The equation $\ln p = A/T + B$ applies to the single phase solutions and to the mixtures of crystals, as is shown in Fig. 2, which is a plot of $\ln p$ versus $1/T \times 10^5$ for the fourteen solutions and three crystalline mixtures. Straight lines result in each case.

This equation is applicable to water also in the temperature range 0 to 60° within the error in plotting on ordinary semi-log paper, but above 60° a third term has to be added to the equation. This condition also applies to our dilute solutions. For the more concentrated solutions the two term equation fits the data even more closely than it does the water data, or the dilute solution data.

Discussion

The vapor pressure measurements are considered of sufficient accuracy to study the variation of Babo's constant, P/P_0 (relative humidity), with temperature. In general, the data available up to this paper indicate that this value is constant within the experimental accuracy. Leopold and Johnston[8] stated that there would be a slight increase in relative humidity with increase of temperature for accurate measurements. Table II confirms this statement; there is a definite rise in Babo's constant with rise in temperature. This trend was found for all of the experimental data except the 20° readings for the two most dilute solutions. Duplicate determinations of these two values, however, fell in the general trend. This trend obtained regardless of the order in which the vapor pressure readings were taken for the various temperatures. This same trend has been obtained in general in all of the measurements on the nitrates in this series of studies.

Quite serious errors would arise in measuring the vapor pressure for a solution at one temperature, and then calculating the vapor pressure at another temperature, far removed, by assuming that P/P_0 is constant. For solution 6 [61.70% $Cd(NO_3)_2$], which may be considered typical, determining P/P_0 at 30° (0.5385) and then calculating the vapor pressure at 60° ($P/P_0 = 0.5661$ actually) would cause an error of 4.61%. This is an error of 3.90 mm. for the vapor pressure at this temperature.

Summary

Complete vapor pressure data for the system cadmium nitrate–water are given from 0 to 86% concentration and for the temperature range 20–60°. These vapor pressures are for the unsaturated, saturated, and supersaturated solutions, and for the mixtures of crystals.

Babo's constant (P/P_0) is shown to increase appreciably with temperature for the binary system cadmium nitrate–water.

BETHLEHEM, PENNA. RECEIVED SEPTEMBER 9, 1938

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[8] Leopold and Johnston, THIS JOURNAL, **49**, 1974 (1927).

[CONTRIBUTION FROM THE LABORATORY OF PHYSIOLOGY, YALE UNIVERSITY SCHOOL OF MEDICINE]

The Standardization of Hydrogen Ion Determinations. II. A Standardization of the *p*H Scale at 38°

BY DAVID I. HITCHCOCK AND ALICE C. TAYLOR[1]

In a recent paper[2] a revision of the *p*H scale was proposed, as a result of hydrogen electrode measurements made with buffer solutions at 25°, in cells including a stationary liquid junction with saturated potassium chloride solution. This revision involved the use of the thermodynamic dissociation constants of the buffer acids together with an extrapolation based, in part, on the Debye–Hückel theory. A consistent scale was obtained for solutions of about *p*H 4 to 9. Since this range includes that part of the *p*H scale which is of primary importance in physiology and biochemistry, it seemed worth while to extend the work by making similar measurements at 38°, a temperature which is close to that of physiological fluids.

Experimental

The materials, apparatus and technique were practically the same as in the earlier work.[2] The concentrations of the solutions were expressed, as before, in moles per liter of solution at room temperature, 21–23°. The series of buffer solutions was extended by preparing mixtures of hydrochloric acid with sodium or potassium acetate or disodium hydrogen phosphate, in such proportions as to yield 1:1 buffers.

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[1] This work was aided by a grant from the Fluid Research Funds of the Yale University School of Medicine.

[2] Hitchcock and Taylor, THIS JOURNAL, **59**, 1812 (1937).

