

show that $\gamma_{\text{Pb}^{++}}$ is given fairly accurately by the Debye-Hückel expression in solutions of alkali chlorides up to 0.16 *M*.

Summary

Solubilities of $\text{Pb}_3(\text{PO}_4)_2$ and PbHPO_4 in aqueous solutions have been measured, lead-ion activities being determined with the lead electrode. The values of the solubility products deduced are as follows: $S_2 = a_{\text{Pb}^{++}} \times a_{\text{HPO}_4^{--}} = 10^{-9.90}$ at 25°; $10^{-9.62}$ at 37.5°. $S_3 = a_{\text{Pb}^{++}}^3 \times a_{\text{PO}_4^{---}}^2 = 10^{-42.10}$ at 25°, $10^{-42.00}$ at 37.5°, when K_3 (the third ionization constant of phosphoric acid) is taken to have the values $10^{-12.30}$ at 25° and $10^{-12.66}$ at 37.5°.

The conditions for equilibrium between the two salts are discussed and the biological bearing of the work is mentioned. $\text{Pb}_3(\text{PO}_4)_2$ is the more stable salt under body conditions.

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THE IONIZATION CONSTANTS OF PHOSPHORIC ACID¹

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In the course of an investigation² on the solubilities of the secondary and tertiary phosphates of lead, it became evident that the values available in the literature for the ionization constants of phosphoric acid were insufficient for the purpose of that work.

We therefore have made measurements to determine the first ionization constant at 25 and 37.5°. A few measurements bearing on the second ionization constant are also reported. Relevant data of other observers are also considered and a value is derived for the third ionization constant. The activity concept is made use of throughout.

Methods

Measurements of hydrogen-ion activity were made by means of cells in which a quinhydrone electrode was connected with a normal calomel electrode by a bridge of saturated potassium chloride solution. This bridge is assumed to eliminate liquid-liquid P. D's.

At 25° the P_{H} is obtained by means of the relation³

$$p\text{H}^+ = \frac{0.4136 - E}{0.05911}$$

¹ This investigation was undertaken on behalf of the Liverpool Medical Research Organization, Professor W. Blair Bell, Director, University of Liverpool.

² Millet and Jowett, *THIS JOURNAL*, 51, 997 (1929).

³ Millet, *Trans. Faraday Soc.*, 23, 521 (1927).

where E , the e.m.f. of the cell, is positive when the quinhydrone electrode is the positive element.

The corresponding formula for 37.5° is⁴

$$pH^+ = \frac{0.4068 - E}{0.06160}$$

When the solutions have a high electrolyte concentration, a correction must be made for the so-called neutral salt error of the quinhydrone electrode. The corrections for an ionic strength of 0.16 have been taken by us as $\Delta pH^+ = -0.008$ at 25° ⁵ and $\Delta pH^+ = -0.006$ at 37.5° .⁶ The hydrogen electrode standard is that of G. N. Lewis, Brighton and Sebastian.⁷

The e.m.f. measurements were carried out in duplicate. Solutions were made up at room temperature from recrystallized salts. No correction has been made for the expansion of the solutions with rising temperature.

The First Ionization Constant.—The first ionization constant of phosphoric acid, K_1 , is defined by the relation

$$pK_1 = pH^+ + pH_2PO_4^- - pH_3PO_4 \quad (1)$$

where pX denotes the negative logarithm of the activity of the chemical species X . It is also useful to define a quantity K'_1 by the relation

$$pK'_1 = pH^+ + pC_{H_2PO_4^-} - pC_{H_3PO_4} \quad (2)$$

where pC_X denotes the negative logarithm of the concentration of the chemical species X .

Older work has not been calculated in terms of the activity concept, with the exception of the conductivity measurements of Noyes and Eastman at 18° given by Abbott and Bray,⁸ which Sendroy and Hastings⁹ state to fit the relation

$$pK'_1 = 2.11 - 0.5\sqrt{\mu}$$

μ being the ionic strength.

The e.m.f. data of Ringer¹⁰ do not lead to a definite value for pK_1 , when calculated according to activity theory.

