not formally analogous. Whether this is real is largely a matter of opinion since in the interpretation of the available ionization potentials different investigators ascribe varying characteristics to the unshared electron-pairs; nevertheless, I consider the point sufficiently interesting to warrant its mention. In the discussion of the structure of carbon monoxide[17] from the molecular orbital point of view, Mulliken describes the slightly antibonding (unshared) pair of electrons attached principally to the carbon atom as occupying an orbital which is essentially an *s*-orbital of carbon. On the other hand, in his discussion of ammonia and its methyl derivatives[18] it is primarily the $2p_z$-orbital of nitrogen which is nonbonding in character. We would accordingly expect that the bonds with borine formed by carbon monoxide and by trimethylamine would be somewhat different, and indeed that the latter would form a stronger bond with borine than the former inasmuch as the bonding power of a *p*-orbital (with greater concentration in the bond direction) is known to be greater than that of an *s*-orbital. Were it convenient to describe the character of the various electrons more quantitatively than is

possible at present so that the effects of polarity and hybridization could be estimated, the 14 kcal. difference between the B–N and B–C bonds predicted above would no doubt become evident.

Acknowledgments.—Sincere thanks are due to Dr. A. B. Burg for providing the samples, to Professor Linus Pauling for a number of very helpful discussions, and to Dr. L. O. Brockway for the use of his electron diffraction apparatus.

Summary

Two derivatives of diborane, borine carbonyl and borine trimethylammine, were investigated by means of an electron diffraction experiment on the vapors. The former compound was found to have its B–C–O atoms linearly arranged with the hydrogen atoms completing the tetrahedron around the boron. The best values for the inter-atomic distances are H–B = 1.20 ± 0.03 Å.; B–C = 1.57 ± 0.03 Å.; C–O = 1.13 ± 0.03 Å. The latter compound has the configuration $H_3BN(CH_3)_3$ with the distances B–N = 1.62 ± 0.15 Å.; N–C = 1.53 ± 0.06 Å. A discussion of the electronic structures of the molecules is then given and an explanation is suggested for the extraordinary difference in the stability of these compounds.

(17) R. S. Mulliken, *Phys. Rev.*, **46**, 549 (1934); *Rev. Modern Phys.*, **4**, 1 (1932).
(18) R. S. Mulliken, *J. Chem. Phys.*, **3**, 506 (1935).

The Standardization of Hydrogen Ion Determinations. I. Hydrogen Electrode Measurements with a Liquid Junction

BY DAVID I. HITCHCOCK AND ALICE C. TAYLOR

Introduction

Since it is not possible to determine the activity coefficient of a single type of ion in solution, or the value of a single liquid junction potential, it has been recognized (*cf.* Clark[1]) that *p*H values of aqueous solutions are expressed on an arbitrary scale. These values are obtained from the e. m. f. of cells such as

H_2, H^+ in aqueous solution, KCl(satd.), HgCl, Hg(+) (A)

by an equation of the form

$$pH = -\log C_H f_H = (E - E_0)/k \qquad (1)$$

in which C_H and f_H are the concentration and the arbitrary activity coefficient of the hydrogen ion, E is the e. m. f. of the cell in volts, E_0 is the po-

tential of the reference electrode with respect to the normal hydrogen electrode, and k is 0.05915 for 25°. Some workers[2] have used in place of E in equation (1) a value corrected for the liquid junction potential, which they have tried to estimate either by the Bjerrum extrapolation or by Henderson's formula. In most cases, however, it has become customary, following Clark,[1] to define *p*H by equation (1) in terms of the observed e. m. f., neglecting liquid junction potentials. These differences in procedure have led to the use of scales of *p*H (or *p*aH) differing by 0.04 or 0.05 (10 to 12% in $C_H f_H$), and to E_0 values dif-

(1) Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, 3rd ed., 1928.