TABLE I

ELECTROMOTIVE FORCE AT 38° OF THE CELL H_2, BUFFER SOLUTION, KCl (SATD.), HCl (0.1 N), H_2 (+)

Dilution factor	Composition of stock solution in moles per liter at 21–23°						
	0.0996 CH_3COOH 0.0990 CH_3COONa	0.0501 CH_3COOH 0.0501 CH_3COONa 0.0501 NaCl	0.0899 CH_3COOH 0.0898 CH_3COOK	0.0501 CH_3COOH 0.0504 CH_3COOK 0.0501 KCl	0.0250 KH_2PO_4 0.0250 Na_2HPO_4	0.0200 NaH_2PO_4 0.0200 Na_2HPO_4 0.0200 NaCl	0.0500 $Na_2B_4O_7$
0.10					0.3682	0.3680	0.4944
.25	0.2231	0.2224	0.2240	0.2232	.3642	.3637	.4936[a]
.50	.2218	.2209	.2230	.2219	.3602	.3592	.4924
.75	.2209	.2197	.2224	.2211	.3573	.3561	.4926
1.00	.2205	.2189	.2220	.2205	.3552	.3537	.4931[b]
E_0	−0.0668	−0.0673	−0.0662	−0.0669	−0.0671	−0.0671	−0.0668

[a] The dilution factor for this borax solution was 0.20 instead of 0.25. [b] Average of seven determinations with different solutions. The figure used in plotting the curve in Fig. 2 was 0.4929.

TABLE II

ELECTROMOTIVE FORCE AT 38° OF THE CELL H_2, HCl + MCl, KCl(satd.), HCl(0.1 N), H_2 (+)

Dilution factor	Composition of stock solution in moles per liter at 21–23°		
	0.1000 HCl (no salt)	0.0100 HCl 0.0900 NaCl	0.0100 HCl 0.0900 KCl
0.10	0.0602	0.1208	0.1211
.25	.0362	.0969	.0973
.50	.0180	.0787	.0793
.75	.0075	.0680	.0687
1.00	.0000	.0604	.0613
E_0	−0.0657	−0.0668	−0.0665

In addition to the control of temperature given by the water-jacketed electrode vessels, which remained at 38 ± 0.05°, the whole apparatus was placed in an electrically controlled air-bath at 38 ± 0.5°. This served to prevent the deposition of solid potassium chloride in the bridge tubes and the condensation of moisture in the hydrogen train. The purity of the commercial hydrogen was tested in a few experiments by passing it over hot reduced copper; since this purification produced no change in the electromotive force obtained with hydrochloric acid (pH 1 or 2) or borax solutions (pH 9), it was generally omitted, and the hydrogen was passed only through distilled water at 38°. As before, the experiments consisted in the measurement of the electromotive force of cells of the type

H_2, acid or buffer solution, KCl (satd.), HgCl, Hg (+) (A)

Several different calomel half cells were used at different times, and their constancy and reproducibility were tested by daily measurements against hydrogen electrodes in 0.1 N hydrochloric acid or an acetate buffer. Since the different calomel cells varied, in some cases, by as much as a millivolt, the results were expressed in terms of the following cell, of which the right half served as a constant reference electrode

H_2, acid or buffer solution, KCl (satd.), HCl (0.1 N), H_2 (+) (B)

The values of the electromotive force of this cell are given in Tables I and II.

Method of Calculation and Extrapolation

Tables I and II include also values of E_0, the extrapolated value of the electromotive force which cell B would have if the activity of hydrogen ions in the solution in the left half cell were unity. The values of E_0 were obtained by extrapolation to zero ionic strength of a function E'', obtained from the experimental results by the following equations

Acetate buffers: $$E'' = E - 0.06173\left(4.766 - \log\frac{C_{HA}}{C_A} - 0.520\sqrt{\mu}\right)$$

Phosphate buffers (1:1): $$E'' = E - 0.06173\,(7.190 - 1.560\sqrt{\mu})$$

Borax buffers: $$E'' = E - 0.06173\left(9.143 - \log\frac{C_{HA}}{C_A} - 0.520\sqrt{\mu}\right)$$

