sponsored by the Ozark Chemical Company, Tulsa, Oklahoma.

Summary

1. Anhydrous monofluorophosphoric acid was prepared by reaction of anhydrous metaphosphoric acid with liquid anhydrous hydrogen fluoride according to the equation $HPO_3 + HF = H_2PO_3F$. The reaction was complete.

2. In the reaction of a 100% orthophosphoric acid with anhydrous hydrogen fluoride in a 1:1 molar ratio, mono- and difluorophosphoric acids

were formed in equilibrium according to the equations

$$H_3PO_4 + HF \rightleftharpoons H_2PO_3F + H_2O \quad (1)$$

$$H_2PO_3F + HF \rightleftharpoons HPO_2F_2 + H_2O \quad (2)$$
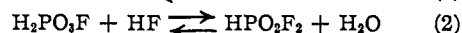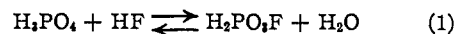
In the reaction product, 33% of the orthophosphoric acid had remained unchanged, 60% was transformed into mono- and 7% into difluorophosphoric acids. The first of the above equilibrium reactions has been described earlier.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

The Molal Electrode Potentials of the Silver–Silver Chloride Electrode in i-Propyl Alcohol–Water Mixtures from 0 to 40°[1]

BY ROBERT LEE MOORE[2] WITH W. A. FELSING

Object of the Investigation.—The purpose of this investigation was the continuation of the study of the effect of changes in solvent media upon the thermodynamic properties of strong electrolytes. Such studies were initiated by Harned and co-workers[3] at Yale University and some work has been reported from this Laboratory by Patterson and Felsing.[4] These latter determined the molal electrode potential of the silver–silver chloride electrode in 10 and 20% ethyl alcohol–water mixtures and the ionization constants of propionic acid in the same solvents as well as in 10 and 20% methyl alcohol–water mixtures. It was intended to extend such measurements to propyl and i-propyl alcohol solutions in order to determine the effect of the lengthening of the aliphatic carbon chain on these quantities. In such determinations, the value of the molal potential of the reference silver–silver chloride electrode is needed for the calculation of the ionization constant of the weak acid. This was determined by the use of cells of the type

$$H_2(g) \mid HCl(m), H_2O(X), \text{Solvent} (Y) \mid AgCl(s) + Ag(s)$$
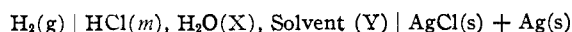
The only report found in the literature on cells containing propyl or i-propyl alcohol was that of Harned and Calmon,[5] who determined the molal potential in 10% i-propyl alcohol at a single temperature, 25°. No work, apparently, has been done in n-propyl alcohol–water mixtures. This is readily understandable in view of our inability to obtain reversible or reproducible behavior with the hydrogen electrode in this solvent.

Experimental Procedures

The preparation and purification of the materials used as well the techniques employed are presented under appropriate headings following

Hydrochloric Acid.—Constant boiling hydrochloric acid was prepared by the method of Foulk and Hollingsworth[6] and the concentrations corresponding to the prevailing barometric pressures were obtained from their tables. In preparing solutions from this material, the molecular weight was taken to be 36.465.

n-Propyl Alcohol.—Eastman Kodak Company "White Label" n-propyl alcohol was dried by the method of Lund and Bjerrum[7] and was then distilled through a one-meter, packed column.

i-Propyl Alcohol.—A commercial 99% material was dried by refluxing over unslaked lime for five hours and was subsequently fractionated through a column packed with glass helices. The middle portion of the distillation was reserved for use.

Hydrogen.—Commercial electrolytic tank hydrogen was washed by passage through a purifying train consisting of sulfuric acid–dichromate solution, sodium hydroxide solution, and water. It was then passed through a drying tube packed with "Drierite" into a heated tube containing copper turnings to remove any traces of oxygen. Upon entering the thermostat, the hydrogen was passed through a twenty-foot coil of copper tubing in order to attain the bath temperature before reaching the pre-saturators.

