diluted and adjusted to a *p*H of 1 to 2 as measured by the glass electrode with the addition of orthophosphoric acid. Silver hypophosphate and silver chloride were precipitated by the addition of an excess of silver nitrate at room temperature and separated by filtration and washing as quickly as possible to prevent the interference of phosphite. The silver hypophosphate was leached out with dilute nitric acid and the hypophosphate oxidized to orthophosphate by repeated evaporation with aqua regia on a steam-bath. The silver ion remaining in solution was removed as silver chloride by the addition of hydrochloric acid. The phosphate was finally precipitated as magnesium ammonium phosphate and ignited to magnesium pyrophosphate.

Orthophosphate was determined essentially by the method of Jones[15] except that the ammonium molybdiphosphate was weighed rather than titrated.

The total phosphorus was determined by repeated oxidation with aqua regia, precipitation of magnesium ammonium phosphate and ignition to magnesium pyrophosphate.

A summary of the analyses is given below, each value being the average of two or more closely agreeing results.

Phosphorus as orthophosphate	0.0054 g. P per ml.
Phosphorus as hypophosphate	.0122 g. P per ml.
Phosphorus as phosphite	.0102 g. P per ml.
Phosphorus as hypophosphite	.0007 g. P per ml.
Total	0.0285 g. P per ml.

The total phosphorus found by oxidation to orthophosphate was 0.0289 g. of phosphorus per ml. which seems to indicate that little, if any, pyrophosphate or metaphosphates are present.

The above results correspond to the following yields of the various products; 19% orthophosphate, 35% phosphite, 2% hypophosphite and 42% hypophosphate.

Summary

A method is presented for the preparation of disodium dihydrogen hypophosphate hexahydrate based upon the oxidation of red phosphorus by sodium chlorite, $NaClO_2$. The method possesses marked advantages over previously published methods. The substances used are cheap and readily available, the method is simple and comparatively rapid, and the yield is good.

It has been shown that the oxidation of red phosphorus by sodium chlorite results in the formation of orthophosphate, phosphite and a small amount of hypophosphite in addition to the hypophosphate.

EAST LANSING, MICHIGAN RECEIVED JANUARY 5, 1949

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(15) Jones, *Ind. Eng. Chem., Anal. Ed.*, **14**, 538 (1942).

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF THE DIVISION OF CHEMICAL ENGINEERING, TENNESSEE VALLEY AUTHORITY]

Electrical Conductivity of Orthophosphoric Acid and of Sodium and Potassium Dihydrogen Phosphates at 25°

BY CHARLES M. MASON[1] AND JULIAN B. CULVERN

Two recent papers[2,3] on the thermodynamic properties of orthophosphoric acid and its salts involved calculation of the extent of ionization of that acid on the basis of conductivity data from the literature. Since the range of concentration covered by those data was not adequate as a basis for extensive thermodynamic calculations, the conductivity of orthophosphoric acid and of potassium and sodium dihydrogen phosphates has been studied more extensively. The study covered the concentration range from 0.001 molar to 100% for the acid and up to saturation for the salts.

The limiting equivalent conductance of the dihydrogen phosphate ion, as determined from the conductance of the salts, was surprisingly low and, therefore, was checked by an alternative experimental method. Measurements of e. m. f. were made with suitable concentration cells by means of the lead–lead phosphate electrode, both with and without transference. Although the results by the two techniques were not in as good agreement as might be desirable, the abnormally low limiting conductance of the dihydrogen phosphate ion was substantiated.

Measurements

Apparatus.—For the conductance measurements, the calibrated bridge was of the Jones and Josephs[4] type as developed by Dike[5] and supplied by Leeds and Northrup as type 4666.

The oscillator and amplifier were standard instruments, supplied by the General Radio Company as types 913B and 1231-A. A 4-inch oscillograph served as a null-point indicator, as suggested by Lamson,[6] and the circuit was that proposed by Jones, Mysels and Juda.[7]

Conductivity cells of the type designed by Jones and Bollinger[8] were standardized with potassium chloride solutions, using the specific conductance values and the directions given by Jones and Bradshaw.[9] The cells were platinized according to the directions of Jones and Bollinger[10] and the absence of a significant change of resist-

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[1] Present address: Explosives Branch, U. S. Bureau of Mines, Bruceton, Pennsylvania.

[2] K. L. Elmore, C. M. Mason and J. H. Christensen, THIS JOURNAL, **68**, 2528-2532 (1946).

[3] C. M. Mason and W. M. Blum, *ibid.*, **69**, 1246-1250 (1947).

[4] G. Jones and R. C. Josephs, *ibid.*, **50**, 1049-1092 (1928).

[5] P. H. Dike, *Rev. Sci. Instruments*, **2**, 379-395 (1931).

[6] H. W. Lamson, *ibid.*, **9**, 272-275 (1938).