Hydrochloric acid solutions: $$E'' = E + 0.06173\,(\log C_H - 0.520\sqrt{\mu})$$

The basis of similar equations was given in the previous paper.[2] Here E is the electromotive force of cell B in volts, 0.06173 is 2.3026 RT/F, 0.520 is the constant of the Debye–Hückel limiting law, μ is the ionic strength of the solution and the numbers 4.766, 7.190 and 9.143 are the negative logarithms of the thermodynamic dissociation constants of the buffer acids, interpolated for 38° from the data of Harned and Ehlers,[3] Nims[4] and Owen,[5] respectively. The ionic strength was calculated on the basis of concentration, in moles per liter at 21–23°, and the same basis was used for C_H of the hydrochloric acid solutions. Strictly this is not consistent with the pK values used, which were obtained on the molal basis. Density determinations showed a maximum discrepancy of 1.2% between the values of C and m for certain solutions at 0.1 ionic strength, but this difference becomes less than 0.25% for very dilute solutions. It was calculated that these differences could not affect the values of E'' and E_0 by more than 0.1 mv., and that the extrapolation therefore yielded

(3) Harned and Ehlers, THIS JOURNAL, **55**, 652 (1933).

(4) Nims, *ibid.*, **55**, 1946 (1933).

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

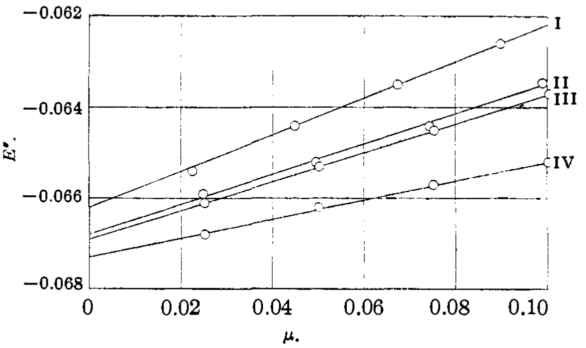

Fig. 1.—Extrapolation of hydrogen electrode data for 1:1 acetate buffers at 38°: I, $CH_3COOH + CH_3COOK$; II, $CH_3COOH + CH_3COONa$; III, $CH_3COOH + CH_3COOK + KCl$; IV, $CH_3COOH + CH_3COONa + NaCl$.

a *p*H scale consistent with thermodynamic dissociation constants expressed in terms of molality. The nature of the extrapolations is illustrated by Figs. 1, 2 and 3.

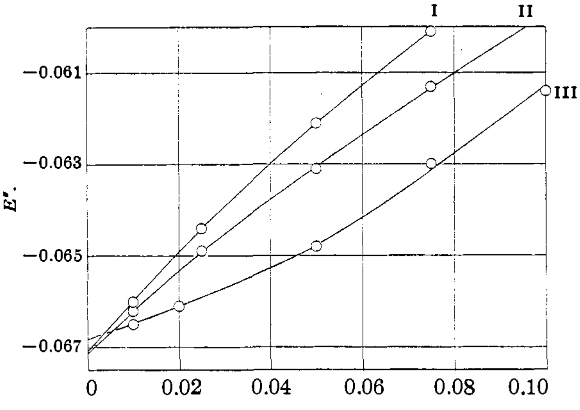

Fig. 2.—Extrapolation of hydrogen electrode data for 1:1 phosphate and borate buffers at 38°: I, $KH_2PO_4 + Na_2HPO_4$; II, $NaH_2PO_4 + Na_2HPO_4 + NaCl$; III, $Na_2B_4O_7$.

Results

The E_0 values for the buffer mixtures at 38°, as given in Tables I and II, are less concordant than those obtained for 25°. There is evidence of a specific effect of different ions, in the order to be expected if the E_0 values include a part of the liquid junction potentials. Solutions containing cations of higher mobility (hydrogen or potassium in place of sodium ions) yielded higher values of E'' and E_0, while those containing anions of higher mobility (chloride in place of acetate or phosphate ions) yielded lower values. If the high figure obtained for the hydrochloric acid solutions without salt is disregarded, as in the previous work[2] at 25°, the mean value of E_0 is −0.0668, with an average deviation of ±0.0002 v. This value, which is identical with that obtained for solutions of hydrochloric acid with sodium chloride (*p*H 2 to 3), acetic acid with sodium acetate (*p*H 4.7), and borax (*p*H 9), was adopted as a basis for a *p*H scale applicable at 38°. The *p*H values were calculated, without correction for liquid junction potentials, by the usual simple equation, which is

