$$[S_8] = 1/\bar{K}_3 \qquad (23)$$

$$W = \frac{1}{\bar{K}_8}([S_8]_0 \bar{K}_3 - 1) \qquad (24)$$

$$N = \frac{1}{\bar{K}_3}\sqrt{8\bar{K}_1([S_8]_0\bar{K}_3 - 1)} \qquad (25)$$

Experimental measurements of magnetic susceptibility[5] and electron spin resonance in liquid sulfur[5,6]

(5) J. A. Poulis, C. H. Massen, and D. V. D. Leeden, *Trans. Faraday Soc.*, **58**, 474 (1962).

(6) J. A. Poulis and W. Derbyshire, *ibid.*, **59**, 559 (1962).

confirm the estimates of polymer sulfur chain length at various temperatures made by Gee.[2] These data, as well as equilibrium monomer concentration as a function of temperature, were exceptionally well explained by the Tobolsky–Eisenberg theory both above and below the transition temperature. Exactly the same mathematical results apply to the new model presented here, with a slight reinterpretation of the numerical values of the equilibrium constants, as shown in eq. 22b.

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Reference Buffer Solutions for pH Measurements in 50% Methanol. Dissociation Constants of Acetic Acid and Dihydrogen Phosphate Ion from 10 to 40°

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Contribution from the National Bureau of Standards, Washington, D. C. Received May 23, 1964

Electromotive force measurements of cells with hydrogen and silver–silver chloride electrodes containing buffer solutions in 50 wt. % methanol–water solvents have been used to determine conventional values of $pa_H{}^*$ *(= $-log\ m_H \cdot {}_s\gamma_H$) for three reference solutions from 10 to 40°. The dissociation constants of acetic acid and dihydrogen phosphate ion in 50% methanol have likewise been determined over the same temperature range, and thermodynamic quantities for the dissociation processes have been derived.*

Introduction

A mixture consisting of equal parts by weight of water and methanol (referred to in this paper as 50% methanol) is a very useful solvent for many compounds whose solubility in water is too small for measurements of acidity and dissociation constants to be made. Progress in this field would be aided by a knowledge of the properties of reference buffer solutions in 50% methanol. In particular, the standardization of the conventional pH meter for use with 50% methanol solutions could then be made with confidence.

The pH values of two solutions, one of which is 0.01 M with respect to both oxalic acid and ammonium hydrogen oxalate and the other 0.01 M with respect to both succinic acid and lithium hydrogen succinate have already been determined[1] in water–methanol solutions at 25°. We now report data for solutions in three buffer series, namely acetate, phosphate, and succinate, over a range of concentration and temperature in 50% methanol as solvent. These values may be regarded as reference points for an operational scale of pH* in this useful mixed solvent.[2]

In addition, the dissociation constant of acetic acid and the second dissociation constant of phosphoric acid have been determined from 10 to 40°, the associated thermodynamic quantities have been calculated, and a comparison has been made with the behavior of these acids in aqueous solution.

Symbols

${}_s\gamma_i$ is the activity coefficient of the species i, on the molal scale, relative to the hypothetical standard state *in 50% methanol;* ${}_s\gamma_i$ approaches unity at infinite dilution in 50% methanol.

${}_sK$ is the equilibrium constant (on the molal scale) of an acid–base reaction, such as $HA \rightleftharpoons H^+ + A^-$.

$${}_sK = \frac{m_H m_A}{m_{HA}} \frac{{}_s\gamma_H \cdot {}_s\gamma_A}{{}_s\gamma_{HA}}$$

Thus $\Delta G° = -RT \ln ({}_sK)$ is the increase in Gibbs energy when a mole of HA (in its standard state *in 50% methanol*) dissociates into a mole of H^+ and a mole of A^-, each in its standard state *in 50% methanol.*

${}_s(a_H\gamma_{Cl}) \equiv m_H \cdot {}_s\gamma_H \cdot {}_s\gamma_{Cl}$ is a well-defined thermodynamic quantity; both ${}_s\gamma_H$ and ${}_s\gamma_{Cl}$ have the properties of ${}_s\gamma_i$ defined above.

$pa_H{}^*$ is, by definition, $p_s(a_H\gamma_{Cl}) + \log\ {}_s\gamma_{Cl}$, where ${}_s\gamma_{Cl}$ is assigned a conventional value (see eq. 4).

