another gaseous substance are produced, and where the total measured pressure may be high.

3. The dissociation pressures for the systems

$MgNH_4PO_4 \cdot 6H_2O$, $MgNH_4PO_4 \cdot H_2O$, H_2O (below 60°)
$MgNH_4PO_4 \cdot 6H_2O$, $MgNH_4PO_4 \cdot H_2O$, $MgHPO_4 \cdot 3H_2O$, H_2O, NH_3 (above 60°)
$MgNH_4PO_4 \cdot H_2O$, $MgNH_4PO_4$, $Mg_2P_2O_7$, NH_3, H_2O
$MgHPO_4 \cdot 3H_2O$, $MgHPO_4 \cdot H_2O$, H_2O

have been determined.

4. The use of Wood's metal as a confining liquid is described.

NEW YORK CITY

RECEIVED AUGUST 13, 1932
PUBLISHED FEBRUARY 9, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

Lead–Mercurous Acetate Voltaic Cell with Acetic Acid as the Solvent[1]

BY GRADY TARBUTTON AND WARREN C. VOSBURGH

The reproducibility that has been attained in the preparation of voltaic cells with non-aqueous electrolytes is in general less than that of cells with aqueous electrolytes. Among those who have attained a reproducibility of within a few tenths of a millivolt are Brodsky,[2] Afanasiew,[3] Isaacs and Partington,[4] and Harned and Fleysher,[5] all with alcoholic electrolytes, and Yoshida,[6] who set up cadmium–mercurous iodide cells with water, methanol, ethanol, propanol and acetone as solvents. The electromotive forces in most other investigations with non-aqueous electrolytes have been reported only to the nearest millivolt.

It seemed worth while to test the reproducibility of cells with acetic acid as the electrolyte solvent. Hutchison and Chandlee[7] have prepared a series of hydrogen–mercurous sulfate cells with acetic acid as the solvent, but the difficulty of either excluding water entirely or keeping its concentration very constant was involved. The cell chosen for this work was a lead–mercurous acetate cell, which when pure acetic acid is the solvent can be represented as follows

$$Pb(Hg) \mid Pb(C_2H_3O_2)_2 \cdot 0.5HC_2H_3O_2 \mid Pb(C_2H_3O_2)_2 \cdot 0.5HC_2H_3O_2, Hg_2(C_2H_3O_2)_2 \mid Hg$$

Materials and Apparatus.—The purification of the acetic acid and of the lead acetate are described in an earlier paper.[8] Mercurous acetate was

---

(1) Part of a thesis submitted by Grady Tarbutton in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University, 1932.

(2) Brodsky, *Z. physik. Chem.*, **121**, 9 (1926).

(3) Afanasiew, *Z. Elektrochem.*, **35**, 221 (1929).

(4) Isaacs and Partington, *Trans. Faraday Soc.*, **25**, 56 (1929).

(5) Harned and Fleysher, THIS JOURNAL, **47**, 82 (1925).

(6) Yoshida, *Chem. Abs.*, **22**, 1893 (1928).

(7) Hutchison and Chandlee, THIS JOURNAL, **53**, 2884 (1931).

(8) Tarbutton and Vosburgh, *ibid.*, **54**, 4537 (1932).

prepared by precipitation and lead amalgam electrolytically, both from purified materials.

An oil-bath was used for temperature control. At 25° fluctuations in temperature were not more than ±0.01°, but at other temperatures about ±0.02°. Temperatures were measured to within ±0.02°.

Electromotive force measurements were made as described by Vosburgh and Elmore.[9]

The cell vessels used were of the "H" form of the sizes given below. For the earlier cells vessel 1 was used. Later, on account of low conductance, vessel 2 was used.

No.	Length, cm.	Width, cm.	Cross arm to base, cm.	Diameter of tube, cm.
1	17	4.7	9	1.1
2	14.8	5.5	4	1.8

Preparation of the Cells.—A lead acetate solution was prepared by adding an excess of lead acetate to acetic acid or a mixture of acetic acid and water. The solution was saturated either by mechanical shaking or by heating until the solid was dissolved and then seeding with the proper crystal form.[10] The latter procedure is preferable. By the former the wrong crystal form was introduced into some of the cells, which made considerable delay in the attainment of equilibrium. The solution so prepared is designated below as solution 1. A sample of solution 1 saturated at a definite temperature, usually 30°, was analyzed by the methods previously described. Previous to introducing into the cells, dissolved air was removed from solution 1.

A portion of solution 1 was saturated with mercurous acetate, giving solution 2.

