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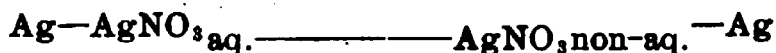
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ELECTROMOTIVE FORCES AND ELECTRODE POTENTIALS IN PYRIDINE AND ITS BINARY MIXTURES WITH WATER, METHYL ALCOHOL AND ETHYL ALCOHOL.

F. S. MORTIMER AND J. N. PEARCE.

HISTORICAL.

The systematic study of the electromotive forces in non-aqueous solvents was begun by Jones.¹ By using cells of the type:



with the same concentration of the salt in each solvent, he hoped to be able to calculate the degree of dissociation in the non-aqueous solutions. It soon became apparent, however, that the solution pressure of a metal varies from solvent to solvent. Substituting the values found by Völlmer² for the degree of dissociation of silver nitrate in ethyl alcohol, he calculated the ratio of the solution pressure of silver in alcohol and in water to be between 0.021 and 0.024. In all of these measurements the alcoholic solutions are positive with respect to the water solutions.

Kahlenberg³ measured the electrode potential of ten different metals in 0.10 N solutions of their salts in about thirty solvents. The electrodes dipped into the solutions which were contained in open vessels, connection between the cells being made by strips of filter paper. The diffusion potential was neglected and apparently no definite temperature was maintained. From his results, which he stated were only qualitative in nature, he concluded that the solution pressure varies not only with the different solvents and their mixtures, but also with the nature of the dissolved substances. He also tested and found that Faraday's laws hold for non-aqueous solutions.

Wilson⁴ measured the electromotive forces of concentration cells in alcoholic solutions of silver nitrate at both 0° and 25°. While the values of the electromotive forces calculated from conductivity data deviated somewhat from those experimentally determined, he concluded that the Nernst equation will be found to hold as well as in non-aqueous solutions.

¹Zeit. physik. Chem., 14, 346, 1894.

²Dissertation, Halle, 1892.

³Jour. Physical Chem., 3, 379, 1899.

Published by the National Bureau of Standards, 1906.
 Am. Chem. Jour., 38, 76, 1906.

Neustadt and Abegg⁵ investigated the electrode potentials and electromotive forces of a number of cells containing solutions of the salts of silver, lead, copper, mercury, cadmium, and zinc. The solvents used were water, methyl alcohol, ethyl alcohol, acetone, and pyridine. In all cases the half cell, Ag-AgNO₃—, constituted one-half of the cell. Since the potential differences in methyl alcohol, ethyl alcohol and acetone are approximately equal to those in water, they concluded that the solution pressures of any one of the metals in these four solvents are approximately equal. The considerably lower values obtained for solutions in pyridine are attributed to extremely low ionic concentration. They also consider that, possibly, silver nitrate is ionized in pyridine solution according to the equation:



Experiments were made using a number of solution chains as liquid junctions in an attempt to eliminate the diffusion potential.

Getman⁶ and Getman and Gibbons⁷ measured the potentials of cadmium and zinc in alcoholic solutions of their salts. In each case the normal calomel electrode constituted the other half of the cell. For both metals it was found that the electrode potentials become more negative as the concentration of the salt increases. Since the effect of concentration is just the reverse of what is found for aqueous solutions, they concluded that the applicability of the Nernst equation is very improbable.

Bell and Field⁸ measured the electromotive forces of concentration cells in water and in ethyl alcoholic solutions of silver nitrate. Rearranging the Nernst equation to the form:

$$\frac{\overline{\pi}}{\log_{10} \frac{c}{c_2}} = \frac{2v}{u+v} \cdot \frac{RT}{nf} \log_e 10 = K$$

they calculated the values of K. The values thus obtained varied between 0.0560 and 0.0623. Assuming the value 0.0623, they calculated the transport number of the anion of silver nitrate in water to be 0.523. Since, however, the value of K varies so widely, they concluded that the transport number must change with the concentration of the salt.

⁵Zeit. physik. Chem., 69, 486, 1909.

⁶Am. Chem. Jour., 46, 117, 1911.

⁷Ibid., 36, 1630, 1914.

Getman and Gibbons⁹ measured the electrode potentials, transport numbers and conductivities in solutions of silver nitrate in methyl alcohol, ethyl alcohol, acetone, and aniline. They concluded that certain abnormalities in non-aqueous solutions may be attributed to the formation of complex solute-solvent compounds which dissociate more or less gradually with the dilution.

The first systematic study of electrode potentials and electromotive forces in mixed solvents was reported by Pearce and Farr.¹⁰ They determined the electromotive forces of concentration cells and the electrode potentials of silver against its ions in water, methyl alcohol and ethyl alcohol and in their binary mixtures at both 0° and 25°. From the close agreement between the observed and calculated values of the electromotive forces it was shown that the Nernst equation can be applied not only to solutions in non-aqueous solvents, but also to solutions in binary mixtures of these solvents. The electrode potentials are relatively greatest in methyl alcohol and least in aqueous solutions, the corresponding values in ethyl alcohol occupying an intermediate position. Further, the values of the electrode potentials are highest in the most concentrated solutions. In all cases they decrease rapidly with dilution at first and then subsequently the decrease proceeds almost linearly with further dilution.

The electrode potentials in the binary mixtures of the alcohols obey the law of mixtures. In the binary mixtures of water and the two alcohols, the electrode potentials increase slowly at first with addition of alcohol from the value in pure water up to mixtures containing about seventy-five per cent of the alcohol and then more rapidly with further increase in the proportion of the alcohol.

The temperature coefficients of the electrode potentials are positive for solutions in both alcohols and their binary mixtures. Those in ethyl alcohol and the aqueous mixtures containing seventy-five per cent and fifty per cent ethyl alcohol, increase with dilution throughout, while those in methyl alcoholic solutions pass through a minimum value. The temperature coefficients in the water and the seventy-five per cent aqueous mixtures are negative throughout, becoming more negative with increasing dilution. The influence of the water as manifested by the temperature coefficients of the electrode potentials is displaced toward higher dilutions as the proportion of the alcohol in the mixture is increased.