(2) Sørensen and Linderstrøm-Lang, *Compt. rend. trav. lab. Carlsberg*, **15**, No. 6 (1924); Bjerrum and Unmack, *Kgl. Danske Videnskab. Selskab., Math.-fys. Medd.*, **9**, 1 (1929); Guggenheim and Schindler, *J. Phys. Chem.*, **38**, 533 (1933).

fering by nearly 4 millivolts for the same reference electrode.[2] Since the e. m. f. of the cells actually used is far more reproducible than these figures seem to imply, there is need of additional evidence in favor of some one scale of E_0 or pH values. Those of the earlier proposals[2] which involve a calculation of liquid junction potentials are not practical for solutions in general. In obtaining pH values by equation (1) with neglect of liquid junction potentials, it would be desirable to use a value for E_0 which would lead to correct values for the dissociation constants of weak electrolytes, since pH measurements are often used to determine such constants. In recent years Harned and his co-workers[3] have obtained exact values for the dissociation constants of weak acids from the e. m. f. of cells without liquid junction, and in the case of acetic acid their value is identical with that obtained by MacInnes,[4] who has applied modern theory to precise conductance measurements. This constant has been used by MacInnes[5] as the basis of a pH scale.

In the present work we have tried to test the possibility of establishing a pH scale which would be consistent with the known values of the thermodynamic dissociation constants of a number of weak acids, covering as wide a range as possible. In order to avoid measurements with extremely dilute solutions, we have tested an extrapolation procedure similar to that suggested[6] for use in obtaining activity coefficients from the e. m. f. of cells without liquid junction. The experiments have consisted in the measurement of the e. m. f. of cell A with buffer solutions, of ionic strength ranging from 0.01 to 0.10.

Experimental

Solutions.—Chemicals of reagent analyzed grade were used as starting materials. All salts were recrystallized except the potassium chloride used for the salt bridge. Acetates, chlorides and lithium glycolate (for which we are indebted to Dr. L. F. Nims) were analyzed by quantitative conversion to sulfates; phosphates, by ignition (cf. Clark[1]); and borax, by ignition and titration against hydrochloric acid (Kolthoff[7]) and against sodium hydroxide in the presence of invert sugar (Gilmour[8]).

Hydrochloric acid was distilled as the constant boiling mixture, and the concentration of a 0.1 N solution prepared on that basis was checked within 0.1% by titration against borax[7] and sodium carbonate. Acetic acid was not purified further. The composition of the acid salts other than phosphates was checked by titration against sodium hydroxide. The distilled water used had a specific conductivity of 1 to 2×10^{-6}. Solutions of ionic strength 0.1 were prepared on a concentration basis, using calibrated weights, and volumetric glassware calibrated at 21–23°. The stock buffer solutions containing acetate or glycolate were further analyzed for both components.

Apparatus and Procedure.—Hydrogen electrodes were of platinum wire, freshly platinized every day or two. Hydrogen was taken from a commercial tank without purification, after tests with dilute acid had shown no change in e. m. f. on passage of the gas over hot reduced copper in a quartz tube. The hydrogen was saturated with water vapor by bubbling through a tube of distilled water at 25°. The electrode vessels were of the type shown in Fig. 1, designed with the aid of Dr. L. F. Nims. Their
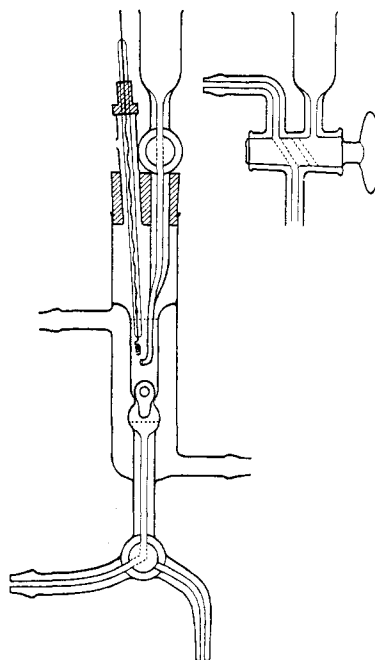

Fig. 1.—Hydrogen electrode cell for measurements with liquid junction.

temperature was kept at 25 ± 0.05° by water circulated from a constant temperature bath through the outer jacket, according to Simms.[9] The upper stopcock served to admit solution or hydrogen, which was kept bubbling continuously after each filling of the cell. The lower stopcock served to empty the cell or to admit potassium chloride solution (saturated at 21–23°) for the liquid junction, which was in the bulb (about 1 cm. wide). The glass bead above the bulb served to minimize disturbance of the junction by convection. The lower tube on the left was connected by glass and rubber tubing (not thermostated) to a reservoir of saturated potassium chloride solution, used for flushing the stopcock and making the liquid junctions, and to the reference electrode, which

(3) Harned and Ehlers, This Journal, **54**, 1350 (1932); also later papers.

