determination of pH

THEORY AND PRACTICE

SECOND EDITION

Roger G. Bates,

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preface

When Sørensen defined the pH unit and outlined the method for determining pH values in his classic papers of 1909, the wide utilization of pH measurements in the research laboratory, the control laboratory, the clinic, and the factory could hardly have been envisioned. The far-reaching application of pH measurements in modern commerce and industry was made possible by the discovery of the hydrogen ion function of glass membranes which led to the development of convenient, practical glass electrodes, pH meters, and controllers that permit the pH of process solutions to be regulated automatically. As so often happens, the technology of pH instrumentation has outdistanced the slow progress toward an adequate understanding and interpretation of the numbers that pH meters furnish so easily, and often with reproducibility and precision of a high order.

With the perfection of chemical thermodynamics, it became evident that Sørensen's experimental method did not, in fact, yield hydrogen ion concentrations. Although the numbers obtained depended in a complex manner on the *activity* of the electrolytes in the "test" solution, they were not an exact measure of the hydrogen ion activity and, indeed, could never be made so. Thus the door was opened to a plurality of "theoretical" pH units, none of which could be matched exactly with the experimental number. The realization that the pH scale must have a defined or *conventional* basis later added to the confusion, for no single convention was generally adopted.

Happily, the situation is somewhat improved today, and substantial agreement on a practical approach to the standardization of pH measurements has been achieved. Regulatory groups in several countries, as well as the International Union of Pure and Applied Chemistry, have endorsed the operational definition of the practical pH value and a standard scale fixed by one or more standard buffer solutions whose assigned pH values are formally consistent with the thermodynamic properties of the solutions and with a single conventional definition of the individual ionic activity. The pH determination is essentially a determination of a difference, and the meaning of the experimental pH value is largely that of the number assigned to the standard. Any interpretation of the pH, if justifiable at all, must begin with a consideration of the significance of the standard pH.

The determination of pH values is a branch of applied electrochemistry, and the latter is inextricably tied to chemical thermodynamics. Yet the pH value is a thermodynamic quantity only in respect to its form; its substance is derived from extrathermodynamic considerations. If there is justification for a theoretical section in a book on pH determinations, it is because the pH unit lacks precise fundamental definition and because it is essential for users of pH numbers to understand the meaning and limitations of the unit in order to employ pH measurements most advantageously. For this reason, an attempt is made here to indicate how far the exact thermodynamic approach can be pursued before empirical standardization begins, and to shed light on the practical consequences of arbitrary conventions in the area where theory can no longer serve as a guide.

A part of this book is a second revision of material that appeared in the volume *Electrometric pH Determinations*, first published in 1954. The work was expanded considerably in 1964 and the title changed to *Determination of pH*. At that time, close attention was given to acid-base behavior in nonaqueous and mixed solvents, and a chapter on indicator pH measurements was added.

The theory and practice of electrometric pH determinations continue to be the chief concerns of this book. Wherever possible the treatment of buffer solutions, dissociation equilibria, salt effects, and medium effects is thermodynamically rigorous instead of "classical". In general, this means simply a strict adherence to the thermodynamic formulation of chemical equilibrium. Most of the earlier material has been brought up to date. Chapter 9 is new and Chapters 7 and 8 largely so. Chapters 4 and 11 have also been extensively revised.

The first four chapters are devoted to an examination of the definitions of pH scales, to conventions which permit an acceptable compromise between theory and experiment to be achieved, and to pH standards. In Chapters 5 and 6, buffer solutions and indicator methods are discussed from the viewpoint of both theory and practice. Chapters 7 and 8 are concerned with our rapidly growing knowledge of acid-base phenomena and measurement scales in nonaqueous and mixed solvents as well as with recent attempts to evaluate medium effects for individual ionic species. The new Chapter 9 examines electrometric determination of hydrogen ion concentrations in constant ionic media, a subject of special importance in coordination chemistry. Chapter 10 describes properties of hydrogen ion electrodes, liquid junctions, and reference electrodes, while a separate chapter (Chapter 11) reviews the properties and behavior of glass electrodes.

Developments in pH instrumentation and in the application of pH measurements to industrial control now clearly exceed the scope of this book. Nevertheless, a general summary of the experimental and theoretical basis for measurement of the electromotive force of pH cells, the general characteristics of pH meters, and the principles of pH control is given in Chapters 12 and 13. No longer is an attempt made to compare features of the many commercial instruments available. In this connection, it should be noted that this book is addressed to chemists rather than to engineers.

