tube H, connection is made by means of a platinum wire with the lead or cadmium amalgam at the bottom of the electrode vessel G.

Summary

Employing electrodes of lead amalgam and of cadmium amalgam, the authors have prepared a series of half-cells which are electromotively equivalent to hydrogen electrodes in contact with solutions in which the hydrogen-ion concentrations are, respectively, 10^{-4}, $10^{-4.7}$, 10^{-5}, 10^{-6}, 10^{-7}, 10^{-8}, 10^{-9}, 10^{-10}.

MINNEAPOLIS, MINNESOTA

MEASUREMENT OF SOLUBILITY BY FLOATING EQUILIBRIUM. THE SOLUBILITY OF LEAD ACETATE

BY MERLE L. DUNDON AND W. E. HENDERSON

Introduction

It has been shown by Richards and Shipley[1] that a small glass float of suitable size and shape, completely immersed in a liquid, is sensitive to very small changes in the density of that liquid. They have applied this principle to the quantitative analysis of solutions and to the calibration of thermometers.

Lamb and Lee[2] have by a slightly different procedure measured the density of various solutions with an accuracy of one part in the seventh

[1] Richards and Shipley, THIS JOURNAL, **34**, 599 (1912); **36**, 1 (1914).
[2] Lamb and Lee, *ibid.*, **35**, 1666 (1913).

decimal place. Their float consisted of an inverted 250cc. flask with an iron rod sealed within it. The densities were determined by weights added to the sinker together with measurement of the current in an electromagnet placed below the float and necessary to cause the latter to sink.

For some time in this laboratory the same general principle has been applied to the measurement of the solubility of a salt at various temperatures. The method that has been developed consists in adding a known weight of solvent to a saturated solution of unknown concentration, until the solution attains the same density as a glass float calibrated at a definite arbitrary temperature. The density of the float used is made less than the density of the most dilute solution to be analyzed, so that it will always be necessary to add solvent to any unknown sample to bring it to the density of the float. It is evident that for a given float and at a fixed temperature, the percentage of solid in the equilibrium solution of any given solute is constant. Therefore, the weight of solute in a given sample of unknown concentration is obtained by first bringing the solution to the same density as the float and then multiplying the weight of the resulting equilibrium solution by that fraction which it is known from the calibration of the float to contain. From the weight of salt obtained in this way and the weight of sample taken the solubility can be calculated with ease.

Purpose of This Investigation.—The purposes of the work herein described were (1) to study the method of determining solubilities by floating equilibrium, and (2) to determine accurately the solubility of lead acetate, $Pb(C_2H_3O_2)_2.3H_2O$, over a definite range of temperature.

Experimental

Preparation of the Pure Salt.—A commercial c. p. lead acetate was recrystallized twice from distilled water made distinctly acid with acetic acid. Residues obtained during the investigation were recrystallized in the same way and used again. Qualitative tests for impurities gave negative results when applied to the prepared salt. The crystals were usually filtered from the mother liquor on a Büchner funnel, washed once with boiled, distilled water and kept in a glass-stoppered bottle from which separate portions were used from day to day. In order to determine whether the crystals ob· tained were really the hydrated normal acetate, $Pb(C_2H_3O_2)_2.3H_2O$, a sample was very carefully dried and analyzed as follows. A current of washed air was drawn through a tube of partially dehydrated crystals and then through the sample to be dried. In this way the loss of any water of hydration and the formation of any basic salt were pre· vented. The dried sample was weighed in a platinum crucible, dil. sulfuric acid added and the crucible placed in an oven at 110° until the water and acetic acid were removed. The resulting lead sulfate was freed from sulfuric acid by heating to a bright red heat in an electric furnace. From the weight of lead sulfate the equivalent weight of lead ace· tate was calculated, all weights being reduced to the vacuum basis. The results of three analyses are as follows: weights taken, 1.0827, 1.2933 and 1.1673 g.; weights calculated from analysis, 1.0827, 1.2936 and 1.1674 g.

