needle and a 3-ml syringe. The needle with syringe is heparinized in the usual fashion. The syringe and needle are then separated and arterial puncture is performed with the butterfly needle. When the artery has been entered, blood will be seen to pulsate up the plastic tubing. When a vein has been punctured, the blood will gradually flow up the tubing. When entry into the artery is ascertained, the syringe is connected to the butterfly needle and the sample is aspirated.

In addition to assuring arterial puncture, the "butterfly" method has two other advantages over the standard approach. With the butterfly needle, small-gauge needles may be used (the smallest needle we have used has been a 25-gauge butterfly needle). In addition, a three-way stopcock can be attached to the

end of the butterfly needle easily, allowing for more blood to be sampled once the blood sample for gas analysis has been obtained.

J. LANCE LICHTOR, M.D.
Resident in Anesthesia

CHRISTINE A. ODELL, M.D.
Resident in Pediatrics

*University of Colorado Medical Center
Denver, Colorado 80262*

REFERENCE

1. Scamman FC: Percutaneous sample for blood-gas analysis: Arterial or venous blood? ANESTHESIOLOGY 51:474, 1979

*p*H Average Rebuttal

To the Editor: — In the recent dispute on the averaging of *p*H values, Giesecke[1] maintained that the average *p*H values should be obtained by first changing the *p*H to the real number by taking the antilog of the negative *p*H value, averaging, then converting back to *p*H by taking the logarithm. He presented an "experimental proof" for the above procedure by measuring the *p*H value of a mixture of equal amounts of five unbuffered solutions whose *p*H values were adjusted to 2.045, 3.114, 4.132, 5.192, and 6.063 by the addition of hydrochloric acid. The *p*H value of the mixture was 2.758, which did not fit the direct arithmetic mean of *p*H 4.109, while the antilog mean showed a perfect fit.

Unfortunately, his experimental design does not address the question to the problem of averaging *p*H. It also ignores the buffer action, as well as the effect of the ionic strength upon the *p*H, not to mention the fact that the *p*H of unbuffered solution has little meaning because it scatters a great deal and the accurate measurement of *p*H of pure water is next to impossible. Before going into the theoretical detail, the following experiment may be most informative for the present argument.

We carefully duplicated his experiment, only replacing hydrochloric acid with sodium hydroxide. With triply distilled water, we prepared each 100-ml solution of *p*H 5.85, 8.81, 9.87, 10.89, and 11.95. The *p*H 5.85 solution was obtained by simply exposing distilled water to air. We mixed 25-ml volumes of all solutions, and measured the *p*H of the mixture by a

combination glass electrode and a Beckman *p*H meter. The resulting *p*H was 11.21.

According to the proposed antilog method, the mean *p*H should be 6.55, and the direct arithmetic mean gives a value of *p*H 9.48. The measured *p*H was not even near the antilog-averaged value or the directly averaged value. This is because the experiment is completely irrelevant to the *p*H average, and is essentially a titration of unbuffered water with acid or base, a meaningless procedure.

What Giesecke has observed (and we have repeated) is partly the effect of dilution of the ionic strength upon the *p*H of a buffer. Dilution of an acidic buffer shifts the *p*H to a higher value (his experiment), and that of an alkaline buffer shifts the *p*H to a lower value (our experiment) (see Appendix). Conversely, addition of a neutral salts such as sodium chloride shifts the *p*H of an acidic buffer to a lower value and the *p*H of an alkaline buffer to a higher value. Here, we refer to hydrochloric acid as a buffer because at the lower *p*H it exists partly in the conjugate form.

These effects occur due to the dependence of the activity coefficient, γ, of an ion on the ionic strength of the solution according to the Debye-Hückel theory (see Appendix).

Disregard of the buffer activity in the above-described experiments is obvious when one considers mixing of a highly buffered solution, say 1 M phosphate buffer, *p*H 6.8, and unbuffered water made acidic by the addition of hydrochloric acid, say to

pH 4.0. The pH of the mixed solution should be close to 6.8 due to the strong buffering action of the phosphate. The pH of a mixed solution can be any value, according to the buffering capacity of each mixing component, and the mathematical average has no relevance to the pH of the mixed solution.

Our view of the thermodynamics of pH and the derived hydrogen ion concentration has already been expressed.[2] Apparently, his error in the experimental design was caused by confusing acidity expressed by the chemical potential and that expressed by the titration.

From the equations in the Appendix, it follows that a decrease of the ionic strength of an acidic buffer increases the pH, while that of an alkaline buffer decreases it, and an increase of the ionic strength works in the opposite way.

HIROSHI KAMAYA, M.D., PH.D.
TAKASHI MASHIMO, M.D.
ISSAKU UEDA, M.D., PH.D.
Department of Anesthesia
University of Utah College of Medicine
Salt Lake City, Utah 84132

REFERENCES

1. GIESECKE AH Jr: Averaging pH *vs.* H^{+} values. In reply. ANESTHESIOLOGY 51:482–483, 1979
2. UEDA I, EYRING H: Hydrogen ion concentration *vs* pH. Anesth Analg (Cleve), 58:487–491, 1979
3. PERRIN DD, DEMPSEY B: Buffers for pH and Metal Ion Control. New York, John Wiley and Sons, 1974

APPENDIX

The concentration (c) of an ion is related to the activity (a) by the activity coefficient (γ)

$$a = \gamma c$$

and the value of γ varies depending upon, among other factors, the ionic strength of the solution.

The ionic strength (I) of a solution is given by

$$I = \tfrac{1}{2} \cdot \Sigma(c_i z^2)$$

where the subscript i refers to the i-th component and z is the valence of the ion.

An approximate form of the Debye-Hückel equation (see, for instance, a textbook by Perrin and Dempsey[3]) in *dilute solutions* gives the following relationship. (Theory for a condensed solution is yet to be formulated).

$$-\log \gamma = Kz^2 I^{1/2}/(1 + I^{1/2}) - 0.1z^2 I$$

where K is a constant that depends only on the temperature.

The approximate generalized equation for a buffer solution is given[3] as follows.
For an acidic buffer

$$p\mathrm{H} = p\mathrm{K_a} + \log \,[\mathrm{H_{n-1}A^{(x+1)-}}]/[\mathrm{H_nA^{x-}}] - (2x + 1)KI^{1/2}/(1 + I^{1/2}) + 0.1(2x + 1)$$

For an alkaline buffer

$$p\mathrm{H} = p\mathrm{K_a} - \log \,[\mathrm{H_{n+1}B^{(x+1)+}}]/[\mathrm{H_nB^{x+}}] + (2x + 1)KI^{1/2}/(1 + I^{1/2}) - 0.1(2x + 1)$$

where $\mathrm{H_nA^{x-}}$ and $\mathrm{H_nB^{x+}}$ are acidic and basic buffer, respectively, and n and x are integer values. The expressions x+ and x− refer to the numbers of positive and negative charges, respectively, carried by the HB and HA ions.

Pulmonary Aspiration Following Antacid Therapy

To the Editor:—Two articles concerning aspiration pneumonitis appeared in the November 1979 issue of ANESTHESIOLOGY.[1,2] The first described a study in dogs in which the antacid Kolantyl Gel® was instilled into the mainstem bronchi, demonstrating a more prolonged pulmonary reaction than occurred after instillation of hydrochloric acid. The second was a report of a case of pulmonary aspiration of gastric contents rendered nonacid (pH 6.4) by prior ingestion of the antacid Riopan®; the patient had hypoxemia for 72 hours, with pulmonary infiltrates visible on chest x-ray for approximately seven days. Despite disclaimers to the contrary in both articles, one is left with the message that pulmonary