The empty cell vessel, which had been properly cleaned, was placed in a beaker of water at about 75°. Lead amalgam, heated to dissolve the solid phase, was placed in one leg of the vessel, covered with a little of solution 1 and allowed to cool slowly to room temperature along with the water in the beaker. It was shown that rapid cooling gave an amalgam of higher lead activity than slow cooling, and that the difference might amount to over 0.1 mv. By slow cooling, amalgam reproducible to less than 0.01 mv. could be obtained.

The amalgam when cool was washed three times with solution 1. Then a portion of the excess solid lead acetate in equilibrium with solution 1 was placed above the amalgam to form a thick layer. This was covered with solution 1.

Mercury was then placed in the other leg of the vessel and washed three times with solution 2.

---

(9) Vosburgh and Elmore, THIS JOURNAL, **53**, 2822 (1931).

(10) See Ref. 8, p. 4539.

Some mercurous acetate was filtered by suction from the solution under which it was kept and washed with solution 2. It was transferred to an agate mortar and mixed well with about a fourth of its volume of lead acetate crystals (some of the excess solid from solution 1) and some solution 2. The paste was then washed three times by decantation with solution 2. A layer of this paste about one centimeter thick was placed above the mercury in the cell vessel.

A thick layer of lead acetate crystals (some of the excess solid from solution 1) was placed above the mercurous acetate paste and enough solution 1 added to fill the vessel to a point above the cross-arm. The upper part of the vessel was flushed out with nitrogen and stoppered with paraffined corks. On top of the corks was poured molten sealing wax or ceresin wax. All cells were made in duplicate.

Electromotive Force Measurements.—It has been shown that three different solid phases can exist in equilibrium with saturated solutions of lead acetate in acetic acid–water mixtures. The cells can be divided into three groups, each group containing a particular solid phase. The electromotive forces over a period of several months are given in Tables I, II and III.

TABLE I

CELLS WITH $Pb(C_2H_3O_2)\cdot 3H_2O$ AS THE SOLID PHASE

Cells	$HC_2H_3O_2/H_2O$[a] ratio by wt.	Electromotive force at 25° 7 Days v.	1 Month v.	6 v.	12–14 v.	15–18 v.
12, 13, 16	0.1969	0.74715	....	0.74729	0.74708	0.74709
17, 18	0.4757	....	0.74480	.74463	.74462	.74462
19, 20	1.144	.73938	.73945	.73921	.73924	....
21, 22	1.552	.73491	.73497	.73444	....	....

[a] The samples analyzed were saturated with lead acetate at 30°. At 25° the ratio would be somewhat larger.

Many of the cells decreased 0.2 to 0.5 mv. between the first and sixth months, but were nearly constant after the sixth month. That the decrease is not continuous is an indication that it is the result of faults of technique. A continuous change might be the result of reaction of the acetic acid with the lead of the amalgam or diffusion of the appreciably soluble mercurous acetate to the amalgam and its reaction with the lead. No evolution of hydrogen at the amalgam was observed. The conductance was sufficient for measuring the electromotive forces to 0.01 mv. The average difference between duplicate cells was 0.07 mv.

Cells 23–26 of Table II decreased appreciably in electromotive force over a period of a year. They may have contained some of the wrong solid phase at the beginning. Cells 38–39 increased. The others changed only a little. Improvements in technique, especially the method of preparing the solutions, were probably responsible for the better results in cells 44–47. The average difference between duplicates omitting cells 25–26 was 0.04 mv.

TABLE II

CELLS WITH $\mathrm{Pb(C_2H_3O_2)_2\cdot 0.5H_2O}$ AS THE SOLID PHASE

Cells	$\mathrm{HC_2H_3O_2/H_2O}$ ratio by wt.	Electromotive force at 25° 7 Days v.	1 Month v.	4–6 v.	10–12 v.
38, 39	3.886[a]	0.72846[c]	0.72851[c]	0.72877	0.72883
23, 24	4.715[a]	.72807	.72802	.72792	.72767
25, 26	4.932[a]	.72940	.72897	.72852	.72832
34	5.617[a]	.72772[c]	.72744[c]	.72760	.72763
46, 47	6.746[b]	.72632	.72632	.72623	....
44, 45	7.730[b]	.72609	.7261	.72614	....

[a] The samples analyzed were saturated at 30°. [b] The samples analyzed were saturated at 25°. [c] Calculated from measurements at 30°.

The solubility of lead acetate was large in the range of the cells of Table II. The solutions were quite viscous, and the conductance was such in some cases that it was difficult to read the electromotive force to better than 0.1 mv. The use of the larger cell vessels helped in this respect.

It can be seen that the electromotive force changes quite appreciably with change in the ratio of acetic acid to water in the electrolyte. This shows that the solid phase is a solvated compound, in agreement with the analytical data presented in the earlier paper.

