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pH scales and proton-transfer reactions in saline media such as sea water

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Abstract—The three approaches to defining pH scales for use in sea water: the N.B.S. scale, the pH(SWS) or 'total' hydrogen ion concentration scale and the 'free' hydrogen ion concentration scale are described, and it is shown how these arise as a direct consequence of alternative experimental procedures for determining practical acidity constants. The advantages of conceptual simplicity and of experimental precision inherent in the use of concentration products to describe proton-transfer reactions in saline media are emphasised. In addition, the problems of theoretical interpretation and of reproducibility which result from the conventional nature of the N.B.S. pH scale are described, and the effect on the corresponding 'apparent' constants outlined. Insofar as it is concentration products rather than 'apparent' constants that are amenable to prediction using models for activity coefficients, the deliberate use of a 'free' hydrogen ion concentration scale should be applicable to many areas of aqueous geochemistry in addition to marine chemistry.

INTRODUCTION

THE FIELD of pH scales and the study of proton-transfer reactions in sea water is one of the more confused areas of marine chemistry. At the moment there are three alternative approaches to defining pH scales for use in sea water: the N.B.S. scale, the pH(SWS) or 'total' hydrogen ion concentration scale and the 'free' hydrogen ion concentration scale. There are also three corresponding definitions of 'constants' to describe proton-transfer reactions in sea water. The reasons for this are primarily historical. They reflect the gradual refinement of the experimentally convenient potentiometric determination of acidity in order that the numbers obtained might be usefully interpreted as a property of hydrogen ion in solution.

Why are pH measurements important? As GUGGENHEIM (1930) forcefully pointed out, it is rarely the hydrogen ion content of a solution that is of itself important. Rather, the hydrogen ion content is indicative of the state of the various proton-transfer equilibria occurring in solution. The case of reaction rates is no exception if we take into account the quasi-equilibrium between the reactants and the critical complex (transition state). It is thus misleading to separate the discussion of pH scales from a consideration of the theoretical and practical aspects of determining the corresponding acidity constants.

In this article, I should like to show how the various pH scales mentioned above arise naturally from alternative approaches to determining practical acidity constants for use in ionic media. I shall review how the conventional nature of the N.B.S. pH scale gives rise to problems both of theoretical interpretation and of reproducibility, and shall discuss the implications of these problems. I shall then describe the 'free' hydrogen ion concentration scale, and would like to point out that such an approach should be generally useful in many areas of aqueous geochemistry apart from marine chemistry. In particular, the 'free' hydrogen ion concentration scale is directly compatible with the various phenomenological models for describing and predicting activity coefficients in electrolyte solutions. In future, it should be possible to discuss proton-transfer reactions in a wide variety of geochemical systems on a common basis.

Although this paper does not discuss the practical determination of pH, the reader is referred to the publications by BATES (1973), CULBERSON (1981), and GRASSHOFF (1983) for a thorough discussion of the pitfalls involved.

PROTON-TRANSFER REACTIONS IN AQUEOUS SOLUTIONS

Introduction

It is safe to say that free protons do not exist in any significant amount in aqueous solutions. Rather the proton is bonded to a water molecule thus forming an H_3O^+ ion; this in turn is hydrogen bonded to three other water molecules to form an $H_9O_4^+$ ion (see CONWAY, 1981—chap. 17). This solvation structure has important consequences for the mechanism and kinetics of a wide range of reactions in aqueous solution (for a detailed discussion see EIGEN, 1964). Nevertheless, it is convenient (and thermodynamically correct) to use the term "hydrogen ion" and the symbol "H^+" as a shorthand for the various hydrates: this is the sense in which I shall employ it.

If HA and A denote an acid and its conjugate base, while HB and B denote another conjugate pair

posed a potentiometric method which they felt measured hydrogen ion activity directly in solution. As a result, it became common practice to define a hybrid acidity constant K'_A (see BRÖNSTED, 1928):

$$\frac{m_{HB}}{m_B} = a_H / K'_A,$$

algebra for a more complex system is similar in principle, although necessarily more involved.) The basic equations which determine the equilibrium relationships fall into two classes:

(a) The mass-action equations: these define the stoichiometry of the various equilibria and the corresponding concentration constants:

$$K_W = m_H m_{OH}$$

$$K_A = m_H m_B / m_{HB}.$$

(b) The mass-balance equations: these relate the concentrations of the various species to the analytical (total stoichiometric) composition of the solution:

$$H_T = m_H - m_B - m_{OH}$$

$$B_T = m_{HB} + m_B.$$

The mass-balance equation for hydrogen ion is calculated relative to a *defined* equivalence point or zero level of protons. This is known as a proton condition (BUTLER, 1964; STUMM and MORGAN, 1981). The zero level chosen here corresponds to H_2O and HB.