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⁹Ibid. 38, 1630, 1914.

¹⁰Jour. Physical Chem., 18, 729, 1914.

They also determined the solution pressure of silver in each of the three solvents, as well as the heats of ionization for the pure solvents and their fifty per cent binary mixtures.

In the hope that still further light may be thrown upon the influence of solvent upon the electrochemistry of solutions, a fourth solvent, pyridine, has been added to the series. To those who are familiar with pyridine and its properties, little need be said. Unlike the three hydroxy-compounds of the previous work, its molecule has the ring structure with one nitrogen atom in the ring. For many salts it is an excellent solvent and the solution of these salts in pyridine is accompanied by a very considerable evolution of heat. Silver nitrate, like many of these salts, separates from its solution in pyridine with pyridine of crystallization; its power to form solvates of high complexity is, therefore, obvious. Of the four solvents named, pyridine has the smallest dielectric constant, yet with many salts it gives solutions possessing fairly good electrical conductivity.

In the present work the electromotive forces of concentration cells and the electrode potentials of silver against solutions of its ions have been redetermined for solutions of the metal in water and the two alcohols at 0° and 25°. Further, similar data have been obtained for solutions of silver nitrate in pure pyridine and for its binary mixtures with water, methyl alcohol and ethyl alcohol, respectively.

MATERIALS AND SOLUTIONS.

Water—The water used was prepared according to the method of Jones and Mackay¹¹. Repeated measurements showed it to have a specific conductivity of approximately 2.0×10^{-6} mhos.

Ethyl Alcohol—Ordinary 95 per cent alcohol was allowed to stand over fresh quicklime for two or three weeks. It was then decanted and distilled. The distillate was allowed to stand over anhydrous copper sulphate for one week and then redistilled. This distillate was refluxed with metallic calcium for ten hours and again distilled. Finally, it was refluxed for two hours with silver nitrate to remove aldehydes and other reducing agents. The distillate from this treatment was collected and preserved in dry glass-stoppered bottles, being protected from the air during distillation by phosphorus pentoxide tubes. In each distilla-

tion a fractionating column was used and only that middle portion which passed over between 77.9° and 78° (uncorr.) was used.

Methyl Alcohol.—Kahlbaum's best grade of alcohol was further purified in the same manner as the ethyl alcohol, except that the treatment with quicklime was omitted. Only that distillate passing over between 64.9° and 65.1° (uncorr.) was used.

Pyridine.—The best grade of pyridine obtainable was allowed to stand over fused potassium hydroxide for two weeks. It was then decanted and distilled. That portion passing over between 115.3° and 115.4° was collected and preserved in dry glass-stoppered bottles, protected during distillation by a train of phosphorus pentoxide and calcium chloride tubes. Because of its great absorptive power for water, extraordinary care was used in handling the pyridine.

Silver Nitrate.—Baker's "Analyzed" silver nitrate was recrystallized by the rapid cooling of a hot saturated solution of the salt in conductivity water. The crystals were filtered on a Büchner funnel, washed with ice-cold conductivity water, sucked dry, and then heated for several hours in a toluol bath at 109° . The salt when thoroughly dry was kept in dark bottles further protected by dark cloths.

Potassium Chloride.—Baker's "Analyzed" potassium chloride was further purified by precipitating a saturated solution by hydrogen chloride gas. The precipitate was filtered on a Büchner funnel, washed with conductivity water, heated to dryness in an air bath at 110° and the crystals preserved in a desiccator over phosphorus pentoxide. The salt was always strongly heated before using.

Mercury.—The mercury was repeatedly washed with dilute nitric acid and the acid removed by repeated washing with conductivity water. It was then distilled under reduced pressure in a current of air.

Calomel.—Kahlbaum's best grade of mercurous chloride was repeatedly washed with a 0.10 N potassium chloride solution after which it was preserved under a fresh sample of the same solution in dark bottles.

Solutions.—All solutions were prepared by direct weighing, or by the suitable dilution of freshly prepared solutions. They

were made up to volume at 25° and, to avoid the possibility of any decomposition occurring in the solutions, all electrometric measurements were made on the same day.

Mixtures.—The solvent mixtures were made up on a percentage basis by weight, the weights of the separate components being accurate to 0.1 gram per liter.

APPARATUS.

The apparatus used in this work was the same as that used by Farr.¹² The constant temperature baths consisted of large deep metal boxes inclosed within larger wooden boxes, the space between being filled with insulating material. The 0°-bath was obtained by clean finely crushed ice moistened with distilled water. The water in the 25°-bath was kept in rapid circulation by a mechanical stirrer. It was electrically heated and maintained at 25° ± .01 by an electrically controlled temperature regulator.

Seven half-cells and two calomel electrodes were used in this investigation. Each half-cell was fitted with a stop-cock in the connecting tube. These were always kept closed except when measurements were being made. Loose plugs of filter paper inserted in the ends of the connecting tubes practically eliminated any possible diffusion potential even when the stop-cocks were momentarily opened for potential readings. The middle vessel was so arranged that the connecting tubes of all the cells could be inserted through tight-fitting rubber stoppers. With this arrangement the solutions were not unduly exposed to the air and the measurements could be made on any combination by simply changing the wire leads and opening the stop-cocks in the connecting tubes. A normal aqueous solution of ammonium nitrate was used in the middle vessel. It was assumed that this solution eliminates the diffusion potential.¹³

The calomel electrodes were prepared in the following manner. In the bottom of the electrode vessel was placed a large globule of pure mercury. This was next covered by a calomel paste prepared by intimately mixing calomel and mercury moistened with 0.1 N solution of potassium chloride. Over this was placed a solution of the 0.1 N potassium chloride which had been shaken with

¹²Loc. cit.

