

Fig. 1.—Mole fraction of $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$.

0.26 mole fraction zinc acetate to lie between 218 and 220°.

At temperatures below 210° the melts were extremely viscous so that great difficulty was experienced in obtaining crystallization and reproducible melting points. If cooling was rapid stable glasses resulted.

An attempt was made to obtain evidence for the existence of the compound 1 sodium acetate: 1 zinc acetate (0.5 mole fraction of zinc acetate).

A number of melting point determinations were made in this region. These freezing points alone, however, did not disprove the existence of this compound, for a slight rise in the curve to a maximum at 50 mole per cent. would not have been detected. However, the point of incipient melting seen on a mixture of 0.49 mole fraction of zinc acetate was 183°. This is wholly inconsistent with the supposition that a maximum in the curve exists at 0.5 mole fraction of zinc acetate. Further, the mixture of mole fraction 0.500 did not behave like a pure compound in that it did not solidify at anything that might reasonably be considered a constant temperature. We found no evidence for the existence of a one to one compound. An attempt was made to check this conclusion by optical and X-ray examination of the mixtures. Neither proved feasible.

The curve definitely points to the existence of the compound $2\text{NaC}_2\text{H}_3\text{O}_2 \cdot \text{ZnC}_2\text{H}_3\text{O}_2$ or $\text{Na}_2\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_4$ —sodium aceto zincate in the unsolvated system. This suggests the existence of the analogous sodium zincate as $\text{Na}_2\text{Zn}(\text{OH})_4$.

Summary

1. The liquidus curve of the binary system zinc acetate–sodium acetate has been determined.
2. The compound $2\text{NaC}_2\text{H}_3\text{O}_2 \cdot \text{ZnC}_2\text{H}_3\text{O}_2$ or $\text{Na}_2\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_4$ was shown to exist.
3. The analogy between this compound and the hydroxyl zincates was discussed.

NEW YORK, N. Y.

RECEIVED SEPTEMBER 9, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SAN FRANCISCO]

Hydrolysis of Stannous Ion in Stannous Perchlorate Solutions

BY MEL GORMAN

The hydrolysis of stannous ion in stannous perchlorate solutions containing free perchloric acid has been investigated by adding sodium hydroxide solution and measuring the pH during the titration with a hydrogen electrode.¹ The purpose of the present investigation is to determine the extent of hydrolysis of stannous ion by a method involving the potentiometric measurement of the mean ion activity of total free perchloric acid and an analysis of total stannous ion concentration.

(1) Prytz, *Z. anorg. allgem. Chem.*, **174**, 355 (1928).

Method and Apparatus

The stannous perchlorate solutions containing free perchloric acid were prepared by the method of Noyes and Toabe,² and the concentration of free acid was determined by their method. A fresh stannous perchlorate solution was prepared for each experiment and stored in contact with metallic tin under nitrogen for at least one day before being used. The concentration of total stannous ion was obtained by titration in an atmosphere of nitrogen with 0.1 *N* iodine using starch indicator.

The mean activity of the hydrogen and perchlorate ions in the solutions of stannous perchlorate and perchloric acid was obtained with the aid of a hydrogen electrode and a

(2) Noyes and Toabe, *THIS JOURNAL*, **39**, 1539 (1917).

normal calomel electrode using cells of the following type
 Pt, H₂, Sn(ClO₄)₂, HClO₄ | saturated NH₄NO₃ | KCl (1 *M*),
 Hg₂Cl₂, Hg (1)

at 25.0°. The commercial hydrogen used was passed through alkaline pyrogallate solution and then through water at 25° before passing into the stannous perchlorate solution. The partial pressure of the hydrogen was obtained by subtracting the vapor pressure of water from the barometric pressure. The platinum electrodes were strips of approximately one square centimeter. They were cleaned and freshly platinized for each experiment.