Measurements in Dilute Solutions.—Solutions were made up by diluting mixtures of decimolar KH_2PO_4 and decinormal HCl. The stoichiometric composition of the solutions and the P_H values obtained are given in Table I.

⁴ Corran and W. C. M. Lewis, *Biochem. J.*, **18**, 1358 (1924).

⁵ Sørensen, Sørensen and Lang, *Ann. chim.*, [9] **16**, 283 (1921).

⁶ P. S. Lewis, *Biochem. J.*, **20**, 986 (1926).

⁷ G. N. Lewis, Brighton and Sebastian, *THIS JOURNAL*, **39**, 2245 (1917); W. M. Clark, "Determination of Hydrogen Ions," 2d ed., Williams and Wilkins Co., Baltimore, Md., 1923, p. 285.

⁸ Abbott and Bray, *THIS JOURNAL*, **31**, 729 (1909).

⁹ Sendroy and Hastings, *J. Biol. Chem.*, **71**, 783 (1926-27).

¹⁰ Ringer, *Chem. Weekblad*, **6**, 446 (1909).

TABLE I
 COMPOSITION AND P_H VALUES OF DILUTE SOLUTIONS

| No. | Composition | | P_H values from quin- hydrone elec. | No. | Composition | | P_H values from quin- hydrone elec. |
|-----|---------------|----------|---|-----|---------------|----------|---|
| | KH_2PO_4, M | HCl, M | | | KH_2PO_4, M | HCl, M | |
| | Temp., 25° | | | | Temp., 37.5° | | |
| 1 | 0.015 | 0.005 | 2.703 | 6 | 0.01667 | 0.010 | 2.406 |
| 2 | .0225 | .0065 | 2.675 | 7 | .0225 | .0065 | 2.718 |
| 3 | .030 | .008 | 2.667 | 8 | .025 | .009 | 2.578 |
| 4 | .045 | .011 | 2.652 | 9 | .0375 | .0195 | 2.807 |
| 5 | .061 | .014 | 2.651 | | | | |

In order to calculate values of pK_1 from the above data, we must evaluate γ_{H^+} and $\gamma_{H_2PO_4^-}$, the activity coefficients of hydrogen ion and the primary phosphate ion. Since the solutions are not very concentrated, approximate relationships will be reasonably accurate.

According to Brönsted,¹¹ in solutions of hydrochloric acid and potassium chloride up to 0.1 molar the following relations hold good

$$-\log \gamma_{H^+} \gamma_{Cl^-} = 0.90 \sqrt{\mu} - \mu$$

$$-\log \gamma_{K^+} \gamma_{Cl^-} = \sqrt{\mu} - 0.8\mu$$

Hence, assuming that $\gamma_{K^+} = \gamma_{Cl^-}$ and that γ_{Cl^-} is the same in corresponding solutions of potassium chloride and hydrochloric acid, we derive the equation

$$-\log \gamma_{H^+} = 0.4 \sqrt{\mu} - 0.6\mu \quad (3)$$

which is assumed to hold for the present cases.

Cohn,¹² working with mixtures of KH_2PO_4 and K_2HPO_4 , was able to represent the activity coefficient of the primary phosphate ion by the relation

$$-\log \gamma_{H_2PO_4^-} = \frac{0.5 \sqrt{\mu}}{1 + 1.5 \sqrt{\mu}} \quad (4)$$

which we likewise take as valid for the systems we are considering.

From the P_H value, Equation 3 allows us to calculate C_{H^+} , a value for μ being assumed and subsequently replaced by a more accurate one. $C_{H_3PO_4}$ is then obtained from the principle of electrical equivalence ($C_{H_3PO_4} = C_{H^+} + C_{K^+} - C_{Cl^-}$), and $pH_2PO_4^-$ calculated with the use of Equation 4. $C_{H_3PO_4}$ is obtained by subtracting $C_{H_2PO_4^-}$ from the total phosphate concentration. Up to the present point we have no basis for any value for $\gamma_{H_3PO_4}$, which is left indeterminate.

Values of $pK_1 - \log \gamma_{H_3PO_4}$ are calculated in Table II. To save space, values of γ_{H^+} and $\gamma_{H_2PO_4^-}$ are omitted; they range from 0.908 to 0.866, and 0.882 to 0.810, respectively. The numbers refer to the solutions given in Table I.

