temperature decomposition of normal lead carbonate gives an undistorted pure red PbO.

3. Comparisons of the catalytic activity of normal and distorted red PbO, yellow PbO and the hydrate toward hydrogen peroxide decomposition are described. The activity of the distorted product is much greater than that of the other products compared and the difference cannot be attributed to particle size. Activity of the distorted oxide is decreased by "annealing" of the sample, which is accompanied by sharpening of the diffraction lines.

4. Comparisons of the heats of reaction of the normal and distorted red PbO with concentrated perchloric acid are made with the result that the distorted red PbO possesses a 1 to 2% greater energy content than normal red PbO.

5. Relative intensity measurements on the distorted and normal red PbO for comparison purposes are described and the results are tabulated showing the great decrease in line intensities on the distorted PbO pattern.

6. The discussion of results includes a review of the active properties found for the distorted red PbO and calculations which show that the distortion cannot be accounted for on the basis of atomic displacements by directional stress, or, except to a very slight extent, on the basis of thermal agitation resulting from the increased energy content of the product. Hence, activity must reside in localized, incompletely crystallized surface areas. An explanation of the formation of yellow PbO at temperatures far below the red to yellow transition temperature is postulated on the basis that lattice impurities, such as water, will cause a metastable form to appear in temperature regions in which it is not usually produced.

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The Activity Coefficients of the Undissociated Part of Weak Acids. I. Acetic Acid in Potassium Acetate Solutions

BY W. D. LARSON AND W. J. TOMSICEK

From measurements of the electromotive forces of the cells

Pt/HOAc(Quinhydrone), HOAc, Hg$_2$(OAc)$_2$ (solid)/Hg

Larson and MacDougall[1] found that the mercurous acetate electrode functioned reversibly, and had a standard e. m. f. of -0.5109 ± 0.0002 v. at 25°, when the concentrations were expressed in moles per liter.

We have studied this electrode by means of the cells

$$\text{H}_2/\text{HOAc}(c_1), \text{KOAc}(c_2), \text{Hg}_2(\text{OAc})_2(s)/\text{Hg} \quad (1)$$
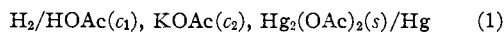
in order to obtain a more precise value of its standard e. m. f. In addition, we have measured cells containing potassium acetate at varying concentrations in a solution of acetic acid of constant molality.

The e. m. f. of cell (1) is given by

$$E = E^0 - \frac{RT}{F} \ln a_{\text{H}^+} a_{\text{OAc}^-} = E^0 - \frac{RT}{F} \ln K c_1 (1 - \alpha) \gamma_u \quad (2)$$

where K is the thermodynamic ionization constant of the acid, α its degree of ionization, c_1 its

(1) W. D. Larson and F. H. MacDougall, *J. Phys. Chem.*, **41**, 493 (1937).

molarity, and γ_u represents the activity coefficient of the acid molecules.

The purpose of measuring the cells containing potassium acetate was to present a method for determining, from e. m. f. measurements, the effect of salts on the activity coefficient of the undissociated part of weak acids. Data for the effect of potassium acetate on acetic acid are presented to illustrate the method.

Experimental

All materials were prepared as described previously.[1] Potassium acetate was from Mallinckrodt, and was dried at 180° for several hours, and then weighed in a closed, previously weighed bottle.

The acetic acid solutions were analyzed with a standard baryta solution. The solutions containing potassium acetate were made up by diluting a weighed amount of the salt with the stock acid solution to one liter in a calibrated, thermostated flask. The density of the solutions was determined by weighing the solution discharged at 25° from an accurately calibrated 25-ml. pipet. All weighings were corrected for buoyancy. The concentrations were known to within 0.1%.

E. m. f. measurements were made with a potentiometer constructed from four L. and N. dial type resistance boxes whose resistances were correct to within 0.04% as deter-

mined by comparison with standard resistances by means of a Jones and Josephs bridge.[2] The potentiometer could be read directly to 0.1 mv. The galvanometer was a portable lamp and scale instrument, L. and N. no. 2420-c; it was sufficiently sensitive to estimate smaller differences in voltage than could be read from the potentiometer. The standard cell was an Eppley unsaturated cadmium cell, certified by the manufacturers.

