solid Catalyzed Liquid to Gas Reaction Occurs

IAN A. WEBSTER

Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

During recent years, considerable effort has been devoted to the examination of temperature stability effects within chemical reactors (see, for example, Aris, 1975). The field's seminal paper appears to have been that of Van Heerden (1953). Concentration stability effects may also manifest themselves under isothermal operating conditions. For example, Matsuura and Kato (1967) have re-

0001-1541-81-3960-0301-$2.00.

ported on multiple isothermal operating conditions for various types of reactors, whereas Pikios and Luss (1977) theoretically investigated isothermal concentration oscillations on catalytic surfaces. The possibility of encountering nonunique conversion steady states has also attracted attention from biochemical engineers (Bruns et al., 1973), especially when the reactor is operating according to substrate inhibited kinetics (Elnashaie et al., 1977). Recent reviews on reactor stability and oscillation behavior have been furnished by Endo et al. (1978) and Sheintuch and Schmitz (1977).

It appears, however, that the concept that a rapid catalytic decomposition of a liquid to a gaseous product can exhibit concentration stability effects, when conducted within the confines of a CFSTR, has been overlooked. That such multiple concentration operating conditions can exist is due to the fact that the reaction rate vs. liquid reactant concentration plot may exhibit a maximum.

The purpose of this note is to describe such a phenomenon and document a realistic example. The a priori prediction of possible multiple operating conditions are important for reactor start-up purposes.

MASS BALANCE AND EXAMPLE

The graphical technique which we employ to display the existence of multiple steady states has been recently adumbrated by Carberry (1976). The example we use is the decomposition of hydrogen peroxide on a metallic silver catalyst. Satterfield and Audibert (1963) measured the rate of this reaction at increasing H_2O_2 concentrations and discovered it went through a maximum at about 45% w/w H_2O_2 and then decreased. The reason for the maximum is due to vapor blanketing of the catalyst surface by oxygen, which is formed as a gaseous product. At low H_2O_2 concentrations, small oxygen bubbles evolve uniformly over the entire catalyst surface and do not hinder the liquid reactant's contact with the catalyst. The rate at which H_2O_2 decomposes increases with its increasing concentration until a point is reached when the reactant is severely retarded in its attempt to contact the catalyst by the outgoing oxygen bubbles. Any further attempts to increase the decomposition rate by increasing the concentration of H_2O_2 in the liquid phase merely results in depressing the rate.

To consolidate ideas with respect to concentration multiplicity phenomena, consider conducting the liquid phase decomposition of H_2O_2 on silver catalyst within a CFSTR. This reaction is used in rockets and space vehicles as a means of providing auxiliary power or thrust. Physically, such a reactor may assume the form of the spinning basket reactor or recycle reactor with a high recycle ratio (Levenspiel, 1972).

A reactant $[H_2O_2(l)]$ mass balance around a well-mixed reactor yields

$$\frac{\rho_i x_i}{\tau MS} \quad \frac{\rho_i x_i}{\tau MS} = r(x_o) \tag{1}$$

where $r(x_o)$ denotes the reaction rate's dependence on the reactor's composition within the reactor. The solution(s) to Equation (1) may be graphically determined by plotting both the left- and right-hand sides as a function of x_o.

In Figure 1 we reproduce in somewhat modified form the experimental rate data obtained by Audibert (1960)* and reported by Satterfield and Audibert (1963). These data can be thought of as comprising an observed or global rate expression, in that they will be altered by fluid mechanic effects. Audibert's (1960) data were collected in an unstirred batch apparatus, although this is not explicitly stated by Satterfield and Audibert (1963).