(4) MacInnes and Shedlovsky, ibid., **54**, 1429 (1932).

(5) MacInnes, "Cold Spring Harbor Symposia on Quantitative Biology," **1**, 190 (1933); MacInnes and Belcher, to be published. We are indebted to Dr. MacInnes for access to unpublished data.

(6) Hitchcock, This Journal, **50**, 2076 (1928).

(7) Kolthoff, ibid., **48**, 1447 (1926).

(8) Gilmour, Analyst, **49**, 576 (1924).

(9) Simms, This Journal, **45**, 2503 (1923).

TABLE I

ELECTROMOTIVE FORCE AT 25° OF THE CELL
H₂, BUFFER SOLUTION, KCl(SATD.), HgCl, Hg(+)

Dilution factor	Composition of stock solution in moles per liter						
	0.0993 CH₃COOH 0.0991 CH₃COOK	0.0251 CH₃COOH 0.0999 CH₃COONa	0.1001 CH₃COOH 0.0994 CH₃COONa	0.4071 CH₃COOH 0.0996 CH₃COONa	0.025 KH₂PO₄ 0.025 Na₂HPO₄	0.05 Na₂B₄O₇	0.0999 CH₂OHCOOLi 0.0500 HCl
0.2	0.5220	0.5574	0.5217	0.4856	0.6596	0.7869	0.4675
.4	.5212	.5563	.5205	.4843	.6559	.7862	.4652
.6	.5206	.5555	.5197	.4835	.6534	.7863	.4638
.8	.5202	.5551	.5192	.4828	.6514	.7866	.4627
1.0	.5200	.5547	.5188	.4824	.6497	.7871	.4618
E_0	.2442	.2441	.2441	.2440	.2442	.2440	.2443

was a single saturated potassium chloride calomel half cell, kept at 25° by a water jacket. The calomel cell was completely filled with solution, so that no flow of liquid occurred when the stopcock was opened.

Duplicate hydrogen electrode cells were always used with the same solution. Before use each cell, with its electrode in place, was rinsed with several changes of distilled water and at least twice with the solution. The cells were then filled, the junctions carefully made, and the hydrogen turned on. Readings were taken at five-minute intervals until they became constant within less than 0.1 millivolt (fifteen to thirty minutes). The cells were then emptied, rinsed, refilled with the same solution, and the readings were repeated until constant. Each result here presented is thus based on at least eight concordant observations. Measurements were made with each solution at ten concentrations, from 0.01 to 0.10 ionic strength.

The constancy of the potential of the calomel half cell and the reproducibility of the method of making liquid junctions were confirmed by daily measurements with the same solution, an acetate buffer or 0.1 M hydrochloric acid. These readings always agreed within 0.1 millivolt throughout the period of this investigation, which occupied four months.

Electromotive force was measured to 0.01 millivolt with a Leeds and Northrup Type K potentiometer and Type R galvanometer, using a calibrated Eppley standard cell.

Results with Buffer Solutions

In Table I are given the concentrations of the components of each stock solution in moles per liter, and the electromotive force in volts, corrected to 1 atm. of dry hydrogen, obtained with each mixture at five concentrations. (In order to save space, less than half of the data are presented.) The values given for E_0 were obtained by extrapolation of these data, making use of the thermodynamic dissociation constants of the buffer acids, as determined by other workers from the electromotive force of cells without liquid junction. The negative logarithms of these dissociation constants are, at 25°: acetic acid, $pK = 4.756$ (Harned and Ehlers[3]); phosphoric acid, $pK_2 = 7.206$ (Nims[10]); boric acid, $pK = 9.237$

(10) Nims, THIS JOURNAL, **55**, 1946 (1933).

(Owen[11]); and glycolic acid, $pK = 3.831$(Nims[12]).

