and barium chlorides, and 4.0 Å. for the lithium chloride solutions. 1.754×10^{-5}[7] and 1.008×10^{-14}[3,4,5] were used for the ionization constants of acetic acid and water, respectively.

Observation of the results in Table II shows that the salt effects on the ionization of acetic acid verify the order found from less accurate results and a less refined method by Harned and Robinson.[8] The order of effect is: $k_A(BaCl_2) > k_A(LiCl) > k_A(NaCl) > k_A(KCl)$ in the concentrated solutions which is the reverse of that found for the activity coefficient of a strong electrolyte, such as hydrochloric acid in these salt solutions.

The variation of the concentration term of the hydrolytic reaction, k_h, with salt concentration is large in lithium and barium chloride solutions. The maximum effect produced by the salt at an ionic strength of 2.01 is approximately 20% in the case of lithium chloride and 30% in the case of barium chloride. Potassium chloride causes a small salt effect at 25° which is of the order of magnitude of the effect of sodium chloride.[2] The maximum variation of k_h, or the deviation from the law of mass action, is about 4%.

Summary

1. From the electromotive forces of the cells

$$H_2 \mid HAc(M),\ MCl_n(m) \mid AgCl\text{-}Ag$$

the ionization, k_A, of acetic acid in lithium, potassium, and barium chloride solutions at 25° has been determined.

2. By combining these results with information derived from the cells

$$H_2 \mid MOH(m_0),\ MCl_n(m_0), \mid AgCl\text{-}Ag$$

the salt effect on the hydrolytic reaction

$$Ac^- + H_2O \rightleftarrows HAc + OH^-$$

have been investigated. The concentration term, $m_{HAc}m_{OH}/m_{Ac}$, in the salt solutions has been computed. Its variation with salt concentration is found to be large in the lithium and barium chloride solutions. In potassium and sodium chloride solutions, however, the total variation from 0 to 3 μ is less than 4% at 25°.

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

[8] Harned and Robinson, *ibid.*, **50**, 3157 (1928).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Ionic Activity Coefficient Product and Ionization of Water in Uni-univalent Halide Solutions—A Numerical Summary

BY HERBERT S. HARNED AND MELVIN A. COOK

As a result of a number of recent investigations, the activity coefficient product, $\gamma_H\gamma_{OH}/a_{H_2O}$, of water in solutions of potassium,[1] sodium,[2] lithium[3] chlorides, and potassium,[4] sodium[4] and lithium bromides[5] have been determined over considerable temperature and concentration ranges. These measurements also lead to the determination of the thermodynamic ionization constant of water, K, defined by the equation

$$K_w = \frac{\gamma_H\gamma_{OH}}{a_{H_2O}} m_H m_{OH} = \gamma_w^2 m_w^2 \qquad (1)$$

Since both K_w and γ_w have been evaluated, the ionization of water, $m_H m_{OH}$, in the salt solutions may be computed. Owing to the voluminous nature of results, complete tabulation was not made in these contributions. In order to render them available in an approximate form at least, we have calculated γ_w by the empirical equation

$$2 \log \gamma_w = \log \frac{\gamma_H\gamma_{OH}}{a_{H_2O}} = -\frac{-2u\sqrt{\mu}}{1 + A\sqrt{2\mu}} + B\mu + C\mu^{3/2} \qquad (2)$$

in which, $u = 1.8143 \times 10^6\ (DT)^{-3/2}$; $A = a$ $35.57\ (DT)^{-1/2}$; $D = 78.54\ [1 - 0.00460\ (t - 25) + 0.0000088\ (t - 25)^2]$; and where B and C may be expressed by the linear equations

$$B = b_0 + b_1 t \qquad (3)$$

$$C = c_0 + c_1 t \qquad (4)$$

the constants of which are given in Table I. For

TABLE I

CONSTANTS OF EQUATIONS

	a	b_0	$b_1 \times 10^4$	c_0	$c_1 \times 10^4$	Δ av.
KCl	3.6	0.266	5.20	−0.0350	−4.88	0.0027
NaCl	3.6	.198	2.00	− .0085	−2.0	.0032
LiCl	3.6	.039	2.00	.0325	−4.0	.0025
KBr	4.2	.205	12.75	− .016	−9.0	.0022
NaBr	4.2	.157	6.75	.010	−6.57	.0035
LiBr	4.2	.000	0.000	.0475	−2.20	.0041

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[1] Harned and Hamer, THIS JOURNAL, **55**, 2194 (1933).