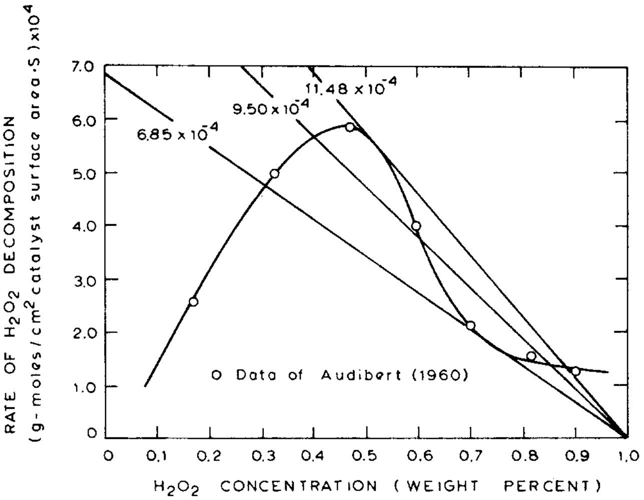

Figure 1. Graphical display of $H_2O_2(l)$ concentration stability effect within a CFSTR. When the curve representative of the rate of $H_2O_2(l)$ decomposition (from Audibert, 1960) on silver catalyst intersects a linear operating line more than once, multiple $H_2O_2(l)$ conversions are possible at the given flow conditions and catalyst size. The numbers on the CFSTR operating lines represent the negative of their gradients. The upper and lower lines represent the bounds for the existence of multiple steady states.

The effect of stirring in a CFSTR would be to disrupt, to some degree, the gas film which blankets the catalyst at high $H_2O_2(l)$ concentrations. With some stirring, the rate curve should still be expected to display a maximum, although different rate curves will prevail, depending on the stirring speed. At extremely high agitation, the observed or global rate should approach the intrinsic rate. While this paper hinges around the applicability of Equation (1), this equation probably holds true at low stirring rates since it only requires that we maintain the liquid bulk concentration uniform. Therefore, at low stirring rates, the rate data of Satterfield and Audibert (1963) and the CFSTR mass balance will be simultaneously applicable.

The data in Figure 1 were obtained for $H_2O_2(l)$ decomposition on the exterior surface of a 0.64 cm O Diameter silver catalyst tube having an exposed length of 0.95 cm. The average bulk liquid temperature was approximately 37°C and did not vary appreciably from run to run, although much higher catalyst surface temperatures were recorded. However, even without stirring, Satterfield and Audibert (1963) never experienced catalyst surface temperatures in excess of the boiling point of the H_2O_2 solution. Thus, the vapor blanketing phenomenon appears to be entirely due to gases evolved during the reaction, and not because of boiling. With a final assumption that none of the silver catalyst dissolves during the course of the reaction and initiates a pseudo homogeneous reaction, the Figure 1 rate data can be taken as being representative of the right-hand side of Equation (1). The left-hand side of Equation (1) is a straight line of slope $-(\rho_o/\tau MS)$ and abscissa intersection of $(x_i\rho_i/\rho_o)$.

Assume we operate our H_2O_2 decomposition CFSTR under the following conditions: $x_i = 0.90$, $\rho_i = 1{\cdot}44$ g/cm^3, $\rho_o = 1{\cdot}30$ g/cm^3, $S = 0.335$ cm^2 of silver catalyst surface area/cm^3 reactant mixture volume and $\tau = 120$ s. These values produce an operating line of slope -9.5×10^{-4} g-moles/cm^2 · s which has an abscissa intersection at unity. In Figure 1 we observe that such an operating line intersects the rate curve in three places, heralding the possibility of three steady operating conditions at effluent H_2O_2 weight fractions of 0.40, 0.61 and 0.85. By the usual

---

*The oxygen values reported by Audibert (1960) were assumed to have been collected at 21°C. This was the temperature used by Sarda (1959) who conducted similar experiments.

arguments, the high and low conversion steady states are both stable, while the intermediate one is unstable.

From Figure 1 it is also clear that with $x_i\rho_i/\rho_o$ set at unity, the multiplicity region extends over the range $6.85 \times 10^{-4} < \rho_o/\tau MS < 11.48 \times 10^{-4}$ g-moles/cm²·s. When the value of $\rho_o/\tau MS$ is such that the CFSTR operates within the multiplicity region, then the ability of the reactor to attain the sought after high conversion steady state depends on the initial conditions and transient response.

In concluding, we have shown in this communication that under certain circumstances, concentration stability effects may exist when a liquid reactant is catalytically decomposed to a gas, within a CFSTR. Our ideas may also be useful in the understanding of electrochemical reactors where gases are commonly evolved in a side reaction (Sakellaropolous and Volintine, 1980).

ACKNOWLEDGMENT

The author acknowledges helpful discussion with Professor Charles N. Satterfield, and financial aid from the Department of Chemical Engineering at Massachusetts Institute of Technology.