Calibration of the Float.—A cigar-shaped float was made from a piece of ordinary soft glass tubing and approximately the desired density ob-

tained by sealing within it a small globule of mercury. The density was made slightly less than that of the saturated solution of lead acetate at 0°. This float was then carefully calibrated as follows. Two separate samples of solution of about 250 cc. each were very carefully brought to floating equilibrium at 25°. Two samples of each were pipetted into a platinum crucible in a glass-stoppered weighing bottle and weighed. Sulfuric acid was then added, the solution evaporated in an oven and the lead sulfate ignited to a bright red heat in an electric furnace. The results are given below with weights reduced to a vacuum. The last two columns are expressed in terms of anhydrous salt.

Sample	Wt. of soln. G.	$PbSO_4$ G.	$PbAc_2$ calculated G.	$PbAc_2$ in solution %
1	19.5958	3.0020	3.2198	16.431
2	16.3442	2.5025	2.6841	16.422
3	18.2169	2.7891	2.9915	16.421
4	18.3582	2.8110	3.0151	16.423

The average of the last three values, which check very closely, is 16.422% and was the value selected to represent the floating equilibrium solution.

Apparatus and General Method.—A large thermostat which could be regulated to 0.01° was kept at 25° and was used in bringing the solution of unknown concentration to floating equilibrium. The thermometer used was graduated in tenths of a degree and had been checked by the Bureau of Standards.

Saturations were attained in a 10-liter thermostat which could be regulated to about 0.02°. The following general procedure was used. An excess of crystals roughly weighed was put into a flask with boiled, distilled water and the solution was stirred with a small propeller-shaped, motor-driven stirrer. The temperature was kept for a few minutes from 0.5° to 3.° higher than that desired and then stirring continued at a constant temperature for about 20 hours. At least two samples were taken for float tests at intervals from 1 to 3 hours apart and one for a gravimetric test within that time. Gravimetric tests were made in the same way as in the calibration of the float.

In making a determination by the float method a 100cc. glass-stoppered weighing bottle was used, and a stirrer was made for it by bending a loop on the end of a small glass rod. The float and stirrer were placed in the weighing bottle and the whole apparatus weighed. The solution for analysis was pipetted into the bottle with a warm pipet and the weight again taken. In case the temperature of the unknown solution differed much from that of the room, this sample was placed in a desiccator for some time before weighing. The stopper was removed, water was added rapidly until the solution began to approach the density of the float,

and the open bottle was then placed in a thermostat regulated at 25°. After sufficient time for the temperature to become constant, water was added a drop at a time from a capillary pipet with constant stirring until floating equilibrium was reached. The end-point was considered to be that point at which the float would just sink when suspended in the solution. It could be determined within one small drop of water. If the end-point was passed, solvent was removed by blowing a current of dry air over the surface for a few minutes. The bottle containing the equilibrium solution was then stoppered, wiped carefully with a piece of clean cheese cloth, and weighed. Before weighing it was placed in a desiccator for about 10 minutes. In a typical analysis of a solution saturated at 20° the vacuum weight of the solution taken was 41.0925 g., and that of the equilibrium solution was 76.7818 g. The salt content of the equilibrium solution as shown by the calibration of the float was 16.422%.

76,7818 × 0.16422 = 12.6091 g. of $Pb(C_2H_3O_2)_2$ in 41.0925 g. of solution.

$$\frac{12.6091}{41.0925} = 30.684 \% \; Pb \; (C_2H_3O_2)_2 \text{ in the solution.}$$

$$\frac{12.6091 \times 100}{41.0925 - 12.6091} = 44.268 \text{ g. of } Pb(C_2H_3O_2)_2 \text{ in 100 g. of water.}$$

The data obtained on the solubility of $Pb(C_2H_3O_2)_2.3H_2O$ and the densities of the saturated solutions are given in Table I. All weighings were reduced to a vacuum basis by the method given in Circular 19 of the Bureau of Standards. Densities obtained from standard tables were used as follows: $Pb(C_2H_3O_2)_2.3H_2O$, 2.5; $PbSO_4$, 6.23. Densities of solutions were determined by weighing the volume contained in a 1cc. pipet. For the equilibrium solution the value was 1.13.

