COMMUNICATIONS TO THE EDITOR

Intraparticle Pressure Gradients in Porous Catalysts

SEIYA OTANI, NORIAKI WAKAO, and J. M. SMITH
University of California, Davis, California

The effectiveness of the intrapellet surface in porous catalysts has been shown (*4*) to depend only upon pore-diffusion and surface-reaction resistances for reactions with no change in number of moles. For the general gaseous reaction an additional factor may be significant—the change in total pressure with position within the pellet. For example, for an increase in number of moles, the steady state pressure will increase from the outer surface of a spherical pellet toward the center. Previous studies on reaction rates in pores have been limited to cases for which there is no change in number of moles, regardless of the order of the rate equation used for the reaction. However, the existence of pressure gradients was noted by Hoogschagen (*3*) and Wheeler (*6*), and the influence of a pressure gradient upon diffusion, without reaction, has been studied by Evans and co-workers (*2*) and by Wicke and Hugo (*7*).

The purpose of this paper is to consider the effect of a change in number of moles on the pressure within the pore for a simple case, an irreversible first-order reaction, at isothermal and steady state conditions.

The reaction may be written

$$A \rightarrow nB \qquad (1)$$

where the rate per unit of pore surface is

$$r_A = k_s C_A \qquad (2)$$

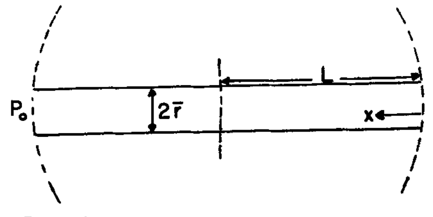

Fig 1. Single-pore model of catalyst pellet.

Equations are presented for the general case in which diffusion occurs by both Knudsen and bulk processes, and hence the diffusion rates are functions of pressure and composition within the pellet. The magnitude of the pressure gradient and its influence on the effectiveness factor can be determined simply when the diffusion is solely of

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Noriaki Wakao is at the University of Tokyo, Tokyo, Japan.

Generalized Peak Heat Flux for Dilute Binary Mixtures

DONALD M. McELIGOT
The University of Arizona, Tucson, Arizona

Boiling of binary mixtures is of particular importance in the chemical process industries. It is also of interest for possible applications to boiling nuclear reactors, where a second component might be added to the primary fluid for metallurgical purposes, and in aerospace engineering for cooling of space probe components during reentry. In these applications it is often only knowledge of the peak heat flux in nucleate boiling q_p'', that is desired by the designer since errors of 50° to 100°F. can be accepted in prediction of the surface temperature.

Experiments by van Wijk, Vos, and von Stralen with small diameter wires yielded peak heat fluxes in excess of that found for either pure component, making the use of binary mixtures seem even more attractive (*1*). The work of Bonilla and Perry (*2*) with a flat heating surface showed comparable results, but the increase was not as striking as in the extreme case noted by van Wijk et al. To date no generalized treatment has been proposed which would adequately predict the variation of q_p'' with respect to mixture composition; the engineer may only use single component correlations evaluated with average properties. In the present paper the author considers a physical analogy between the boiling of binary mixtures and subcooled single component boiling. A correlation is obtained for the significant case of the peak heat flux for dilute binary mixtures.

First, visualize the process physically. For a large volume the liquid depth and transverse dimensions may be considered infinite. As the liquid vaporizes, the mixture in the vicinity of a bubble tends toward being denuded of the component with the lower boiling point. The turbulent mixing action of the bubbles and the effects of mass diffusion act to alleviate this situation; but it is expected that, on a time-averaged basis, a concentration gradient will be produced perpendicular to the surface. This gradient determines the saturation temperature gradient in the liquid, which, in turn, approximates the liquid temperature variation except in close proximity to the heated surface, where it is slightly superheated. For a mixture which is dilute in *B*, the volatile component, it is expected that only component *A* will be present at the heater surface, except at very low heat fluxes. As a bubble rises, with vapor temperature corresponding to the bubble composition, it transfers heat to the cooler surrounding liquid, condensing vapor, until thermal equilibrium is approached. In addition, the concentration difference between vapor and liquid at any height above the heater induces some degree of mass transfer. A steady state is set up and the bubble continues its rise towards the surface. If the volume of the system is large, as hypothesized, the cooler surrounding liquid is expected to be at the saturation temperature of the initial mixture. Thus, the imposed subcooling is the difference between the saturation temperature of component A and the saturation temperature of the initial mixture. Since the bubble does not collapse on or near the surface, the increase in convective heat transfer is less than would be the case for single component subcooled boiling at the same enthalpy difference. The physical analogy is seen to be in the boundary conditions in terms of enthalpy. Other governing equations and conditions are not completely analogous, so a different mathematical solution would be expected.