These four equations thus uniquely define the four concentrations m_H, m_{OH}, m_{HB} and m_B.

In the potentiometric determination of acidity constants, it is convenient to use the cell

Reference half-cell	Solution in which equilibria take place	Electrode reversible to hydrogen ion

whose e.m.f. is given by

$$E = E^0 + (RT/F) \ln h,$$

where h is proportional to m_H (*i.e.* $h = m_H k$, see next section). The determining equations can therefore be rewritten as a single expression which combines the independently measurable parameters $E(h)$, B_T and H_T:

$$H_T = h/k - B_T/(1 + h/K''_A) - K''_W/h$$

(where $K''_A = K_A k$ and $K''_W = K_W k$). This equation is the basis for all determinations of acidity constants.

In order to obtain values for h, it is necessary to specify a value for E^0. The alternative approaches to defining pH scales, and hence the corresponding acidity constants, each represent alternative procedures for defining or estimating E^0. Once such a procedure has been defined, then the corresponding value of K''_A can be estimated from a set of e.m.f. data as a function of composition.

THE POTENTIOMETRIC DETERMINATION OF ACIDITY

Introduction

The special influence of the hydrogen ion concentration on a variety of processes in aqueous solution was first recognised and described by SØRENSEN (1909), who proposed a potentiometric procedure for the determination of hydrogen ion concentrations which he expressed as the "hydrogen ion exponent":

$$P_H = -\log c_H.$$

Development of the modern formulation of the concepts of thermodynamics, and of the newer theories of electrolyte solutions, showed that the e.m.f. of galvanic cells is related more directly to activity than to concentration; thus SØRENSEN and LINDERSTRØM-LANG (1924) proposed a new acidity unit:

$$pa_H = -\log a_H.$$

It is now well recognised that the activity of a single ion plays no real part in the e.m.f. of a galvanic cell, whether or not the cell is of the type with liquid junction (GUGGENHEIM, 1930). There is nevertheless a need for a reproducible pH scale based on the experimentally convenient potentiometric determination of acidity (MACINNES, 1948), and this has led to a wide acceptance of an *operational* definition of the measurement of pH.

The operational definition of pH

The pH of a solution is defined in terms of measurements on the particular cell

Reference electrode	Concentrated KCl sol.	Test sol.	Electrode reversible to hydrogen ion

The reference electrode is usually reversible to chloride ion, and the e.m.f. of this cell can be formally written as (after BATES, 1973)

$$E = \{E^0 + (RT/F) \ln a_{Cl(KCl)} + E_J\} + (RT/F) \ln a_H$$

$$= E^{0'} + (RT/F) \ln a_H,$$

where E_J is the (formal) liquid junction potential between the two half cells. This formula is actually a conventional definition of $E^{0'}$ and a_H, the value of each depending on the value assigned to the other. In the operational definition of pH (see BATES, 1973; IUPAC, 1979), the pH of solution X is related to the pH of standard S:

$$pH(X) = pH(S) + \frac{E_S - E_X}{(RT \ln 10/F)}.$$

Therefore

$$\frac{E_S - E_X}{(RT \ln 10/F)} = \frac{E^{0'}_S - E^{0'}_X}{(RT \ln 10/F)} - \log a_H(X) + \log a_H(S).$$

It is clear that pH(X) can only be identified with the conventional activity term if two conditions are met: (a) The term $E^{0'}_S - E^{0'}_X$ is *assumed* to be zero. (b) pH(S) is defined as $-\log a_H(S)$, where $a_H(S)$ has been *conventionally* assigned.

Although it has been widely recognised that $E^{0'}_S - E^{0'}_X$ is rarely equal to zero, its finite value is usually ascribed to differences in the liquid junction potential (see *e.g.* CULBERSON, 1981; BREZINSKI, 1983). It is thus only possible to measure this term accurately in other solutions for which the conventional value of a_H is known, *i.e.* other solutions with assigned pH(S) values (see *e.g.* BATES *et al.*, 1950; COVINGTON *et al.*, 1983).