Electrodes.—The hydrogen electrodes were constructed from platinum foil (1 × 1½ cm.) sealed into soft glass tubes; they were platinized in the usual manner. The silver–silver chloride electrodes were of two types. Those employed in the majority of the measurements were of the type described by Patterson and Felsing,[4] in which a silver oxide–silver chlorate paste was thermally decomposed. In one series of measurements the Harned Type-2 electrode[8] was also employed. Apparently, the two types were equally satisfactory, the observed cell voltages agreeing to within the precision of measurement. The electrodes were always allowed to age several days in small portions of the solutions on which determinations were made prior to the actual voltage measurements.

Solutions.—Stock solutions somewhat less than one-half molal in hydrochloric acid were prepared in the desired solvent mixtures by weighing out suitable quanti-

(1) Constructed from a portion of the thesis to be presented to the graduate faculty of the University of Texas by Robert Lee Moore in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1947.

(2) du Pont Fellow, 1945–1946, 1946–1947.

(3) Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Co., New York, N. Y., 1942.

(4) Patterson with Felsing, THIS JOURNAL, **64**, 1478 (1942).

(5) Harned and Calmon, ibid, **61**, 1491 (1939).

(6) Foulk and Hollingsworth, ibid., **45**, 1229 (1923).

(7) Lund and Bjerrum, Ber., **64B**, 210 (1931).

(8) Harned, THIS JOURNAL, **51**, 416 (1929).

ties of the constant boiling acid, anhydrous alcohol, and conductivity water; the balance was sensitive to 1 milligram. Ten-liter quantities of 5, 10 or 20% i-propyl alcohol were prepared by weight on a balnce sensitive to 0.05 g. The solutions on which measurements were to be made were prepared by weight dilution of the concentrated stock solutions with the appropriate solvent mixtures. The solutions thus prepared were stored in one-liter Pyrex flasks equipped with a siphon tube, sintered-glass gas dispersor, and an exit tube. Dissolved oxygen was removed by passage for ten minutes of a rapid stream of fine bubbles of oxygen-free, solvent-saturated hydrogen. The exit tubes were then closed and the solution stored under an atmosphere of purified hydrogen until transfer to the cells. In order to detect any error in preparation, two stock solutions prepared from different batches of constant boiling hydrochloric acid were used in making dilutions for each series of measurements. Eight to ten solutions, ranging from 0.003 to 0.1 molal, were utilized in each solvent mixture.

Densities.—The densities of the solvent mixtures over the range of temperatures involved were determined by the usual pycnometric technique.

Vapor Pressures.—The vapor pressure of these solvent mixtures, needed in correcting the observed cell voltages to one atmosphere pressure of hydrogen, were determined by the method of Felsing and Thomas.[9] The dielectric

TABLE I

CHARACTERISTIC CONSTANTS OF THE BINARY SOLUTIONS

Temp., °C.	Density, g./ml.	Vapor press., mm.	Dielectric constant	Debye–Hückel constants	
				u	A
5% i-Propyl Alcohol					
0	0.99146	5.0	84.4	0.521	1.425
5	.99160	7.2	82.4	.526	1.428
10	.99123	10.4	80.5	.530	1.431
15	.99054	14.6	78.6	.535	1.437
20	.98961	20.5	76.7	.541	1.442
25	.98838	28.1	74.9	.546	1.447
30	.98687	38.2	73.2	.552	1.453
35	.98515	51.5	71.5	.558	1.457
40	.98327	68.5	69.8	.565	1.464
				$M_{XY} = 18.65$	
10% i-Propyl Alcohol					
0	0.98550	5.6	80.5	0.5595	1.459
5	.98526	8.2	78.6	.5645	1.464
10	.98464	11.8	76.7	.570	1.468
15	.98367	16.8	74.9	.575	1.473
20	.98246	23.7	73.1	.5815	1.477
25	.98096	32.7	71.4	.587	1.483
30	.97915	44.6	69.7	.594	1.488
35	.97723	60.2	68.1	.601	1.494
40	.97498	80.5	66.4	.6085	1.500
				$M_{XY} = 19.36$	
20% i-Propyl Alcohol					
0	0.97751	6.9	72.5	0.655	1.537
5	.97582	10.1	70.7	.662	1.543
10	.97384	14.6	69.0	.668	1.547
15	.97165	20.7	67.4	.674	1.553
20	.96922	28.9	65.7	.682	1.558
25	.96667	40.0	64.1	.691	1.564
30	.96389	54.9	62.6	.698	1.571
35	.96100	73.5	61.1	.707	.1577
40	.95696	97.5	59.6	.7155	.1584
				$M_{XY} = 20.94$	

