LETTERS TO THE EDITOR

LETTER TO THE EDITOR: MISUSE OF YOUNG-DUPRE EQUATION

If a sessile drop of liquid resting on a solid surface at a condition of thermodynamic equilibrium has a contact angle θ as shown in Figure 1, then surface tensions of the three interfaces are related by the Young-Dupré equation (Adamson, 1967):

$$\sigma_{LV} \cos\theta = (\sigma_{SV} - \sigma_{SL}) \qquad (1)$$

Surface tension of the liquid-vapor interface (σ_{LV}) may be measured by a variety of methods. Contact angle (θ) is directly observable. Unfortunately there is no way to measure either σ_{SV} or σ_{SL}. In fact, it is not even clear what the structure of the solid-vapor interface might be. Is it clean, solid surface? Or is it solid surface covered by a monolayer of liquid, or perhaps several layers? The answer is related to the fact that a surface over which a liquid is advancing is often different from that of the same surface after a drop has passed over it. Since the quantities on the right-hand side of Equation (1) cannot be measured, one can only say that the difference ($\sigma_{SV} - \sigma_{SL}$) is defined by Equation (1). It follows that there is no way to prove or disprove Equation (1) and this has led many to the conclusion that Equation (1) is not very useful.

If Equation (1) for a binary mixture is differentiated with respect to activity of one species (a_1), an application of Gibbs' equation yields an equation of the form (Boyes and Ponter, 1972):

$$\frac{d\theta}{da_1} = f\,[\sigma_{LV}, \theta, \Gamma_{LV}, \Gamma_{SV}, \Gamma_{SL}] \qquad (2)$$

where Γ is surface excess per unit area. In a recent paper Boyes and Ponter (1972) tried to use Equation (2) to explain their experimental data on contact angle (θ) as a function of concentration in the liquid. It should be apparent that it is impossible, either in principle or in practice, to do this. Equation (2) does not give the variation of contact angle with concentration because Γ_{SV} and Γ_{SL} are undefined, for the same reason that σ_{SV} and σ_{SL} are undefined. Therefore, the reasoning of Boyes and Ponter (1972) is invalid.

LITERATURE CITED

Adamson, A. W., *Physical Chemistry of Surfaces,* 2nd Edit., p. 353, Interscience, New York (1967).

Boyes, A. P., and A. B. Ponter, "The Wetting Behavior of Azeotropic Systems at Atmospheric and Reduced Pressures," *AIChE J.*, 18, 935 (1972).

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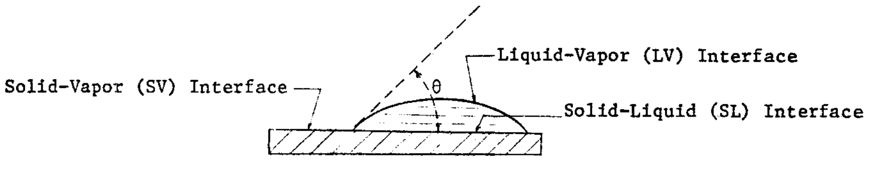

Fig. 1. Drop of liquid on solid surface.

TO THE EDITOR

Contact angles were measured on both polytetrafluoroethylene and copper surfaces under distillation conditions. At near-terminal compositions it was noted that an inflexion occurred with concentration increase in the copper experiments which was absent when using polytetrafluoroethylene. Professor Myers asks if the solid surface is covered or not with a monolayer of liquid or perhaps several layers and questions the usefulness of the Young-Dupré equation here.

With polytetrafluoroethylene it has been shown by a number of workers that no adsorption of vapor takes place although this is not the case for the high energy surface. Therefore, a change in liquid concentration will not affect σ_{sv} using the polymer although it will for the other surface considered. This difference in behavior has been used to explain qualitatively the form of the contact angle-concentration curves obtained employing the two equations presented in the paper.

There is no inconsistency.

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TO THE EDITOR:

In their comments on our paper (Rieke and Pigford, 1971), Garcia, Grace, and Clift (1973) have expressed disagreement with two of our conclusions:

1. Our experimental evidence from photographs of rising bubbles containing colored tracer gas indicates that the bubble roofs were continually collapsing, leading to release of gas from the particulate phase above into the bubble cavities.
2. The observed rapid increase of a wake region, composed of solid particles and tracer gas below each bubble, indicated that tracer gas did not return to the bubble by upward flow through the bubble's base.

The potential flow theory on which they base their criticisms has two main steps: the computation of the particle velocities corresponding to assumed potential flow around a spherical cavity and the computation of fluid velocities past the solid particles from the pressure gradients. There is no doubt that the theory is confirmed by some of the evidence, notably the approximate agreement between observed and calculated bubble rising velocities. But the point on which we intended to express some doubt about the theory concerns the estimates of the rates of leakage of tracer gas from bubbles into the particulate phase around them and, particularly, the conclusion in the theory that gas flows into the bases of bubbles at the same rate at which it leaks out. Garcia et al. believe that our observations of rapid accumulation of tracer gas in the wake region behind a bubble can be accounted for by the shedding of tracer from the outer edge of our thin tracer clouds in the particulate phase above our bubbles; we believe that it can be accounted for by the continual release of solid particles from the unstable roof of a bubble, leading to addition of interstitial gas to the bubble at the top and entrapment of bubble-cavity gas at the floor.

