The final end-points of the titrations were found only after the lapse of several weeks although only minor changes were observed after the first week or two.

The bulb and the silver were weighed by substituting carefully calibrated weights. The crucibles with the quartz were weighed by substituting a similar tare crucible and the necessary weights.

Two analyses subject to known errors of uncertain magnitude are omitted from the foregoing table. Analyses 1 and 2 are subject to uncertainty owing to the use of glass during the synthesis and collecting of the trichloride. Analyses 3–5 yield a definitely higher value than those of Analyses 6 to 13, presumably owing to the lesser purity of the indium which served for the synthesis. The averages of Analyses 6 to 8 of the trichloride and Analyses 9 to 13 of the tribromide are nearly identical, although the concordance of the bromide analyses is less satisfactory. The average atomic weight of indium found in Analyses 6 to 13, 114.76, represents fairly the outcome of our work.

CAMBRIDGE, MASSACHUSETTS

RECEIVED DECEMBER 16, 1932
PUBLISHED MAY 6, 1933

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

The Second Dissociation Constant of Phosphoric Acid from 20 to 50°

BY LESLIE FREDERICK NIMS

The author has determined the second dissociation constant of phosphoric acid, by using the method employed by Harned and Ehlers[1] in their investigation of acetic acid. The research was undertaken in order to obtain accurate values of the dissociation constant at room and blood temperatures, and to test the applicability of the method to other than uni-univalent electrolytes.

Discussion of the Method

The essence of the method employed is that the dissociation constant is obtained from electromotive force measurements upon cells without liquid junctions, containing appropriate buffer mixtures. No extrathermodynamical methods are employed other than the use of the Debye–Hückel limiting function for the activity coefficients of the ions involved. The cells

$$H_2/NaH_2PO_4(m_1),\ Na_2HPO_4(m_2),\ NaCl(m_3)/AgCl/Ag\ +$$
$$H_2/KH_2PO_4(m_1),\ Na_2HPO_4(m_2),\ NaCl(m_3)/AgCl/Ag\ +$$

were employed. The electromotive force of either is given by the equation

$$E = E_0 - \frac{RT}{F} \ln \gamma_H \gamma_{Cl} m_H m_{Cl} \qquad (1)$$

---

[1] Harned and Ehlers, THIS JOURNAL, **54**, 1350 (1932).

The equation for the second dissociation constant of phosphoric acid is

$$K = \frac{\gamma_{H}\gamma_{HPO_4}}{\gamma_{H_2PO_4}}\frac{m_{H}m_{HPO_4}}{m_{H_2PO_4}} \tag{2}$$

By eliminating m_H from equations (1) and (2), equation (3) is obtained

$$-\log K = \frac{(E - E_0)F}{2.3026\,RT} + \log\frac{m_{Cl}m_{H_2PO_4}}{m_{HPO_4}} + \log\frac{\gamma_{Cl}\gamma_{H_2PO_4}}{\gamma_{HPO_4}} \tag{3}$$

By applying the equation of Debye and Hückel in approximate form the last term of equation (3) is seen to be given by

$$\log\frac{\gamma_{Cl}\gamma_{H_2PO_4}}{\gamma_{HPO_4}} = 2A\sqrt{\mu} - B\mu \tag{4}$$

By substituting this result in equation (3) there is finally obtained

$$-\log K + B\mu = \frac{(E - E_0)F}{2.3026\,RT} + \log\frac{m_{Cl}\,m_{H_2PO_4}}{m_{HPO_4}} + 2A\sqrt{\mu} \tag{5}$$

E represents the measured electromotive force, E_0 the normal electrode potential of the cell

$$H_2/HCl(m)/AgCl/Ag +$$

m the molal concentration of the respective ions, A the theoretical constant of the Debye–Hückel equation, μ the ionic strength of the solution, K the second dissociation constant of phosphoric acid and B a complicated function of the concentration which, while essentially constant over the concentration range employed, need not be evaluated. It is important to note that any slight error involved in using equation (4) becomes progressively less as the concentration decreases and that $m_{H_2PO_4}$ and m_{HPO_4} are essentially equal to the molalities of the salts making up the solutions, since the dissociation constant is small compared with the concentrations employed.

The right-hand side of equation (5), whose terms are known or may be evaluated, is plotted against the ionic strength. The intercept at zero ionic strength gives the true thermodynamic value of $-\log K$. This extrapolation is very easy to carry out, as the plot both by theory and in practice is nearly a straight line.