The *definitive* method for pH measurement in dilute aqueous solutions is based on measuring the e.m.f. (E) of the cell

$$\mathrm{Ag(s)}\left|\mathrm{AgCl(s)}\right|\begin{matrix}\text{Dilute aq. sol.}\\ \text{with added NaCl}\end{matrix}\left|\mathrm{H_2(g,\ 1atm)}\right|\mathrm{Pt(s)}.$$

The calculated function is

$$\mathrm{pH} = \lim_{m_{\mathrm{NaCl}}\to 0}\left\{\frac{E^0 - E}{(RT\ln 10/F)} + \log m_{\mathrm{Cl}} + \log \gamma_{\mathrm{Cl}}\right\}.$$

E^0 is the standard potential of the Ag/AgCl half cell. The present convention (BATES and GUGGENHEIM, 1960) is based on the assumption that the molal activity coefficient of chloride ion in dilute aqueous solution ($I_m \leq 0.1$ mol kg^{-1}) can be estimated by means of the equation

$$\log \gamma_{\mathrm{Cl}} = -AI_m/(1 + 1.5I_m),$$

where A is the usual temperature dependent Debye-Hückel constant. This is essentially the procedure that has been used to determine the pH in a series of primary aqueous calibration solutions, the so-called N.B.S. buffers (BATES, 1973). It is also the approach taken by COVINGTON *et al.* (1983) in order to assess the magnitude of the error in pH measurements in low ionic strength media such as lake water.

The measurement of hydrogen ion concentration

In ionic media (*i.e.* where the activity coefficients of the various reacting species are dominated by the presence of the bulk electrolyte—the ionic medium), it is possible to measure hydrogen ion concentration directly using the cell

$$\begin{matrix}\text{Reference}\\ \text{half-cell}\end{matrix}\left|\begin{matrix}\text{Solution in which}\\ \text{equilibria take place}\end{matrix}\right|\begin{matrix}\text{Electrode reversible}\\ \text{to hydrogen ion}\end{matrix}$$

A number of reference half-cells have been used. The best systems (stablest, most reproducible e.m.f.) use an electrode which responds to one of the non-reacting ions of the ionic medium, *e.g.* a sodium glass electrode (see BIEDERMANN *et al.*, 1974):

$$E = E^0 + (RT/F)\ln(a_{\mathrm{H}}/a_{\mathrm{Na}}),$$

or a silver-silver chloride electrode (*e.g.* BATES *et al.*, 1943; THURMOND and MILLERO, 1982):

$$E = E^0 + (RT/F)\ln(a_{\mathrm{H}}a_{\mathrm{Cl}}).$$

Other experimenters have used cells with liquid junctions (*e.g.* HANSSON, 1972, 1973a,b,c,d; DICKSON and RILEY, 1979a,b). In these cases the e.m.f. of this cell is given by the formal expression

$$E = E^0 + (RT/F)\ln a_{\mathrm{H}} + E_J,$$

(see discussion by GUGGENHEIM, 1936; DICKSON and WHITFIELD, in prep.).

In every one of these cases, the e.m.f. can be expressed by the classical Nernst equation:

$$E = E^0 + (RT/F)\ln m_{\mathrm{H}}.$$

A comparison of this with the previous equations shows that, in the case of cells without liquid junction, the constancy of E^0 depends on the constancy of the activity coefficients despite any compositional variations which might occur during the course of an experiment (usually a titration). In the case of cells with liquid junction, there is the additional possibility that the liquid junction e.m.f. might vary. To a first approximation, this is the result of the highly mobile proton and $\Delta E_J \approx j_{\mathrm{H}}m_{\mathrm{H}}$ (see BIEDERMANN and SILLÉN, 1953; ROSSOTTI and ROSSOTTI, 1961). The value of j_{H} in sea water media is approximately 30 mV mol^{-1} kg (DICKSON and RILEY, 1979a), and thus the variation in liquid junction e.m.f. can often be neglected. BATES and MACASKILL (1975) also imply that this is the case.

APPLICATION TO SALINE MEDIA SUCH AS SEA WATER

Introduction

The discussion so far has implicitly assumed that none of the various reacting species were complexed by the medium. In a solution which can complex these species, *e.g.* sea water, it is possible to get side-reactions such as

$$\mathrm{H^+ + SO_4^{2-} = HSO_4^-}$$

$$\mathrm{Mg^{2+} + OH^- = MgOH^+}$$

etc. The formal simplicity of the mass-action, mass-balance and Nernst equations can however be retained by defining them in terms of total concentrations:

$${}^{\mathrm{T}}m_{\mathrm{H}} = m_{\mathrm{H}} + \sum \textit{complexes with medium ions}$$

$${}^{\mathrm{T}}m_{\mathrm{OH}} = m_{\mathrm{OH}} + \sum \textit{complexes with medium ions}$$