The constancy of the reference electrode was checked from time to time during the investigation by connecting it through a bridge of saturated potassium chloride to a solution of 0.05 *M* potassium acid phthalate into which dipped a hydrogen electrode, and noting the electromotive force developed. The observed and calculated voltages agreed to within 0.5 millivolt.³

Experimental Results and Calculations

The calculation of the composition of each solution based on the equation



was performed as follows. The activity of the total perchloric acid was computed from the voltage of the cell. The activity of the total hydrogen ion was assumed equal to the mean ion activity of the total perchloric acid, and in turn the activity of the total hydrogen ion was assumed equal to its concentration. The concentration of free acid subtracted from the concentration of total hydrogen ion gives the concentration of SnOH⁺ and of hydrogen ion due to hydrolysis. By subtraction of SnOH⁺ from total stannous ion the concentration of unhydrolyzed stannous ion can be found. The values of the equilibrium quotient, *K*₁, were computed from the relation

$$K_1 = c_{\text{SnOH}^+} a_{\text{H}^+} / c_{\text{Sn}^{++}} \quad (1)$$

in which *c* is concentration in moles per liter and *a* is activity. The experimental results and values of *K*₁ are listed in Table I. *μ* is the ionic strength.

In Fig. 1, curve I represents log *K*₁ against *μ*^{1/2}. The shape of the curve demonstrates that the equilibrium quotient is varying with ionic strength in accord with the theory of Debye and Hückel. However, extrapolation of this curve to zero ionic strength does not give the true equilibrium constant for the reaction because of

(3) When the saturated potassium chloride bridge was replaced by a bridge of saturated ammonium nitrate the electromotive force was five millivolts lower. An attempt to use this difference as a correction factor to the observed voltages of cells of type (1) in calculating the mean ion activity of perchloric acid was unsuccessful.

TABLE I

E. m. f. H ₂ = 1 atm.	Total H ⁺ activity	Free HClO ₄ moles/l.	Total Sn ⁺⁺ moles/l.	<i>μ</i> ^{1/2}	<i>K</i> ₁ × 10 ²
0.3199	0.2520	0.2390	0.0935	0.71	4.06
.3363	.1330	.1173	.1189	.68	2.02
.3341	.1450	.1356	.0939	.64	1.61
.3323	.1552	.1520	.0565	.56	0.92
.3674	.0403	.0342	.0449	.42	.63
.3671	.0404	.0346	.0455	.42	.59
.3817	.0227	.0151	.0389	.35	.55
.3914	.0157	.0109	.0184	.24	.56
.3955	.0132	.0104	.00936	.18	.56
.4009	.0108	.00846	.00672	.16	.59
.4078	.00822	.00651	.00396	.12	.62

the uncertainty introduced by the assumption that the activity of total hydrogen ion equals the concentration of total hydrogen ion in making the calculation for SnOH⁺ by difference between total acid and acid from hydrolysis. Actually this difference term is the subtraction of a concentration from an activity and hence the result is neither of these quantities. In order to obtain the actual concentration of SnOH⁺ the hydrogen ion concentration must be known. By retaining

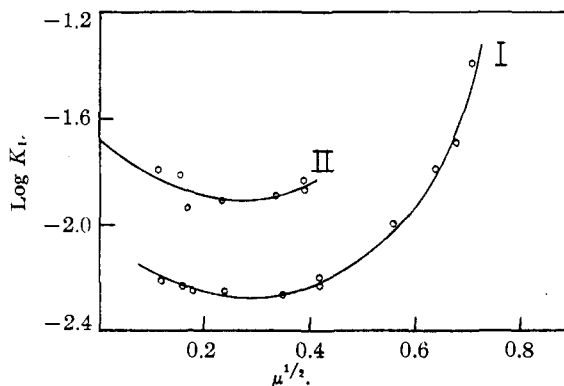


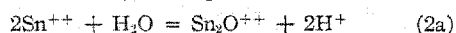
Fig. 1.—Plot of log *K*₁ against square root of ionic strength.

the assumption that the mean ion activity of the perchloric acid is equal to the activity of the hydrogen ion, the concentration of the latter can be obtained by dividing its activity by its activity coefficient. The activity coefficient of hydrogen ion in a solution of given ionic strength can be calculated from the values of the mean ion activity of perchloric acid and of sodium perchlorate at the stated ionic strength, if in the latter we consider that the activity coefficients of the sodium ion and perchlorate ion are equal.⁴

(4) The activity coefficients of perchloric acid and sodium perchlorate were obtained from Landolt-Börnstein, "Physikalisch-chemische Tabellen," Erg. III, pp. 2144 and 2153 (1936), respectively.