The simplest idealization, saturated pool boiling from a horizontal surface, was analyzed by nondimensionalizing the governing equations. For this purpose it was assumed that viscous effects, interface velocities, and conduction are negligible, that both phases are incompressible, and that mass diffusivities are constant in the realm of interest. From the equations of continuity, mass continuity for a single component, momentum and energy (all for both phases), and appropriate boundary conditions, one may obtain the following parameters for description of system behavior:

$$\frac{gg_c\sigma(\rho_l-\rho_v)h^4{}_{fg}\rho_v{}^2}{q_p{}''^4}, \frac{\rho_l}{\rho_v},$$

$$\frac{(\mathcal{D}_A{}^4 g)^{1/3}\rho_v}{\sigma g_c}, \frac{g\sigma}{g_c\,\rho_l\,h^2{}_{fg}}, \frac{h_{l,A}-h_{l,o}}{h_{fg}}$$

The first parameter is identical to that derived by Kutateladze in applying the same procedure to single component saturated pool boiling (*3*), while the last is equivalent to $c_p\Delta t_{\text{sub}}/h_{fg}$ when applied to subcooled single component boiling.

As far as the author knows, the only published set of data for binary pool boiling from a horizontal surface is that of Bonilla and Perry in 1941 (*2*). They noticed a difference between organic and aqueous mixtures when considering the variation of q_p'' with respect to concentration, but they were not able to generalize the results beyond comparison to an ideal mixture prediction. The only other flat-plate investigation, that of Bobrovich et al., does not appear to be available (*4*). The extensive data by van Wijk et al., both in reference *1* and later papers, is not deemed applicable; the low values of q_p'' for the single component boiling (for water: about three-fifths of accepted value) and bubble sizes comparable to heater dimensions indicate a different mechanism is controlling the peak heat flux than would be the case for a flat plate. Furthermore, Kutateladze shows a striking difference between flat-plate and fine wire results with binary liquids (*4*). The extensive heat transfer data with a moderate diameter heater by Sternling and Tichacek did not approach q_p'' since they wished to avoid damage to the tube (*5*).

From the data of Bonilla and Perry, the author calculated the above parameters for each experimental point. The values for the diffusion coefficient, $\mathcal{D}_A$, were more uncertain than other properties since in most cases it was necessary to extrapolate from room temperature data. In general, there is a dearth of fluid property information for mixtures near their saturation temperatures; fortunately, Bonilla and Perry measured the viscosity, surface tension, and density of the mixtures at their boiling points. In examining the calculated values, the author found no significant dependence on the parameters

$$\rho_l/\rho_v,\ (\mathcal{D}_A{}^4 g)^{1/3}\rho_v/\sigma g_c \text{ or } g\sigma/g_c\,\rho_l\,h_{fg}{}^2$$

For the range, $0.02 \lesssim (h_{l,A}-h_{l,o})/h_{fg} \lesssim 0.3$, it appears that a correlation of the form

$$\frac{q_p''}{h_{fg}\rho_v{}^{1/2}\,[gg_c\sigma(\rho_l-\rho_v)]^{1/4}} = 0.37\left[\frac{h_{l,A}-h_{l,o}}{h_{fg}}\right]^{1/7}$$

will both describe the behavior for dilute mixtures and provide a limiting relation for others (Figure 1). Use of a fractional power dependence is a matter of convenience; as with most data in this field, a linear form or an exponential form could be applied for a stated range. From inspection of the equilibrium diagrams, one sees agreement with the correlation when the mixture parameter $\dfrac{y-x}{x}$ is approximately unity or greater. Values below 0.7 plot erratically. Thus, this parameter is proposed as defining the dilute regime with respect to the problem investigated.

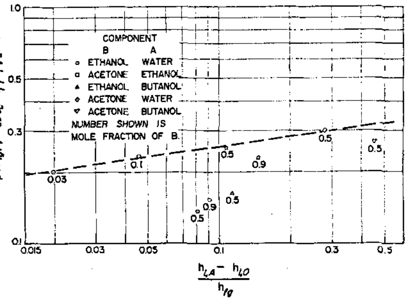

Fig. 1. Saturated pool boiling of binary mixtures. Peak heat flux data of Bonilla and Perry (2).

The author realizes that additional data should be obtained to substantiate the empirical conclusions reached. Single component subcooled data is not expected to yield the same correlation since the bubble behavior after leaving the heater is not the same. However, results from tubular heaters should show comparable trends when the tube diameter is large compared to the bubble size. It is hoped that this note will stimulate such investigations, either with horizontal surfaces or large tubes in the near future.

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NOTATION

c_p = specific heat, B.t.u./lb.$_m$°F.
$\mathcal{D}$ = liquid diffusion coefficient, sq. ft./hr.
g = acceleration of gravity, ft./hr.^{2}
g_c = consistency factor, lb.$_m$ ft./lb.$_f$ hr.^{2}
h = enthalpy; $h_{fg} = h_v - h_l$, B.t.u./lb.$_m$
q'' = heat flux; q_p'', peak heat flux, B.t.u./sq.ft.hr.
t = temperature; t_{sat}, saturation temperature, °F.
x = mole fraction of component B in liquid phase
y = mole fraction of component B in vapor phase
ρ = density, lb.$_m$/cu.ft.
σ = vapor-liquid surface tension of initial liquid concentration, lb.$_f$/ft.

Subscripts

A = higher boiling component
l = liquid
o = initial
v = vapor
w = wall or heated surface

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