etc. The utility of this approach clearly depends on the assumption that the ratio ${}^{\mathrm{T}}m_{\mathrm{X}}/m_{\mathrm{X}}$ is constant over the range of conditions considered. This is certainly true for acids and bases present in sea water at low concentrations (see for example the discussions by PYTKOWICZ *et al.*, 1974; DICKSON and WHITFIELD, in prep.): it is implicit in the original proposal of BUCH (1930) that the equilibria involving carbonic acid in sea water might be successfully treated using apparent constants. For example, in a medium containing sulphate (but no other protophilic ligands)

$${}^{\mathrm{T}}m_{\mathrm{H}} = m_{\mathrm{H}} + m_{\mathrm{HSO_4}}$$

$$= m_{\mathrm{H}}(1 + \beta(\mathrm{HSO_4})m_{\mathrm{SO_4}});$$

thus

$${}^{\mathrm{T}}m_{\mathrm{H}}/m_{\mathrm{H}} = 1 + \beta(\mathrm{HSO_4})m_{\mathrm{SO_4}},$$

and will remain essentially constant as long as $m_{HSO_4} \ll m_{SO_4}$ (*i.e.* at low m_H values). A similar reasoning applies also to the other reacting species.

The mass-balance equation for hydrogen ion is therefore

$$H_T = {}^Tm_H - {}^Tm_B - {}^Tm_{OH},$$

and similarily

$$B_T = {}^Tm_{HB} + {}^Tm_B.$$

(In the remainder of the text ${}^Tm_{HB}$ and ${}^Tm_B$ should strictly be used in place of m_{HB} and m_B to signify that complexes with medium ions are included. However no real ambiguity is introduced by omitting the T superscript.)

The three alternative approaches to defining pH scales (and thus acidity constants) for use in sea water (see *e.g.* BATES, 1982) reflect alternative approaches to interpreting the potentiometric determination of acidity

$$E = E^0 + (RT/F) \ln h.$$

The N.B.S. pH scale and 'apparent' constants

In this approach, $-\log h$ is defined as equal to pH(N.B.S.), *i.e.* using the operational definition of pH. Then

$$E^0 = E_S + (RT \ln 10/F) \cdot pH(S)$$

and the apparent constant

$$K'_A = 10^{-pH} m_B / m_{HB}.$$

Then

$$H_T = 10^{-pH}/k^* - B_T/(1 + 10^{-pH}/K'_A) - K'_w/10^{-pH},$$

and therefore in order to describe the system over a wide range of pH it is necessary to measure both k^* and K'_w in addition to K'_A.

This approach has been taken by a number of recent workers who have used the N.B.S. pH scale in order to determine acidity constants (see *e.g.* CULBERSON and PYTKOWICZ, 1973; MEHRBACH *et al.*, 1973; ATLAS *et al.*, 1976; SASS and BEN-YAAKOV, 1977) who have each determined

$$k^* = 10^{-pH}/{}^Tm_H$$

in their various media. The authors cited use symbols such as f_H or even γ_{H^+} to denote this parameter which they think of as an 'apparent activity coefficient' for hydrogen ion (see DISCUSSION).

pH(SWS) and 'stoichiometric' acidity constants

This approach was first suggested for use in sea water by Lars Gunnar Sillén (SILLÉN, 1967; DYRSSEN and SILLÉN, 1967). The key feature of this approach is that h is defined as equal to ${}^Tm_H$, and the stoichiometric constant

$$K^*_A = {}^Tm_H m_B / m_{HB}.$$

The mass balance equation for hydrogen is thus

$$H_T = {}^Tm_H - B_T/(1 + {}^Tm_H/K^*_A) - K^*_W/{}^Tm_H.$$

The essence of this approach therefore, is that the electrode system is calibrated simultaneously with the determination of the constants. Usually this is achieved by some least squares minimisation procedure which treats both E^0 and K^*_A as adjustable parameters. It is usually sound practice to determine K^*_W from a separate experiment in which $B_T = 0$. A wide variety of computer programs have been written for such problems (see LEGGETT, 1983). A number of workers in the past have calibrated glass electrodes as a hydrogen ion probe, and then transferred them to the test cell (see *e.g.* ROSSOTTI and ROSSOTTI, 1961): this is not now considered the optimal technique (ROSSOTTI, 1974), as it has been shown that there are small changes in E^0 resulting from the transfer of glass electrodes from one solution to another (PEHRSSON *et al.*, 1976).

Values of K^*_A (*i.e.* using a 'total' hydrogen ion concentration scale) have been determined for a wide range of proton-transfer reactions in sea water media: the ionic product of water (HANSSON, 1972, 1973b; DICKSON and RILEY, 1979a), carbonic acid (HANSSON, 1973b,c), boric acid (HANSSON, 1973a,c), hydrogen sulphide (ALMGREN *et al.*, 1976), phosphoric acid (DICKSON and RILEY, 1979b; JOHANSSON and WEDBORG, 1979), ammonia (JOHANSSON and WEDBORG, 1980).