[7] G. Jones, K. J. Mysels and W. Juda, THIS JOURNAL, **62**, 2919-2922 (1940).

[8] G. Jones and G. M. Bollinger, *ibid.*, **53**, 411-451 (1931).

[9] G. Jones and B. C. Bradshaw, *ibid.*, **55**, 1780-1800 (1933).

[10] G. Jones and D. M. Bollinger, *ibid.*, **57**, 280-284 (1935).

ance with change of frequency assured the adequacy of the platinization.

The conductance measurements were made with the cells immersed in a Leeds and Northrup precision oil thermostat type 4956-Al, which maintained a temperature of 25.000 ± 0.0005°. The thermostat was set at 25.000° by means of a platinum resistance thermometer in conjunction with a Mueller bridge, both having been calibrated by the National Bureau of Standards. The measurements were corrected for the conductivity of the solvent.

The measurements of e. m. f. were made with the equipment, technique and materials described in the development of the lead–lead phosphate electrode.[3] The cell for measurement of the e. m. f. with transference was an adaptation of a pair of the half-cells for lead amalgam, as described by Bates, Edelstein and Acree,[11] the pair of cells being connected by a transference junction for phosphoric acid similar to that devised for hydrochloric acid by Harned and Dreby.[12]

It was discovered that if the cell vessels were filled with the reference solution on one side and unknown on the other, the more dilute of the two solutions being used to flush and fill the center tube and stopcock bore, introduction of the amalgam into the solution-filled cell resulted in much quicker attainment of equilibrium at a given e. m. f. than did the reverse procedure described by Mason and Blum.[3] The small amount of crystalline secondary lead phosphate was added last. The liquid junction was effected, through the stopcock, only during actual e. m. f. readings. Absolute exclusion of oxygen was necessary. The solutions were swept free of oxygen by oxygen-free nitrogen which had been passed through a solution of the same concentration as the test solution in a series of two saturators of the design described by Brown and Felger.[13] After evacuation of the cells, they were flushed with nitrogen, and the oxygen-free solutions were introduced without contact with the air.

Purification of Materials.—Conductance water was prepared by redistillation of ordinary distilled water in a Barnstead conductance water still. The conductance of the product was uniformly less than 1×10^{-6} mho.

Orthophosphoric acid was dehydrated carefully

TABLE I

ELECTRICAL CONDUCTANCE OF SODIUM DIHYDROGEN PHOSPHATE AT 25°

C, moles per liter	$\Lambda_{\text{obs.}}$	$\Lambda_{\text{cor.}}$	$\Lambda_{\text{smoothed}}$	$\Lambda^{\circ\prime}$	Density, ρ
0.001020	84.634	81.288	81.116	83.636	0.99716
.002064	81.821	80.471	79.985	83.569	.....
.004007	79.996	78.308	78.554	83.547	.....
.006859	77.924	76.632	77.059	83.593	.99786
.008265	77.537	76.368	76.442	83.615	.99802
.01030	76.809	75.782	75.684	83.693	.99836
.01372	75.310	74.399	74.665	83.914	.99840
.02000	74.079	73.324	73.085	84.262	.99896
.02566	72.873	72.202	71.926	84.600	.99966
.02751	71.619	70.978	71.599	84.731	.99980
.03878	70.500	69.957	69.785	85.407	1.0007
.05152	68.880	68.411	68.280	86.330	1.0019
.06864	67.018	66.709	66.663	87.619	1.0035
.07778	66.138	65.757	65.896	88.192	1.0038
.09274	65.135	64.779	64.802	89.215	1.0060
.1030	64.410	64.077	63.905	89.666	1.0065
.1374	61.937				1.0093
.1935	59.291				1.0140
.2754	55.810				1.0215
.3091	54.883				1.0247
.4128	51.732				1.0333
.5152	49.281				1.0423
.6183	47.031				1.0509
.7783	43.868				1.0642
.9274	41.504				1.0767
1.367	35.493				1.1129
2.061	28.115				1.1676
3.885	15.513				1.3053

