pirical techniques are used to good advantage for a very understandable treatment. The number of problems presented is generous.

In addition to analytical treatment of steady and transient conduction, numerical techniques are also presented. For both forced and natural convection, an integral analysis is given, followed by presentations of empirical results. The nature of thermal radiation is discussed and exchange analysis is by the network method. An introduction to two phase heat transfer systems is given in Chapter 9 on condensation and boiling. The treatment is more abbreviated than one would perhaps wish, but serves as a good starting point. Heat exchanger design presents both the log mean temperature difference and the NTU effectiveness methods. The mass transfer chapter (Ch. 11) is far too brief to be effective. Special topics in Chapter 12 give a helpful introduction to several topics and the final chapter on Heat Transfer in the Environment is timely and undoubtedly will provoke student interest.

The primary set of units used is the SI, with conversion tables given to the English units for those of us who still "think" in the old system.

To restate my initial appraisal: this is an excellent, well put together introductory text on heat transfer. I recommend it.

Philip F. Dickson
Colorado School of Mines

Thermochemical Kinetics, 2nd. Ed., Sidney W. Benson, Wiley Interscience, 320 pp., $22.50, New York, 1976.

This book has a subtitle: *Methods for the Estimation of Thermochemical Data and Rate Parameters.* This is more descriptive than the somewhat arcane title and almost directly suggests that the book represents an effort to make accessible to the chemical engineer and the industrial chemist the vast resources of chemical kinetics to predict, understand and control a host of phenomena.

In chemical engineering, group additivity methods have been used for many years to estimate thermochemical quantities dealing with equilibrium systems. Professor Benson has perfected such methods but his originality has been to use these for the estimation of entropies and heat capacities pertaining to the most elusive species of all: those dealing with the so-called activated complex or transition state of chemical kinetics. Many examples are discussed in this book to illustrate the sometimes embarrassing agreement between estimated and experimental quantities. The treatment of S. W. Benson is unique in its scope and it reflects a lifetime of expertise in the field.

Two limitations must be mentioned. First, the treatment is limited to ideal gas phase reactions excluding specifically all reactions with ionic or adsorbed intermediates. Of course, the wealth of processes covered is nonetheless impressive: oxidation, combustion, atmospheric and stratospheric chemistry, pyrolysis etc. The second limitation is more serious: the methods described do not apply to the estimation of activation energies. For the calculation of the latter, Benson and Alfassi have proposed some special semi-empirical rules, the generality of which remains to be tested.

Perhaps the success of this book which amply deserves this second edition, is that its author is not primarily an applied kineticist but a leading theoretical one whose previous work *Foundations of Chemical Kinetics* has been a lasting monument since 1960. This being said, it seems entirely fair to this reviewer to point out an error on page 2 of the present book. For a reaction with a general stoichiometric equation, it is not generally correct to state [eqn. (1.3)] that the ratio of rate constants forward and reverse is equal to the equilibrium constant for the reaction. This was already pointed out years ago by several authors including Denbigh in his classical book on Thermodynamics and discussed again recently [M. Boudart, *J. Phys. Chem.*, **80,** 2869 (1976)].

In spite of this venial sin, Professor Benson's little book is too valuable to be left on library shelves: it belongs to the desk of anyone dealing with thermodynamics or kinetics and who doesn't?

M. Boudart
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LETTERS TO THE EDITOR

To the Editor:

In a recent article LeVan and Newman [*AIChE J.*, **22,** 695 (1976)] are critical of boundary layer methods [D. A. Saville, *Chem. Eng. J.*, **5,** 251 (1973); J. F. Harper, *Q. J. Mech. Appl. Math.*, **27,** 89 (1974)] when applied to estimate the distribution of soluble surfactant in the interface around a small gas bubble rising through a liquid. Here the distribution of surfactant fixes the variation of interfacial tension around the periphery and the resultant change in stress changes the terminal velocity of the bubble.

Since boundary layer solutions for problems of this sort are asymptotic representations, the question is mainly one of deciding whether or not the Peclet number is large enough for the desired accuracy. LeVan and Newman used a numerical method to solve the full conservation equation for a Peclet number of 60 and found that the terminal velocity of a small bubble is lower than the Hadamard-Rybczynski velocity by an amount $\kappa C_\infty U_0$. Here C_∞ is the surfactant concentration far from the bubble, U_0 is the Hadamard-Rybczynski velocity and κ is a numerical factor, 1.9×10^8 cm^3/g-mole according to their numerical solution. Boundary layer theory gives precisely the same functional form and κ, calculated using Eq. 16 of Saville (1973), turns out to be 2.1×10^8 cm^3/g-mole.

