Generally speaking, redefinition of terms is unwise in my opinion. I have therefore cast about for a suitable word. The Greek  $\kappa_{OUVOS}$  (common) comes to mind, since its primary meaning is "shared in common." The angles mentioned above are common to various crystal species.

My colleague, Raymond Harriman, of the Classics Department, called my attention to the fact that in using the expression "cenogonal angle" one is repeating the idea of angle, since  $\gamma_{00}\nu_{i\alpha}$  is the Greek word for angle, but in spite of this, the term seems the best one available.

Cenogonal angles include the angles in the tetragonal zone [001] of the tetragonal system as well as the angles in the hexagonal zone  $[00-1]^3$  of the hexagonal system and all the angles between the faces of crystals in any of the zones of the isometric system. In Dana's *System of mineralogy* (6th ed., 1892) a fairly complete list of these angles may be found (pp. xx-xxvi). It should be emphasized that cenogonal angles are predictable; that is, they may be calculated in advance of any knowledge of the axial ratio. The use of a special term such as "cenogonal" emphasizes the importance of the predictable angles.

I wish to acknowledge my indebtedness to my colleagues, Harry Caplin, J. D. H. Donnay, H. F. Fränkel, S. A. Francis, R. D. Harriman, Philip Harsh, Stanley Herold, R. F. Jones, Louis H. Kanter, Lionel Pearson, K. C. Peer, G. Polya, and Julian Smith, for the opportunity of discussing various terms.

Stanford University

AUSTIN F. ROGERS

## Criticism of a Definition of pH

The following definition has appeared in a long series of editions of the Chemical Rubber Publishing Company's Handbook of chemistry and physics: "Hydrogen ion concentration or pH value is the logarithm of the reciprocal of the gram ionic hydrogen equivalents per liter; i.e.,  $pH = log \frac{1}{(H^+)}$  per liter." Thus, it would appear that pH is the negative logarithm of pH, like the man in the popular song who was his own grandfather. Several times I have called the attention of the editor of the Handbook to this error, but so far without result.

The relation,  $pH = -\log (H^+)$ , in which  $(H^+)$  is the hydrogen ion concentration, as given by Sorensen in 1909,

<sup>3</sup> In zones of the hexagonal system the writer prefers the method of omitting the third index.

represented the prevailing ideas sufficiently well at that time. Since then the meaning and the calibration of the pH scale have received both theoretical and experimental attention with the result that quite a number of papers have accumulated on the subject (Cohn, Heyroth, and Menkin. J. Amer. chem. Soc., 1928, 50, 696; Guggenheim and Schlinder. J. phys. Chem., 1934, 38, 533; Hitchcock and Taylor. J. Amer. chem. Soc., 1937, 59, 1812; MacInnes, Belcher, and Shedlovsky. J. Amer. chem. Soc., 1938, 60, 1094; R. G. Bates. Chem. Rev., 1948, 42, 1; etc.). In possibly all but one case in a thousand it is not necessary to consider the meaning of pH in terms of solution theory at all, but only to accept the numbers as a practical scale of acidity and alkalinity.

From an operational point of view, pH values are the result of measurements of the potentials, E, of galvanic cells of the type:  $(Pt)H_2$ ; solution X : sat'd KCl; reference electrode with the aid of the equation,

$$pH = \frac{E - E_0}{2.306 \text{ RT/F}}$$

Here "solution X" is the fluid whose pH is desired,  $E_0$  is a constant depending upon the nature of the reference electrode and the temperature, and R, T, and F are the gas constant, the absolute temperature, and the faraday, respectively. For most purposes, therefore, it is only necessary to agree on values of the constant  $E_0$ . However, studies have been made leading to closely agreeing values of this constant at a series of temperatures such that, if the pH measurements are interpreted in terms of thermodynamic ionization constants, no serious errors will be made.

According to present theories of electrolytes, there is no simple relation between the hydrogen ion concentration and the pH value of a solution. The relation  $pH = -\log (H^+)$  is an approximation only, and using it as a definition may lead to serious errors. The expression  $pH = -\log a_{H^+}$ , in which  $a_{H^+}$  is the activity of the hydrogen ion, is also open to objection, since the activity of a single ion species is not an operational concept.

It is the author's rather forlorn hope that compilers of handbooks and authors of textbooks will someday indicate that the expression  $pH = -\log (H^+)$  is not a definition and that it may be, in some cases, only a very rough approximation.

D. A. MACINNES

Laboratories of the Rockefeller Institute for Medical Research, New York City