TABLE II

ELECTRICAL CONDUCTANCE OF POTASSIUM DIHYDROGEN PHOSPHATE AT 25°

C, moles per liter	$\Lambda_{\text{obs.}}$	$\Lambda_{\text{cor.}}$	$\Lambda_{\text{smoothed}}$	$\Lambda^{\circ\prime}$	Density, ρ
0.001	107.091	103.715	102.914	105.567	.....
.001401	106.868	104.015	102.381	105.521	.....
.002	104.565	102.177	101.759	105.510	.....
.002564	102.804	100.694	101.236	105.483	.....
.004	101.585	99.896	100.190	105.495	0.99768
.005	100.788	99.278	99.558	105.488	.99776
.006	99.902	98.525	99.035	105.533	.00786
.007	99.291	98.016	98.541	105.560	.99796
.008	98.914	97.720	98.087	105.591	.....
.009	98.362	97.237	97.682	105.643	.99806
.01	98.003	96.936	97.307	105.700	.99776
.02	94.903	94.149	94.415	106.302	.99872
.03	92.682	92.066	92.371	106.957	1.0001
.04	91.107	90.578	90.792	107.645	1.0010
.05	90.704	90.209	89.509	108.413	1.0021
.06	88.482	88.046	88.452	.....	1.0030
.07	88.395	87.993	87.495	.....	1.0038
.08	86.480	86.104	86.616	.....	1.0049
.09	86.369	86.015	85.836	.....	1.0057
.1	85.641	85.303	85.155	.....	1.0062
.2	79.279			.....	1.0161
.3	75.119				1.0252
.4	71.826				1.0344
.5338	68.200				.....
.6	66.627				1.0523
.7	64.017				.....
.8	62.059				1.0696
.9	60.159				1.0777
1.0	58.581				1.0870
1.1445	56.415				.....
1.885	48.391				.....

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[11] R. G. Bates, M. Edelstein and S. F. Acree, *J. Research Natl. Bur. Standards*, **36**, 159–170 (1946).

[12] H. S. Harned and E. C. Dreby, THIS JOURNAL, **61**, 3113–3120 (1939).

[13] E. H. Brown and M. M. Felger, *Ind. Eng. Chem., Anal. Ed.*, **17**, 277–280 (1945).

and recrystallized *thrice* by the method described by Simon and Schulze.[14] Stock solutions were prepared by dissolving the crystalline acid in conductance water. Potassium and sodium dihydrogen phosphate were *thrice* recrystallized from conductance water and made into stock solutions that were just short of saturation. Spectrographic analyses of the acid and the salts showed their content of impurities not to exceed a few thousandths of 1%. Solutions for the conductance measurements were prepared by dilution of the analyzed stock solutions of the purified materials in a calibrated volumetric flask at 25.000 ± 0.0005°.

Results.—The results of the conductance measurements are given in Tables I to III. For each of the tabulated concentrations, measurements were made in two cells with different constants, thus minimizing errors attributable to the characteristics of the cell. Checks were made at various multiples of the standard frequency, 1000 cycles per second, to assure absence of significant error from polarization.

TABLE III

ELECTRICAL CONDUCTANCE OF ORTHOPHOSPHORIC ACID AT 25°

C, moles per liter	$\Lambda_{obs.}$	Density, ρ	*C*, moles per liter	$\Lambda_{obs.}$	Density, ρ
0.001	336.38		0.9523	58.20	1.0457
.003	291.82		1.820	55.44	1.0890
.004	276.21		2.6188	53.95	1.1290
.006	253.71		3.3495	51.63	1.1654
.008	236.99		4.0220	49.02	1.1988
.01	223.00[a]		4.6420	46.07	1.2287
.02	180.95		5.7510	40.18	1.2825
.02593	166.34		6.2463	37.32	1.3062
.04	143.73		6.7059	34.56	1.3278
.04777	134.63		7.0	33.03	1.3422
.05	133.05		8.0	27.53	1.3882
.07	117.89		9.0	22.52	1.4346
.08	112.59		10.0	18.16	1.4806
.09	108.00		11.0	14.47	1.5255
.09927	104.43	1.0025	12.0	11.43	1.5719
.10	104.05	1.0026	13.0	9.04	1.6152
.1976	83.10	1.0075	14.0	7.16	1.6591
.2951	73.96	1.0125	15.887	4.80	1.7345
.6759	61.17	1.0318	18.02[b]	3.14	1.8224

[a] Smoothed value from a plot of Λ against log *C*. [b] Molten 100% orthophosphoric acid.

The smoothed results of the e. m. f. measurements on cells with transference are given as E_t in Table IV. The tabulated results represent two series of experiments—one in which solutions of concentrations from 0.01 to 1 molal were tested against a 0.1-molal reference solution and one in which solutions of concentrations from 0.10 to 10 molal were tested against a 1.0-molal reference solution. The two series of results were interconverted to yield one series of values with a 0.01-molal solution as the reference. A number of runs were made with a solution of a given concentration, the results were treated statistically, and those which deviated from the mean by an amount greater than that predicted by standard methods were discarded. The mean was recorded. For the cell with transport the error appeared from the original data to be ±0.1 mv. except below 0.1 *m* where it increased to ± 0.4 mv.