It is true, as pointed out by LeVan and Newman, that a boundary layer model neglects (in the first approximation) diffusion in the θ-direction along and near the surface. However, the qualitative features of the concentration field are very similar to those predicted by the full numerical solution except near the rear stagnation point. There, although the boundary layer solution exhibits weakly singular character, the fact that the singularity is integrable [Harper (1974)] means that the total drag can still be calculated accurately.

Upon comparing the numerical solution given by LeVan and Newman with the results obtained by boundary layer methods I conclude that the latter still offer a reasonably accurate picture even at Peclet numbers as low as 60.

D. A. Saville
Department of Chemical Engineering
Princeton University

Reply

We derived equations in our paper for the terminal and interfacial velocities of a bubble or drop with an arbitrary surface tension gradient at its interface. The boundary layer approach to diffusion, which could have been used in an example problem to calculate a distribution of surfactant at the interface of a freely circulating bubble, was mentioned only in the context that its use "would not result in reasonable *interfacial* velocities."

A profile of interfacial surfactant concentration obtained by the boundary layer method for a freely circulating bubble or drop is not consistent with the fluid mechanic problem. Our argument is based on analysis of two boundary conditions. The first is the tangential force balance:

$$\frac{1}{R}\frac{d\sigma}{d\theta} = \tau_{r\theta} - \hat{\tau}_{r\theta} \text{ at the interface.}$$

Here R is the radius of the bubble or drop, $d\sigma/d\theta$ is the surface tension gradient, and $\tau_{r\theta}$ and $\hat{\tau}_{r\theta}$ are the tangential shear stresses in the outer and inner fluids respectively. The second is a boundary condition on the diffusion equation:

$$\frac{\partial c}{\partial \theta} = 0 \text{ along the rear axis.}$$

Because of the neglect of diffusion in the θ-direction, the second boundary condition is not satisfied by a boundary layer solution. As a result, the surface tension gradient at the rear stagnation point is not equal to zero. In reality, however, it must be zero because both of the shear stresses in the tangential force balance are zero.

Our series solution for the interfacial velocity was derived using the tangential force balance as a boundary condition. If a surface tension gradient which is not consistent with this boundary condition is substituted into the series, reasonable results are not obtained. In fact, if the surface tension gradient at the rear stagnation point is not equal to zero, the series will not converge. (This point can be deduced from Equations 24, 26, and 29 of our paper.)

In his letter Saville writes that compared to a solution of the full convective diffusion equation, boundary layer theory gives precisely the same functional form for the terminal velocity of a bubble. Actually, this functional form is independent of the rate model adopted. It is obtained from fluid mechanic results and surface chemistry assumptions, as shown in our paper. For example, the same functional form would also be obtained if either surface diffusion or adsorption kinetics were the dominant mechanism controlling the distribution of surfactant.

M. Douglas LeVan
Amoco Production Company

John Newman
University of California, Berkeley

To the Editor:

In a recent paper [*AIChE J.*, **23** (1), 10-16 (1977)] S. W. Churchill employs a regression parameter, *n*, for estimating the combined effect of free and forced convection on heat transfer rates in the laminar flow regime via the relationship (Eq. 9)

$$[Nu/Nu_N]^n = 1 + [Nu_F/Nu_N]^n \quad (1)$$

and proposes that its generalized form (Eq. 10, etc . . .) is ". . . presumed to be valid for component transfer . . . although confirmatory data are not available."

In recent publications Mohanta and Fahidy [*Electrochim. Acta*, **21**, 143-147; 149-152 (1976)] have shown that using experimental limiting current density data in electrochemical mass transfer systems, the relative importance of the two modes may be estimated via an interaction parameter:

$$[i/i_N]^{1/n} = 1 + [i_F/i_N]^{1/n} \quad (2)$$

Eq. 2 is isomorphic to Churchill's equation except that the two parameters "*n*" are reciprocal to each other. For ionic mass transfer in open channel flow our range, $2/3 < n < 2$ corresponds to $1/2 < n < 3/2$ in Churchill's relationship, whereas for magnetoelectrolysis our range, $1/3 < n < 3/4$ corresponds to $4/3 < n < 3$ in Eq. 1. Thus, the parameter "*n*" concept for combined free and forced convection has, indeed, experimental justification in the analysis of mass transfer, at least in the quoted surface/flow configurations.