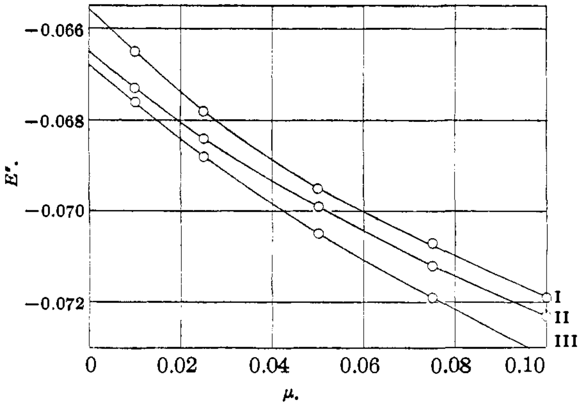

Fig. 3.—Extrapolation of hydrogen electrode data for hydrochloric acid solutions at 38°: I, HCl without salt; II, HCl + KCl (1:9); III, HCl + NaCl (1:9).

$$pH = (E + 0.0668)/0.06173$$

for cell B at 38°.

In Table III are given the *p*H values obtained in this way for a number of standard solutions which may be used for checking electrodes. Values obtained for the same solutions at 25° are included for comparison. Except for 0.1 *N* hydrochloric acid, whose *p*H value is determined by that of E_0 for cell B, the results are reported only to the nearest 0.005 *p*H, which corresponds to 0.3 mv. Since more measurements were made with 0.1 *N* hydrochloric acid and with the 0.1 *N* acetic acid–sodium acetate buffer than with other

TABLE III

STANDARD SOLUTIONS FOR CHECKING ELECTRODES AT 38 AND 25°

Composition in moles per liter at 21–23°	*p*H (38°)	*p*H (25°)
0.1 HCl	1.082	1.085
.1 $KH_3(C_2O_4)_2 \cdot 2H_2O$	1.495	1.480[a]
.01 HCl + 0.09 KCl	2.075	2.075
.05 $KHC_8H_4O_4$	4.025	4.010
.1 CH_3COOH + 0.1 CH_3COONa	4.655	4.645
.025 KH_2PO_4 + 0.025 $Na_2HPO_4 \cdot 2H_2O$	6.835	6.855
.05 $Na_2B_4O_7 \cdot 10H_2O$	9.070	9.180

[a] The *p*H value 1.490, which was published previously[2] for 25°, referred to a tetroxalate solution of lower concentration, 0.0965 *M*.

solutions, their values are particularly recommended as a basis for a *p*H scale applicable at 38°.

Discussion

Table III includes *p*H values for 0.1 *N* hydrochloric acid, although the E_0 values obtained from experiments with this acid alone were not used. This procedure did not invalidate the use of this solution in the reference half cell, since the *p*H scale was determined by the behavior of the various solutions in the left half of cell B. In spite of the discordant E_0 value obtained from data with more dilute hydrochloric acid, it seemed desirable to assign to 0.1 *N* hydrochloric acid, which is a reproducible standard solution, *p*H values consistent with those of the acid–salt mixtures and the buffer solutions.

There is practically no difference between the *p*H values obtained for hydrochloric acid of ionic strength 0.1, either with or without salt, at 25 and 38°. It may be calculated from the data of Harned and Ehlers[6] that the negative logarithm of the mean activity of the ions in 0.1 molal hydrochloric acid is 1.099 at 25° and 1.102 at 38°. Evidently the effect of temperature on these thermodynamic activities is of the same small magnitude as its effect on the non-thermodynamic *p*H values for hydrochloric acid solutions.