At high acidity, ${}^Tm_H$ is no longer directly proportional to m_H. It is therefore preferable to allow explicitly for the formation of species such as HSO_4^- and HF (see *e.g.* HANSSON and JAGNER, 1973; DICKSON and RILEY, 1979a). If desired, the final data can be presented on a "sea water scale" of hydrogen ion concentration:

$$m_H(SWS) = m_H(1 + \beta(HSO_4){}^Tm_{SO_4} + \beta(HF){}^Tm_F)$$

$$\approx {}^Tm_H.$$

This form of presentation achieves a measure of independence from systematic errors resulting from the use of inaccurate values for $\beta(HSO_4)$ and $\beta(HF)$ (DICKSON, 1977; DICKSON and RILEY, 1979a).

There has been no agreement as to whether to include HF in the definition of a 'total' hydrogen ion concentration scale. It was included implicitly by MEHRBACH *et al.* (1970), who used natural sea water for their experiments: it was included explicitly by Dickson in his work in synthetic seawater media. Other workers who have used a synthetic sea water without fluoride have of course not included the effect of fluoride in a definition of ${}^Tm_H$ (see *e.g.* Hansson's work).

The 'free' hydrogen ion concentration scale

Although the 'total' hydrogen ion scale is thermodynamically rigorous and well suited to the determination of acidity constants by titration techniques, it is however much clearer to use a 'free' hydrogen ion

concentration scale, and to write the full equation explicitly incorporating the formation of bisulphate and hydrogen fluoride. In 1975, at the Dahlem Conference on "The Nature of Seawater," a working group on conventions for sea water equilibria proposed that it would be worth considering a 'free' hydrogen ion concentration scale, thus allowing a clear description of proton-transfer processes in sea water (HANSSON *et al.*, 1975). Professor Roger G. Bates, together with a variety of co-workers at the University of Florida, has therefore pursued this goal.

The basis of this approach has been to use the highly reproducible hydrogen/silver—silver chloride cell in a synthetic sea water whose chloride concentration is known. Then

$$E = E^0 + (RT/F)\ln(m_H m_{Cl}) + (2RT/F)\ln \gamma_{\pm}(HCl),$$

or, at trace hydrogen ion concentrations

$$E = \{E^0 + (RT/F)\ln m_{Cl} + (2RT/F)\ln {}^{tr}\gamma_{\pm}(HCl)\} + (RT/F)\ln m_H$$

$$= E^0 + (RT/F)\ln m_H.$$

If ${}^{tr}\gamma_{\pm}(HCl)$ is known in the synthetic sea water, it is then possible to measure m_H directly in solution. Two approaches have been used to determine ${}^{tr}\gamma_{\pm}(HCl)$:

(i) Values have been measured in a chloride mixture which is thought to approximate the synthetic sea water (see KHOO *et al.*, 1977a).

(ii) Values of ${}^{tr}\gamma_{\pm}(HCl)$ and $\beta(HSO_4)$ are obtained simultaneously from a minimisation procedure using data for various concentrations of HCl in synthetic sea water (see *e.g.* BATES and CULBERSON, 1977).

This latter approach has been applied by DICKSON *et al.* (in prep.), in order to obtain a self-consistent suite of values over a wide range of temperature and ionic strength. Once the value of ${}^{tr}\gamma_{\pm}(HCl)$ is known, it is possible to estimate accurate values of acidity constants defined as

$$K_A = m_H m_B / m_{HB}.$$

This is best achieved by extrapolating e.m.f. data obtained using buffer mixtures of known composition to zero buffer concentration (*i.e.* the ionic medium standard state):

$$\ln K_A = \lim_{B_T \to 0} \left\{ \frac{E - E^0}{(RT/F)} + \ln(m_B/m_{HB}) \right\}.$$

This can be done with high precision (see *e.g.* KHOO *et al.*, 1977b).

Although no-one has yet used a 'free' hydrogen scale for evaluating titration data in a sea-water medium in order to determine acidity constants, there is no reason in principle why this should not be done provided that an accurate value of $\beta(HSO_4)$ is known for the medium. The mass balance equation for hydrogen ion could then be written as

$$H_T = m_H + {}^T m_{SO_4}/(1 + (1/\beta(HSO_4)m_H)) - B_T/(1 + m_H/K_A) - K_W/m_H,$$

and E^0 and K_A evaluated simultaneously as has been done for the 'total' hydrogen ion scale.