T. Z. Fahidy
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Reply

This confirmation of the utility of Equation (9), in my article [*AIChE* Journal **23**, 10-16 (1977)], for the correlation of data for combined free and forced convection in electrochemical and magnetoelectrical systems is indeed welcome. I regret that this work of Professor Fahidy was not available to me when the manuscript was prepared.

Stuart W. Churchill
Department of Chemical and
Biochemical Engineering
University of Pennsylvania

To the Editor:

McDuffies' paper "Vortex Free Downflow in Vertical Drains" [*AIChE J.*, **23**, 37 (1977)] provides neat design equations for the critical conditions for which supernatent fluid will be drawn into the bottom outflow pipe of a cylindrical tank with its axis vertical. It seems advantageous to quote, at the same time, the similar critical conditions for a cylindrical tank with its axis horizontal. The designer then has equations for his two most important systems.

The problem was dealt with by Gardner and Crow (1971) and Gardner, Crow and Neller (1973). It was shown that, at larger liquid levels, the flow of water is restricted under critical conditions by its ability to flow along the base of the vessel to the outflow. The restriction is of similar kind to that for a broad-crested weir. An empirical fit to the numerical solution of the theoretical equations gives

$$N = \left[\frac{\rho Q^2}{\Delta\rho g R^5}\right]^{1/2} = 0.619\left(\frac{h_c}{R}\right)^{1.94} \quad (1)$$

which is valid in the range of (h_c/R) from 10^{-2} to unity. h_c is the liquid level far from the outflow, R is the radius of the cylinder, Q is the flowrate to one side of the outflow, ρ is the liquid density, $\Delta\rho$ is the density difference between phases and g is acceleration due to gravity.

It should be added that equation (1) is valid for the case where there is a steady state, with liquid being added to the vessel normal to the liquid interface.

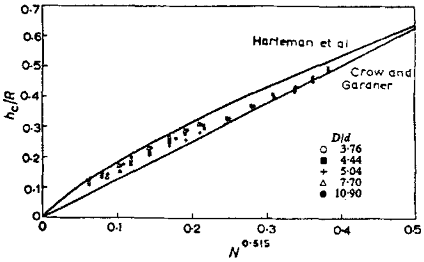

Fig. 1. Critical conditions compared with theory.

Fig. 1 shows experimental results obtained with a wide range of flowrates and of the ratio of the vessel diameter D to the outflow diameter d. It is clear that Gardner and Crow's relation fits the results for $(h_c/R) > 0.23$ but that there is a trend towards Harleman, Morgan and Purple's relation for smaller values of (h_c/R). This is not unexpected since the flow pattern towards the outflow might be expected to become more axisymmetric with respect to outflow at low liquid levels. It is noted that the outflow diameter does not appear to be a significant parameter.

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LITERATURE CITED

Gardner, G. C. and I. G. Crow, "Onset of Drawdown of Supernatent Fluid in Surge Tanks," *Chem. Engng. Sci.*, **26**, 211 (1971).

Gardner, G. C., I. G. Crow, and P. H. Neller, "Carryunder Performance of Drums in High Pressure Circulation Boilers," *Pro. Inst. Mech. Engrs.*, **187**, 207 (1973).

Reply:

Gardner's letter provides quite a fitting supplement to my paper. It might be concluded from his letter and related references for drains of cylindrical tanks with horizontal axes that there are two downflow regimes for H/D ratios above those producing simple weir flow (D = drain diameter). The first of these is for the lower range of H/D values. It is one in which the controlling flow is in the drain itself. The second is for the higher range of H/D values (and Froude numbers). There the flow is limited to a maximum critical horizontal Froude number, $Fr_c' = V/\sqrt{g'h} = 1.0$, where h is the height of the liquid in the horizontal flow channel.

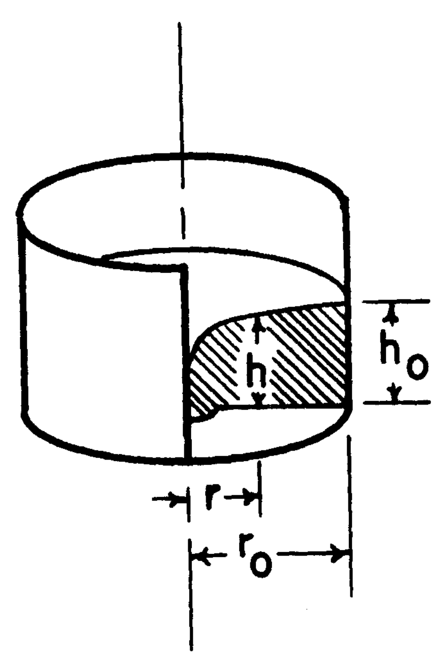

Fig. 1. Downflow system for cylindrical tank with vertical axis.