Experimental Procedure

Disodium phosphate, monopotassium phosphate and sodium chloride were purified by recrystallization of high grade analyzed salts from distilled water. A standard solution of hydrochloric acid was prepared from constant boiling acid and analyzed by precipitation of silver chloride. A solution of disodium phosphate was made and analyzed by evaporating weighed samples and igniting gently to constant weight, sodium pyrophosphate being weighed.

In order to vary the conditions as much as possible, two separate series of experiments were run. The stock solution for the first had the following composition: 0.06165 molal in disodium phosphate, 0.06146 molal in monosodium phosphate and 0.06146 molal in sodium chloride. The solution was made from weighed portions of the standard hydrochloric acid and disodium phosphate solutions. The second stock solution had the composition: 0.03090 molal in disodium phosphate, 0.03090 molal in sodium chloride, and 0.03956 molal in monopotassium phosphate. The solution was made by adding weighed amounts of dry sodium chloride and dry monopotassium phosphate crystals to a known quantity of the disodium phosphate solution and diluting with a weighed amount of water. The solutions used in the cells were made by dilution of weighed amounts of the stock solutions with distilled water. The solutions were weighed after boiling *in vacuo* to remove dissolved air. In this way the concentrations were known to 0.1% or better.

The silver chloride electrodes were of type (2) described by Harned.[2] The platinum electrodes were of platinum foil, coated with a light deposit of platinum black. No grayish cast of the platinum underneath was discernible. Both the silver chloride and platinum electrodes were freshly prepared for every cell. Tank hydrogen, freed from oxygen by passage over reduced copper oxide at 500°, was used for the hydrogen electrode.

A simple "H" cell was used, so designed that diffusion of silver ions from the silver chloride electrode into the hydrogen electrode compartment did not take place during the time the cells were running. The cells were filled by a vacuum technique. Duplicate cells usually checked to within a few hundredths of a millivolt, remaining constant for ten hours or more in test cases. Ordinarily the cells were kept about two and one-half hours at the first temperature, and one-half to one hour at other temperatures. Cells were considered to be constant if two or three readings at fifteen minute intervals agreed to within 0.02 millivolt, and if at the final temperature they remained constant for an hour or more. The temperature was controlled to within ±0.01° by a large thermostated water-bath, so arranged that the temperature could be easily and quickly changed through a five degree interval.

Experimental Results

In Table I are given the experimentally determined electromotive force values in volts, corrected to one atmosphere of hydrogen. The first column

Table I

Series 1. Electromotive Force of the Cell

$H_2/NaH_2PO_4(m_1)$, $Na_2HPO_4(m_2)$, $NaCl(m_3)/AgCl/Ag$ +

D.F.	E_{25}	E_{30}	E_{35}	E_{40}	E_{45}	E_{50}
0.04375	0.79433	0.80002	0.80573	0.81146	0.81724	0.82301
.08897	.77383	.77917	.78453	.78989	.79524	.80073
.10204	.76974	.77497	.78025	.78555	.79087	.79623
.14236	.75985	.76490	.77000	.77513	.78027	.78540
.19356	.75057	.75553	.76046	.76541	.77037	.77537
.3397	.73333	.73798	.74260	.74724	.75188	.75659
.4675	.72327	.72774	.73218	.73667	.74112	.74559

Series 2. Electromotive Force of the Cell

$H_2/KH_2PO_4(m_1)$, $Na_2HPO_4(m_2)$, $NaCl(m_3)/AgCl/Ag$ +

D.F.	E_{20}	E_{25}	E_{30}	E_{35}	E_{40}	E_{45}
0.07935	0.78485	0.79051	0.79616	0.80186	0.80750	0.81316
.10252	.77773	.78322	.78876	.79425	.79979	.80533
.18715	.76055	.76570	.77092	.77613	.78135	.78656
.2986	.74683	.75173	.75672	.76174	.76666	.77161
.5169	.73057	.73517	.73983	.74455	.74909	.75383
.6650	.72297	.72749	.73201	.73656	.74113	.74571
1.0204	.70980	.71409	.71839	.72270	.72701	.73135

---

(2) Harned, This Journal, **51**, 416 (1929).

of the table contains the dilution factor (D. F.) by which the concentrations of the respective stock solutions are multiplied to obtain the concentrations in the cells concerned.

In Table II the first column gives the values of the ionic strength of the solutions. The remaining columns give values for the expression on the right-hand side of equation (5), calculated from the experimental data obtained at the various temperatures. The first row in each series gives the values obtained by extrapolating these figures to zero concentration; these extrapolated values are the values of $-\log K$ or pK at the several temperatures.