TABLE IV

ELECTROMOTIVE FORCE AND CALCULATED TRANSFERENCE NUMBERS FROM LEAD–LEAD PHOSPHATE CELLS WITH LIQUID JUNCTION

Pb (2-phase amalgam), $PbHPO_4(s)$, $H_3PO_4(m)$; H_3PO_4 (m_r), $PbHPO_4(s)$, Pb (2-phase amalgam)

Molality, *m*	E^a	E_t (meas.)	ΔE^c	t_+
0.00	......	......	......	0.914
.02	0.0120$_9$	0.0102$_6$	0.00062	.89
.03	.0187$_7$	.0157$_5$	.00028	.88
.05	.0269$_8$	.0224$_2$	−.00012	.86
.07	.0322$_7$	.0267$_0$	−.00028	.85
.1	.0378$_7$	.0311$_0$	−.00061	.84
.2	.0479$_7$	.0395$_0$	−.00052	.82
.3	.0537$_3$	.0443$_5$	−.00032	.81
.5	.0610$_2$	.0505$_3$	.00007	.80
.7	.0660$_5$	.0543$_7$	−.00003	.79
1.0	.0714$_2$	.0587$_1$	.00016	.78
2.0	.0828$_6$	.0673$_6$	.00014	.76
3.0	.0905$_1$	.0732$_1$	.00034	.74
4.0	.0967$_1$	.0778$_3$	.00046	.73
5.0	.1020$_3$	.0815$_5$	.00038	.72
6.0	.1068$_6$	.0848$_1$	.00023	.71
7.0	.1115$_2$	.0878$_3$	.00001	.70
8.0	.1157$_1$	.0907$_9$	.00000	.69
9.0	.1196$_1$	.0931$_9$	−.00059	.69
10.0	.1229$_5$	.0950$_5$[b]	......	...
10.224	.1246$_2$[b]	.0959$_7$	.00073	.68

[a] Calculated from data in ref. 3. [b] Interpolated. [c] $\Delta E = E_t$ (meas.–calcd.).

Discussion

Dihydrogen Phosphates of Sodium and Potassium.—In dilute solutions, potassium and sodium dihydrogen phosphates cannot be considered as simple uni-univalent electrolytes, because there may be secondary ionization of the dihydrogen phosphate ion. Abbott and Bray,[15] as well as Lugg,[16] have shown that, where β represents the degree of dissociation of the $H_2PO_4^-$ ion in sodium and potassium dihydrogen phosphate solutions

$$\Lambda_{cor.} = \Lambda_{obs.} - \beta\Lambda_{H^+} - 2\beta\Lambda_{1/2HPO_4^-} + \beta\Lambda_{H_2PO_4^-} \quad (1)$$

Λ being the equivalent conductance as indicated by the subscripts. If β is small, it may be approximated from the equation

$$\beta = \sqrt{K_2/C} \quad (2)$$

where K_2 is the second ionization constant of phosphoric acid.

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[14] A. Simon and C. Schulze, *Z. anorg. allgem. Chem.*, **242**, 313–368 (1939).

[15] G. A. Abbott and W. C. Bray, THIS JOURNAL, **31**, 729–763 (1909).

[16] J. W. H. Lugg, *ibid.*, **53**, 1–8 (1931).

Primary ionization of the salts was assumed to be complete, and activity coefficients were assumed to be unity or to cancel. The limiting ionic conductances were used for the conductance terms in equation 1 after trials demonstrated that values calculated for different concentrations from the Onsager equation were without significant effect upon the absolute value of the corrections. The value for Λ_{0H^+}, 349.82, was taken from MacInnes.[17] The values for the phosphate ions, $\Lambda_{0^1/_2HPO_4^=} = 57$ and $\Lambda_{0H_2PO_4^-} = 36$, were taken from Landolt–Börnstein.[18] Change of the value for the $H_2PO_4^-$ ion to 33.0, as a result of the present study, proved to be without significant effect on the corrected equivalent conductance of the salts. For the second ionization constant of phosphoric acid, K_2 in equation 2, a value of 6.226×10^{-8} was taken from Nims.[19] The corrected equivalent conductances for sodium and potassium dihydrogen phosphate are shown as $\Lambda_{cor.}$ in Tables I and II.

The corrected equivalent conductances for the two salts then were smoothed through application of the method suggested by Lautie,[20] whereby the equivalent conductance of the salt being investigated is plotted against the equivalent conductance of a simple one–one electrolyte for which the conductance–concentration relationship is known. The data reported by Shedlovsky, Brown and MacInnes[21] for potassium chloride were used for the comparative plot.

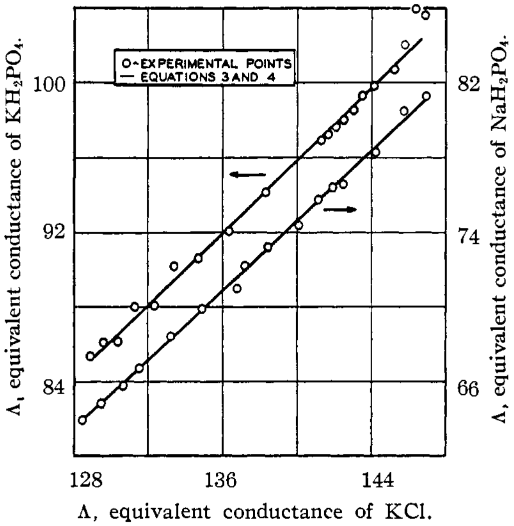

Fig. 1.—Smoothing plot for conductance data.