Thus, there are alternative explanations of bubble behavior, each acceptable, we think, on the basis of presently available evidence.

Garcia, Grace, and Clift (1973) refer to their own observations of upward gas velocities inside bubbles using very light solid particles inside a fluid bed composed mainly of coal particles four to six times larger than our glass beads. Their observations are contrary to our own conclusion that, for our smaller glass beads, the direction of net gas flow probably was downward, with a rather large uncertainty which we reported. Our calculated downward flow rate came from a material balance which we believe is valid. We suggested that one way to account for the rapid growth of tracerfilled gas volume below each bubble, exceeding the flow rate down the bubble's sides, is to assume that there was entrapment of gas at the floor between solid particles that land there. Garcia et al. believe instead that the observed accumulation rates come entirely from diffusive shedding of tracer from the theoretical cylindrical cloud of gas outside each bubble. As we pointed out, our numerical results agreed approximately with the theoretical expectation. We think that either point of view about the rate of loss can be taken on the basis of the available data. The unsettled question seems to us to be whether tracer gas returns to a bubble or not.

Garcia et al. criticize our conclusions about solid volumetric flow rates which we derived from a similar material balance. They are correct in their assertion that we did not evaluate the contribution in this balance from solid particles which cross the tracer-gas streamline enclosing the wake region. The potential flow theory is clearly invalid for the base region below the flat floor of a bubble and there are no particle velocities available for making such estimates. Their direction is known, however. Because of the vertical pressure gradient in our bed, the gas tends to flow upward about 1.3 in/s faster than the solid. If such a downward flux of solid had been included in the balance for our wake regions, the derived value of the downward flow of solids onto the floor of our typical bubble would have been even greater than the value we reported.

We believe, finally, that the potential flow theory is supported by much of the available evidence but we continue to believe, as we stated, that conclusions from it about the mechanism by which tracer gas is lost from bubbles and whether tracer gas returns may be wrong.

LITERATURE CITED

1. Garcia, A., J. R. Grace, and R. Clift, "Behavior of Gas Bubbles in Fluidized Beds," *AIChE J.*, **19**, 369 (1973).
2. Rieke, R. D., and R. L. Pigford, "Behavior of Gas Bubbles in Fluidized Beds," *AIChE J.*, **17**, 1096 (1971).

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TO THE EDITOR

In a recent issue of this Journal, Angus, Edwards and Dunning (1) presented a helpful discussion of signal broadening in laser doppler velocimeters. In the Appendix to that paper they add an analysis of the beam in the region of the geometrical focus.

Additional diagrams of intensity for truncated gaussian beams that may be helpful to the reader are contained in the following article:

"Design of Optical Systems for use With Laser Beams" by Daphne J. Innes and Arnold L. Bloom published as the Spectra-Physics Laser Technical Bulletin Number 5, Mountain View, California.

LITERATURE CITED

Angus, John C., Robert V. Edwards, and John W. Dunning, Jr., "Signal Broadening in the Laser Doppler Velocimeter," *AIChE J.*, **17**, 1509 (1971).

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BOOKS (continued from page 414)

Europe and, likewise, industrial and academic professionals. Future International Symposia (such as that held in Amsterdam in May, 1972, and that to be held in Chicago in 1974) will also have state-of-the-art reviews. In summary, the book contains "chemical reaction engineering 1970" as it is seen by a wide range of experts in the field.

Thus, this book should be a very useful consolidation of the recent progress in chemical reaction engineering. The research contributions indicate the current directions of research and serve to alert both investigators and users to the next problems that will be attached and hopefully be solved.

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Editor's Note: Professor Bischoff was the chairman for this First International Symposium and, since the subject area was so broad, it was felt that he could best present a summary of the objectives of the symposium as well as to review its contents.

Guide for Safety in the Chemical Laboratory, Manufacturing Chemists Association, Van Nostrand Reinhold, New York (1972). $17.50.

This book provides the chemical laboratory supervisor with a practical guide for controlling laboratory safety problems.

Information on safety storing, handling, and disposing of chemicals in a laboratory is given. You might say that the coverage is weak because all details are not given. On the other hand, the coverage is strong in that the most frequently occurring accidents are treated and up-to-date references are given for follow-up details. This is as it should be so that the reader can personalize his own action for his particular circumstances.

The book provides safety guidelines for scale-up from the laboratory bench to the pilot plant that are not readily available elsewhere.

This book should be a welcome addition on safety designs and practices for all personnel involved in chemical laboratory operation.

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