TABLE III

CELLS WITH $\mathrm{Pb(C_2H_3O_2)_2\cdot 0.5HC_2H_3O_2}$ AS THE SOLID PHASE

Cells	$\mathrm{HC_2H_3O_2/H_2O}$ ratio by wt., 25°	Electromotive force at 25° 7 Days v.	1 Month v.	3 v.	6 v.
42	10	0.7268	0.7270	0.7272	0.7272
43	10	.7271	.7270	.7272	.7272
40	26	.7216[a]	.7279	.7279	.7279
41	26	.7216[a]	.7279	.7279	.7279
48	90[b]	.72902	.72903	.72900	...
49	90[b]	.72908	.72903	.72902	...
54	..[c]	.72895[d]	.72864[d]	.72908	...
55	..[c]	.72895[d]	.72866[d]	.72908	...

[a] These cells had fine needle-like crystals when prepared. After a week the cells were opened and seeded with the stable solvated crystals. The solid phase began to change over immediately, and the electromotive force became constant within a few hours. [b] The solution was nearly anhydrous; the ratio is subject to considerable error of method. [c] The solution was made to duplicate that of cells 48–49, but was not analyzed. [d] Calculated from measurements at 30°.

With regard to constancy and reproducibility the cells of Table III were the most satisfactory yet considered. Cells 42–43 were not as good as the others at first, but became constant later. Cells 40–43 had so much solid phase in them that the resistance was high and the electromotive force could not be measured to better than ±0.05 mv. Cells 48–49 and 54–55 had not as much solid phase and could be measured more precisely.

The change in electromotive force with composition again shows that the solid phase is solvated. As the water content decreases, the solubility of lead acetate decreases rapidly, and the mole fraction of acetic acid increases. The increase in electromotive force with increase in mole fraction of acetic acid would be expected if the solid phase is an acetic acid solvate, because in this case acetic acid is one of the reactants in the cell reaction. The cell data again confirm the solubility results previously reported.

The electromotive force of cells 40–41 after seven days is of interest. These cells contained a solid phase obtained by spontaneous crystallization from a supersaturated solution. It consisted of fine needle-like crystals. The electromotive force after seven days is nearly in agreement with that of an earlier pair of cells, which was 0.72166 and 0.72173 v., respectively. These latter cells were made with an electrolyte containing quite a bit of water and with dehydrated lead acetate as the solid phase. The constant electromotive force with the different composition in the two pairs indicates that both had the unsolvated salt as the solid phase.

The unsolvated lead acetate of cells 40–41 changed over to the solvated form on being seeded, and the electromotive force increased. The electromotive force of the earlier cells increased slowly without seeding.

While the electromotive force is dependent on the composition of the solution in all the cells having stable solid phases, it should be noted that at the transition points the composition is fixed when both solid phases are present. Eight cells were made with the two hydrated solid phases in equilibrium with the saturated solution. The solutions did not have the composition of the transition point when first prepared but approached it gradually after the cells were set up. The cells were not constant at first and did not agree until constancy was attained.

TABLE IV

CELLS WITH BOTH $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ AND $Pb(C_2H_3O_2)_2 \cdot 0.5H_2O$ AS SOLID PHASES, 25°

Cells	Initial v.	7 Days v.	1 Month v.	6 v.	12 v.
27	0.72994	0.72974	0.73002	0.73033	0.73031
28	.72994	.72922	.72956	.73018	.73032
36	.72929[a]	.72992[a]	.73011[a]	....	....
37	.72937[a]	.73001[a]	.73019[a]	.73018	.73017
50	.73098	.73055	.73015	....	....
51	.73068	.73047	.73017	....	....
52	.73088[a]	.73078[a]	.73072[a]	.73044[b]	....
53	.73090[a]	.73078[a]	.73073[a]	.73044[b]	....

[a] Calculated from measurement at 30°. [b] Three months.

It can be considered that the reaction for the cells of Table IV does not involve the electrolyte. The anhydrous lead acetate produced by reaction of lead with mercurous acetate must become hydrated at the expense of the trihydrate present, since the composition of the solution cannot change. The reaction, therefore, is

$$5Pb(amalgam) + 5Hg_2(C_2H_3O_2)_2 + Pb(C_2H_3O_2)_2\cdot 3H_2O \longrightarrow 6Pb(C_2H_3O_2)_2\cdot 0.5H_2O + 10Hg \quad (1)$$

The change of electromotive force with temperature was therefore determined in order to calculate the heat of reaction.