The plot was linear, as shown in Fig. 1, and application of the method of least squares yielded the equations

$$\Lambda_{NaH_2PO_4} = 0.93488\ \Lambda_{KCl} - 56.246 \qquad (3)$$

$$\Lambda_{KH_2PO_4} = 0.98716\ \Lambda_{KCl} - 42.1489 \qquad (4)$$

where Λ_{KCl} was chosen at the same concentration at which $\Lambda_{\text{phosphate}}$ was desired.

The limiting conductance of potassium chloride being known, 149.86, equations 3 and 4 provided a means for calculation of the limiting conductance of sodium and potassium dihydrogen phosphate, the results being $\Lambda_{0NaH_2PO_4} = 83.855$ and $\Lambda_{0KH_2PO_4} = 105.787$. Introduction of the ionic conductances given by MacInnes[17] for sodium and potassium ions yielded 33.745 and 32.267, respectively, for the limiting conductance of the dihydrogen phosphate ion. The average value, $\Lambda_{0H_2PO_4^-} = 33.01$, is considered to be near the actual limiting conductance. These values are compared with those from the literature in Table V.

TABLE V

THE LIMITING CONDUCTANCE, λ_{0^-}, OF DIHYDROGEN PHOSPHATE ION AT 25°

Method of determination	λ_{0^-}	Source
E. m. f. concentration cells	33.0	This investigation
Unknown	36.0	Landolt–Börnstein[18]
Calculation from conductance data for H_3PO_4	29.7	Elmore, *et al.*[2]
Calculation from conductance data for salts	34.2	International Critical Tables
Calculation from conductance data for salts	42.0	Buehrer[22]
Estimated from the solubility of lead phosphate	33.5	Böttger[23]
Conductance of NaH_2PO_4	33.35	This investigation
Conductance of KH_2PO_4	32.18	This investigation

According to the Onsager equation

$$\Lambda = \Lambda_0 - (\alpha^*\Lambda_0 + \beta^*)\sqrt{C} \qquad (5)$$

where α^* and β^* are theoretical constants, a plot of Λ as a function of $\sqrt{C}$ should approach the axis of infinite dilution linearly along the theoretical slope, $\alpha^*\Lambda_0 + \beta^*$. Such plots for sodium and potassium dihydrogen phosphate are shown in Figs. 2 and 3. The values, $\alpha^* = 0.2289$ and $\beta^* = 60.18$, were taken from Benson and Gordon.[24]

The experimental data for sodium dihydrogen phosphate fall along the theoretical slope, as shown in Fig. 2. The data for potassium dihydrogen phosphate (Fig. 3) approach the zero axis of concentration from slightly below the limiting slope, however, a result which Harned and Owen[25] considered to be indicative of in-

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(17) D. A. MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corp., New York, N. Y., 1939, p. 342.

(18) Landolt-Börnstein, "Physikalisch-chemische Tabellen," Vol. III, Supplement 3, 5th ed., Julius Springer, Berlin, 1936, pp. 2059–2060.

(19) L. F. Nims, THIS JOURNAL, **55**, 1946-1951 (1933).

(20) R. Lautie, *Bull. soc. chim.*, 345-348 (1946).

(21) T. Shedlovsky, A. S. Brown and D. A. MacInnes, *Trans. Electrochem. Soc.*, **66**, 165-178 (1934).

(22) T. F. Buehrer, *Ariz. Agr. Expt. Sta. Tech. Bull.*, **42**, 155-212 (1932).

(23) W. Böttger, *Z. physik. Chem.*, **46**, 521-619 (1903).

(24) G. C. Benson and A. R. Gordon, *J. Chem. Phys.*, **13**, 473-474 (1945).

(25) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp , New York, N. Y., 1943.

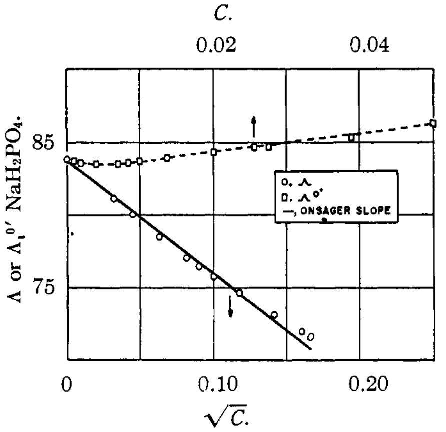

Fig. 2.—Extrapolation of conductance data for NaH_2PO_4.