(9) Felsing and Thomas, *Ind. Eng. Chem.*, **21**, 1269 (1929).

constants used were those of Åkerlöf.[10] These various quantities are presented in Table I.

Voltage Measurements.—The Pyrex cell vessels were similar to those used in the previous investigation[4] and to those employed by Harned and Morrison.[11] The presaturators were equipped with sintered-glass discs, which performed very satisfactorily. Provision was made to mount six cells simultaneously in a covered kerosene-filled thermostat equipped with mechanical refrigeration, control heaters, stirrer, etc. The temperature control was of the order of 0.01°. All voltages were measured with a Leeds and Northrup Type K-2 potentiometer; the working standard cell was frequently compared to several standard cells calibrated by the National Bureau of Standards, one of which had been certified only a short time ago.

The cells were filled by partially evacuating the vessels, flushing several times with hydrogen, and then admitting the solution under slightly reduced pressure. The cells were transferred to the thermostat and the flow of hydrogen to the hydrogen half-cell commenced. Each solution was investigated in triplicate. In one series of measurements, the cells were placed into the bath at 0° and then brought up to 25° in 5° steps. A second series was then begun at 25° and carried up to 40°. Thus six observations were obtained on each solution at 25° and three at each of the other temperatures. It was found that, after placing the cells in the thermostat, one to four hours were required for equilibrium to be attained; this time was found to be longest in those solutions which were least concentrated in hydrochloric acid and most concentrated in alcohol. Upon raising the temperature to a new value, constant voltage was usually attained in thirty minutes or less. The agreement between voltages of cells containing the same solution and the voltages at 25° of the low (0–25°) and the high (25–40°) temperature series was generally better than 0.05 mv. A few values deviating by more than 0.1 mv. were discarded.

Calculations and Results

The molal potentials were calculated by means of the equation

$$E' = E + 2k \log m - \frac{2ku\sqrt{md_0}}{1 + A\sqrt{md_0}} - 2k\log(1 + 0.002\,mM_{xy})$$
$$= E_m^0 + f(m),$$

where E' is the apparent molal potential; E is the cell voltage at 1 atmosphere; u and A are the Debye–Hückel constants; m is the weight molality of hydrochloric acid; d_0 is the density of the solvent; M_{xy}, the average molecular weight, is given by Harned and Owen[3] to be $100/[X/M_x + Y/M_y]$ where X and Y represent the composition in weight per cent. and M_x and M_y are the molecular weights of the components of the binary solution; E_m^0 is the true molal potential, and $f(m)$ is a function of the molality. A value of 4.3 Å. was taken as the mean distance of approach, since this value has been found valid in aqueous solutions as well as in several solvent media. The k values were those recommended by Harned and Owen.[3] Straight lines were obtained when E' was plotted against the weight molality, m. The best straight lines at each temperature were calculated by the method of least squares and the values of E_m^0 determined in this manner. The results obtained in 10% i-propyl alcohol are pre-

(10) Åkerlöf, THIS JOURNAL, **54**, 4125 (1932).