${}_sE°$ is the standard e.m.f. of the cell: H_2, HCl in 50% methanol, AgCl; Ag. Thus, $\Delta G° = -F({}_sE°)$ is the increase in Gibbs energy for the reaction $0.5H_2 + AgCl \rightarrow Ag + H^+ + Cl^-$, both H^+ and Cl^- being in their standard states *in 50% methanol.*

(1) C. L. De Ligny, P. F. M. Luykx, M. Rehbach, and A. A. Wieneke, *Rec. trav. chim.*, **79**, 713 (1960).

(2) R. G. Bates, M. Paabo, and R. A. Robinson, *J. Phys. Chem.*, **67**, 1833 (1963).

Experimental

Acetic acid was cooled until approximately one-half had frozen. This portion, on analysis by means of the mass spectrometer and by gas chromatography, was found to contain 0.6 mole % acetic anhydride and less than 0.01 mole % water.[3] An equimolal stock solution of acetic acid, sodium acetate, and sodium chloride (each about 0.1 M) was prepared by the addition of the requisite amounts of sodium carbonate (dried at 275°) and sodium chloride to a standardized aqueous solution of acetic acid. This solution was then diluted with water and methanol to form a solvent medium consisting of 50% methanol and 50% water by weight. Spectrograde methanol was used. The aqueous stock solution was prepared several days before the measurements were begun, thus assuring complete hydrolysis of the small amount of acetic anhydride which the purified acetic acid contained.

NBS standard samples 186Ib and 186IIb of potassium dihydrogen phosphate and disodium hydrogen phosphate, respectively, were used to prepare the phosphate buffer solutions. Succinic acid of reagent grade was recrystallized once from hot water. Analysis by titration with standard alkali indicated an amount of titratable hydrogen corresponding to 100.02% of the theoretical. Sodium succinate hexahydrate, which lost 39.99% by weight on heating (calcd. 40.01%), was rendered anhydrous by heating at 110°. The sodium hydrogen succinate buffer solutions were then prepared by combining equimolal amounts of succinic acid and sodium succinate.

Calculation of pa_H*

The e.m.f. of the cell

Pt; $H_2(g)$ (1 atm.), buffer soln., Cl⁻ (in 50% MeOH), AgCl; Ag (I)

is given by

$$E = {}_sE° - k \log {}_s(a_H\gamma_{Cl}m_{Cl}) \qquad (1)$$

where k is written for $(RT \ln 10)/F$, or, alternatively

$$p_s(a_H\gamma_{Cl}) \equiv -\log {}_s(a_H\gamma_{Cl}) = (E - {}_sE°)/k +$$
$$\log m_{Cl} \qquad (2)$$

The e.m.f. of cell I has been measured[4] with 50% methanol as solvent for solutions of hydrochloric acid ranging from 0.005 to 0.05 m in composition and over the temperature range 10 to 40°. Details of the cell construction and values of the standard potential, $_sE°$, have already been reported.[4]

Table I contains values of $p_s(a_H\gamma_{Cl})$ for ten equimolal solutions of acetic acid (HAc), sodium acetate, and sodium chloride, for ten equimolal solutions of sodium hydrogen succinate (NaHSuc) and sodium chloride, and for ten equimolal solutions of potassium dihydrogen phosphate, disodium hydrogen phosphate, and sodium chloride. The values of the measured e.m.f., not given in Table I, can be obtained if desired by eq. 2 with the use of $_sE°$, the composition of the solution, and values of $p_s(a_H\gamma_{Cl})$ given in Table I.

(3) Analysis by E. E. Hughes of the Analysis and Purification Section.
(4) M. Paabo, R. A. Robinson, and R. G. Bates, *J. Chem. Eng. Data*, 9, 374 (1964).