The method of extrapolation which was adopted is based on the following considerations. The ionization of a weak acid must follow exactly the law of mass action, using thermodynamic activities. If pK is the negative logarithm of the thermodynamic ionization constant and pH is the negative logarithm of the hydrogen ion activity, this may be written

$$pH = pK - \log \frac{C_{HA}}{C_A} - \log \frac{f_{HA}}{f_A} \qquad (2)$$

Since the scale of pH values is to be so defined as to make equation (1), which is arbitrary, consistent with equation (2), which is exact, the right members of these equations may be equated. This makes it possible to define an experimental quantity, E', by the relation

$$E' = E - kpK + k \log \frac{C_{HA}}{C_A} = E_0 - k \log \frac{f_{HA}}{f_A} \qquad (3)$$

Since activity coefficients, by definition, approach unity at infinite dilution, an extrapolation of E' to zero concentration should give E_0. A plot of E' against either μ or $\sqrt{\mu}$, for the range here studied, gives a line of considerable curvature, and this extrapolation is uncertain. Straighter curves may be obtained by making use of the Debye–Hückel theory in the approximate form

$$\log \frac{f_{HA}}{f_A} = A \sqrt{\mu} - B\mu \qquad (4)$$

where A is 0.506 for 25° and B may or may not be a constant. The combination of equations (3) and (4) makes it possible to define another experimental quantity, E'', by the relation

$$E'' = E - kpK + k \log \frac{C_{HA}}{C_A} + kA \sqrt{\mu} = E_0 + kB\mu \qquad (5)$$

For the phosphate mixtures equations (4) and (5) were altered, in accordance with theory, by the use of $3A$ instead of A.

(11) Owen, *ibid.*, **56**, 1695 (1934).

(12) Nims, *ibid.*, **58**, 987 (1936).

The left member of equation (5) contains only known quantities. The ratio C_{HA}/C_A is almost equal to the ratio of the acid and salt components of the buffer. For the phosphate mixture the two ratios are identical. For the ace-
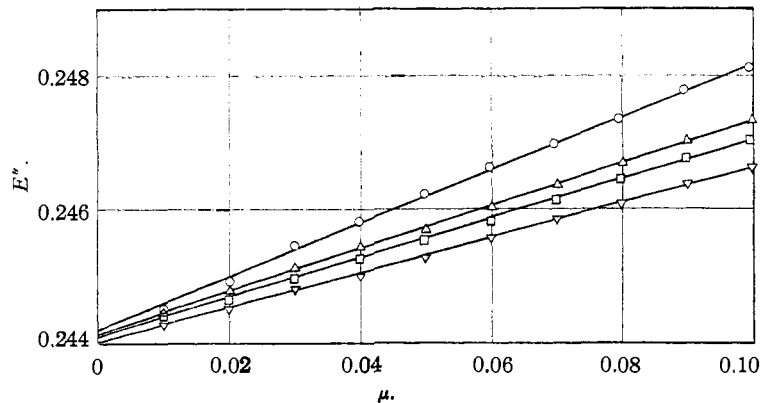

Fig. 2.—Extrapolation of hydrogen electrode data for acetate buffers: circles, acetic acid:potassium acetate = 1:1; triangles, acetic acid:sodium acetate = 1:4; squares, acetic acid:sodium acetate = 1:1; inverted triangles, acetic acid:sodium acetate = 4:1.

tate and glycolate buffers a more exact value for C_{HA}/C_A was obtained by subtracting the concentration of hydrogen ions from the acid concentration and adding it to the salt concentration, thus allowing for the ionization of the weak acid. The values used for C_H were obtained with sufficient accuracy (1 or 2 significant figures) by assuming the validity of the ionic strength principle and using in equation (1) values for E_0 and f_H obtained from results with hydrochloric acid (Table II). For the borax solutions hydrolysis was assumed, according to the equation