The *p*H values given in Table III for the buffer solutions show a somewhat larger variation with temperature, although the effect exceeds 0.02 *p*H in only one case. For the acetate, phosphate and borate solutions the differences, *p*H (25°) − *p*H (38°), are −0.01, +0.02 and +0.11, respectively. The corresponding differences in the *pK* values of the buffer acids at the two temperatures are −0.010, +0.016 and +0.094. Although it is recognized that *p*H values cannot have a strictly thermodynamic significance, it seems worth while to point out that an agreement between these two sets of differences might be deduced from the thermodynamic law of mass action if *p*H were a measure of either the concentration or the activity of hydrogen ions and if the variation with temperature of the activity coefficients of the buffer acids were negligibly small.

The only previous work in which a scale of *p*H values has been based on thermodynamic dissociation constants is that of MacInnes.[7] His experimental data, which have appeared in a paper by MacInnes, Belcher and Shedlovsky,[8] were obtained principally with very dilute acetate buffers, 0.001 to 0.01 in ionic strength, and were extrapolated by a method which gives marked curvature when applied to results for higher concentrations. If their data for 25° are reduced to our reference electrode and plotted by our method, they agree fairly well with ours at 0.01 ionic strength. Below that point, where we have no data, their results approach an E_0 value about 0.5 mv. higher than ours. Hence their *p*H scale should be lower than ours by about 0.008 *p*H. A comparison of their Table VII with Table III of the present paper shows that this is approximately true, except for their 0.1 *N* acetate buffer at 38°. Here they give a *p*H value slightly lower than their value for 25°, while our *p*H value, like that of *pK*, is about 0.01 unit higher for 38 than for 25°. For many purposes a discrepancy of 0.01 *p*H is not significant. It may be concluded that either our scale or theirs gives *p*H values which are reasonably consistent with thermodynamic dissociation constants.

Our work on the standardization of hydrogen ion determinations is being continued by an experimental study of a measure of acidity obtained from cells without liquid junction, according to ideas expressed by Guggenheim[9] and by one of us.[10]

Summary

Measurements of electromotive force at 38° are reported for cells of the type

H_2, buffer or acid solution, KCl (satd.), HCl (0.1 *N*), H_2 (+)

Acetate, phosphate and borax buffers were used, as well as solutions of hydrochloric acid with and without an added chloride. On the basis of the thermodynamic dissociation constants of the buffer acids and a nearly linear extrapolation, a value of E_0 was obtained for the reference electrode: KCl (satd.), HCl (0.1 *N*), H_2. On this basis *p*H values for 38° were assigned to several standard solutions, including 0.1 *N* hydrochloric acid (*p*H 1.082) and 0.1 *N* acetic acid in 0.1 *N*

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[6] Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933).

[7] MacInnes, *Cold Spring Harbor Symposia on Quantitative Biology*, 1, 190 (1933). We wish to acknowledge again the courtesy of Dr. MacInnes in supplying us with unpublished data for comparison with our own, and to express our regret over the premature publication of two *p*H values ascribed to him in Table III of our previous paper.[2] These values should be replaced by those given later by MacInnes, Belcher and Shedlovsky.[8]

[8] MacInnes, Belcher and Shedlovsky, THIS JOURNAL, **60**, 1094 (1938).

[9] Guggenheim, *J. Phys. Chem.*, **34**, 1758 (1930).

[10] Hitchcock, THIS JOURNAL, **58**, 855 (1936); **59**, 2753 (1937).

sodium acetate (pH 4.655). These pH values, without correction for liquid junction potentials, serve to establish a pH scale which may be used to obtain the values of thermodynamic dissociation constants at 38°.

New Haven, Conn. Received July 29, 1938

[Contribution from the Chemical Laboratory of the University of Illinois and the Williams Oil-O-Matic Heating Corporation]

Hydrogen Bonds Involving the C–H Link. V. The Solubility of Methylene Chloride in Donor Solvents

By M. J. Copley, G. F. Zellhoefer and C. S. Marvel

Recent publications[1–3] by the authors have shown that hydrogen bonding, involving the C–H link, occurs in solutions of the haloforms in solvents containing the donor atoms, oxygen or nitrogen. In one article[1] data were included on the solubilities of the two dihalogenated methanes, methylene chloride and monofluoromonochloromethane, in three donor solvents (diethylene glycol dimethyl ether, ethyl ether of diethylene glycol acetate and tetraethylene glycol dimethyl ether). Their solubilities were in considerable excess of the values predicted by Raoult's law and almost comparable with the solubilities observed for the haloforms in the same solvents. These results led the authors to suggest that a hydrogen atom of a dihalogenated methane is also capable of forming a hydrogen bond with an oxygen or nitrogen atom having an exposed pair of electrons. Such an activity for hydrogen bonding on the part of the hydrogen atoms, in these very stable compounds, was somewhat unexpected and it seemed important to extend the investigation to include a larger number of types of solvents.