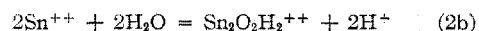
In the range of concentration up to an ionic strength of 0.2 the sodium ion and perchlorate ion activity coefficients are no doubt equal to within two or three per cent. Therefore the activity coefficients of hydrogen ion were computed and used in conjunction with the hydrogen ion activities in solutions of this investigation up to an ionic strength of 0.2 in the calculation of the concentrations of total hydrogen ion. With the aid of these latter values corrected concentrations of SnOH^+ and stannous ion were calculated. Using these figures new equilibrium quotients were calculated according to equation 1 and their logarithms plotted against $\mu^{1/2}$ as in Fig. 1, Curve II. The extrapolation to zero ionic strength was accomplished by the method of Randall and Vietti,⁵ and the value of the equilibrium constant, K_1^0 , is estimated to be 0.02.

According to Prytz¹ the hydrolysis of stannous ion is represented by the equation



(5) (a) Randall and Vietti, *THIS JOURNAL*, **50**, 1526 (1928); (b) Randall, *J. Chem. Ed.*, **8**, 1062 (1931); (c) see also Bray and Hershey, *THIS JOURNAL*, **56**, 1889 (1934).

or



The analytical data of Table I were used to calculate the composition of each stannous perchlorate solution and the equilibrium quotients based on equation 2. The logarithms of these equilibrium quotients when plotted against $\mu^{1/2}$ give a U-shaped curve which does not permit extrapolation to zero ionic strength according to the limiting law of Debye and Hückel. Since Randall and Vietti have shown that in such a plot the curve will resemble one of the family of logarithm of activity coefficient *vs.* $\mu^{1/2}$ for single electrolytes, it is obvious that equation 1, and not equation 2, represents the hydrolysis of stannous ion.

Summary

Solutions of stannous perchlorate containing free perchloric acid have been analyzed. The variation of the equilibrium quotient, K_1 , with ionic strength proves that the hydrolysis follows the equation $\text{Sn}^{++} + \text{H}_2\text{O} = \text{SnOH}^+ + \text{H}^+$. The value of the equilibrium constant, K_1^0 , at 25° is 0.02.

SAN FRANCISCO, CALIF. RECEIVED SEPTEMBER 25, 1939

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY, UNIVERSITY OF MINNESOTA]

A Study of Diffusion Processes by Electrolysis with Microelectrodes¹

BY H. A. LAITINEN AND I. M. KOLTHOFF

Introduction

The diffusion of an electro oxidizable or reducible substance in solution can be studied by measuring the current obtained using suitable electrodes in an electrolysis cell if the supply of electro reducible or oxidizable material is determined only by the rate of diffusion of the material to one of the electrodes, and if well-defined boundary conditions of concentration can be maintained at the electrode surface. The latter condition is fulfilled if the concentration of diffusing material is maintained at a value of practically zero at the electrode surface by maintaining a potential at the electrode such that the diffusing material is immediately oxidized or reduced upon reaching the electrode surface.

The theory of the diffusion process in the vicinity of an electrode depends upon the geometric

characteristics of the electrode and surrounding solution. Two extreme geometric cases are represented by a flat electrode, to which diffusion can occur from only one direction (linear diffusion), and a spherical electrode, to which diffusion can occur from all directions (spherically symmetrical diffusion). The equations for the current as a function of time, for linear and spherically symmetrical diffusion, are given below, as well as experimental results on the determination of current-time curves with microelectrodes of various types to determine the conditions under which theoretical diffusion conditions in electrolysis can be fulfilled.

The theoretical relation between current and time for linear diffusion has been derived by Cottrell² and MacGillavry and Rideal³ and is

$$i = -A \sqrt{\frac{D}{\pi t}} nFC \quad (1)$$

(1) This paper is based on a thesis to be submitted by H. A. Laitinen to the Graduate Faculty of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1940.

(2) F. G. Cottrell, *Z. physik. Chem.*, **43**, 385 (1902).

(3) D. MacGillavry and E. K. Rideal, *Rec. trav. chim.*, **56**, 1013 (1937).