TABLE II

Series 1, The Value of $\frac{(E - E_0)F}{2.3026\,RT} + \log \frac{m_{Cl}\, m_{H_2PO_4}}{m_{HPO_4}} + 2A\sqrt{\mu}$

μ	25°	30°	35°	40°	45°	50°
0.0	7.2061	7.1977	7.1922	7.1892	7.1892	7.1912
.01347	7.2142	7.2056	7.2001	7.1976	7.1983	7.2009
.02739	7.2260	7.2177	7.2126	7.2104	7.2104	7.2146
.03142	7.2281	7.2192	7.2140	7.2121	7.2128	7.2163
.04383	7.2381	7.2293	7.2242	7.2227	7.2235	7.2264
.05959	7.2497	7.2425	7.2374	7.2359	7.2368	7.2404
.10458	7.2830	7.2761	7.2715	7.2706	7.2720	7.2766
.14393	7.3082	7.3017	7.2976	7.2977	7.2993	7.3035

Series 2

μ	20°	25°	30°	35°	40°	45°
0.0	7.2178	7.2055	7.1969	7.1914	7.1888	7.1884
.01295	7.2273	7.2158	7.2076	7.2029	7.2001	7.1998
.01673	7.2319	7.2197	7.2117	7.2058	7.2035	7.2035
.03054	7.2434	7.2308	7.2229	7.2176	7.2155	7.2154
.04872	7.2566	7.2441	7.2367	7.2326	7.2299	7.2301
.08434	7.2853	7.2730	7.2654	7.2617	7.2583	7.2604
.10850	7.3032	7.2920	7.2846	7.2806	7.2802	7.2822
.16649	7.3417	7.3310	7.3246	7.3211	7.3211	7.3238

In Fig. 1 the values of the function

$$\frac{(E - E_0)\,F}{2.3026RT} + \log \frac{m_{Cl}\, m_{H_2PO_4}}{m_{HPO_4}} + 2A\sqrt{\mu}$$

given in Table II are plotted against the ionic strength. The points for each series lie on a straight line. The lines for the two series have slightly different slopes (values of B in equation (5)). This is to be expected, for the solutions of the first series contained a 1 to 1 mixture of the sodium phosphates, while the second contained a 3 to 4 mixture of the sodium and potassium phosphates. It can be seen from Fig. 1 and Table II that the extrapolated values for the two series are in excellent agreement, well within the experimental error.

Table III gives the values of the second dissociation constant of phosphoric acid at the various temperatures, the theoretical Debye–Hückel constant A, and the E_0 values of Harned and Ehlers,[3] which were used in evaluating the terms of equation (5). Even though the values of A and E_0 may be subject to slight revision, the use of the values given does not affect the final results for the dissociation constant, since the E_0 values were obtained by Harned and Ehlers by the use of these values of A. The present electromotive force determinations are strictly comparable with those of Harned and Ehlers, since electrodes of the same type were used, and the technique was practically identical with theirs. Hence any constant errors should cancel out in the determination of the dissociation constant.