The above values of $pK_1 - \log \gamma_{H_3PO_4}$ show no trend with concentration and hence we take $\gamma_{H_3PO_4} = 1$, and derive values for pK_1 at 25° of 2.10, and at 37.5° of 2.16.

¹¹ Brönsted, *Trans. Faraday Soc.*, **23**, 419 (1927).

¹² Cohn, *THIS JOURNAL*, **49**, 173 (1927).

TABLE II
 CALCULATION OF pK_1 IN DILUTE SOLUTIONS

| Temp., °C. | No. | μ | C_{H^+} | $C_{H_2PO_4^-}$ | $C_{H_3PO_4}$ | $pK_1 - \log \gamma_{H_3PO_4}$ |
|------------|-----|-------|-----------|-----------------|---------------|--------------------------------|
| 25 | 1 | 0.017 | 0.00218 | 0.01218 | 0.00282 | 2.122 |
| | 2 | .025 | .00236 | .01836 | .00414 | 2.092 |
| | 3 | .0325 | .00243 | .02443 | .00557 | 2.096 |
| | 4 | .0475 | .00255 | .03655 | .00845 | 2.098 |
| | 5 | .0635 | .00258 | .04958 | .01142 | 2.105 |
| 37.5 | 6 | .021 | .00435 | .01102 | .00565 | 2.176 |
| | 7 | .025 | .00214 | .01814 | .00436 | 2.163 |
| | 8 | .028 | .00297 | .01897 | .00603 | 2.147 |
| | 9 | .043 | .00562 | .02362 | .01388 | 2.156 |

Britton's data¹³ obtained by electrometric titration of phosphoric acid with caustic soda at 20°, using the hydrogen electrode, have been re-calculated by us on the same basis as our own data, the mean value of pK_1 deduced being 2.01. This is lower than the value 2.08, which would be derived at 20° from our values at 25 and 37.5° if a constant temperature coefficient were assumed, and lower than the value calculated by Sendroy and Hastings for 18°, namely, 2.11.

Measurements at Total Ionic Strength 0.16.—For the purpose of the investigation already referred to,² values of pK_1' at an ionic strength of 0.16 were required. Solutions of similar composition to those already used were made up, sodium chloride being added to raise the ionic strength to approximately 0.16.

Since no suitable value for γ_{H^+} was available in the literature, γ_{H^+} was measured for a solution containing 0.01 *M* HCl and 0.15 *M* NaCl.

 TABLE III
 COMPOSITION AND P_H VALUES OF SOLUTIONS ($\mu = 0.16$)

| No. | KH_2PO_4 , <i>M</i> | HCl, <i>M</i> | NaCl, <i>M</i> | P_H (25°) | P_H (37.5°) |
|-----|-----------------------|---------------|----------------|-------------|---------------|
| 1 | 0.03 | 0.0053 | 0.1281 | 2.825 | 2.885 |
| 2 | .03 | .0080 | .1270 | 2.607 | 2.659 |
| 3 | .03 | .0120 | .1252 | 2.407 | 2.466 |
| 4 | .03 | .0176 | .1224 | 2.194 | 2.255 |

 TABLE IV
 CALCULATION OF pK_1' AND pK_1 ($\mu = 0.16$)

| Temp., °C. | No. | C_{H^+} | $C_{H_2PO_4^-}$ | $C_{H_3PO_4}$ | pK_1' | pK_1 |
|------------|-----|-----------|-----------------|---------------|---------|--------|
| 25 | 1 | 0.00166 | 0.02636 | 0.00364 | 1.965 | 2.138 |
| | 2 | .00275 | .02475 | .00525 | 1.934 | 2.107 |
| | 3 | .00435 | .02235 | .00765 | 1.941 | 2.114 |
| | 4 | .00711 | .01951 | .01049 | 1.925 | 2.098 |
| 37.5 | 1 | .00143 | .02613 | .00387 | 2.056 | 2.222 |
| | 2 | .00241 | .02441 | .00559 | 2.019 | 2.185 |
| | 3 | .00376 | .02176 | .00824 | 2.044 | 2.210 |
| | 4 | .00611 | .01851 | .01149 | 2.048 | 2.214 |

¹³ Britton, *J. Chem. Soc.*, 1927, 614.