NOTATION

M = molecular weight of reactant (H_2O_2)
r = reaction rate (g-mole H_2O_2/cm² catalyst surface area · s)
S = surface area of catalyst per unit volume of reactor (cm²/cm³ total reactant mixture)
x = weight fraction of reactant (H_2O_2)
ρ = density (g/cm³)
τ = CFSTR residence time (s)

Subscripts

i = reactor inlet
o = reactor effluent

LITERATURE CITED

Aris, R., *The Mathematical Theory of Diffusion and Reaction in Permeable Catalysts*, Clarendon Press, Oxford, England (1975).

Audibert, F. P., "Vapor Binding Phenomena in the Decomposition of Concentrated Hydrogen Peroxide on Silver," S.M. thesis, Mass. Inst. Technol., Cambridge (1960).

Bruns, D. D., J. E. Bailey and D. Luss, "Steady State Multiplicity and Stability of Enzymatic Reaction Systems," *Biotechnol. Bioeng.*, **15**, 1131 (1973).

Carberry, J. J., *Chemical and Catalytic Reaction Engineering*, pp. 129-131, McGraw-Hill, New York (1976).

Elnashaie, S. S., A. H. Gaber and M. A. El-Rifai, "Dynamic Analysis of Enzyme Reactors Exhibiting Substrate Inhibition Multiplicity," *Chem. Eng. Sci.*, **32**, 557 (1977).

Endo, I., T. Furusawa and H. Matsuyama, "Stability of Catalytic Reactors: A Critical Review," *Catal. Rev. - Sci. Eng.*, **18**, No. 2, 297 (1978).

van Heerden, C., "Autothermic Processes - Properties and Reactor Design," *Ind. Eng. Chem.*, **45**, 1242 (1953).

Levenspiel, O., *Chemical Reaction Engineering*, 2 ed., pp. 485-486, Wiley, New York (1972).

Matsuura, T., and M. Kato, "Concentration Stability of the Isothermal Reactor," *Chem. Eng. Sci.*, **22**, 171 (1967).

Pikios, C. A., and D. Luss, "Isothermal Concentration Oscillations on Catalytic Surfaces," *ibid.*, **32**, 191 (1977).

Sakellaropoulos, G. P., and B. G. Volintine, "Multiple Steady States in Electrochemical Reactors," *ibid.*, **35**, 396 (1980).

Sarda, P. K., "Catalytic decomposition of Hydrogen Peroxide on Metal Surfaces," Sc.D. thesis, Mass. Inst. Technol., Cambridge (1959).

Satterfield, C. N., and F. P. Audibert, "Nucleate and Film Boiling in the Catalytic Decomposition of Hydrogen Peroxide," *Ind. Eng. Chem. Fundamentals*, **2**, 200 (1963).

Sheintuch, M., and R. A. Schmitz, "Oscillations in Catalytic Reactions," *Catal. Rev. - Sci. Eng.*, **15**, No. 1, 107 (1977).

Manuscript received October 3, 1979; revision received March 3, and accepted March 13, 1980.

A Group Contribution Molecular Model of Liquids and Solutions: II. Groups and Their Interactions in Water and Aqueous Solutions of Paraffins, Ketones, and Alcohols

C. H. CHIEN,
R. A. GREENKORN,
AND
K. C. CHAO

School of Chemical Engineering
Purdue University
West Lafayette, Indiana 47907

INTRODUCTION

Groups are structural units of molecules. There has been a sustained interest in the literature about group contribution to activity coefficients in solutions. This interest stems from the fact that large numbers of molecules are made up of a few groups. Group contribution models, therefore, offer the potential of making wide ranging predictions of numerous molecular systems using the properties of a few groups. Nitta, et al. (1977) developed a molecular model of group contributions for pure liquids and solutions, including heats of mixing and activity coefficients. Properties of four groups (CH_3, CH_2, CO, OH) and their interactions were reported, allowing the model to be applied to liquid paraffins, alcohols, ketones, and their solutions. The equations of the model of Nitta et al. (1977) will not be repeated here.

In this communication we report the description of water and aqueous solutions of non-electrolytes using the model of Nitta et al. (1977). Aqueous systems are characterized by strong hydrogen bonds and highly unusual non-ideal solution properties. The difficulty of their description coupled with their great practical importance present an unparalleled challenge to any molecular model.

Interactions of Water Molecules

The interactions of water molecules are represented in this model in two types: the hydrogen bonds WOH and the cavities CVT.

For each water molecule there are four hydrogen bonds: two through the molecule's "own" hydrogen atoms, and two through

---