$$Na_2B_4O_7 + H_2O = 2Na^+ + 2BO_2^- + 2HBO_2$$

or

$$Na_2B_4O_7 + 5H_2O = 2Na^+ + 2H_2BO_3^- + 2H_3BO_3$$
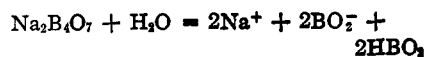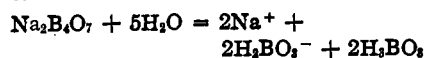
If these reactions went to completion, borax would be a perfect 1:1 buffer. Actually the alkalinity of the solutions corresponded to $C_{OH} = 2 \times 10^{-5}$, indicating a reaction of borate ion with water to form 2×10^{-5} moles of additional undissociated acid. Hence C_{HA} was obtained by adding C_{OH} to the equivalent concentration of sodium ion, and C_A by subtracting C_{OH} from the same concentration. Only in the

case of the glycolate mixtures did these corrections have any significant effect on the extrapolation.

The ionic strength, μ, in equation (5) was taken as equal to the concentration of sodium or potassium acetate in the acetate buffers, four times the molar concentration of either salt in the 1:1 phosphate mixtures, twice the molar concentration of borax ($Na_2B_4O_7$), and $C_{Li} + C_H$ in the mixtures of lithium glycolate with hydrochloric acid.

The extrapolation, illustrated in Figs. 2 and 3, consisted in plotting E'' against μ, drawing the best line to represent the observed points, and reading off the intercept at zero ionic strength. The points for the acetate buffers, as shown in Fig. 2, fell on straight lines, having practically the same intercept, $E_0 = 0.2441 \pm 0.0001$. The phosphate and borate data, as shown in Fig. 3, fell on curved lines, and accordingly the extrapolation is less certain. Some doubt may be justified as to the extrapolation of the glycolate data because of the relatively large correction due to C_H in calculating the ratio C_{HA}/C_A; the effect of this
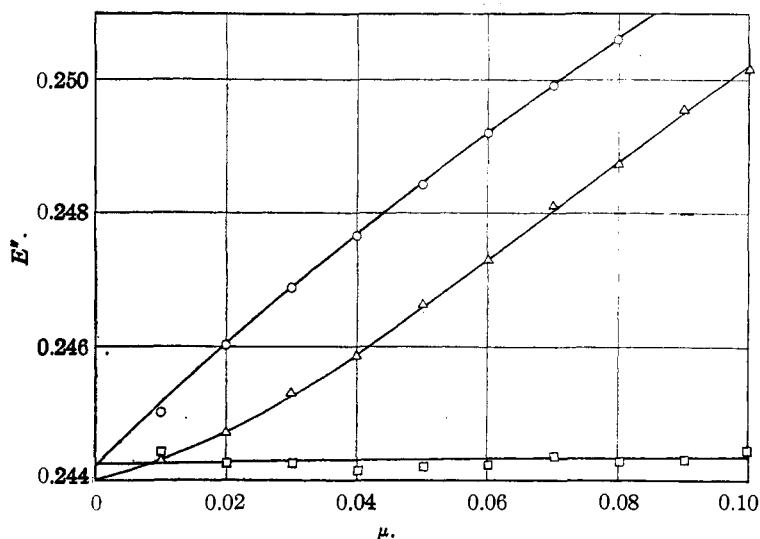

Fig. 3.—Extrapolation of hydrogen electrode data for 1:1 buffers: circles, phosphate; triangles, borate; squares, glycolate.

in E'' amounted to 0.2, 0.4 and 1.7 millivolts at ionic strengths of 0.10, 0.05 and 0.01, respectively. It may be concluded from Fig. 3, however, that the E_0 derived for the acetate buffers is not inconsistent with the measurements on the three

other buffers, since the average intercept of their curves is 0.2442 ± 0.0002 volt. From these results it was concluded that the use of 0.2441 for E_0 with our cells would lead to a pH scale, between pH 4 and 9 at least, consistent with the true pK values of weak acids.