¹³Ostwald-Luther, *Measurements*, 3d Ed., p. 448.

calomel and allowed to stand in contact with it until saturated. The single potential of the calomel electrode was calculated from the value given by Richards,¹⁴ the values taken being $+0.5986$ volts at 0° and $+0.6186$ volts at 25° . These electrodes were renewed alternately every two weeks and were found to be reproducible to within two-tenths of a millivolt.

The electromotive forces were measured by means of a Wolff potentiometer in connection with a Leeds-Northrup, "Type H," wall galvanometer. In aqueous solutions it was easily sensitive to .01 millivolt, but the high resistance in non-aqueous solutions made it almost impossible to detect differences of less than 0.1 millivolt. A Cadmium-Weston cell which had been recently standardized against a similar element certified by the Bureau of Standards was used as the standard of reference. It had an electromotive force of 1.01745 volts of 25° . While its temperature coefficient is practically negligible, it was kept at this temperature by insulating it in a beaker immersed in the 25° -bath.

The silver electrodes were prepared according to the method described by Farr.¹⁵ Short pieces of pure silver wire were fused into the ends of glass tubes. To the ends sealed into the glass were soldered copper wires, each the length of the glass tube. The tubes were then filled to within an inch of the top with hard paraffine which prevented the mercury with which the contact was made with the wire leads, from amalgamating the silver. Before being used the electrodes were plated by connecting them in series in a solution of potassium-silver cyanide. After a current of ten milliamperes had been passed for three hours, they were removed, rinsed with distilled water and allowed to stand for forty-eight hours in contact with a button of pure silver under a pure aqueous solution of silver nitrate. Ten or twelve electrodes were thus prepared. The choice of the electrodes was made in the following manner. They were all grouped in a single cell containing a 0.1 N solution of silver nitrate which was in turn connected with a calomel electrode through an intermediate solution of ammonium nitrate. Only those electrodes were chosen which gave an electromotive force varying not more than 0.1 millivolt from 0.3886 volts.

It was observed early in the work that the electrode potential of a freshly prepared half-cell changes on standing. This

change, for any given electrode, is most rapid at first, the rate of change then gradually decreasing to zero at equilibrium. In order to eliminate any errors from this source, the whole battery of half-cells with their respective electrodes and solutions was set up and allowed to stand for at least one and one-half hours at constant temperature. That this time sufficed for the attainment of equilibrium between electrode and solution may be seen from the following table:

Time	30	60	75	90	105 min.
Electrode potential....	.6559	.6571	.6577	.6578	.6578 volts

THEORETICAL.

There are four sources of electromotive force in any cell: the thermo-electric potential at the junction of the wire leads with the electrodes, the diffusion potential at the junction of the two solutions, and the electrode potentials at the surfaces of contact between the electrodes and their respective solutions. The first is entirely eliminated by compensation, and it is assumed that the diffusion potential has been made negligible by the interposition of the 0.1 N solution of ammonium nitrate. There is left for consideration, therefore, only the two electrode potentials.

According to the equation of Nernst, based on the osmotic theory of the cell, the electrode potentials of a metal in contact with two solutions of its ions are given by the expressions:

$$\pi_2 = \frac{RT}{nf} \cdot \ln \frac{P}{p_2} \text{ and } \pi_1 = \frac{RT}{nf} \cdot \ln \frac{P}{p_1} \quad (1)$$

where R represents the gas-constant, (1.985 calories), T the absolute temperature, n the valence of the cation, and f the faraday (96540 coulombs), P represents the solution pressure of the metal, and p₁ and p₂ the osmotic pressures of the cation in the two solutions, the pressure being measured in atmospheres.

Assuming the absence of a diffusion potential, the electromotive force of a concentration cell is therefore given by the expression:

$$\pi = \pi_2 - \pi_1 = \frac{RT}{nf} \cdot \ln \frac{P}{p_2} - \frac{RT}{nf} \cdot \ln \frac{P}{p_1}, \text{ — } (p_1 > p_2).$$

This by rearrangement becomes,

$$\pi = \frac{RT}{nf} \cdot \ln \frac{p_1}{p_2} \quad (2)$$

Since the osmotic pressures of the ions are proportional to their concentrations and since for normal electrolytes the concentrations are in turn proportional to the equivalent conductivities of the solutions, then

$$\frac{p_1}{p_2} = \frac{\alpha_1 c_1}{\alpha_2 c_2} = \frac{\lambda_1 c_1}{\lambda_2 c_2}$$

Substituting in (2), we have

$$\pi = \frac{RT}{nf} \ln \frac{\lambda_1 c_1}{\lambda_2 c_2}, \tag{3}$$

where c , α and λ represent the concentration, the degree of dissociation and the equivalent conductance of the electrolyte, respectively.

The temperature coefficients of the electrode potentials were calculated by means of the relation,

$$\frac{d\pi}{dT} = \frac{\pi_{25} - \pi_0}{\pi_0 \cdot 25} \tag{4}$$

The relation between the electrical and chemical energies in a cell is given by the well-known Helmholtz equation,

$$\pi = \frac{Q}{f} + T \frac{d\pi}{dT}$$

By rearranging and multiplying by .2387 in order to convert joules into calories

$$Q = f \left(\pi - T \frac{d\pi}{dT} \right) \cdot .2387, \tag{5}$$

where Q is the heat of ionization.

By rearranging (1), the solution pressure of a metal is given by the expression,

$$\ln P = \frac{\pi nf}{RT} + \ln p$$

By substituting for the osmotic pressure p its value calculated from the gas laws, i. e.,

$$p = 22.4 \cdot \alpha \cdot c \cdot \frac{T}{273},$$

there is obtained for the solution pressure of the metal, the relation

Published by UN# ScholarWorks (22.4 \cdot \alpha \cdot c \cdot \frac{T}{273}). \tag{6}

RESULTS.

The results obtained are given in the following tables and curves:

TABLE I.

ELECTRODE POTENTIALS IN WATER-PYRIDINE SERIES AT 25°.