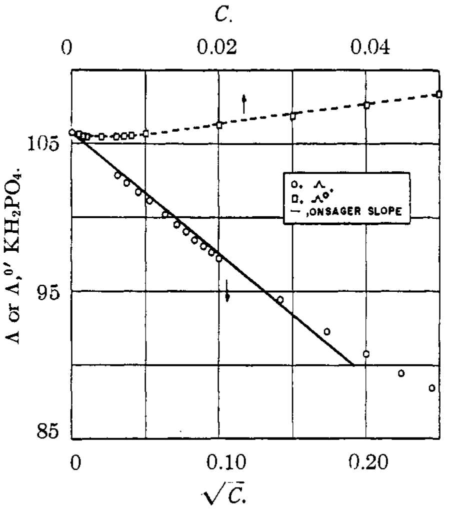

Fig. 3.—Extrapolation of conductance data for KH_2PO_4.

complete dissociation. In both Figs. 2 and 3 the points in the dilute region extrapolate to the calculated limited conductances within experimental error.

Shedlovsky[26] noted that when the limiting equation 5 is rearranged so that Λ_0 may be calculated directly from individual values of Λ, the difference between successive computed values of Λ_0 becomes proportional to the difference in concentration. The limiting conductances thus calculated are represented by Λ_0', which is defined by the expression

$$\Lambda_0' = \frac{\Lambda + \beta^*\sqrt{C}}{1 - \alpha^*\sqrt{C}} \qquad (6)$$

Figures 2 and 3 include values of the function Λ_0', in relation to C. The form of the equation deviates from strict linearity to yield the flat minimum near the axis, a phenomenon noted by Harned and Owen[23] as characteristic of electrolytes of the higher-valence type and which may be due to imperfections in the assumptions that have to be made in the evaluation of the corrections for secondary ionization.

Orthophosphoric Acid.—The first ionization constant of phosphoric acid is defined by

$$-pK_1 = \log K_1 = \log \frac{\alpha^2 C}{1 - \alpha}\,\frac{f_{\pm}^2}{f_u} \qquad (7)$$

where K_1 is the constant, α the degree of dissociation, C the concentration in moles per liter, and f_u and $f_{\pm}$ the respective activity coefficients of undissociated acid and ions. The ionic activity coefficients have been shown in this case to be represented adequately by the limiting law of Debye and Hückel,[2] and the activity coefficient of the undissociated acid may be represented by $\log f_u = B\mu$. Substitution of these quantities into equation 7 gives

$$pK_1' + 1.017\sqrt{\mu} = pK_1 - B\mu \qquad (8)$$

where

$$pK_1' = -\log \frac{\alpha^2 C}{1 - \alpha}$$

A plot of $pK_1' + 1.017\sqrt{\mu}$ against the ionic strength, μ, should yield a straight line of slope B and should intercept the zero axis of concentration at the point where $pK_1' = pK_1$. Lugg[16] used the foregoing method of calculation with equation 8 to obtain a value for pK_1 for orthophosphoric acid at 18°. This method, as devised by Lugg, was used as a means to test the validity of the conductivity data for orthophosphoric acid at 25°. Calculation of α by the method of Banks[27] and by the method of Shedlovsky[28] gave identical values within the known experimental error of the measurements.

Figure 4 shows a plot of $pK_1' + 1.017\sqrt{\mu}$ against μ for the experimental data. A straight line passed through the points intersects the zero axis of ionic strength at $pK_1' = pK_1 = 2.126$. Nims[29] used the more accurate e. m. f. method to obtain 2.124 for this quantity. The agreement is evidence of the validity of the measurements when the error indicated by the scattering of the points is taken into consideration.

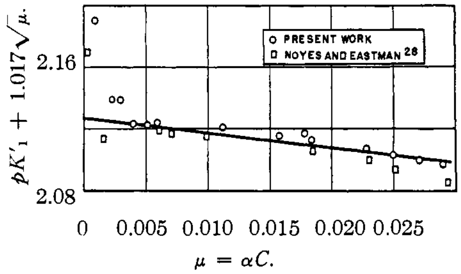

Fig. 4.—Extrapolation of conductance data to obtain pK_1.

The data of Noyes and Eastman[30] are included in Fig. 4. From the sensitive comparison repre-

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(26) T. Shedlovsky, This Journal, **54**, 1405-1411 (1932).

(27) W. H. Banks, *J. Chem. Soc.*, 3341-3342 (1931).

(28) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739-743 (1938).

(29) L. F. Nims, This Journal, **56**, 1110-1112 (1934).

(30) A. A. Noyes and G. W. Eastman, *Carnegie Institution Publications*, **63**, 239-281 (1907).

sented by the plot, it is evident that the two sets of data agree well within the limits of experimental error.