Sea water buffers

The idea of using buffers made up in a synthetic sea water background was first proposed by SMITH and HOOD (1964) who suggested that there were experimental advantages to doing so. These authors suggested that such buffers should have the position of secondary standards, and that they should be calibrated with respect to the N.B.S. pH scale. More recently, in an attempt to use the experimentally convenient potentiometric determination of pH to estimate hydrogen ion concentration in sea water, some workers (*e.g.* HANSSON, 1973d; RAMETTE *et al.*, 1977) have proposed values of pH(S) for buffer solutions made up in a background of synthetic sea water. The key to the successful application of this approach lies in the matching of the buffer composition with that of the sample. This is apparent from the following equations.

The e.m.f. of the pH cell in sea water can be written as

$$E = E^0 + (RT/F)\ln m_H$$

(see last section), therefore

$$\frac{E_S - E_X}{(RT\ln 10/F)} = \frac{E_S^0 - E_X^0}{(RT\ln 10/F)} - \log m_H(X) + \log m_H(S).$$

Again this is only useful if $E_S^0 - E_X^0$ is zero, and if $m_H(S)$ is accurately known, otherwise pH(X) is strictly only an operational value. The calibration of the buffers is no different in principle from measuring an acidity constant and is achieved in much the same manner. Thus HANSSON (1973d) titrated his buffer with HCl in order to calibrate his electrode system and thus assign a value of ${}^T m_H(S)$. Bates's group (RAMETTE *et al.*, 1977) use the value of ${}^{tr}\gamma_{\pm}(HCl)$ to estimate E^0 and thus assign $m_H(S)$.

The use of buffers based on a sea water background has not yet found any following within the oceanographic community. The reasons for this are various (see the excellent discussion by CULBERSON, 1981), but predominantly reflect the feeling that the considerable effort required to prepare such buffers is not repaid by commensurate gains in precision. In a regime where it is not possible to match the background composition of the buffer with that of the sample (*e.g.* estuaries or brines) the use of such buffers is impractical.

DISCUSSION

It has been claimed by a number of authors (PYTKOWICZ, 1969; BEN-YAAKOV and SASS, 1978;

CULBERSON, 1981) that the pH-apparent constant approach is equivalent to the use of stoichiometric acidity constants to describe proton-transfer reactions in ionic media. This claim, although correct in principle, is misleading. It is apparent from the discussion of the previous section, that

$$10^{-pH} = m_H\gamma_? \approx {}^Tm_Hk^*,$$

(see also the discussions by HAWLEY and PYTKOWICZ, 1973; CULBERSON, 1981). In addition the 'apparent' dissociation constant

$$K'_A = K_A\gamma_? = K^*_Ak^*$$

incorporates the same constant term and thus the ratio

$${}^Tm_{HB}/{}^Tm_B = 10^{-pH}/K'_A$$

will be unambiguously defined if k^* is a constant. Unfortunately, it is not.

A number of workers have measured k^* (or f_H as it is often termed) in sea water media and it is apparent that considerable systematic differences exist (see Fig. 1). The value of $\gamma_?$ (and hence of k^*) is dependent on the physical design of the liquid-liquid junction in the pH cell—see the discussion of reference electrodes by CULBERSON (1981). As a result, for each well-defined value of a stoichiometric acidity constant, there will exist a multitude of possible 'apparent' constants, each corresponding to a particular reference half-cell. This problem has been acknowledged by some workers using apparent constants (see *e.g.* MEHRBACH *et al.*, 1973; ATLAS *et al.*, 1976) who are careful to specify the exact reference electrode used, and the particular reference buffer employed. Even this is not always sufficient; both MEHRBACH *et al.* (1973) and myself (DICKSON, 1977) have compared data for supposedly identical reference electrodes, and have obtained systematic differences equivalent to more than 0.01 pH units.

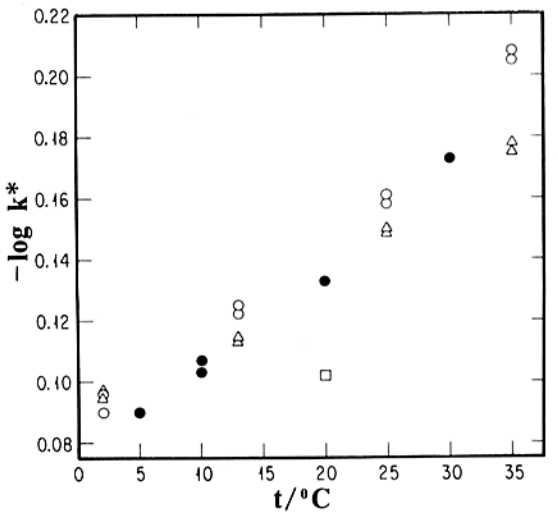

FIG. 1. Values of $-\log k^* = pH(NBS) + \log {}^Tm_H$ for sea water of S ≃ 35. Δ, CULBERSON and PYTKOWICZ (1973), O, MEHRBACH *et al.* (1973), □, ATLAS *et al.* (1976), ●, DICKSON (1977).