Results with Hydrochloric Acid Solutions

In order to determine whether the same scale could consistently be applied to more acid solutions, measurements were made with hydrochloric acid, with and without 9 equivalents of the chloride of another univalent cation. Here the quantities E' and E'' were given a slightly different significance, since complete dissociation was assumed and the Debye theory was applied to f_H.

$$E' = E + k \log C_H = E_0 - k \log f_H \qquad (3a)$$
$$- \log f_H = A\sqrt{\mu} - B\mu \qquad (4a)$$
$$E'' = E + k \log C_H - kA\sqrt{\mu} = E_0 - kB\mu \qquad (5a)$$

Since these solutions contained only uni-univalent strong electrolytes, the ionic strength was taken as the sum of the acid and salt concentrations.
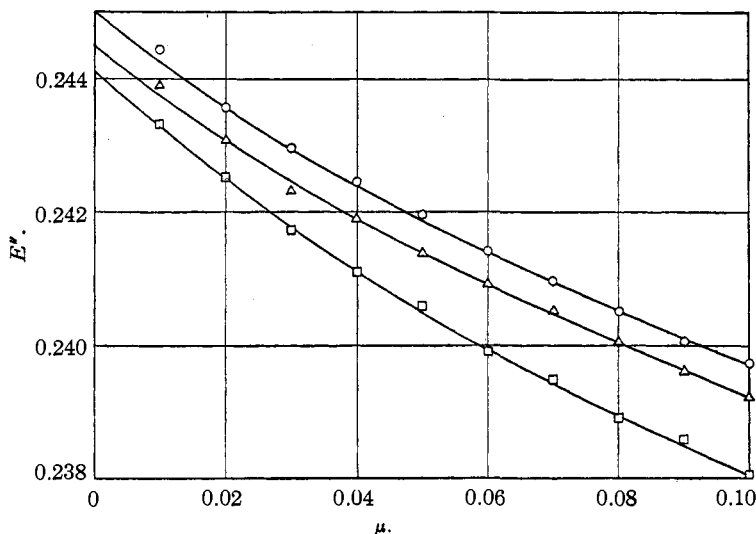

Fig. 4.—Extrapolation of hydrogen electrode data for hydrochloric acid solutions: circles, without salt; triangles, with 9 equivalents of potassium chloride; squares, with 9 equivalents of sodium chloride.

The results obtained with hydrochloric acid alone, and with potassium or sodium chloride, are given in Table II and Fig. 4. It was found that ammonium chloride gave a curve slightly lower than that for potassium chloride, while lithium chloride had about the same effect as sodium chloride. None of these curves was a straight line, and their intercepts were not concordant with one another nor with those given by the buffer mixtures, ex-

TABLE II

ELECTROMOTIVE FORCE AT 25° OF THE CELL

H_2, HCl + MCl, KCl(SATD.), HgCl, Hg(+)

Dilution factor	Composition of stock solution, moles per liter		
	0.1 HCl (no salt)	0.01 HCl 0.09 KCl	0.01 HCl 0.09 NaCl
0.2	0.3483	0.4069	0.4064
.4	.3311	.3897	.3889
.6	.3210	.3797	.3787
.8	.3139	.3726	.3714
1.0	.3083	.3670	.3658
E_0	.2450	.2445	.2441

cept in the case of the acid sodium chloride solutions, for which E_0 was 0.2441. Apparently at the junction of the saturated potassium chloride solution with even a very dilute solution of hydrochloric acid there was a potential difference nearly a millivolt higher than that at the junctions with the buffer solutions. The fact that the effect of the salts shown in Fig. 4 was in the order of the mobilities of their cations also suggested an influence of liquid junction potentials. Accordingly an attempt was made to correct the data of Table II for liquid junction potentials by the use of Henderson's formula. This procedure lowered the curves by 2.5 to 3.5 millivolts, but it did not make them coincide and the divergence of their intercepts was even greater than before. This result is in accordance with the conclusion of Hamer and Acree[13] that partial corrections for liquid junction potentials lead to larger errors than no corrections, as it is generally admitted that Henderson's formula gives only a partial correction, which may be counteracted in part by a term involving the activity coefficients of the ions.

It may be concluded that the calculation of pH values from a single E_0 leads only to an arbitrary scale for these strongly acid solutions, except for mixtures of sodium chloride and hydrochloric acid of pH 2 to 3, for which this extrapolation gave the same E_0 as that obtained for the buffer solutions.

Standard Solutions for Checking Electrodes

In Table III are given pH values, based on the E_0 value of Table I, for a number of reproducible solutions. The hydrochloric acid solutions and the 0.1 N acetate buffers were found to give un-

(13) Hamer and Acree, *J. Research Nat. Bur. Standards*, **17**, 605 (1936).