N	100 WATER VOLTS	75 W-25 P VOLTS	50 W-50 P VOLTS	25 W-75 P VOLTS	100 PYRIDINE VOLTS
1.0	1.0513	-----	.7513	.7002	.6112
.50	1.0430	.7603	.7026	.6496	.5866
.10	1.0097	.7075	.6578	.6070	.5470
.05	.9944	.6820	.6371	.5878	.5367
.025	.9774	.6650	.6178	.5714	.5255
.01	.9578	.6426	.6023	.5504	.5055
.005	.9403	.6343	.5928	.5328	.4853

TABLE II.

ELECTRODE POTENTIALS IN WATER-PYRIDINE SERIES AT 0°.

N	100 WATER VOLTS	75 W-25 P VOLTS	50 W-50 P VOLTS	25 W-75 P VOLTS	100 PYRIDINE VOLTS
1.0	1.0456	-----	.7282	.6836	.5810
.50	1.0411	.7382	.6842	.6361	.5678
.10	1.0095	.7034	.6324	.5946	.5296
.05	.9913	.6739	.6258	.5758	.5216
.025	.9820	.6571	.6085	.5630	.5081
.01	.9625	.6405	.5973	.5421	.4928
.005	.9471	.6334	.5866	.5309	.4740

MEAN TEMPERATURE COEFFICIENTS OF ELECTRODE POTENTIALS.

	-.000045	+.000430	+.000762	+.000771	+.001293
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TABLE III.

CONCENTRATION CELLS IN WATER-PYRIDINE AT 25°.

N_1-N_2	100 WATER	75 W-25 P	50 W-50 P	25 W-75 P	100 PYRIDINE
1. —.1	.042	-----	.094	.093	.065
.05	.057	-----	.114	.112	.074
.025	.074	-----	.134	.129	.086
.01	.093	-----	.149	.150	.104
.005	.111	-----	.159	.169	.126
.1 —.05	.015	.025	.021	.019	.010
.025	.032	.042	.039	.039	.021
.01	.052	.065	.055	.056	.039
.005	.069	.074	.065	.077	.062
.05 —.025	.017	.017	.020	.016	.011
.01	.037	.039	.035	.037	.030
.005	.054	.049	.045	.055	.052
.025 —.01	.019	.022	.015	.021	.019
.005	.037	.031	.024	.038	.041
.01 —.005	.017	.008	.010	.021	.022

TABLE IV.

CONCENTRATION CELLS IN WATER-PYRIDINE AT 0°.

N_1-N_2	100 WATER	75 W-25 P	50 W-50 P	25 W-75 P	100 PYRIDINE
1. —.1	.036	-----	.096	.089	.051
.05	.054	-----	.090	.107	.059
.025	.064	-----	.119	.120	.073
.01	.083	-----	.131	.142	.088
.005	.098	-----	.142	.153	.105
.1 —.05	.018	.030	.003	.018	.008
.025	.027	.046	.025	.031	.021
.01	.047	.063	.034	.052	.037
.005	.062	.072	.046	.064	.051
.05 —.025	.009	.017	.027	.013	.013
.01	.029	.033	.036	.035	.029
.005	.044	.041	.048	.045	.047
.025 —.01	.019	.016	.009	.021	.016
.005	.035	.024	.021	.033	.033
.01 —.005	.015	.007	.012	.011	.018

TABLE V.

ELECTRODE POTENTIALS IN ETHYL ALCOHOL-PYRIDINE SERIES AT 25°.

N	100 ETHYL VOLTS	75 E-25 P VOLTS	50 E-50 P VOLTS	25 E-75 P VOLTS	100 PYRIDINE VOLTS
.5	-----	.7986	.6872	.6380	.5866
.1	1.0826	.7348	.6391	.5921	.5470
.05	1.0686	.7084	.6222	.5790	.5367
.025	1.0592	.7007	.6148	.5655	.5255
.01	1.0391	.6821	.5906	.5363	.5066
.005	1.0277	.6684	.5667	.5204	.4853

TABLE VI.

ELECTRODE POTENTIALS IN ETHYL ALCOHOL-PYRIDINE SERIES AT 0°.

N	100 ETHYL VOLTS	75 E-25 P VOLTS	50 E-50 P VOLTS	25 E-75 P VOLTS	100 PYRIDINE VOLTS
.5	-----	.7698	.6621	.6190	.5678
.1	1.0696	.7144	.6195	.5741	.5296
.05	1.0571	.6866	.6036	.5603	.5215
.025	1.0466	.6739	.5952	.5473	.5061
.01	1.0251	.6583	.5726	.5108	.4926
.005	1.0131	.6397	.5512	.5083	.4746

MEAN TEMPERATURE COEFFICIENTS OF ELECTRODE POTENTIALS.

	+ .000506	+ .001457	+ .001280	+ .001295	+ .001293
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TABLE VII.

CONCENTRATION CELLS IN ETHYL ALCOHOL AND PYRIDINE AT 25°.

N ₁ -N ₂	100 ETHYL	75 E-25 P	50 E-50 P	25 E-75 P	100 PYRIDINE
0.5 — .1	-----	.064	.048	.046	.039
.05	-----	.090	.065	.059	.050
.025	-----	.099	.073	.073	.061
.01	-----	.116	.097	.102	.080
.005	-----	.130	.121	.117	.101
0.1 — .05	.014	.026	.017	.013	.010
.025	.024	.034	.024	.027	.021
.01	.043	.052	.049	.056	.039
.005	.055	.066	.072	.071	.062
0.05 — .025	.010	.008	.007	.013	.011
.01	.029	.026	.032	.043	.030
.005	.041	.040	.055	.058	.052
0.025 — .01	.031	.018	.024	.029	.019
.005	.032	.032	.048	.044	.041
0.015 — .005	.012	.014	.024	.016	.022

TABLE VIII.

CONCENTRATION CELLS IN ETHYL ALCOHOL AND PYRIDINE AT 0°.