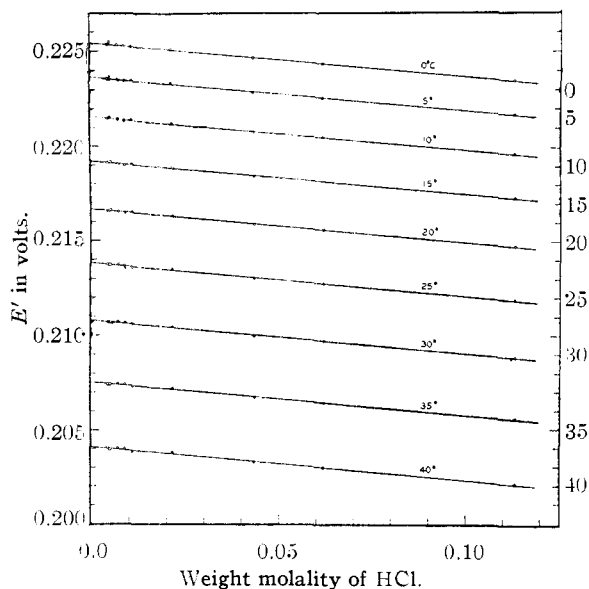(11) Harned and Morrison, *Am. J. Sci.*, **33**, 161 (1937).

Fig. 1.—The molal electrode potentials of the silver-silver chloride electrode in 10% isopropyl alcohol.

sented graphically in Fig. 1; these are representative of all three solvent mixtures. The *average* deviation of the points from these lines was less than 0.05 mv. in the 5 and 10% *i*-propyl alcohol and about 0.08 mv. in the 20% solution. The values obtained for E_m^0 are presented in Table II.

TABLE II

THE MOLAL ELECTRODE POTENTIALS OF THE SILVER-SILVER CHLORIDE ELECTRODE IN VOLTS

Temp., °C	Voltages in *i*-propyl alcohol composition, %		
	5	10	20
0	0.23106	0.22543	0.21612
5	.22892	.22365	.21492
10	.22654	.22158	.21336
15	.22390	.21922	.21138
20	.22107	.21667	.20906
25	.21807	.21383	.20637
30	.21494	.21081	.20341
35	.21164	.20754	.20009
40	.20809	.20410	.19652

It was also found possible to relate E_m^0 to the temperature by means of equations of the form

$$E_m^0 = a + b(t - 20) + c(t - 20)^2$$

The molal potential–temperature equations represent the experimental results with an average deviation of less than 0.05 mv. The constants obtained by least squares treatment are

i-Propyl alcohol, %	a	$10^4 b$	$10^6 c$
5	0.22110	−5.7425	−3.8357
10	.21666	−5.3324	−4.7405
20	.20905	−4.9001	−6.8362

Similar equations were determined relating cell voltages (corrected to 1 atmosphere) to the temperature. These are presented in Table III.

TABLE III

ELECTROMOTIVE FORCES OF THE CELLS

5% *i*-Propyl Alcohol

m	$a(E_{20})$	$b \times 10^4$	$c \times 10^6$
0.003303	0.51300	4.280	−3.65
.005668	.48658	3.416	−3.77
.007738	.47146	2.896	−3.68
.01313	.44585	2.030	−3.93
.02654	.41228	0.950	−3.81
.03927	.39368	.333	−3.65
.05808	.37523	− .265	−3.71
.10890	.34449	−1.178	−3.80

10% *i*-Propyl Alcohol

.004377	.49500	4.253	−4.55
.004864	.48990	4.044	−4.72
.005121	.48739	3.940	−4.55
.007084	.47164	3.470	−4.54
.008809	.46107	3.125	−4.48
.01074	.45159	2.790	−4.76
.02153	.41834	1.713	−4.57
.04331	.38519	0.628	−4.59
.06191	.36840	.093	−4.57
.11326	.34004	− .797	−4.55

20% *i*-Propyl Alcohol

.004163	.49043	4.760	−6.70
.006163	.47160	4.162	−6.71
.007822	.46018	3.778	−6.74
.01179	.44031	3.146	−6.63
.02069	.41392	2.280	−6.70
.04142	.38119	1.253	−6.59
.06213	.36229	0.650	−6.51
.11183	.33497	− .200	−6.41