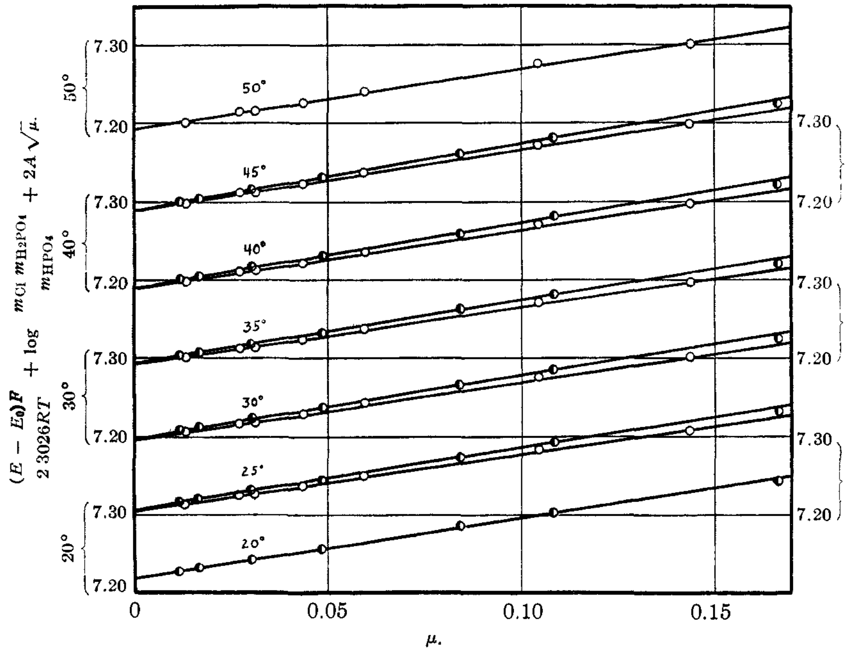

Fig. 1.—The value of $\frac{(E - E_0)F}{2.3026RT} + \log \frac{m_{Cl}\, m_{H_2PO_4}}{m_{HPO_4}} + 2A\sqrt{\mu}$ as a function of the ionic strength. The intercept at zero ionic strength is $-\log K$: ○, series 1; ◐, series 2.

TABLE III

THE SECOND DISSOCIATION CONSTANT OF PHOSPHORIC ACID

Temp., °C.	A	E_0	$K \times 10^8$ Series 1	Series 2	Average
20	0.502	0.22554		6.056	6.056
25	.506	.22239	6.222	6.230	6.226
30	.511	.21908	6.343	6.355	6.349
35	.516	.21561	6.424	6.436	6.430
40	.522	.21200	6.468	6.474	6.471
45	.528	.20825	6.468	6.482	6.475
50	.534	.20436	6.439		6.439

---

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

Figure 2 contains the plot of *K* (average) against the temperature. Also for comparison are given the values determined by Bjerrum and Unmack.[4] At 18 and 25° the agreement with Bjerrum and Unmack is excellent. At 37° their measurement seems to indicate too high a degree of dissociation. Cohn's[5] determination of 7.16 for the negative logarithm of *K* was based upon the value 0.3380 for the calomel electrode at 18°. Using 0.3357[6] for the calomel electrode, Cohn's figure for *pK* would become somewhat higher than 7.20 at room temperature, which is in fair agreement with the present determinations. Although the previous investigators made use of somewhat comparable methods, the uncertainties of liquid junction potentials and single electrode potentials do not enter into the present determinations.

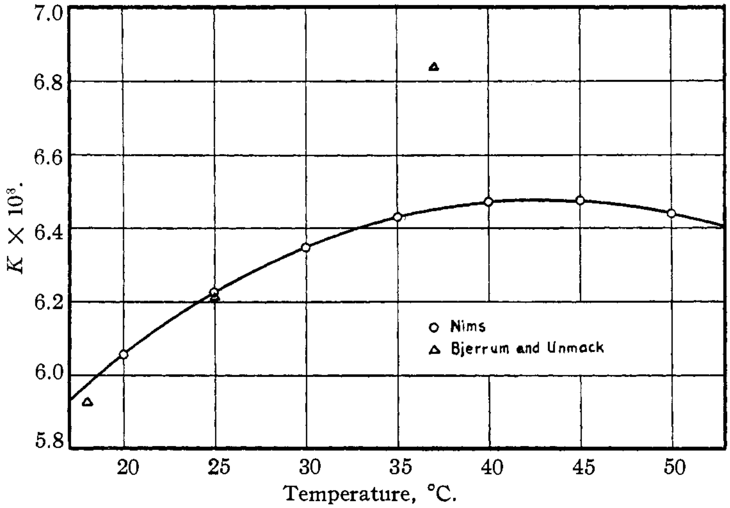

Fig. 2.—The second dissociation constant of phosphoric acid as a function of the temperature.

Summary

1. The second dissociation constant of phosphoric acid has been determined from electromotive force measurements of cells without liquid junction at 5° intervals from 20 to 50°.

2. A maximum value of the second dissociation constant is reached in the neighborhood of 43°.

3. The second dissociation constant of phosphoric acid has the value of 6.46×10^{-8} or a *pK* of 7.190 at blood temperature (37.5°) and at this temperature is changing but very slightly with the temperature.

NEW HAVEN, CONNECTICUT

RECEIVED DECEMBER 16, 1932
PUBLISHED MAY 6, 1933

---

(4) Bjerrum and Unmack, *Kgl. Danske Videnskab. Selskab, Math.-fys. Medd.*, **9**, 129 (1929).

(5) Cohn, THIS JOURNAL, **49**, 173 (1927).

(6) Sörensen and Linderström-Lang, *Compt.-rend. trav. laboratoire Carlsberg*, **15**, No. 6 (1924).