Table I. Values of $p_s(a_H\gamma_{Cl})$ in 50 Wt. % Methanol

I	Temp., °C.						
---	10	15	20	25	30	35	40
Buffer: $KH_2PO_4(m)$ + $Na_2HPO_4(m)$ + $NaCl(m)$; $I = 5\ m$							
0.01	8.343	8.325	8.311	8.301	8.294	8.292	8.293
0.02	8.292	8.273	8.259	8.248	8.241	8.238	8.238
0.03	8.254	8.235	8.221	8.210	8.202	8.198	8.198
0.04	8.224	8.204	8.189	8.178	8.170	8.166	8.165
0.05	8.197	8.178	8.163	8.151	8.143	8.138	8.137
0.06	8.173	8.154	8.139	8.127	8.119	8.114	8.112
0.07	8.152	8.132	8.117	8.105	8.097	8.091	8.089
0.08	8.132	8.113	8.097	8.085	8.076	8.071	8.068
0.09	8.113	8.094	8.078	8.066	8.057	8.051	8.048
0.10	8.096	8.077	8.061	8.049	8.040	8.033	8.031
Buffer: $HAc(m)$ + $NaAc(m)$ + $NaCl(m)$; $I = 2\ m$							
0.01	5.674	5.666	5.661	5.660	5.662	5.667	5.676
0.02	5.674	5.666	5.661	5.660	5.662	6.667	5.676
0.03	5.674	5.666	5.661	5.659	5.662	5.667	5.676
0.04	5.675	5.666	5.661	5.659	5.661	5.667	5.675
0.05	5.675	5.666	5.661	5.659	5.661	5.667	5.675
0.06	5.676	5.666	5.661	5.659	5.661	5.666	5.675
0.07	5.676	5.666	5.661	5.659	5.661	5.666	5.675
0.08	5.676	5.666	5.660	5.659	5.661	5.666	5.675
0.09	5.676	5.666	5.660	5.659	5.660	5.666	5.675
0.10	5.677	5.667	5.660	5.658	5.660	5.666	5.675
Buffer: $NaHSuc(m)$ + $NaCl(m)$; $I = 2\ m$							
0.01	5.968	5.951	5.938	5.929	5.923	5.921	5.922
0.02	5.950	5.933	5.919	5.910	5.903	5.901	5.901
0.03	5.935	5.917	5.902	5.892	5.886	5.882	5.883
0.04	5.921	5.902	5.888	5.877	5.870	5.866	5.866
0.05	5.910	5.890	5.875	5.864	5.857	5.853	5.852
0.06	5.900	5.880	5.865	5.853	5.846	5.841	5.841
0.07	5.891	5.872	5.857	5.845	5.836	5.831	5.829
0.08	5.885	5.865	5.850	5.838	5.830	5.826	5.826
0.09	5.881	5.861	5.845	5.833	5.826	5.822	5.822
0.10	5.878	5.858	5.842	5.831	5.824	5.820	5.821

The quantity, pa_H*, related to $p_s(a_H\gamma_{Cl})$ by

$$pa_H* \equiv p_s(a_H\gamma_{Cl}) + \log {}_s\gamma_{Cl} \qquad (3)$$

can only be evaluated if a convention is adopted for calculating the single ion activity coefficient, $_s\gamma_{Cl}$, of chloride ion in 50% methanol.

For aqueous solutions of ionic strength (I) less than 0.1, Bates and Guggenheim[5] recommended the convention

$$-\log \gamma_{Cl} = \frac{AI^{1/2}}{1 + \rho I^{1/2}} \qquad (4)$$

Here

$$A = \frac{1.8246 \times 10^6}{(\epsilon T)^{3/2}} d_0^{1/2}$$

where d_0 and ϵ are the density and dielectric constant, respectively, of the solvent, and ρ ($= B\mathring{a}$) was taken as 1.5 mole$^{-1/2}$ kg.$^{1/2}$. As B is given by the expression

$$B = \frac{50.29 \times 10^8}{(\epsilon T)^{1/2}} d_0^{1/2}$$

this is equivalent to assigning a value of 4.56 Å. for the ion-size parameter ($\mathring{a}$) of chloride ion in aqueous solution at 25°. It would appear reasonable to use this value of $\mathring{a}$ at other temperatures and for methanol-water solvents unless the methanol content is very high (>80%). This convention for $_s\gamma_{Cl}$ thus becomes

(5) R. G. Bates and E. A. Guggenheim, *J. Pure Appl. Chem.*, 1, 163 (1960).

entirely consistent with the convention on which γ_{Cl} and standard pH values in aqueous solution are based.