The value found was 0.90 at 25° and 0.91 at 37.5°, and this was taken as valid for the solutions of which the P_H was measured, the composition of which is given in Table III.

The value of pK'_1 obtained is 1.94 at 25° and 2.04 at 37.5°. The values of pK_1 , 2.11 and 2.21, have been calculated from values of $\gamma_{H_2PO_4^-}$ deduced elsewhere,² namely 0.67 and 0.68.

The agreement of these values of pK_1 with those obtained in more dilute solutions is sufficiently good to confirm the conclusion that $\gamma_{H_2PO_4}$ does not depart appreciably from a value of unity.

The Second Ionization Constant.—Many measurements have been made of the P_H values of mixtures of the primary and secondary alkali phosphates but the majority are unsuitable for the accurate evaluation of the second ionization constant of phosphoric acid, K_2 , since the ionic strengths of the systems investigated are too high.

K_2 may be defined by the relation $pK_2 = pH^+ + pH_2PO_4^- - pHPO_4^{--}$ and the quantity pK'_2 is defined similarly to pK'_1 .

Cohn¹² has, however, recently made an extensive investigation of mixtures of primary and secondary phosphates at 18°, and this author's measurements, which are in concordance with those of Sørensen and Michaelis, lead to a value of pK_2 which is probably very accurate. Reduced to the G. N. Lewis standard for the hydrogen electrode, this value is 7.130.

For other temperatures no values of any great accuracy appear to be available. Sendroy and Hastings⁹ state that unpublished measurements at 20° give a value of about 7.18, and suggest that the value at 38° may be 7.15.

We have made a number of measurements of the P_H of mixtures containing 0.0025 M KH_2PO_4 and 0.0025 M Na_2HPO_4 ($\mu = 0.01$). The mean values obtained are 6.997 at 25° and 6.928 at 37.5°, probably accurate to about 0.003 pH^+ . From these values, using Cohn's relation

$$pK_2 = pK'_2 + \frac{1.5 \sqrt{\mu}}{1 + 1.5 \sqrt{\mu}}$$

pK_2 is calculated to be 7.127 at 25° and 7.058 at 37.5°. The value at 25° is close to the value 7.130 obtained by Cohn at 18°.

The data of Michaelis and Garmendia¹⁴ for the three most dilute solutions measured, when similarly calculated and reduced to the G. N. Lewis standard, give a value for pK_2 at 25° of about 7.11. Britton's data¹³ on the same basis give a value of about 7.04 at 20°.

Measurements made by us on mixtures containing 0.0025 M KH_2PO_4 and 0.0025 M Na_2HPO_4 , of which the ionic strength was raised to 0.16 with NaCl, gave pH^+ (and also pK'_2) values of 6.680 at 25° and 6.589 at 37.5°.

¹⁴ Michaelis and Garmendia, *Biochem. Z.*, **67**, 431 (1914).

The Third Ionization Constant.—Sendroy and Hastings⁹ have made P_H measurements at 38° on mixtures of secondary and tertiary phosphates and found that pK'_3 could be represented approximately by the relation

$$pK'_3 = 12.66 - 2.25 \sqrt{\mu}$$

pK_3 and pK'_3 are defined in a manner similar to pK_1 and pK'_1 . As the data used lie between the limits $\sqrt{\mu} = 0.25$ and $\sqrt{\mu} = 0.50$, the extrapolation to infinite dilution is somewhat uncertain.

Suitable data for the calculation of pK_3 at other temperatures are scanty. Prideaux and Ward's measurements¹⁵ were made at ionic strengths of 0.085 upward. Kolthoff's measurements¹⁶ were also made at high ionic strengths; by a method not clearly explained this author calculates pK_3 at 18° to be about 12.30.

The electrometric titrations of Britton¹³ at 20°, however, were carried out in the range $\mu = 0.033$ to $\mu = 0.047$, and the values obtained may be used in attempting to evaluate pK_3 .