Inevitably, the passage of two decades has brought a change in the demands placed on pH measurements and in the areas where such measurements are of critical concern. In this edition, for example, special needs for accurate pH measurements in clinical chemistry and biomedical research, as well as in nonaqueous solutions, are acknowledged. An attempt has nonetheless been made to introduce new contributions and new emphasis without slighting the orderly development of ideas from which present-day concepts have emerged.

ROGER G. BATES

Gainesville, Florida
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A number of the tables and figures have appeared earlier in other publications, and I am grateful for permission to reproduce them. Figures 4–4, 4–5, and 4–8 appeared in *The Analyst* and are reproduced with acknowledgment to the Society of Public Analysts and Other Analytical Chemists. Table 8 of the Appendix and Figs. 5–2, 5–3, and 11–2 were taken from *Analytical Chemistry*. Tables 2–3 and 6–10 and Figs. 2–2 and 4–1 are from *Chemical Reviews*. Figure 13–3 is from *The Industrial Chemist*. Table 3–3 and Figs. 7–3 and 10–1 appeared first in the *Journal of the American Chemical Society*. Figure 11–6 is from the *Journal of the Electrochemical Society*. Figure 3–1 was published in the *Journal of Physical Chemistry*, and Fig. 10–10 is from *Science*.

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R.G.B.

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CHAPTER 1

fundamental principles and conventions

The electrometric determination of pH is essentially the evaluation of a quasi-thermodynamic constant from a measurement of the electromotive force of a suitable galvanic cell. It is accordingly necessary to examine the cell process in the light of thermodynamic concepts in order to comprehend fully the meaning of the experimental pH value and its limitations. It should be noted also that pH measurements made with indicator dyes relate indirectly to the pH scale defined in terms of galvanic cells. Some of the basic principles of electromotive force measurements and of the thermodynamics of electrolytic solutions needed for an understanding of the theory and practice of pH measurements are considered briefly in this introductory chapter.[1]

Reversible Cells and Potential

When current is drawn from a galvanic cell, an oxidation-reduction process called the *cell reaction* always takes place, and chemical energy is transformed into electrical energy. Oxidation-reduction reactions can conveniently be regarded as the sum of two half-reactions, one an oxidation and the other

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[1] Symbols and terminology relating to pH and its measurement are in accord with recommendations accepted by the International Union of Pure and Applied Chemistry; see R. G. Bates and E. A. Guggenheim, *Pure Appl. Chem.*, **1**, 163 (1960), and *Manual of Symbols and Terminology for Physicochemical Quantities and Units*, IUPAC, Butterworths, London, 1970. In general, the International System of Units (SI) is used. The few exceptions include the atmosphere (atm) as a unit of pressure and the symbol m to represent both the quantity molality and its unit (mol kg^{-1}). Thus a solution containing 0.1 mol kg^{-1} of HCl will be designated either by HCl, 0.1 m or by HCl ($m = 0.1$).

a reduction, the former providing the electrons utilized by the latter. The sites of the half-reactions are the *electrodes*, and, if these are suitably placed, the passage of electrons, necessary for the reaction to occur, can take place in significant amounts only through a circuit external to the cell. When this circuit is closed, oxidation will occur spontaneously at one electrode and reduction at the other; electrons will continue to pass from one electrode to the other until a state of equilibrium has been attained. The electrode at which spontaneous oxidation takes place and electrons appear is the negative electrode; that at which reduction occurs spontaneously, consuming electrons, is the positive electrode.

Any reversible electrode can suffer an oxidation or a reduction, that is, can either supply or remove electrons. The *potential* or tendency of a given electrode to supply electrons depends on the Gibbs energies of the oxidized and reduced states of the chemical substances, the temperature, and the pressure. Indeed, it is often convenient to regard the electron as a chemical element, a reactant or product in the oxidation or reduction process.[2]

The potentials of the two electrodes with respect to each other determine the direction of the flow of current. The potential difference, or *electromotive force* (e.m.f., E) is the driving force of the reaction. If the e.m.f. of a reversible cell is balanced externally by an equal and oppositely directed e.m.f., there will be no chemical change within the cell. However, if the external e.m.f. is then increased by an infinitesimal amount, a small current will flow and a small amount of reaction will occur. When, on the other hand, the applied e.m.f. is decreased infinitesimally, current begins to flow in the opposite direction and the chemical reaction is reversed. The measurement of the e.m.f. of a galvanic cell by the compensation method, where the e.m.f. supplied by the potentiometer balances almost exactly that of the cell, approaches very closely the condition of thermodynamic reversibility; hence the principles of equilibrium thermodynamics can be applied to these systems.