N ₁ -N ₂	100 ETHYL	75 E-25 P	50 E-50 P	25 E-75 P	100 PYRIDINE
0.5 — 0.1	-----	.055	.042	.045	.038
.05	-----	.087	.058	.059	.046
.025	-----	.096	.067	.072	.060
.01	-----	.112	.089	.109	.075
.005	-----	.130	.111	.111	.093
0.1 — .05	.013	.031	.016	.014	.008
.025	.023	.040	.024	.027	.021
.01	.044	.056	.047	.063	.037
.005	.056	.074	.069	.066	.055
.05 — .025	.010	.009	.008	.013	.013
.01	.032	.025	.031	.049	.029
.005	.044	.043	.053	.052	.047
.025 — .01	.020	.016	.022	.036	.016
.005	.034	.034	.044	.039	.033
.01 — .005	.012	.018	.022	.003	.018

TABLE IX.

ELECTRODE POTENTIALS IN METHYL ALCOHOL-PYRIDINE SERIES AT 25°.

N	100 METHYL VOLTS	75 M-25 P VOLTS	50 M-50 P VOLTS	25 M-75 P VOLTS	100 PYRIDINE VOLTS
.5	-----	.8105	.7177	.6386	.5866
.1	1.0975	.7306	.6541	.5911	.5470
.05	1.0799	.7145	.6369	.5690	.5367
.025	1.0707	.6959	.6201	.5520	.5255
.01	1.0507	.6766	.6000	.5426	.5066
.005	1.0286	.6612	.5834	.5280	.4853

TABLE X.

ELECTRODE POTENTIALS IN METHYL ALCOHOL-PYRIDINE AT 0°.

N	100 METHYL VOLTS	75 M-25 P VOLTS	50 M-50 P VOLTS	25 M-75 P VOLTS	100 PYRIDINE VOLTS
.5	-----	.7811	.6934	.6175	.5678
.1	1.0916	.7126	.6233	.5658	.5296
.05	1.0706	.6970	.6184	.5522	.5216
.025	1.0611	.6814	.6017	.5369	.5081
.01	1.0330	.6628	.5851	.5243	.4926
.005	1.0167	.6493	.5614	.5120	.4746

MEAN TEMPERATURE COEFFICIENTS OF ELECTRODE POTENTIALS.

+ .000508	+ .00098	+ .001419	+ .001352	+ .001293
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TABLE XI.

CONCENTRATION CELLS IN METHYL ALCOHOL AND PYRIDINE AT 25°.

N_1-N_2	100 METHYL	75 M-25 P	50 M-50 P	25 M-75 P	100 PYRIDINE
.5 —.1	-----	.080	.064	.047	.039
.05	-----	.096	.081	.069	.050
.025	-----	.115	.098	.087	.061
.01	-----	.134	.117	.096	.080
.005	-----	.149	.134	.111	.101
.1 —.05	.018	.016	.017	.021	.010
.025	.027	.035	.035	.039	.021
.01	.047	.054	.054	.049	.039
.005	.069	.069	.072	.063	.062
.05 —.025	.010	.018	.017	.017	.011
.01	.030	.038	.037	.027	.030
.005	.052	.053	.054	.041	.052
.025—.01	.020	.019	.020	.009	.019
.005	.042	.035	.037	.024	.041
.01 .005	.022	.015	.017	.014	.022

TABLE XII.

CONCENTRATION CELLS IN METHYL ALCOHOL AND PYRIDINE AT 0°.

N_1-N_2	100 METHYL	75 M-25 P	50 M-50 P	25 M-75 P	100 PYRIDINE
.5 —.1	-----	.068	.070	.052	.038
.05	-----	.084	.075	.065	.046
.025	-----	.099	.092	.081	.060
.01	-----	.118	.107	.093	.075
.005	-----	.132	.131	.106	.093
.1 —.05	.021	.016	.005	.013	.008
.025	.031	.031	.021	.028	.021
.01	.059	.050	.038	.041	.037
.005	.075	.063	.062	.054	.054
.05 —.025	.010	.015	.016	.015	.013
.01	.037	.034	.033	.028	.029
.005	.053	.047	.058	.040	.047
.025—.01	.028	.019	.016	.012	.016
.005	.044	.032	.041	.015	.033
.01 —.005	.017	.014	.025	.012	.018

ELECTROMOTIVE FORCES IN PYRIDINE

TABLE XIII.

CONCENTRATION CELLS IN PURE PYRIDINE.

N_1-N_2	OBSERVED 0°	CALCULATED	OBSERVED 25°	CALCULATED
1.0 -0.1	+0.051	-0.021	+0.065	-0.015
.05	+0.059	-0.005	+0.074	+0.0001
.01	+0.088	+0.032	+0.104	+0.037
.5 -0.1	+0.038	+0.031	+0.039	+0.033
.05	+0.046	+0.046	+0.050	+0.049
.01	+0.075	+0.084	+0.080	+0.086
.1 -0.05	+0.008	+0.015	+0.010	+0.015
.01	+0.037	+0.053	+0.039	+0.052
.05-.01	+0.029	+0.037	+0.030	+0.037

TABLE XIV.

HEATS OF IONIZATION.

SOLVENT	ELECTRODE POTENTIAL	MEAN OF THE TEMP. COEFF.	HEAT OF IONIZATION	DIELECTRIC CONSTANT
100 water -----	1.0097	-0.00069	23728	80.5
75 W-25 P -----	.7075	+0.00430	13352	56.9
50 W-50 P -----	.6578	+0.00762	9925	41.1
25 W-75 P -----	.6070	+0.00691	9243	31.5
100 Pyridine -----	.5470	+0.001293	3726	11.2
100 Ethyl -----	1.0826	+0.00506	21472	-----
75 E-25 P -----	.7348	+0.001457	6927	-----
50 E-50 P -----	.6391	+0.001280	5938	-----
25 E-75 P -----	.5921	+0.001354	4346	-----
100 Methyl -----	1.0975	+0.00415	22440	32.8
75 M-25 P -----	.7306	+0.000989	10045	24.5
50 M-50 P -----	.6541	+0.001420	5321	18.2
25 M-75 P -----	.5911	+0.001356	4310	-----

TABLE XV.