TABLE V

CHANGE OF ELECTROMOTIVE FORCE WITH TEMPERATURE

	$E_t - E_{25}$						
Cells	t = 16° mv.	20° mv.	30° mv.	35° mv.	40° mv.	45° mv.	50° mv.
27–28	−1.02	−0.59	0.20	0.50	0.77	0.97	0.76
36–37	−0.63	− .18	.20	.53	.70	0.82	.91
Calcd.	− .45	− .25	.25	.50	.75	1.00	..

The variation with temperature is linear within the limits of error and follows the relationship

$$E_t = E_{25} + 0.000050\,(t - 25)$$

as shown in the table.

For the cell Pb(Solid)/Pb^{++}/Pb(Hg) Gerke[11] found the value $E = 0.0057 + 0.000016\ (t - 25)$. Combining the two cells gives the electromotive force of the lead–mercurous acetate cell with a solid lead electrode, of which the electromotive force is $E = 0.7359 + 0.000066\ (t - 25)$. Application of the Gibbs–Helmholtz equation gives $\Delta H = -165.26$ kg. cal. with an uncertainty of not more than 0.2 kg. cal. If this is substituted in Equation 1 along with the values for the heats of formation of lead acetate trihydrate and mercurous acetate, namely, 446.12 and 203.34 kg. cal., respectively,[12] the heat of formation of $Pb(C_2H_3O_2)_2\cdot 0.5H_2O$ is found to be 271.35 kg. cal. The precision of this value depends mainly on that of the heats of formation of lead acetate trihydrate and mercurous acetate.

The temperature coefficients of the other cells were determined also. The cells with the higher water concentrations had negative temperature coefficients. The temperature coefficient approached zero as the ratio of acetic acid to water increased, and was positive for the cells with the higher ratios. It is interesting to note that a cell with the trihydrate as the solid phase and a ratio of acetic acid to water a little larger than that of cells 21–22 should have a zero temperature coefficient.

In connection with the temperature coefficient measurements, during which the cells were heated to 52°, no tendency of any of the solid phases to change to a more stable form was noted.

Summary

Lead–mercurous acetate voltaic cells have been set up with solvents covering a wide range of acetic acid–water mixtures and including nearly anhydrous acetic acid, and with three different solid phases.

---

[11] Gerke, THIS JOURNAL, **44**, 1684 (1922).

[12] "International Critical Tables," Vol. V, pp. 184, 187.

Duplicate cells with nearly pure acetic acid as the solvent could be reproduced to within 0.1 mv. and were constant in electromotive force for several months at least.

A cell containing two solid phases in equilibrium with the saturated solution was prepared.

The heat of formation of the compound $Pb(C_2H_3O_2)_2 \cdot 0.5H_2O$ was determined.

DURHAM, NORTH CAROLINA

RECEIVED AUGUST 17, 1932
PUBLISHED FEBRUARY 9, 1933

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Viscosity of Aqueous Solutions as a Function of the Concentration

BY GRINNELL JONES AND SAMUEL K. TALLEY

It has long been known that the viscosity of aqueous solutions is approximately a linear function of the concentration. In 1876 Sprung[1] published measurements on many salts at many temperatures. His viscosity–concentration curves are approximately linear but have an upward trend at higher concentrations which indicates an increasing deviation from a linear limiting law. Arrhenius[2] also found that the linear relationship holds approximately over the lower part of the concentration range but that the viscosity increases more rapidly than the concentration at high concentrations. He proposed an equation which is reducible to the form $\eta = A^c$, η is the relative viscosity compared to that of water at the same temperature and A is an empirical constant for any salt and temperature. This equation has been much used by later experimenters although it is only a rough approximation.

Most salts give solutions with viscosity greater than that of water at all concentrations. Some salts (including most but not all of the iodides, bromides, chlorides, bromates, chlorates, nitrates and thiocyanides, of cesium, rubidium, potassium, ammonium, thallium and hydrogen) give solutions having a viscosity less than that of water.[3] In such cases it is usual for the viscosity–concentration curve to go through a minimum and for some salts at sufficiently high concentrations the viscosity may become greater than that of water. This type of curve cannot be reproduced by the Arrhenius equation.

(1) A. Sprung, *Pogg. Ann. Phys. Chem.*, **159**, 1 (1876).

(2) S. Arrhenius, *Z. physik. Chem.*, **1**, 285 (1887).

(3) A. I. Rabinovich, THIS JOURNAL, **44**, 954 (1922), discusses the hypotheses which have been suggested to account for this phenomenon. An interesting suggestion has recently been made by Z. W. Wolkowa and W. S. Titow [*Z. physik. Chem.*, **A155**, 53 (1931)], who say "We may therefore suspect (vermuten) that an aqueous solution can only have a greater fluidity than water if the heat of dilution is negative."