Values of A and B ($= \rho/\hat{d}$) can be calculated using the known dielectric constants of methanol–water solvents; those for 50% methanol from 10 to 40° have already been published.[4] The pa_H^* values for each of the three series of buffer solutions calculated with the aid of this convention are summarized in Table II.

Table II. Values of pa_H^* in 50 Wt. % Methanol

| I | Temp., °C. | | | | | | |
	10	15	20	25	30	35	40
Buffer: $KH_2PO_4(m)$ + $Na_2HPO_4(m)$ + $NaCl(m)$; $I = 5\ m$							
0.01	8.277	8.258	8.243	8.232	8.225	8.221	8.221
0.02	8.204	8.184	8.168	8.157	8.148	8.144	8.142
0.03	8.151	8.131	8.115	8.102	8.093	8.088	8.086
0.04	8.109	8.088	8.071	8.058	8.049	8.043	8.040
0.05	8.072	8.051	8.034	8.021	8.011	8.004	8.001
0.06	8.040	8.019	8.002	7.988	7.978	7.971	7.967
0.07	8.011	7.990	7.973	7.959	7.948	7.940	7.936
0.08	7.984	7.963	7.946	7.932	7.921	7.913	7.908
0.09	7.960	7.939	7.921	7.907	7.896	7.887	7.882
0.10	7.937	7.916	7.898	7.884	7.872	7.863	7.858
Buffer: $HAc(m)$ + $NaAc(m)$ + $NaCl(m)$; $I = 2\ m$							
0.01	5.608	5.599	5.593	5.591	5.592	5.597	5.604
0.02	5.586	5.577	5.571	5.568	5.569	5.573	5.580
0.03	5.571	5.561	5.555	5.552	5.553	5.556	5.563
0.04	5.560	5.549	5.543	5.540	5.540	5.543	5.550
0.05	5.550	5.539	5.532	5.529	5.529	5.533	5.540
0.06	5.542	5.531	5.524	5.520	5.520	5.524	5.530
0.07	5.535	5.523	5.516	5.512	5.512	5.515	5.522
0.08	5.529	5.517	5.509	5.505	5.505	5.508	5.515
0.09	5.523	5.511	5.503	5.499	5.499	5.502	5.508
0.10	5.518	5.506	5.498	5.493	5.493	5.496	5.502
Buffer: $NaHSuc(m)$ + $NaCl(m)$; $I = 2\ m$							
0.01	5.902	5.884	5.870	5.860	5.854	5.850	5.850
0.02	5.863	5.844	5.829	5.818	5.811	5.806	5.806
0.03	5.832	5.812	5.797	5.785	5.777	5.772	5.770
0.04	5.806	5.786	5.770	5.757	5.748	5.743	5.741
0.05	5.784	5.764	5.747	5.734	5.725	5.719	5.716
0.06	5.766	5.745	5.728	5.714	5.705	5.698	5.696
0.07	5.750	5.729	5.712	5.698	5.688	5.680	5.676
0.08	5.738	5.716	5.698	5.684	5.675	5.668	5.666
0.09	5.728	5.705	5.688	5.674	5.664	5.658	5.656
0.10	5.720	5.697	5.680	5.666	5.656	5.650	5.648

Dissociation Constants

The dissociation constant of acetic acid in 50% methanol was determined in the following manner. With the aid of the definition

$$_sK = \frac{a_H m_{A^-} \gamma_{A^-}}{m_{HA} \gamma_{HA}} \tag{5}$$

where A^- denotes acetate ion and HA the undissociated acetic acid molecule, eq. 1 can be written

$$E - {}_sE° = -k \log \left[{}_sK \frac{m_{Cl} m_{HA}}{m_{A^-}} \cdot \left(\frac{\gamma_{Cl} \gamma_{HA}}{{}_s\gamma_{A^-}} \right) \right] \tag{6}$$

or, since $m_{A^-} = m_{HA} = m_{Cl} = m$

$$p({}_sK) - \log {}_s\left(\frac{\gamma_{Cl} \gamma_{HA}}{\gamma_{A^-}} \right) = \frac{E - {}_sE°}{k} + \log m \tag{7}$$

Thus a plot of the right side of eq. 7 against m should give $p({}_sK)$ as the limiting value when m approaches 0. This simplified treatment is possible because acetic acid

is so weak in 50% methanol that the correction for its dissociation is negligible.