E. m. f. Measurements on Transference Cells.—When the lead–lead phosphate electrodes previously investigated[3] are combined to form a concentration cell without transference, this cell may be represented by

Pb (2-phase amalgam), $PbHPO_4$ (s), H_3PO_4 (m), H_2–H_2,
E_1
H_3PO_4 (m_r), $PbHPO_4$ (s), Pb (2-phase amalgam) (9)
E_2

and the e. m. f. will be

$$E = E_1 - E_2 \tag{10}$$

where E_1 and E_2 represent values taken for the e. m. f. of the cell as reported by Mason and Blum.[3]

Cell 9 involves the reversible transport of one equivalent of phosphoric acid from concentration m to concentration m_r, the reference, per faraday of current passed through the cell.

When the same electrode elements are combined as a cell with transference

Pb (2-phase amalgam), $PbHPO_4$ (s), H_3PO_4 (m); H_3PO_4 (m_r), $PbHPO_4$ (s), Pb (2-phase amalgam) (11)

MacInnes[17] has shown that there will be a transfer of t_{H^+} equivalents through the concentration range from m to m_r.

For cell 11

$$-nF\mathrm{d}E_t = t_{H^+}\,\mathrm{d}\mu' \tag{12}$$

where n is the number of equivalents, F the faraday-per-volt equivalent, E_t the e. m. f. of the cell, t_{H^+} the transference number of hydrogen ion, and μ' the chemical potential.

For cell 9

$$-nF\mathrm{d}E = \mathrm{d}\mu' \tag{13}$$

whence

$$t_{H^+} = \frac{\mathrm{d}E_t}{\mathrm{d}E} \tag{14}$$

A measurement of the e. m. f. of cells 9 and 11 and a determination of the slope of E_t as a function of E will yield the transference number of the hydrogen ion. Since $t_+ + t_- = 1$, the transference number of the dihydrogen phosphate ion is obtained readily.

A plot of E against E_t yielded a function that was almost linear and the deviation of the slope, particularly at low concentrations below 0.1 molal, was almost within the known experimental error in this concentration range, about ± 0.4 mv. The method of least squares then was used to fit the simple quadratic equation

$$E_t = -0.00116 + 0.9041E - 0.95202E^2 \tag{15}$$

to the data. The ΔE column in Table IV shows the fit of this equation where $\Delta E = E_t$ (meas.–calcd).

Equation 15 did not fit the data as well as might be desired. Attempts to fit equations of several other forms were even more unsuccessful. ΔE was then incorporated into the expression for the e. m. f. with transference as a function of the e. m. f. without transference to yield on differentiation the equation

$$t_+ = \frac{\mathrm{d}E_t}{\mathrm{d}E} = \frac{\mathrm{d}(\Delta E)}{\mathrm{d}E} + 0.9041 - 1.904E \tag{16}$$

for the cation transference number. In order to obtain the first term on the right-hand side of equation 16, ΔE was plotted against E. It was found that a straight line, with a slope of 0.01, could be drawn through the points for concentrations above 0.1 molal. The points below 0.1 molal give a negative slope of 0.05 but these were ignored on the assumption that an extrapolation of reliable data into dilute solutions would be more reliable than the measurements below 0.1 molal. Previous experience had shown that for all these cells, the e. m. f. becomes very erratic below 0.1 molal.

Longsworth[31] has demonstrated that a plot of $t_+^{0\prime}$ as a function of C will give a linear extrapolation to the true value of t_+^0 at infinite dilution. The term $t_+^{0\prime}$ is defined by

$$t_+^{0\prime} = \frac{t_+\Lambda' + {}^1/_2\beta^*\sqrt{\alpha C}}{\Lambda' + \beta^*\sqrt{C}} \tag{17}$$

where

$$\Lambda' = \Lambda_0 - (\alpha^*\Lambda_0 + \beta^*)\sqrt{\alpha C} \tag{18}$$

Limiting transferences for the hydrogen ion in phosphoric acid and for the dihydrogen phosphate ion were calculated from equation 17 by the following procedure.

The ionic strength of phosphoric acid solutions was calculated[2,3] from the relationship, $\mu = \alpha C$, where α, the degree of dissociation, was calculated from conductance data for the solutions. Values of $(t_+^{0\prime})_1$ were calculated from α and the value of Λ_0, 378.3, previously used for phosphoric acid.[2] A plot of $(t_+^{0\prime})_1$ as a function of μ yielded a preliminary value of 0.914 for t_+^0. The value of λ_{0+} for the hydrogen ion is 349.82, from which Λ_0 for phosphoric acid is calculated to be 382.74 or, within the probable limits of experimental error, 383. A recalculation of $t_+^{0\prime}$ was made to test the effect on the intercept of changing the value of Λ_0. Within the limits of experimental error, the limiting value of t_+^0 was not affected by these variations in Λ_0. The value, 383, for Λ_0 results in a value of 33 for Λ_{0-}, a result which is compared in Table V with those in the literature.