This problem has further ramifications. It is common practice in the field of geochemistry to assume that the N.B.S pH scale gives activities for the proton. As has been pointed out in the preceding discussion, this is not the case. As a result the magnitude of any 'single ion activities' calculated using this assumption will be dependent on the liquid junction potential, and thus do not even represent a useful *conventional* scale.

Culberson suggests that this problem would be overcome by the development of a reproducible liquid-liquid junction (and presumably the use of such a junction to determine K'_A). This systematic error is however not the only problem in obtaining apparent acidity constants. The definition of apparent constants, *i.e.* using the pH cell, automatically precludes the use of cells without liquid junction for the measurement of acidity constants. This is unfortunate, as the cell without liquid junction effectively eliminates problems resulting from possible variation of the liquid junction during a titration. A further technique used to improve the quality of hydrogen ion concentration data obtained using glass electrodes is to design the experiment so that the electrode pair can be calibrated directly in the test solution, if possible before the introduction of the reacting system of interest (see ROSSOTTI, 1974; DICKSON and RILEY, 1979b). This approach obviates the shift in E^0 that has sometimes been observed when an electrode pair is shifted from one solution to another. Again, this avenue is of necessity closed to those wishing to determine apparent constants.

Although I have cited a number of disadvantages above, I do not feel that they represent the *major* drawback to the use of apparent constants. Rather, as WHITFIELD (1975) points out:

> "If we are to explain rather than describe the chemistry of protolytic species in sea water it is important that pH scales should be available that are defined on some thermodynamically acceptable scale rather than specified in terms of particular procedures."

The concentration constant K_A is unambiguously related to the standard acidity constant:

$$K^0_A = K_A\frac{\gamma_H\gamma_B}{\gamma_{HB}}.$$

This allows a number of possibilities which are not easily available to the assiduous user of apparent constants:

(1) Measured values of K^0_A/K_A can be used to assess the performance of models of interactions in electrolyte solutions (which attempt to predict the magnitude of the activity coefficient term). If K_A is measured in simple ionic solutions, this information can even be used to obtain parameters for such models (see *e.g.* THURMOND and MILLERO, 1982).

(2) Models of electrolyte solutions could be used to estimate values for K_A from a knowledge of K^0_A

and the composition of the solution. This would be invaluable for the study of brines and other geologically important solutions where it will be an impossible task to measure acidity constants for every composition of interest.

(3) Models of electrolyte solutions can be used in order to assess the effect of compositional changes on the values of K_A (see *e.g.* BEN-YAAKOV and GOLDHABER, 1973). This will probably be the most accurate method for treating the compositional changes that occur in marine pore waters during early diagenesis.

Although at the moment such models are at an early stage of development (see WHITFIELD, 1979), they hold promise for the future as a framework for linking together a variety of measurements in solutions of different compositions (see *e.g.* HARVIE, 1981; HARVIE *et al.*, 1984). A knowledge of analytical parameters such as the equilibrium partial pressure of CO_2—$P(CO_2)$—and the total inorganic carbon—C_T—will allow the calculation of hydrogen ion concentration, without recourse to the measurement of pH. This in turn will allow the calculation of m_{HB}/m_B for any other acid-base system. The accurate measurement of parameters such as $P(CO_2)$ or C_T requires however fairly sophisticated instrumentation; there will thus always be a call for a method of determining hydrogen ion concentration which has the convenience and simplicity of the pH measurement.

One such approach which would be of widespread applicability, is to calibrate ones own pH cell to measure hydrogen ion concentration. The technique would be to determine experimentally an estimate of the factor k^* as a function of composition. This could be achieved using either synthetic (CULBERSON and PYTKOWICZ, 1973; DICKSON, 1977) or natural samples (MEHRBACH *et al.*, 1973). This approach would be particularly appropriate to estuarine studies where matched buffers for hydrogen ion concentration are clearly impractical. The resulting pH data could then be reported as hydrogen ion concentrations. As I have pointed out above, such a value constitutes an *empirical* correction for a particular electrode system, and it would be most unwise to use a value that had been obtained for another reference electrode.