Table III

Standard Solutions for Checking Electrodes at 25°

Composition in moles per liter	New scale	pH according to Previous workers
0.1 HCl	1.085	1.075 (Scatchard[17])
.1 KH$_3$(C$_2$O$_4$)$_2$·2H$_2$O (tetroxalate)	1.490	
.01 HCl + 0.09 NaCl	2.058	2.068 (Sørensen,[2] paH, 18°)
.01 HCl + 0.09 KCl	2.078	2.078 (Sørensen,[2] paH, 18°)
.03 KHC$_4$H$_4$O$_6$ (tartrate)	3.567	
.1 KH$_2$C$_6$H$_5$O$_7$ (citrate)	3.719	3.72 (Kolthoff,[14] paH)
.05 KHC$_8$H$_4$O$_4$ (phthalate)	4.008	4.015 (MacInnes[5])
.1 HC$_2$H$_3$O$_2$ + 0.1 NaC$_2$H$_3$O$_2$ (acetate)	4.648	4.62^a (Clark,[1] Michaelis)
.01 HC$_2$H$_3$O$_2$ + 0.01 NaC$_2$H$_3$O$_2$	4.714	4.703 (MacInnes[5])
.025 KH$_2$PO$_4$ + 0.025 Na$_2$HPO$_4$	6.857	6.85^a (Clark,[1] 20°, interp.)
.05 Na$_2$B$_4$O$_7$	9.180	9.19^a (Clark,[1] from Walbum)

^{a} These older values probably should be increased by 0.04 to put them on the paH scale of Sørensen.[2]

changed e. m. f. readings after several weeks or months in ordinary glass bottles. The phosphate and borax solutions were reproducible to 0.1 millivolt only when freshly prepared. Solutions of a single anhydrous acid salt are more readily prepared and analyzed than any of these. Potassium hydrogen phthalate was used successfully by Clark[1] with his rocking electrode, but we repeatedly have found it to give drifting potentials with bubbling hydrogen unless it had been recrystallized 3 times at 25°. Potassium dihydrogen citrate was found by Kolthoff[14] not to remain anhydrous, and we have observed molds in its solution, as well in that of the acid tartrate; the addition of thymol as an antiseptic led to erratic hydrogen electrode readings. One acid salt which may make a desirable standard solution is potassium tetroxalate. Its crystals were found to have the theoretical composition, KH$_3$(C$_2$O$_4$)$_2$·2H$_2$O, after drying in ordinary air at room temperature. A solution of this salt, saturated at 0°, has been recommended by Schomaker and Brown[15] for the preparation of a standard quinhydrone electrode, but we have preferred to weigh the salt and check the concentration of the solution by titration with standard alkali and permanganate solutions.

Comparisons with the Work of Others

Since our scale of pH values does not depend on the reproducibility but only on the constancy of our calomel half cell, it is not suggested that its E_0 value be used by others. The solutions of Table III, when used with a hydrogen electrode, are probably better standards for the calculation

of pH values than is any calomel half cell. It may be noted, however, that our figure of 0.3083 volt for the hydrogen electrode in 0.1 N hydrochloric acid against the saturated calomel half cell is identical with that given by La Mer and Baker,[16] who made their liquid junction around a ground glass stopper. A value of 0.3084 or 0.3085 may be calculated from results obtained by Scatchard[17] after the flow of solutions at his junction had been stopped. Clark,[1] however, selected 0.3094 for this cell, and earlier workers who used capillary or plugged junctions obtained values nearly 1 millivolt higher. Our figure for 0.1 N acetic acid in 0.1 N sodium acetate is 0.5190, which is identical with that chosen by Clark.[1]

In the last column of Table III are given pH values obtained by others for some of the solutions which we have studied. They agree with our values, in most cases, within 0.01 pH, but this is true only because they were obtained, generally, by authors who tried to define pH (or paH) on an activity basis, with little or no correction for liquid junction potentials. Of these workers only, MacInnes[5] has based his scale on thermodynamic dissociation constants, and his scale will agree with ours within a few tenths of a millivolt. He concluded that E_0 was 0.3358 for the tenth-normal potassium chloride calomel electrode with neglect of liquid junction potentials. Direct measurements of this cell against the saturated potassium chloride calomel electrode were made by Fales and Mudge,[18] who found the latter to be 0.0918 ± 0.0002 volt less positive, by Bjerrum and Unmack,[2] who reported 0.0912, and by Riehm,[19] who found 0.0913. If the average,

(14) Kolthoff and Vleeschhouwer, Biochem. Z., 179, 410 (1926); 183, 444 (1927).