[2] Harned and Mannweiler, *ibid.*, **57**, 1873 (1935).

[3] Harned and Copson, *ibid.*, **55**, 2206 (1933).

[4] Harned and Hamer, *ibid.*, **55**, 4496 (1933).

[5] Harned and Donelson, *ibid.*, **59**, 1280 (1937).

the ionization constant, K_w, the equation

$$\log K_w = -\frac{4787.3}{T} - 7.1321 \log T - 0.010365T + 22.801 \quad (5)$$

given by Harned and Hamer[1] may be employed. From these values of K_w and the values of γ_w obtained from equation (2), $m_H m_{OH}$ may be computed by equation (1). The limits of validity of these equations are as follows: (1) they may all be applied from 0 to 3 M salt concentration; (2) the temperature ranges of validity of these computations are from 0 to 50° for potassium and sodium chloride solutions, 10 to 40° for lithium chloride solutions, and 0 to 40° for the bromide solutions.

If we had allowed all the parameters of equation (2) to be unrestricted, a more accurate reproduction of the results derived from the experimental data could have been made. The calculations are greatly simplified by the use of only two values of a, by using the same value of a at all temperatures, and by expressing B and C by simple linear equations. The average deviations of 2 log γ_w, calculated and observed, are given in the last columns of the table. From these, it is clear that γ_w^2 may be computed with an accuracy between ±0.5 and ±1% depending on which salt solution is under consideration.

Summary

Equations and numerical parameters are given by means of which the ionization constant, the ionic activity coefficient product and ionization of water in potassium, sodium, and lithium chlorides and bromides may be computed throughout wide temperature ranges and at all concentrations up to 3 M.

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A New Study of the Preparation and Properties of the Higher Oxides of Lead

BY G. L. CLARK, N. C. SCHIELTZ AND T. T. QUIRKE

Because of its presence in the charged positive plate of the storage battery, the evidences from X-ray examination of highly characteristic distortion in the lattice under certain conditions and the very significant researches of LeBlanc and Erebius,[1] which have demonstrated that the tetragonal PbO_2 lattice persists through a range of compositions from PbO_2 down to $PbO_{1.66}$, unusual interest is attracted to this well-known oxide. It has become evident that a great deal of careful research work upon the structure of lead dioxide is essential in order better to understand the peculiar characteristics of the oxide under various conditions. To this end the preparation of a single crystal of lead dioxide, in order that diffraction patterns may be made, is very desirable. In the estimation of LeBlanc and Erebius, Simon[2] was the first person ever to succeed in preparing large crystals corresponding exactly to the formula PbO_2. Hydrated, crystalline sodium plumbate and water were heated at 250° for three days in an autoclave to produce large crystals supposedly of lead dioxide. Twin crystal clusters (similar to Pb_2O_3 crystals in Fig. 3) were illustrated in this paper. The crystals were reported as doubly refracting in polarized light with a range of interference colors from dark to light blue, dichroism from red to green or blue, and an X-ray diffraction pattern corresponding to the well-known rutile structure of PbO_2. These crystals were reported to be more resistant to thermal decomposition and the dissolving action of sulfurous acid, nitric acid and other reagents than found for the usual preparations of lead dioxide. Simon reported only the presence of these large black crystals, which are illustrated in photomicrographs, and did not mention the granular powder of similar color (Fig. 3), which he kindly submitted upon request to aid investigations in this work.

In the present work, the effort has been made to duplicate the Simon preparation exactly in order to obtain single crystals of lead dioxide for quantitative investigation. The original method of preparation of sodium plumbate due to Fremy[3] consisted in fusing lead dioxide and sodium hydroxide in excess. The mass is taken up with water, filtered, and the filtrate evaporated.

In the course of this investigation serious dif-

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(1) LeBlanc and Erebius, *Z. physik. Chem.*, **A160**, 69 (1932).

(2) Simon, *Z. anorg. Chem.*, **185**, 300 (1930).

(3) Fremy, *Ann. chim. phys.*, [3] **12**, 488 (1844). or *Z. anorg. Chem.*, **177**, 109–16 (1928).