No very satisfactory basis is available for calculating the required activity coefficients— γ_{OH^-} , $\gamma_{H_2PO_4^{--}}$ and $\gamma_{PO_4^{---}}$.

As an approximate relation we have made use of an equation analogous to that used by Sendroy and Hastings

$$-\log \gamma = 0.45 n^2 \sqrt{\mu}$$

K_w has been taken as 0.68×10^{-14} . To Britton's P_H values 0.04 has been added to correct them to the G. N. Lewis standard.

Then pK_3 is defined by the relation

$$pK_3 = pH^+ + pC_{PO_4^{---}} - pC_{H_2PO_4^{--}} + 2.25 \sqrt{\mu}$$

From P_H and γ_{OH^-} , C_{OH^-} is evaluated, and $C_{PO_4^{---}}$ and $C_{H_2PO_4^{--}}$ obtained from the principle of electrical equivalence.

Values at either end of the series have been omitted as being less accurate. The mean value of pK_3 obtained is 12.11. It should be noted that Britton's data give values for pK_1 and pK_2 about 0.1 lower than do other data. An additional error of the same order may be introduced into pK_3 owing to our having used a tentative formula for the activity coefficients. Thus the value 12.11 may be in error by 0.1–0.2. Sendroy and Hastings' value of 12.66 at 38° may be in error to a similar extent. Thus the temperature coefficient is a doubtful quantity, but a value of 12.3 might be interpolated for 25°.

Heats of Ionization of Phosphoric Acid.—The heats of ionization of phosphoric acid, as far as the first two stages are concerned, may be calculated as follows from the values of pK_1 and pK_2 obtained in this paper.

¹⁵ Prideaux and Ward, *J. Chem. Soc.*, **125**, 429 (1924).

¹⁶ I. M. Kolthoff, *Rec. trav. chim.*, **46**, 350 (1927).

| Reaction | pK (25°) | pK (37.5°) | Heat evolved |
|--|------------|--------------|--------------|
| $H_3PO_4 \longrightarrow H^+ + H_2PO_4^-$ | 2.10 | 2.16 | +2000 |
| $H_2PO_4^- \longrightarrow H^+ + HPO_4^{--}$ | 7.127 | 7.058 | -2300 |

The calculated heats of ionization, which are in calories per mole, refer, of course, to the ionization at infinite dilution.

The values of pK_3 calculated are insufficiently accurate for the heat effect of the third ionization step to be calculated. Heat, however, is evolved in this ionization.

Summary

With the quinhydrone electrode measurements of the P_H values of phosphate mixtures have been made which lead to the following values for the ionization constants of phosphoric acid

$$pK_1 (25^\circ) = 2.10, \quad pK_1 (37.5^\circ) = 2.16$$

$$pK_2 (25^\circ) = 7.13, \quad pK_2 (37.5^\circ) = 7.06$$

These figures are compared with those derived from other data.

From the data of Britton pK_3 at 20° is calculated to be about 12.1.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 192]

THE PRINCIPLES DETERMINING THE STRUCTURE OF COMPLEX IONIC CRYSTALS

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1. **The Relative Stability of Alternative Structures of Ionic Crystals.**—The elucidation of the factors determining the relative stability of alternative crystalline structures of a substance would be of the greatest significance in the development of the theory of the solid state. Why, for example, do some of the alkali halides crystallize with the sodium chloride structure and some with the cesium chloride structure? Why does titanium dioxide under different conditions assume the different structures of rutile, brookite and anatase? Why does aluminum fluosilicate, $Al_2SiO_4 \cdot F_2$, crystallize with the structure of topaz and not with some other structure? These questions are answered formally by the statement that in each case the structure with the minimum free energy is stable. This answer, however, is not satisfying; what is desired in our atomistic and quantum theoretical era is the explanation of this minimum free energy in terms of atoms or ions and their properties.

Efforts to provide such a treatment for simple alternative structures, such as the sodium chloride and cesium chloride structures and the fluoride and rutile structures, have been made with the aid of the Born potential expression and modifications of it. Assuming that all ions repel each