Stonehill[32] has shown that for nitric acid a plot of $\sqrt{\mu}$ against t_+ intersects the zero axis of concentration at t_+^0. The data are not at sufficiently low concentration for a determination of t_+^0 by this mean but the limiting slope was apparently approached.

Although the data of Table V show considerable variation from the reported values of the limiting conductance of the dihydrogen phosphate ion,

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(31) L. G. Longsworth, THIS JOURNAL, **54**, 2741–2758 (1932).

(32) H. I. Stonehill, *J. Chem. Soc.*, 647–651 (1943).

it is believed that the actual value is within one unit of 33.0.

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Summary

Conductance measurements for phosphoric acid were made over a wide range of concentration.

Conductance measurements for sodium and potassium dihydrogen phosphate were made from dilute solutions practically up to saturation.

The cation transference numbers were measured in dilute orthophosphoric acid.

The limiting conductance of the dihydrogen phosphate ion was determined to be 33.0 ± 1.0.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

A Spectrophotometric Investigation of Bismuth Thiocyanate Complexes[1]

BY WM. DAVID KINGERY[2] AND DAVID N. HUME

Both the normal salt, $\mathrm{Bi(SCN)_3 \cdot 14H_2O}$, and a series of red complex salts with the type formulas $\mathrm{M_3^{I}[Bi(SCN)_6]}$ and $\mathrm{M_3^{II}[Bi(SCN)_6]_2}$ are well known and have been prepared as crystalline compounds by previous workers.[3,4] The amber to red color obtained by addition of excess alkali thiocyanate to an acidic bismuth nitrate or chloride solution has been observed to migrate to the anode in transference experiments[4] and is generally assumed to be due to the presence of the $\mathrm{Bi(SCN)_6^{\equiv}}$ ion. The color reaction is quite sensitive and has been suggested for the colorimetric determination of small amounts of bismuth.[5] The existence of $\mathrm{TlBi(SCN)_4}$ has also been claimed,[4] leading to the inference that the $\mathrm{Bi(SCN)_4^-}$ ion may also exist in solution.

The purpose of this research has been to determine the bismuth thiocyanate complexes present in solution by means of spectrophotometric analysis. A combination of the method of continuous variations, introduced by Job[6] and further developed by Vosburgh and Cooper,[7] with a logarithmic analysis similar to that used by Bent and French[8] has served to demonstrate the existence of several complex ions in the mixture and permit their stability constants to be measured.

Experimental

Measurements.—Absorption measurements below 355 mμ were made with a Beckman model DU Quartz Photoelectric Spectrophotometer. Measurements at wave lengths above 355 mμ were made with a Coleman model 14 Photoelectric Spectrophotometer using a Coleman PC 6 filter for all readings given, except those at 400 mμ shown in Fig. 2, which were made using a Coleman PC 4 filter. The same cells were used for all measurements on each instrument, and oriented in the same direction. In all cases, measurements were made with reference to a blank solution containing all constituents save one, namely, the color-forming constituent in lowest concentration. This technique served to compensate for the effects due to small amounts of impurities in the reagents. All measurements were made at room temperature, 20–25°, and the measurements of optical density are accurate within about 1% under the conditions used in this investigation.

Materials.—Solutions were prepared from freshly opened bottles of commercial C.P. bismuth oxide, perchloric acid and sodium thiocyanate. Small amounts of color-forming impurities varied with each container. However, by using materials from the same containers for all measurements involving intercomparisons, and by the uniform use of "blank" corrections, any small effects of these impurities were cancelled.

Perchloric acid was used for acidification since it transmits well in the ultraviolet as well as in the visible section of the spectrum, and is known to have little or no tendency to form complexes.

Results and Discussion

A large number of mixtures of bismuthyl perchlorate and sodium thiocyanate in perchloric acid were prepared and their absorption characteristics determined. The bismuth concentration was varied between 0.00003 and 0.8 *M*, and the thiocyanate concentration was varied between 0.00005 and 4.0 *M*. When all the measurements were corrected to a common path length for comparison, it was found that curves for all intermediate concentrations and ratios of bismuth to thiocyanate fell between two extremes. The solutions with very low thiocyanate and high bismuth concentrations showed maximum absorption in the vicinity of 270 mμ and no absorption above 350 mμ. The other limiting case, the solutions with very high thiocyanate and low bismuth concentrations, showed absorption peaks at 335 and 270 mμ with the absorption extending well into the visible region (Fig. 1). All curves for high thiocyanate solutions were observed to have the same shape above 350 mμ suggesting that only one complex was absorbing in this region. Similarly, with very high bismuth to

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