(15) Schomaker and Brown, Ind. Eng. Chem., Anal. Ed., 9, 34 (1937).

(16) La Mer and Baker, This Journal, 44, 1961 (1922).

(17) Scatchard, ibid., 47, 641, 696, 3107 (1925).

(18) Fales and Mudge, ibid., 42, 2434 (1920).

(19) Riehm, Z. physik. Chem., A160, 1 (1932).

0.0914, is added to our E_0, 0.2441, we get, as E_0 for the tenth-normal electrode, 0.3355, in fair agreement with MacInnes.

Summary

Measurements of electromotive force were made at 25° using the cell: H_2, buffer solution, KCl (satd.), HgCl, Hg. By extrapolation of the data obtained with acetate, phosphate, borate and glycolate buffer solutions, a single value of E_0 for this calomel half cell was obtained, on the basis of the thermodynamic dissociation constants of the acids used. The same value was · obtained from measurements with hydrochloric acid in sodium chloride solutions, but not with the acid alone nor with potassium chloride. This E_0 value was used to assign pH values to a series of standard solutions from pH 1 to 9, without correction for liquid junction potentials. It is suggested that this pH scale may be used as a basis for the exact determination of the thermodynamic dissociation constants of weak acids from hydrogen electrode measurements with buffer solutions, containing the acid and its sodium salt, provided that the pK of the acid lies between 4 and 9.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

The Apparent Molal Volume of Inorganic Salts in Methanol Solution[1]

BY J. B. STARK AND E. C. GILBERT

Since the work of Masson[2] showing that the apparent solution volume of a large number of salts in aqueous solution is a linear function of the square root of the volume concentration, considerable interest has been attached to the problem and it has been studied extensively in numerous laboratories.[3]

Redlich and Rosenfeld[4] have attempted to justify this behavior on the basis of the Debye–Hückel theory, although the linear relationship where observed often seems to hold in solutions far too concentrated for such treatment. Johnson and Martens[5] found the relationship to hold for alkali halides in liquid ammonia. However, as the number of substances investigated has increased and the experimental precision has improved, it is becoming more evident that the rectilinear relationship is by no means universally valid.

Deviations from relationships which are based on interionic attraction frequently are more pronounced in solvents of low dielectric or become evident at lower concentration, hence it was be-lieved that a study of the apparent molal volume of salts in alcoholic solution might provide useful information, particularly if salts were chosen for which data are also available for their aqueous solutions. Methanol was chosen as the solvent for this study because of its higher solvent power for salts and its relative ease of purification. Density data in the literature for alcoholic solutions of inorganic salts are for the most part somewhat unsatisfactory and few calculations of the apparent molal volume have been made. Vosburgh, Connell, and Butler[6] studied the electrostriction produced by alkali halides in aliphatic alcohols and calculated apparent molal volumes. Gibson and Kincaid[3] have recently reported the apparent volumes, also of alkali halides, in methanol and glycol. The data of Jones and Fornwalt[8] obtained for viscosity measurements, also permit easy and accurate calculation of the apparent molal volumes of alkali and ammonium halides.

Experimental

Ammonium nitrate, potassium thiocyanate, calcium nitrate, and mercuric chloride were chosen as suitable salts, and the densities of a series of solutions of varying concentrations were determined at 25°, using methanol as solvent.

Materials.—Synthetic methanol was purified by the method of Lund and Bjerrum,[7] omitting the treatment with tribromobenzoic acid from their procedure. The density of the alcohol obtained was 0.786644. The

(1) This paper is taken from a thesis presented by J. B. Stark in partial fulfilment of the requirements for the M.S. degree at the Oregon State College, June, 1937.

(2) Masson, *Phil. Mag.*, [7] **8**, 218 (1929).

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