The plot was found to be linear and almost horizontal, as would be expected from the presumed approximate equality of γ_{Cl} and γ_{A^-}. The value of $p({}_sK)$ at each temperature was evaluated by the method of least squares. The results are given in Table III, together with the standard deviation of the intercept.

Table III. p_sK Values of Acetic Acid and Dihydrogen Phosphate Ion in 50% Methanol

| Temp., °C. | Acetic acid | | | Dihydrogen phosphate ion | | |
	p_sK (exptl.)	σ_i	p_sK (calcd.)	p_sK (exptl.)	σ_i	p_sK (calcd.)
10	5.673	0.002	5.674	8.480	0.001	8.482
15	5.665	0.002	5.665	8.469	0.002	8.465
20	5.662	0.001	5.661	8.452	0.001	8.453
25	5.660	0.001	5.660	8.443	0.002	8.445
30	5.662	0.001	5.662	8.441	0.002	8.441
35	5.665	0.001	5.668	8.442	0.001	8.440
40	5.677	0.002	5.676	8.443	0.002	8.444

Shedlovsky and Kay[6] made conductance measurements from which they derived the dissociation constant of acetic acid at 25° in water–methanol mixtures of compositions ranging from 10 to 100% methanol. Although they did not make measurements in 50% methanol as solvent, we can interpolate from their results at 20, 40, 60, and 80% methanol a value of $p_sK = 5.654$ in 50% methanol, which compares very well with our value of 5.660.

Bacarella, Grunwald, Marshall, and Purlee[7] also derived values of p_sK from e.m.f. data of suitable cells at 25°; from their results, we interpolate a value of $p_sK = 5.657$ at 50% methanol, again in good agreement with our value.

When applied to the second dissociation constant of phosphoric acid, eq. 7 becomes

$$p({}_sK_2) - \log {}_s\left(\frac{\gamma_{Cl} \gamma_{H_2PO_4^-}}{\gamma_{HPO_4^{-2}}} \right) = \frac{E_s - E°}{k} + \log m \tag{8}$$

The activity coefficient term is no longer small but can be approximated by the expression

$$\log {}_s\left(\frac{\gamma_{Cl} \gamma_{H_2PO_4^-}}{\gamma_{HPO_4^{-2}}} \right) = \frac{2A\sqrt{I}}{1 + B\hat{d}\sqrt{I}} - \beta I \tag{9}$$

where A and B are the appropriate Debye–Hückel constants (on the molal scale) for 50% methanol[4] and $\hat{d}$ is the "ion-size" parameter. As I is 5 m, eq. 8 becomes

$$p({}_sK_2) + 5\beta m = \frac{E - {}_sE°}{k} + \log m + \frac{2A\sqrt{I}}{1 + B\hat{d}\sqrt{I}} \tag{10}$$

A satisfactory linear plot of $[p({}_sK_2) + 5\beta m]$ vs. m was obtained with $\hat{d} = 4.4$ Å., and $p({}_sK_2)$ was evaluated in the usual way by the method of least squares. These $p({}_sK_2)$ values from 10 to 40° are given in Table III along with the standard deviations.

(6) T. Shedlovsky and R. L. Kay, *J. Phys. Chem.*, **60**, 151 (1956).
(7) A. L. Bacarella, E. Grunwald, H. P. Marshall, and E. L. Purlee, *J. Org. Chem.*, **20**, 747 (1955).

Thermodynamic Quantities

The values of $p(_sK)$ for both acetic acid and phosphoric acid have been fitted to the equation[8]

$$p(_sK) = A_1/T - A_2 + A_3T \qquad (11)$$

where T is the Kelvin temperature, $t(°C.) + 273.15$, again using the method of least squares. The numerical values found for the three constants are summarized in Table IV.