ENERGY OF THE CELL REACTION

Measurement of the potential difference between two reversible electrodes provides one of the most accurate means of studying the driving force of the reaction taking place within the cell and the change in Gibbs energy

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[2] M. Randall, *Amer. Phys. Teacher*, **6**, 291 (1938); **7**, 292 (1939). The concepts of "electrode potential" and "electromotive force" will be used in this book instead of "tension" as recommended by the International Committee for Electrochemical Thermodynamics and Kinetics (now International Society of Electrochemistry, ISE), because the author believes these terms and concepts to be more familiar to the general reader. The ISE recommendations have been summarized by P. Van Rysselberghe, *Electrochim. Acta*, **5**, 28 (1961); *J. Electroanal. Chem.*, **2**, 265 (1961). The unit of e.m.f. and electrode potential used consistently in this book is that formerly termed the "absolute volt."

as the reaction proceeds. Let us consider, for example, the following important reaction,

$$\tfrac{1}{2}H_2(g) + AgCl(s) = Ag(s) + HCl(m) \qquad (1)$$

The letters g and s in this equation represent gas phase and solid phase, respectively, and the letter m indicates, first, that the hydrochloric acid is present in solution and, second, that its molality (moles per kilogram of solvent) is m. This is an oxidation-reduction process which proceeds spontaneously from left to right at room temperature when the hydrogen pressure is 1 atm and the solution of hydrochloric acid is less than $9m$.[3]

When the reaction proceeds as written, hydrogen atoms are oxidized and silver chloride is reduced. In the cell[4]

$$Pt; H_2(g), HCl(m), AgCl(s); Ag(s) \qquad (2)$$

the "oxidizing agent" is isolated from the "reducing agent." If diffusion through the cell is negligible, no appreciable reduction of silver chloride by hydrogen can ensue. To sustain the process, a transfer of electric charge must take place. If this transfer is not possible, chemical change at the electrodes ceases. Nevertheless, the difference of electrical potential between the platinum and silver electrodes reveals the *tendency* for reaction 1 to take place.

The reversible electromotive force E multiplied by the quantity of electric charge that must be transferred to bring about the unit amount of reaction gives the maximum electrical work[5] that this amount of chemical reaction is capable of producing at constant temperature, pressure, and concentration. This is the decrease in Gibbs energy $-\Delta G$ which accompanies the reaction, namely

$$-\Delta G = nFE \qquad (3)$$

where F is the Faraday constant and n is an integer.[6]

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[3] G. Akerlof and J. W. Teare, *J. Amer. Chem. Soc.*, **59**, 1855 (1937).

[4] Finely divided platinum, which catalyzes the dissociation of hydrogen molecules into atoms and the oxidation of the latter, is the common site for the hydrogen electrode.

[5] In accordance with the recommendations of the IUPAC Manual (reference 1), the symbol G is used for the Gibbs energy, $H - TS$, where H and S are the heat content (enthalpy) and entropy, respectively, and T is the thermodynamic temperature in kelvins.

[6] For E in volts, F in coulombs per mole, and n in faradays per reaction unit as written, $-\Delta G$ is in joules. The value of n is readily determined by separating the cell reaction into its oxidation and reduction parts; n is then seen to be the number of moles of electrons necessary to balance each half-reaction electrically. Energy in thermochemical calories is obtained by the defined relationship 1 cal = 4.184 J.

ABSOLUTE POTENTIALS

The only possible way that atoms can furnish electrons to metallic conductors (or vice versa) is through a change in charge, that is, a change of valence. Hence the passage of current between metallic and electrolytic conductors is accompanied by a chemical reaction. Thermodynamics can furnish information only about the complete reaction and the *differences* of potential between the electrodes. The peculiar demands of pH measurements, however, focus attention on the half-reaction that occurs at the electrode reversible to hydrogen ion and on the half-cell potential. The "absolute" scale of single electrode potentials has long been sought by both experimental and theoretical means, but these efforts have thus far not met with success.