Such a pragmatic empirical approach is not entirely satisfactory, and it may be better in the future to consider the possibility of using cells without liquid junction. A promising candidate would be the combination of a hydrogen glass electrode and a sodium glass electrode. If the composition of the test solution is known, it should be possible to obtain thermodynamic information which could be unambiguously related to m_H. This suggestion is originally credited to George Scatchard (see HITCHCOCK, 1936), although it has been considered more recently by WILDE and ROGERS (1970).

It is apparent therefore that useful quantitative information about the concentration of hydrogen ion can be obtained only in systems whose composition is known. This is what one should expect. pH can thus retain its utility as a semi-quantitative measure of acidity in those systems where the detailed acid-base chemistry is not known (MACINNES, 1948). The question then arises as to which is the more useful, 'free' or 'total' hydrogen ion concentration. This is by no means a clear cut choice. The use of the 'free' hydrogen ion scale is certainly conceptually clearer in that the species HSO_4^- is well established, and ignoring its existence (although thermodynamically permissible) is inherently confusing. In order to use the 'free' hydrogen ion scale it is necessary to know a value for $\beta(HSO_4^-)$. This however is quite a weak association, and thus it is not a simple matter to determine an accurate value for the association constant. Any error in this value will result in a systematic error in the estimated 'free' hydrogen ion concentration. In those circumstances where an investigator believes that the value of $\beta(HSO_4^-)$ appropriate to his system is poorly known, it is probably better (although potentially more confusing) to employ a 'total' hydrogen ion concentration scale.

CONCLUSIONS

CULBERSON (1981) has recently reviewed the current status of pH measurements in sea water. In his discussion (pp. 202–204), he states that:

> "The major problem with the NBS pH scale for equilibrium measurements in sea water is the unreproducibility of its liquid junction potential, not its lack of theoretical meaning. . . . hydrogen ion concentration scales have no practical advantages for pH measurements in low (estuaries) or high (brines) salinity environments. . . . Adoption of one of the hydrogen ion concentration scales will still require the use of the NBS pH scale for measurements in estuaries and brines, and will mean that oceanographers use a pH scale different from that used by geochemists and biochemists."

Culberson then concludes that it would be more profitable to design a reproducible liquid junction than to adopt the 'free' or 'total' hydrogen ion pH scales.

Although I concur fully with the need for a reproducible liquid junction, and would refer the interested reader to the results of BIEDERMANN and DOUHÉRET (1980a,b,c) in this regard, I do not agree with Culberson's other comments.

In the preceding sections I hope to have brought out the advantages of experimental precision and conceptual simplicity that are inherent in using concentration constants rather than 'apparent' constants for the study of proton-transfer reactions in saline media, whether in the laboratory or in the field. These advantages are briefly summarised here.

(1) Constants based on hydrogen ion concentration scales (*i.e.* ionic medium standard states) are clear and unambiguous. In addition, they allow where desired the optimal precision in their determination.

(2) As a result of this, the relationship between such constants and the so-called "infinite dilution" values is readily apparent. This can be used either to test models of activity coefficients, or to predict

values of the stoichiometric constants for use in solutions where they have not been measured.

(3) If one is prepared to take the trouble, an estimation of hydrogen ion concentration is probably possible in any solution *whose composition is known.*

The measurement of pH *per se* (even if the problems of the reproducibility of the liquid junction are overcome) should only be a method of last resort. Its utility as a quantitative indication of the state of acid-base equilibria is tenuous at best, and is particularly so in solutions where the composition is not well known. Even in physiological media (~0.16 M NaCl), where the liquid junction problems are not as acute as they are for geochemical brines, there is no clear consensus as to the desirability of N.B.S. pH measurements compared to a hydrogen ion concentration scale (BATES, 1973; ANON., 1976).

Although the operational pH (NBS) scale is widely used by those geochemists studying lakes, streams, ground water etc., the same problems exist. In waters at a low ionic strength, it may be possible to utilize specially developed low ionic strength buffers together with a flowing cell (COVINGTON *et al.*, 1983). Such pH measurements would be expected to lie on the conventional hydrogen ion activity scale and could be used together with other thermodynamic data for modelling acid base processes in low ionic strength systems. In ground waters, or brines where the ionic strength is somewhat higher (>0.1*m*), it is not possible to ascertain to what extent such pH measurements are bedevilled by liquid junction problems. In these systems, the investigator will have to decide what accuracy is required for their investigation in order to ascertain whether conventional pH measurements are adequate, or whether an alternative approach is justified.

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