Table IV. Thermodynamic Quantities for the Dissociation of Acetic Acid and Dihydrogen Phosphate Ion[a]

| | — Acetic acid — | | — Dihydrogen — phosphate ion | |
	Water	50% methanol	Water	50% methanol
A_1	1170.48	1755.02	1979.5	2092.05
A_2	3.1649	6.1509	5.3541	5.2254
A_3	0.013399	0.019870	0.019840	0.022316
$\Delta G°$	6488	7721	9823	11,521
$\Delta H°$	−95	−52	987	496
$\Delta S°$	−22.1	−26.1	−29.6	−37.0
$\Delta C_p°$	−37	−54	−54	−61
Temp.$_{max}$ (°K.)	295.6	297.2	315.9	306.2
$-\log (_sK_{max})$	4.756	5.660	7.180	8.440

[a] $\Delta G°$ and $\Delta H°$ in cal. mole^{-1}; $\Delta S°$ and $\Delta C_p°$ in cal. deg.$^{-1}$ mole^{-1}.

The $p(_sK)$ values calculated with the aid of these constants are given in Table III. By standard procedures, the Gibbs energy change, $\Delta G°$, the enthalpy change, $\Delta H°$, the entropy change, $\Delta S°$, and the heat capacity change, $\Delta C_p°$, for the dissociation process at 25° have been calculated, as well as the temperature at which $_sK$ has its maximum value and the value of $p(_sK)$ at this temperature. The results are compared with the corresponding data for aqueous solutions. In Table IV the thermodynamic data are given in thermochemical calories, 1 thermochemical calorie being defined as 4.1840 joules.

Discussion

There is reason to believe that the methanol molecule is intrinsically a weaker base than the water molecule. The apparent increase in the total basicity of the medium when the aqueous solvent is enriched with methanol may thus result from a breakdown of the water structure, increasing the number of free water molecules.[9] It is noteworthy that the entropy change for the dissociation of acetic acid and dihydrogen phosphate ion

in 50% methanol is not greatly different from that in the aqueous solvent. It seems likely therefore that the primary protolytic process is the *hydration* of protons in both solvents and that the small increases in the negative value of $\Delta S°$ observed are the result of the different electrostatic effects on the processes concerned.

It was suggested earlier[2] that pa_H* (referred to the standard state s rather than that in pure water) constitutes the most useful unit for a practical pH scale in alcohol-water media that is available at the present time. Inasmuch as the pH response of many glass electrodes is substantially unimpaired in 50% methanol[7, 10] and, furthermore, the liquid-junction potential also displays satisfactory reproducibility,[2] the glass electrode pH meter can be used.

The operational pH* is defined in terms of a standard pH*(S) just as pH is defined in terms of pH(S).

$$pH* = pH*(S) + \frac{E_x - E_s}{(RT \ln 10)/F} \qquad (12)$$

For selected standard reference solutions

$$pH*(S) \equiv pa_H* \qquad (13)$$

The values of pa_H* given in Table II may thus be regarded as standard values of pH*(S) for the determination of the operational pH* in 50% methanol by eq. 12.

Operational pH* values obtained in this way may therefore be expected *to approach* the dimensions of pa_H* under ideal conditions and as such have a definite significance in terms of chemical equilibria in water-alcohol solvents. The measurement of pH* and the use of pH* values have been considered in some detail elsewhere.[11]

The question of the "accuracy" of these reference values is a difficult one to assess. The reproducibility of the e.m.f. of cell I is of the order of 0.1 to 0.2 mv. The *precision* of $p_s(a_H\gamma_{Cl})$ is accordingly about 0.003 unit, but a further uncertainty of about this magnitude is inherent in the values of $_sE°$ used. As the conventional values of $_s\gamma_{Cl}$ are considered exact, the accuracy of the conventional values of pa_H* is of the order of 0.005 unit, the accuracy being somewhat less at 10 and 40° than at 25°. The accuracy of the scale of pH* fixed by these reference solutions involves the additional question of internal consistency, that is, the constancy of the liquid-junction potential when one of the three reference solutions is replaced by another. Until more information on this matter has been obtained, it seems reasonable to assign an over-all uncertainty of ±0.01 unit to the pH* scale in 50% methanol.

(8) H. S. Harned and R. A. Robinson, *Trans. Faraday Soc.*, 36, 973 (1940).
(9) E. A. Braude and E. S. Stern, *Nature*, 161, 169 (1948); *J. Chem. Soc.*, 1976 (1948).

(10) M. Paabo, M. S. Thesis, George Washington University, 1962.
(11) R. G. Bates, "Determination of pH," John Wiley and Sons, Inc., New York, N. Y., 1964, pp. 222–229, 378.