The variation of E_m^0 with the dielectric constant of the solvent is well illustrated in Fig. 2, in which the molal electrode potential is plotted as a function of $1/D$. The values of the molal potential
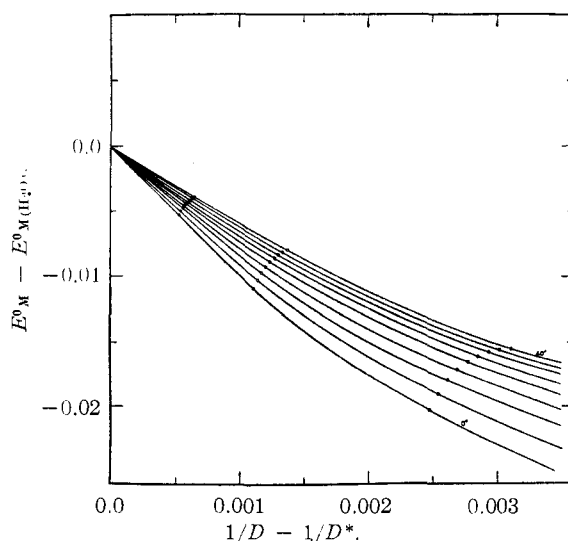

Fig. 2.—Variation of molal potential with dielectric constant in isopropyl alcohol–water mixtures: D^* is dielectric constant of water.

and $1/D$ for aqueous solution at the same temperature have been subtracted in order that the family of curves might possess a common origin. The general shape of the curves is typical of graphs of this type, deviating somewhat from straight lines.

A comparison of the E_m^0 in 10% i-propyl alcohol at 25° obtained in this investigation with the value of Harned and Calmon,[5] 0.21363 volt, reveals a difference of 0.2 mv. This is partially accounted for by the different values used for the vapor pressure of the solvent medium. The value determined in this investigation was 32.7 mm. whereas the value used by Harned and Calmon[5] was 27.0 mm.; no source reference for this latter value is given in their paper. Use of the value of 32.7 mm. corrects their E_m^0 to 0.21373 volt. which is still 0.1 mv. lower than the value obtained in this investigation. This difference is within the sum of the respective errors of these investigations; it is to be noted that solutions were employed which were prepared from two different stock solutions and that two types of silver–silver chloride electrodes were used. All points fell essentially on the same curve.

Activity Coefficients.—Since the relations between E' and m were linear, the activity coefficients of hydrochloric acid in these solutions may be represented by the Debye–Hückel equation with a linear term added

$$\log \gamma \pm = - \frac{u \sqrt{c}}{1 + A \sqrt{c}} + Bm - \log (1 + 0.002\, m\, M_{xy})$$

It was found, for the data obtained, that for a given solvent mixture, B was inversely proportional to the absolute temperature. Hence, the series of values of B for the various temperatures may be replaced by the single constant B' ($= BT$). The values found for this constant in 5, 10 and 20% isopropyl alcohol were 42.96, 44.24 and 51.15, respectively. Since the primary concern in this investigation was the determination of molal electrode potentials, no observations were extended to high concentrations. The equations could probably be applied with fair accuracy up to a concentration of 1 molal provided that the densities of the solution rather than that of the solvent were used in converting from weight molality to volume concentration.

Observations in n-Propyl Alcohol.—As previously stated, an attempt was made to carry out a similar series of measurements in n-propyl alcohol–water mixtures. It was found that the silver–silver chloride electrodes apparently behaved normally in this solvent, as was evidenced by a zero voltage when different electrodes were measured against one another in the same solvent. However, the hydrogen electrodes did not behave normally in this solvent. The cell voltages failed to attain constancy even after periods of ten hours or longer. Furthermore, cells containing the same solution would often differ by as much as 0.03 volt. It was noted that the electrodes which were least platinized gave the highest values and approached a near steady state most rapidly; however, none actually reached the equilibrium state. In addition, foaming difficulties were encountered at the lower temperatures. Temporarily, at least, work has been discontinued on this solvent.

Preliminary measurements in 10% acetone–water mixtures also indicated the same difficulty of non-reproducible results.

Summary

1. Electromotive force measurements have been made on cells of type $H_2(g)\,|\,HCl(m$ in 5, 10 and 20% isopropyl alcohol–water)$\,|\,AgCl(s) +$ Ag(s).

2. The molal electrode potential of the silver–silver chloride electrode has been determined in these solvents from 0 to 40°.

3. Vapor pressure and density measurements on the solvent have been made and tabulated over this temperature range.

4. Equations are presented for the mean activity coefficients of hydrochloric acid.