It can be shown that a critical horizontal Froude number also exists for radial inflow at the base of a cylindrical tank with a vertical axis as well (see Figure 1). At any radius, r, the total head, H_T, is

$$H_T = \frac{V^2}{2g'} + h \qquad (1)$$

where V is the radial fluid velocity toward the axis of the cylinder. At a critical maximum horizontal Froude number, $Fr_c' = V/\sqrt{g'h} = 1.0$, the situation is such that inflow to a smaller radius must be accompanied by an increase in liquid height, h. It follows that, for the general case of horizontal inflow, at any radius, r,

$$\frac{3}{2} h_o \geq h \geq \frac{2}{3} h_o \qquad (2)$$

assuming that V can have nonzero values at $r = r_o$ and that the horizontal Froude number at this boundary is equal to, or less than the critical value of 1.0. If this condition of choked horizontal inflow occurs at the edge of the drain, where $r = D/2$, the maximum superficial Froude number within the drain is given by the relationship,

$$Fr = \frac{V}{\sqrt{g'D}} = 4.0\left(\frac{h}{D}\right)^{1.5} \qquad (3)$$

This equation fits my data at drain Froude numbers above 4.0 better than the Kalinske, or the Harleman equation. The concept of a choked horizontal flow condition can also be invoked to explain the fact that in my experiments the liquid downflow rate could not be increased beyond a given value at any one liquid height, even with increasing vessel pressure and air flow rate through the drain. With the incorporation of this third type of flow limit the equations best fitting my data are:

Flow Type	H/D	Equation
Weir	$\frac{H}{D} \leq 0.4$	$Fr = 2.36(H/D)^{1.5}$ (Souders)
Drain Limited	$0.4 < \frac{H}{D} \leq 1.0$	$Fr = 4.28(H/D)^2$ (Kalinske)
Choked Horizontal Radial Inflow	$1.0 < \frac{H}{D}$	$Fr = 4.0(H/D)^{1.5}$

where $H = h$ at $r = D/2$. I would not recommend any revision of the design equations suggested in my paper to fit this three-regime concept. The complexity is not justified for design.

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Errata

In "A Simple Method for Safety Factor Evaluation" by Ygàl Volkman [*AIChE J.*, **23**, 203-20 (1977)], the illustration for Figure 2 should appear as follows:

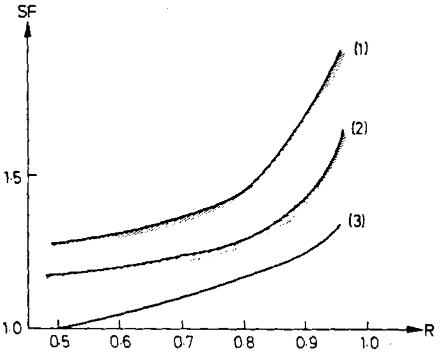

Fig. 2. Sample calculations of safety factors: ($\sigma_c/\overline{c} = 0.2$).
(1) General (bound)
(2) Unimodal symmetrical (bound)
(3) Normal distribution

In "A Generalized Expression for the Effectiveness Factor of Porous Catalyst Pellets," [*AIChE J.*, **23**, 208-210 (1977)] by S. W. Churchill, a factor of τ_1 is missing from an entry in both Tables 1 and 2 and $2\tau_1^*$ from an entry in Table 1. These entries under *Infinite Cylinders* should read

(after η): $2I_1\{\tau_1\}/\tau_1 I_o\{\tau_1\}$
and $I_1\{2\tau_1^*\}/\tau_1^* I_o\{2\tau_1^*\}$

$$\left(\text{after}\,\frac{1}{\eta}\right):\ \frac{\tau_1^2}{2Bi} + \frac{\tau_1 I_o\{\tau_1\}}{2I_1\{\tau_1\}}$$

This error does not influence the balance of the paper.

The second term on the left side of Equation (6) should read $(C_s/C_b)_\infty$ and the second term from the right of Equation (7) should read $k_c(C_b - C_s)/s$.

It should have been noted that the results of this paper can also be interpreted as the effectiveness factor for heat transfer by fins and spines.