The mercurous acetate electrode vessels were those used in the previous work, and the hydrogen electrode vessels were of Pyrex glass. The hydrogen electrodes were 1 cm. squares of platinum gauze rolled into cylinders. They were lightly platinized in a 1% chloroplatinic acid solution containing a trace of lead acetate.

Cells were run at least in duplicate, and always agreed to within 0.1 mv. Their electromotive forces became constant after about two hours, and remained so for periods as long as four days.

Air was removed from some of the solutions by bubbling oxygen-free nitrogen through them. These solutions gave results in the cells identical with those from which the air had not been removed.[3]

The hydrogen was electrolytic tank hydrogen; oxygen was removed by passing it over copper turnings at 480°. It was saturated at the temperature of the thermostat with the vapor of the solution being studied.

Standard E. m. f. of the Mercurous Acetate Electrode.

—In order to check the value of the standard e. m. f. previously reported, thirteen cells were studied with acetic acid concentrations varying from 0.5 to 1.0 molar. These cells contained no potassium acetate; it was assumed that $\gamma_u = 1$ in such solutions. K has the value 1.754×10^{-5}.[4] c_1 is the analytically determined concentration of the acetic acid. α, for these solutions containing no added salt, was approximated from K and c_1 as described by Larson and MacDougall.[1] Thus, when E is measured, E^0 becomes known. The results are given in Table I. We have used the value 0.05913 for $2.303 \, RT/F$ at 25°.

TABLE I

STANDARD E. M. F. OF THE MERCUROUS ACETATE ELECTRODE AT 25°

c	E	$-E^0$
0.4992	0.8100	0.5109
.5170	.8092	.5109
.5087	.8096	.5109
.7433	.7999	.5109
1.035	.7914	.5109

The first column gives the molarity of acetic acid, the second the e. m. f. corrected to 760 mm. hydro-

(2) We wish to thank Prof. George Glockler of the School of Chemistry of the University of Minnesota for making the bridge available to us.

(3) H. S. Harned and W. J. Hamer, Report of the Naval Research Laboratories, No. P-1071, Sept. 14, 1934, found that air had no effect on mercurous sulfate electrodes.

(4) H. S. Harned and R. W. Ehlers, THIS JOURNAL, **54**, 1350 (1932); D. A. MacInnes and T. Shedlovsky, ibid., **54**, 1429 (1932).

gen pressure, and the third the value of the standard e. m. f. of the electrode, $Hg/Hg_2(OAc)_2(s)$, OAc^- at 25°. These results are much more precise than those previously given, probably due to more careful analytical work.

It should be pointed out that this value of the standard e. m. f. is calculated on a molarity basis. If it is calculated from eq. (2) using moles of acid per 1000 grams of water, the E^0 becomes -0.5117 v., since if we take $\gamma_u = 1$ on a molarity basis, $\gamma_u \gtrless 1$ on a molality basis.

The Activity Coefficients of the Undissociated Acid.

—When the cells contain potassium acetate, as well as when they contain no salt, their electromotive forces are given by eq. (2). The effects of the added salt are first, to change the value of α, and second, to change the value of γ_u. α is computed from the ionization values of Harned and Hickey[5] for acetic acid in the presence of potassium chloride at the ionic strengths used. Since E^0 is known from measurements of the cells with no added salt, reported in Table I, γ_u can be calculated when E is measured. It must be remembered that E is computed on the basis that $\gamma_u = 1$ when no salt is present. Therefore, the values of γ_u for any one concentration of acid in the presence of salt are relative to those in pure acid solutions.

In this work, the variation of the activity coefficient of undissociated acetic acid in a 0.5147 molal acid solution with varying amounts of potassium acetate was studied. Table II gives the experimental results. The activity coefficients are reported for concentrations in moles per liter of solution. The molality activity coefficients (i. e., those for concentrations in moles per 1000 g. of water) may be obtained from those reported by multiplying by the ratio of molarity to molality.

TABLE II

EFFECT OF POTASSIUM ACETATE ON THE ACTIVITY OF THE UNDISSOCIATED ACETIC ACID IN 0.5147 MOLAL ACETIC ACID AT 25°

c_1	c_2	d	E	γ_u
0.4992	0.0	0.9999	0.8100	1.000
.4990	.01120	1.0006	.8096	1.016
.4989	.02016	1.0013	.8096	1.016
.4987	.02970	1.0018	.8097	1.012
.4979	.05043	1.0022	.8098	1.008
.4971	.09873	1.0053	.8099	1.004
.4930	.2936	1.0141	.8101	0.996
.4864	.4986	1.0233	.8109	.966
.4739	.9911	1.0465	.8123	.914

(5) H. S. Harned and F. C. Hickey, ibid., **59**, 2303 (1937).