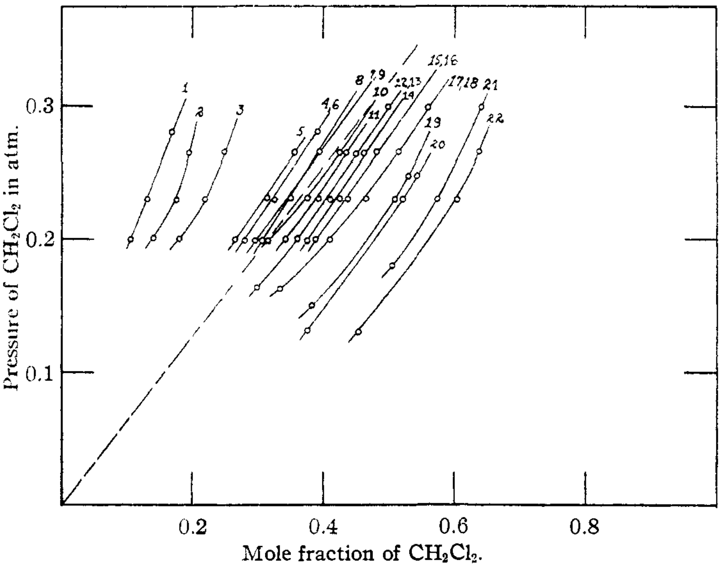

Fig. 1.—The solubility of methylene chloride as a function of pressure in alcohols, ethers, acids, esters, aldehydes, and ketones: 1, phenol; 2, acetic acid; 3, propionic acid; 4, anisole; 5, salicylaldehyde; 6, phenyl vinyl ether; 7, benzaldehyde; 8, Δ^2-cyclohexenone; 9, acetylacetone; 10, paraldehyde; 11, heptaldehyde; 12, ethyl acetoacetate; 13, triphenyl phosphite; 14, cyclohexanone; 15, acetonylacetone; 16, 1,4-dimethoxycyclohexane; 17, ethyl diethylacetoacetate; 18, tri-*o*-cresol phosphate; 19, ethyl ether of diethylene glycol acetate; 20, diethyl ether of diethylene glycol; 21, tri-*n*-butyl phosphate; 22, dimethyl ether of tetraethylene glycol.

The present paper reports the solubilities of methylene chloride in the same group of solvents[3] as was used by the authors in their study of the effect of solvent association on the solubility of haloforms. The remarkable similarity we have observed in the behaviors of dihalogenated methanes and haloforms clearly demonstrates that a hydrogen atom in either type of compound interacts with an unshared pair of electrons on an oxygen or nitrogen atom of a solvent and thus gives rise to the phenomenon called hydrogen bonding.

Experimental

The method[4] used in making the solubility determinations has been described previously in detail. The solvents tested were purified carefully and their boiling or melting points checked. The solubilities were determined over a range of pressure at a temperature of 32.2°. The results of the solubility measurements are plotted in Figs. 1 and 2. To compare the solvents conveniently, the gram per gram and mole fraction solubilities at a partial pressure of methylene chloride corresponding to its vapor pressure at 4.5° are given, re-

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[1] Zellhoefer, Copley and Marvel, This Journal, **60**, 1337 (1938).

[2] Zellhoefer and Copley, *ibid.*, **60**, 1343 (1938).

[3] IV, Copley, Zellhoefer and Marvel, *ibid.*, **60**, 2666 (1938).

[4] G. F. Zellhoefer, *Ind. Eng. Chem.*, **29**, 584 (1937).