TABLE I

SOLUBILITY OF $Pb(C_2H_3O_2).3H_2O$ PER 100 GRAMS OF WATER

Expressed in terms of anhydrous salt

Temperature	Float method	Gravimetric method	Density of solution saturated
°C.	G.	G.	
0.10	19.84	19.82	1.14
0.20	19.93	....	..
10.00	29.46	29.37	1.195
...	29.38	....	..
15.00	35.84	35.82	1.22(interp.)
...	35.81	....	..
20.00	44.27	44.25	1.26
...	44.24	....	..
25.00'	55.195	55.21	1.33
30.02	69.95	69.95	1.41
...	69.92	....	..
35.04	88.96	89.01	1.48

TABLE I (continued)

Temperature °C.	Float method G.	Gravimetric method G.	Density of saturated solution
. . .	89.05	. . . .	. .
40.07	116.69	116.55	1.60
. . .	116.73	. . . .	. .
45.10	155.71	155.49	1.73
	155.66		
	155.66		
50.14	221.44	220.27	1.88
	221.14		
50.14[a] (Next day)	222.42		

[a] See discussion under behavior of lead acetate in neutral solution.

TABLE II

THE SOLUBILITY OF $Pb(C_2H_3O_2)_2.3H_2O$ AS TAKEN FROM A CURVE PLOTTED FROM THE VALUES IN TABLE I AND EXPRESSED IN TERMS OF THE ANHYDROUS SALT

Temperature °C.	Grams per 100 g. of water	Per cent. solution
0	19.7	16.5
5	23.7	19.4
10	29.3	22.8
15	35.6	26.4
20	44.3	30.7
25	55.2	35.6
30	69.7	41.1
35	88.9	47.1
40	116.0	53.7
45	153.0	60.7
50	221.0	67.6

Conclusions in **Regard to the Float Method.**—From the results obtained we can safely say that analyses by the float method can easily be made to check within 0.1% without taking extraordinary precautions. With as soluble a salt as lead acetate the change of solubility with temperature is so great that slight variations in the temperature of saturation have a large effect upon the concentration of the solution. For example, at $35°$ a change of $0.02°$ corresponds to a change of solubility of about 0.1%. Thus it seems probable that in this work the method of analysis was much more accurate than the attainment of solubility equilibria. The attainment of floating equilibrium is a process capable of great exactness, and if we assume that density under standard conditions is a true measure of concentration, as it undoubtedly is in most cases, then the accuracy of this method of analysis is determined largely by two factors, thermostat regulation and weighing in a large glass vessel. If, however, the weighings are done with great care such errors will be less than the weight of the last drop used in bringing the solution to equilibrium. The

average weight per drop as we worked was 0.035 g. (added to about 40 g. of solution). For the best results the density of the float should be such that the weight of solution taken for analysis is about the same as the weight of solvent to be added. This will minimize errors in weighing. The larger the volume of the equilibrium solution the more accurately the end-point can be reached; but a very large volume is more difficult to weigh with precision. From 50 to 75 g. of equilibrium solution is a very satisfactory quantity. Care must be taken that bubbles of air do not cling to the float, and in determining an equilibrium the float must be pushed into the center of the solution as it clings to the upper surface with great tenacity.

The time necessary for a complete analysis is determined largely by the time required for weighing. With some practice the float can easily be brought to equilibrium within 15 minutes. Altogether the method is capable of considerable speed and accuracy.

In working with a substance which can readily be obtained in a pure form the float may be calibrated most easily by weighing directly the pure substance and the resulting equilibrium solution which is obtained by adding the solvent.

The Behavior of Lead Acetate in Solution.—The value for the solubility of normal lead acetate which seems to us most accurate is that given by Jackson.[3] He worked only at 25°, and in a study of the basic acetates of lead by interpolating the curve across the neutral point, obtained the value for the normal salt. His value is 35.5%, or 55.05 g. per 100 g. of water. The only other value of any importance which we have found is that of Osaka and Hara[4] who determined the solubility in dil. acid solutions and extrapolated to neutral solution. Their value at 25° is 54.38 g. per 100 g. of water.

From 12 gravimetric analyses on 4 different solutions we obtained the average value 55.21. After the values at other temperatures had been obtained we returned to 25°, and on a solution of carefully prepared crystals, two float tests checked at 55.46 which is considerably higher than before. Some well formed crystals were then very carefully washed and immediately placed in the saturation flask. By the float method 55.50 and 55.53 g. per 100 g. of water were obtained; by the gravimetric method, 55.46 g.