SOLUTION PRESSURES IN THE PURE SOLVENTS.

SOLVENT	SOLUTION PRESSURE
Water -----	2.46×10^{-17}
Ethyl Alcohol -----	2.02×10^{-18}
Methyl Alcohol -----	3.55×10^{-19}
Pyridine -----	1.77×10^{-16}

DISCUSSION.

The observed electromotive forces of all the possible concentration cells of the type:



may be found in Tables III, IV, VII, VIII, XI and XII. The observed values are small, as we should expect. While they are incumbered, doubtless, with slight errors, they are approximately of the right order of magnitude. In all cases the positive electrode was found in the more concentrated solution. Conductivity data are not available for the solutions in the binary mixtures containing pyridine as one of the components. It is therefore impossible to give the calculated values in the mixed solvents. In the pure solvents, water, methyl alcohol, and ethyl alcohol, the values obtained agree closely with those obtained by Farr,¹⁶ thus confirming his statement that the Nernst equation does hold for concentration cells in these solvents.

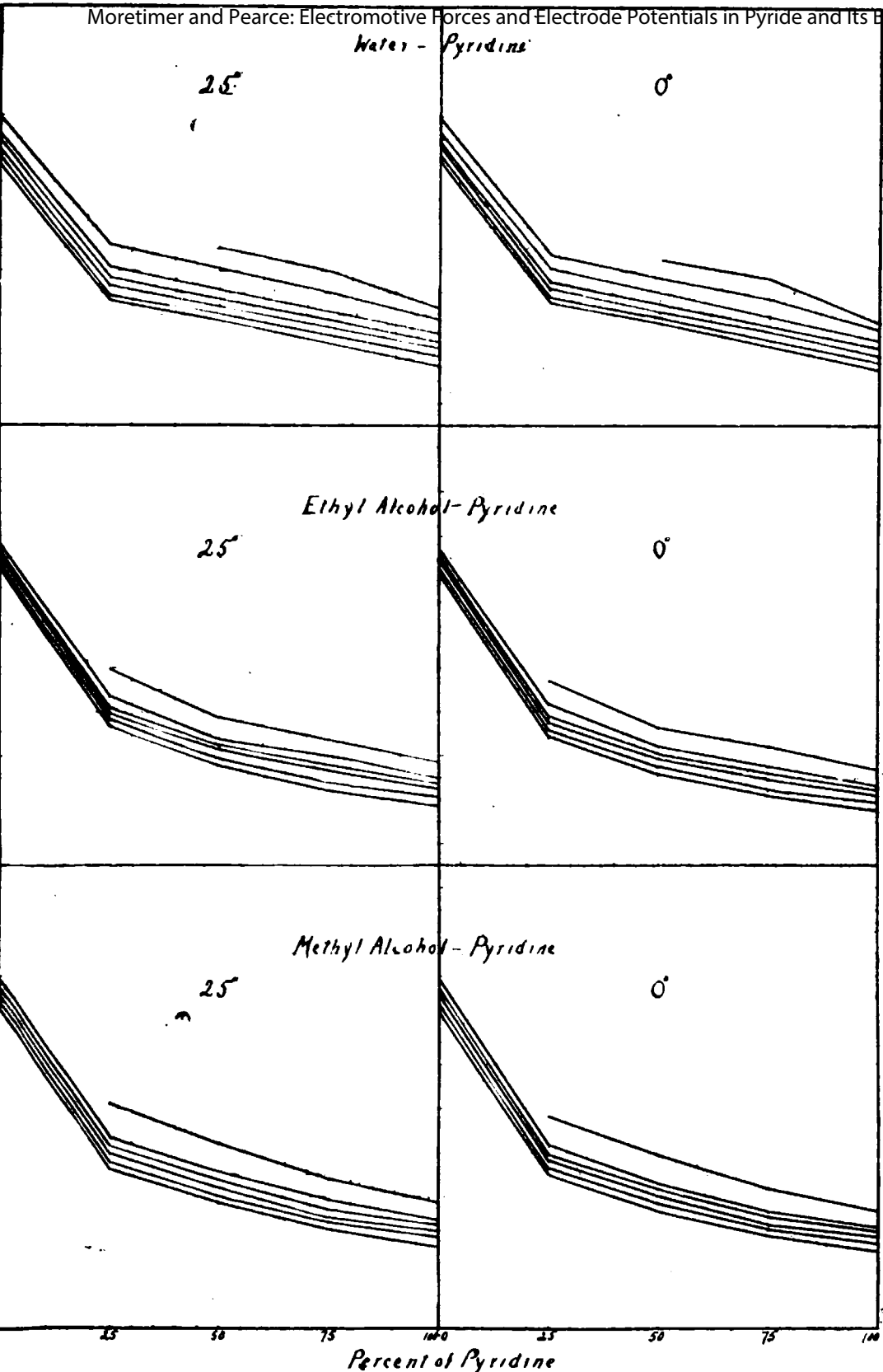
During the present year the equivalent conductances of solutions of silver nitrate in pure pyridine have been carefully determined by Mr. H. L. Dunlap of this laboratory. Repeated determinations give the following values for the equivalent conductance at infinite dilution:

$$\lambda_\infty \text{ at } 0^\circ = 51, \lambda_\infty \text{ at } 25^\circ = 71.$$

In attempting to calculate the electromotive forces of concentration cells in pyridine from Mr. Dunlap's conductivity data, it was found that the calculated values deviate considerably from those observed. They are peculiar in the following respects: When the normal solution constitutes one-half of the concentration cell they are smaller than the observed values, but if the concentrations in each of the half-cells are less than .5 N they are larger. Furthermore, it will be observed that with the more concentrated solutions the calculated electromotive forces show reversal of sign.