The first column gives the number of moles of acetic acid per liter of solution, the second, the number of moles of potassium acetate per liter of solution, the third, the density, the fourth, the electromotive force corrected to 760 mm. of hydrogen, and the last, the relative activity coefficients of the undissociated acid.

Discussion

A review of data on the activity coefficients of the un-ionized part of weak acids has been given by Randall and Failey.[6]

The methods available for studies of this quantity have been distillation and distribution experiments, and studies on the solubilities of slightly soluble acids. The first two methods lack precision, and the last one obviously is limited to weak acids whose solubility is not large. The method presented in this paper is simple and unambiguous. It can be applied to any weak acid having a slightly soluble mercurous salt. The relative activity coefficients obtained are thermodynamically exact.

The usual method of calculation of the activity of hydrogen ions in a buffer mixture is based on

(6) M. Randall and C. F. Failey, Chem. Rev., 4, 291 (1927).

the assumption that the undissociated part of the acid has an activity equal to its concentration. From our results it appears that such an assumption is valid if the salt content does not exceed 0.3 molar, at least in the case of acetic acid–potassium acetate buffers.

Further studies of the effects of other acetates upon acetic acid as well as of other weak acid buffer systems are being undertaken in this Laboratory.

Acknowledgment.—We wish to thank Mr. Joseph Norris for his assistance in preparing the chemicals and in measuring many of the cells.

Summary

The standard e. m. f. of the electrode Hg/Hg_2-$(OAc)_2(s)$, OAc^- is -0.5109 v. at $25°$.

A method for determining the activity coefficient of the undissociated part of weak acids has been described. This method can be applied to any weak acid whose mercurous salt is slightly soluble.

Values of the relative activity coefficients of acetic acid molecules in the presence of potassium acetate are presented.

Volume Changes in the Methyl Alcohol–Toluene System

BY L. S. MASON AND HOMER PAXTON

There has been little systematic study of the changes in volume which attend the formation of a large number of binary systems of organic liquids, and the data which are available seem to permit no satisfactory generalizations. Few investigators consider such changes due to purely physical factors. Possibly relative inter- and intramolecular volumes are significant in some, if not in all, cases, but it is more probable that the seemingly ubiquitous association, dissociation and solvation effects are predominant, particularly when considered in conjunction with the deviations of other physical constants from additivity.

Solutions of methyl alcohol in toluene at $25°$ show a negative volume change over the entire range of composition, in contrast with solutions of ethyl alcohol and of isopropyl alcohol in toluene and in benzene. Moreover, measurements on this system at two different temperatures have indicated that further measurements over a range

of temperatures might yield interesting information.[1,2] We have therefore measured the densities of representative solutions of these two substances at -21.1, 0.0, 25.0 and $49.7°$.

Methyl alcohol and toluene were used without further purification, their densities being 0.78693 and 0.86228, respectively, in close agreement with the best recent values of 0.78705[3] and 0.78675[4] for methyl alcohol and 0.86106,[5] 0.8625[6] and 0.86233[7] for toluene. The solutions were prepared by weight and precautions taken to reduce the evaporation and distillation effects to a minimum. The

(1) E. R. Washburn and A. Lightbody, J. Phys. Chem., 34, 2701 (1930).

(2) L. S. Mason and E. R. Washburn, ibid., 40, 481 (1936).

(3) H. H. Willard and G. F. Smith, THIS JOURNAL, 45, 286 (1923).

(4) K. K. Kelley, ibid., 51, 180 (1929).

(5) D. Tyrer, J. Chem. Soc., 105, 2534 (1914); "International Critical Tables," Vol. III, p. 29.

(6) J. F. W. Schulze, THIS JOURNAL, 36, 498 (1914); "International Critical Tables," Vol. VII, p. 77.

(7) J. Timmermans and F. Martin, J. chim. phys., 23, 755 (1926); "International Critical Tables," Vol. III, p. 27.