It should be noted that an absolute scale of potential is not essential for the establishment of a single scale of acidity for all solvent media. One needs rather a scale of potential for each solvent relative to a conventional scale in one solvent (for example, in water). Proposals for interrelating hydrogen electrode potentials[7] in a variety of solvent media are discussed in Chapters 7 and 8.

THE HYDROGEN SCALE

In spite of the progress that has been made, the validity and accuracy of a basis for an absolute scale of potential have not been established. Fortunately, a numerical scale of potential that meets nearly all practical requirements in the aqueous medium can be based on an arbitrary conventional reference point. The arbitrary zero of potential is defined as follows. The potential of the reversible hydrogen electrode in contact with hydrogen gas at 1 atm partial pressure and immersed in a solution containing hydrogen ions at unit activity,

$$\mathrm{Pt}; \mathrm{H_2}(g,\ 1\ \mathrm{atm}), \mathrm{H^+}(a = 1) \tag{4}$$

is taken as zero at all temperatures. The scale of potentials based on this zero point is called the *hydrogen scale*.

The potential of a single electrode on the hydrogen scale is evidently the e.m.f. of a complete cell consisting of the electrode in question combined with this standard hydrogen electrode. The e.m.f. should not include the diffusion potentials that arise at the liquid-liquid boundary between the two half-cells. Inasmuch as the standard hydrogen electrode is not a convenient reference for practical measurements, potentials on the hydrogen scale are

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[7] V. A. Pleskov, *Usp. Khim.*, **16**, 254 (1947); H. M. Koepp, H. Wendt, and H. Strehlow, *Z. Elektrochem.*, **64**, 483 (1960); N. A. Izmailov, *Dokl. Akad. Nauk SSSR*, **127**, 104 (1959). The subject of absolute and relative electrode potentials has been reviewed by G. Milazzo and G. Bombara, *J. Electroanal. Chem.*, **1**, 265 (1959–60).

usually calculated from the measured e.m.f. of other electrode combinations —for example, from the potential of the given electrode with respect to the calomel reference element. The sign of the single electrode potential must be decided by convention. This matter will be considered in a later section.

Chemical Potential and Activity

E.M.F. AND THE CELL REACTION

Equation 3 expresses the relationship between the electromotive force of a galvanic cell and the decrease of Gibbs energy when the cell reaction proceeds reversibly. Both the (Gibbs) free energy change and the e.m.f. measure the tendency for the cell reaction to take place. It is appropriate to consider next the effect on the e.m.f. of changes in the concentration or activity of the individual reactants or products.[8] For this purpose we shall write a cell reaction in general terms, as follows:

$$iI + jJ + \cdots = uU + vV + \cdots \tag{5}$$

The Gibbs energy of the system represented by equation 5 is a function of the temperature T, the pressure P, and the composition, expressed in terms of the numbers of moles n_I, n_J, n_U, n_V, etc., of each of the components of the system. When the system is subjected to small changes in these variables, the change dG in free energy is (at constant charge)

$$dG = -S\,dT + V\,dP + \sum \mu_X\,dn_X \tag{6}$$

where S and V are the entropy and volume of the system, respectively, and μ_X is a quantity called the *partial molar free energy* or *chemical potential* of the species (X) indicated by the subscript. The summation is made for all species of which the system is composed. Mathematically, the chemical potential of the species X is the partial derivative of the free energy with respect to moles of species X, when the temperature, pressure, and amounts of the other substances remain constant:

$$\mu_X = \left(\frac{\partial G}{\partial n_X}\right)_{T,P,n} \tag{7}$$

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[8] Excellent authoritative discussions of the thermodynamics of cells and of electrolytic solutions have been given by D. A. MacInnes, *The Principles of Electrochemistry*, Reinhold Publishing Corp., New York, 1939; Dover Publications, New York, 1961; S. Glasstone, *Introduction to Electrochemistry*, D. Van Nostrand Co., New York, 1942; H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, 3rd ed., Reinhold Publishing Corp., New York, 1958; and R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, 2nd ed. revised, Butterworths, London, 1970.