The deviations between the observed and calculated values for the electromotive forces of concentration cells in pure pyridine must be attributed to one or both of two causes,—either the solution pressure of the metal varies with the concentration of the dissolved silver nitrate, or, owing to polymerization and subsequent ionization, the equivalent conductivity is not a true

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Percent of Pyridine

Curves showing the influence of pyridine upon the electrode potentials of silver against solutions of silver ions in water, methyl alcohol, ethyl alcohol and pyridine, and in the binary solvents containing pyridine as one component. The upper curve in each plot represents the most concentrated solution.

measure of the concentration of the silver ions. The latter alternative is in accord with the observation of Neustadt and Abegg¹⁷ that in the electrolysis of pyridine solutions of silver nitrate both the silver ion and the nitrate radicle migrate to the cathode, probably as a complex ion.

Walden and Centnerszwer¹⁸ have found that the molecular weight of silver nitrate in dilute pyridine solutions is normal, while in the more concentrated solutions it is greater than normal, thus indicating association. Since simple silver ions must be present, if an electromotive force is to exist, it is probable that silver nitrate may ionize both as simple and as complex ions. If the ionization of the complex molecule is just sufficient to form as many particles as there would be if the substance existed as a simple molecule, then the molecular weight should appear to be normal. This is probably the case in the more dilute solutions of silver nitrate in pyridine.

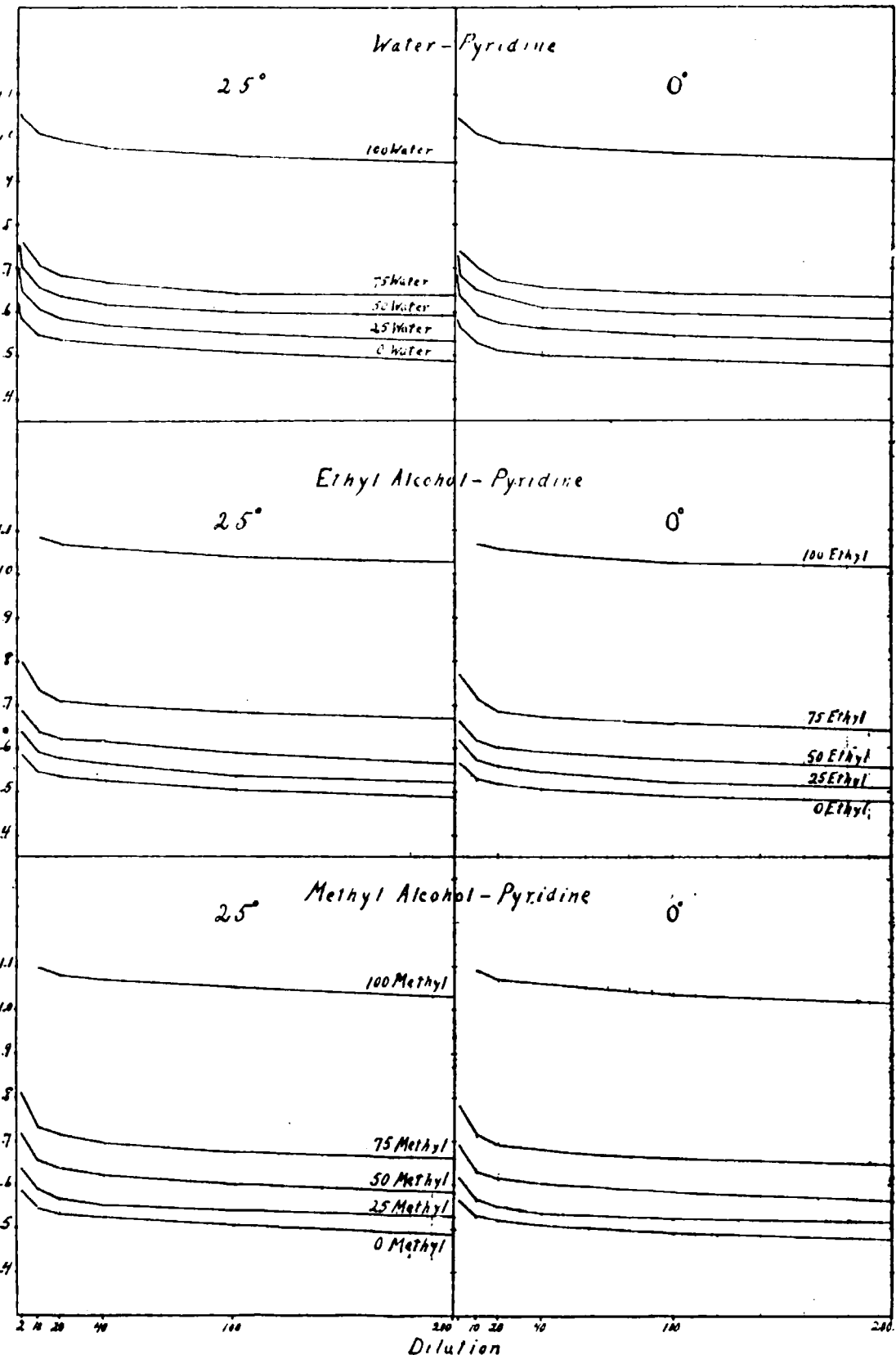
It is evident from Tables I, II, V, VI, IX, X and from Plate II A that the electrode potentials of silver are much higher for solutions in water, methyl alcohol and ethyl alcohol than for equivalent concentrations in pyridine. On comparing the equivalent concentrations, it will be observed that for all binary mixtures of pyridine with water and with the two alcohols the electrode potential increases with the decrease in the proportion of pyridine in the mixture. This increase is very gradual until seventy-five per cent of the pyridine has been replaced by the second solvent. For the water-pyridine mixtures the initial increase is apparently a linear function of the per cent of water present. With further decrease in the proportion of pyridine there is a rapid increase in the value of the electrode potential to its value in the second solvent. The curves for the water-pyridine series show a strong resemblance to the curve found by Hartley, Thomas and Appleby¹⁹ for the surface tensions of the same system. Whether or not any relation exists between surface tension and electrode potential is a question still unanswered.

For all solvents, simple and mixed, the electrode potentials increase as the concentration of the salt increases. From the curves, Plate II B, it will be observed that, starting with the most

¹⁷Loc. cit.

¹⁸Zeit. physik. Chem., 55, 321, 1906.

¹⁹Trans. Chem. Soc., 1906, 119, 1198.



Published by JNU ScholarWorks, 1916
 Curves showing the relation between the electrode potentials and the concentration of the silver nitrate in the pure and binary solvents. 9

concentrated solution, the electrode potential drops very rapidly with the first dilutions, and then decreases almost linearly in the more dilute regions. It will also be observed from the volume-electrode potential curves for any set of binary mixtures and hence for all of the pure solvents as well, that the curves obtained are practically parallel to each other. If they were exactly parallel, it would follow, as was stated by Farr,²⁰ that, "if the electromotive force at the junction of the two solutions has been entirely eliminated, and since the electromotive force of a concentration cell at a given temperature is proportional to the logarithm of the ratio of the ionic concentrations in the two solutions, it follows that the ratio between the ionic concentrations for equivalent concentrations of the salt in the separate solvents is constant and independent of the dilution."

The mean temperature coefficient of the electrode potentials in each solvent has been calculated for both the pure solvents and their mixtures and tabulated at the bottom of the tables for the electrode potentials. All of the temperature coefficients are positive except those in the more dilute solutions in the pure water. In all solutions containing pyridine the temperature coefficients are extremely large. In the water-pyridine series they increase continually from the value in pure water to the value in pure pyridine as the per cent of pyridine is increased. In the ethyl alcohol-pyridine solutions they increase rapidly with the first addition of pyridine, then decrease to practically the value in pure pyridine after fifty per cent of the alcohol is replaced by the pyridine. In the methyl alcohol-pyridine series the temperature coefficients increase rapidly to a maximum value in the fifty per cent mixture, then decrease slowly to the value in pure pyridine as the proportion of alcohol is diminished. The same relations obtain for binary mixtures of pyridine and ethyl alcohol, except that the maximum occurs in the presence of a smaller proportion of pyridine.

The heats of ionization are given in Table XIV. They were calculated by substituting the mean temperature coefficients and the electrode potentials for the 0.1 N solutions in equation (5). The heat of ionization in pyridine is very low. In any series of solvent mixtures, the heats of ionization decrease the most rapidly upon the first addition of pyridine to the second solvent, and then more slowly as the per cent of pyri-

²⁰Loc. cit.

dine is increased. The heats of ionization decrease with increase of pyridine relatively more rapidly in each of the alcoholic-pyridine mixtures than in the water-pyridine mixtures.

In the last column of Table XIV are given a few dielectric constants²¹. It will be observed that in this respect also, the first addition of pyridine to the other solvent produces relatively the greatest change. Are then, the electrode potentials and heats of ionization functions of the dielectric constants?

The solution pressure of silver in contact with pyridine solutions of silver nitrate is found to be much higher than when in contact with aqueous or alcoholic solutions. These calculations were made by substituting in (6) the electrode potentials obtained for the 0.1 N solutions in each of the pure solvents, and the values of α calculated from the following values of the equivalent conductivities: Water, $\lambda_{10}=99.46^{22}$ and $\lambda_{\infty}=128.54^{23}$. Methyl alcohol, $\lambda_{10}=38.575^{22}$ and $\lambda_{\infty}=98.0$. Ethyl alcohol $\lambda_{10}=13.215^{22}$ and $\lambda_{\infty}=35.6^{23}$. Pyridine, $\lambda_{10}=27.585^{22}$ and $\lambda_{\infty}=71.22$

The solution pressures in water and the alcohols are in good agreement with those calculated by Farr. The values calculated for water also are very close to the values 2.3×10^{-17} , given by Neumann²⁴. Assuming from conductivity data that silver nitrate is one-fourth as highly ionized in pyridine as it is in aqueous solutions, Kahlenberg calculated the solution pressure of silver in pyridine to be 3.4×10^{-10} , a value very close to the one herein reported.

SUMMARY.

The electromotive forces of concentration cells containing solutions of silver nitrate in the pure solvents: water, methyl alcohol, ethyl alcohol, pyridine, and in the binary mixtures of pyridine with each of the other solvents have been determined at 0° and 25°. It has been shown that the Nernst equation cannot be applied to solutions of silver nitrate in pyridine, possibly because of a change in the solution pressure of the metal with the concentration of the salt or because of the association and subsequent complex ionization of silver nitrate in pyridine solutions. The equivalent conductance is not a measure of the concentration of the silver ions.

²¹Determined by Mr. Richard Beeson.

²²This laboratory.

²³Kohlrausch, *Sitzungsber. Berd. Akad.*, 26, 570, 1902.

²⁴*Zeit. physik. Chem.*, 14, 193, 1894.

The electrode potentials have been determined for the same solvents at both temperatures. They are much higher in water, methyl alcohol and ethyl alcohol than in pyridine. In all solvents they are highest in the most concentrated solution, decreasing rapidly with the first dilutions and then almost linearly with further dilution. The electrode potentials in the binary mixture of pyridine with each of the other solvents decrease very rapidly with the first addition of pyridine. With further increase in the per cent of pyridine the values decrease gradually to that in pure pyridine. For the water pyridine series, beginning with twenty-five per cent pyridine, the decrease in the value of the electrode potential is linear with the per cent of pyridine.

The average temperature coefficients of electrode potentials have been calculated for each of the pure solvents and their binary mixtures. All are found to be positive except those in the dilute solutions in pure water. In water-pyridine mixtures the temperature coefficients increase continuously to the value in pyridine. In both alcoholic mixtures with pyridine they go through maximum values.

The heats of ionization of silver in the pure solvents and their binary mixtures are found to be much higher in water, methyl alcohol and ethyl alcohol than in pyridine. As the per cent of pyridine is increased in its mixtures with each of the other solvents, the heat of ionization decreases at first very rapidly and then more slowly to its value in pure pyridine.

The solution pressure of silver nitrate has been calculated for each of the pure solvents. It is much higher in pyridine than in either of the two alcohols or water.

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