It seemed as a result of these experiments that the more carefully we prepared the salt the higher were the values and the more deviation they showed from the results obtained indirectly by Jackson. Moreover, another very interesting fact came to light in the temperature curve. Below 35° the float values and the gravimetric values checked very well,

[3] Jackson, This Journal, 36, 2350 (1914).
[4] Osaka and Hara, Mem. Coll. Sci. Kyoto Imp. Univ., 2, 147 (1917).

but at higher temperatures the gravimetric curve began to fall definitely below the curve obtained by the float method. These facts seemed to require some explanation.

Jackson[3] has shown that upon the addition of lead hydroxide to solutions of normal acetate a very soluble salt of the composition $3Pb(C_2H_3O_2)_2 . PbO . 3H_2O$ is formed. Parsons[5] has also shown that the freezing point of a solution of normal lead acetate is actually raised by the addition of lead hydroxide, which confirms this fact. By these two salts dissolving independently it is evident that the presence of a slight amount of basic lead would increase very greatly the apparent solubility of the normal salt. At high temperatures the hydrated salt decomposes with the evolution of water and acetic acid so readily that it is impossible to determine its melting point in an open tube. Löfman[6] has shown that at 20° hydrolysis is considerably more than 1%. This hydrolysis would produce a basic salt and free acetic acid. As the acid concentration increased the hydrolysis would be retarded, unless the temperatures were high enough to drive off the acid, in which case the action would proceed indefinitely. Because of the very small ionization of lead acetate a very low acid concentration should effectually retard hydrolysis. A mass of fine crystals taken from an acid solution might carry with them a slight amount of acid which would affect the apparent solubility. This could account for the variable results at 25°. At higher temperatures the formation of basic salt would be greater, and a calculation of normal salt based on total lead content would necessarily be different from a calculation based on the density of the solution. This result is in accordance with the facts. It is probable, therefore, that the values obtained by both methods are influenced to some extent by this effect.

Jackson gives the following figures for slightly acid and slightly basic solutions at 25°.

	PbO %	Pb(C₂H₃O₂)₂ %	Density of sol.
1	-0.27	35.19	1.326
2	$+0.10$	35.60	1.334
3	$+1.01$	37.14	1.367

Calculating total lead as $Pb(C_2H_3O_2)_2$ these would be (1) 54.30, (2) 55.43, and (3) 60.57 g. per 100 g. of water. The density of one of our solutions which analyzed 55.23 was 1.333 which agrees quite well.

The assumption made above that the variable results are due to the presence of basic salt seems to be justified by all available experimental data. If, therefore, solubility is the amount of salt that goes into solution with water, our values are reasonably accurate. If it is a measure of

[5] Parsons, *J. Phys. Chem.*, **11**, 659 (1907).

[6] Löfman, *Z. anorg. allgem. Chem.*, **107**, 241 (1919).

the number of molecules of normal salt in the solution, our values are probably a little high. For all practical purposes, however, the difference is not appreciable.

For assistance rendered in the earlier stages of this work, credit should be given to Mr. Gebhard Stegeman.

Summary

A method of determining solubilities by the use of floating equilibrium is described. This method has been shown to be capable of considerable speed or great accuracy and a reasonable amount of both.

The solubility of lead acetate, $Pb(C_2H_3O_2)_2 \cdot 3H_2O$, has been determined between $0.0°$ and $50°$.

Evidence has been produced which supports an explanation for the variation in the values obtained for the solubility of lead acetate.

COLUMBUS, OHIO

THE INFLUENCE OF ELECTROLYTES ON THE SOLUBILITY OF NON-ELECTROLYTES

BY ANDREW MCKEOWN

The mutual relations existing between the solubilities of different substances in the same solution have received much attention in the past, both from the theoretical and from the practical standpoint, and semi-empirical relations have been obtained which represent the experimental facts in particular cases in a more or less satisfactory manner.[1] Investigations have recently been carried out by Dawson[2] on the salting out of phenol from water solution by sodium sulfate, and by Thorne[3] on the solubility of ethyl ether in aqueous solutions of sodium chloride. The data in the latter case are of special interest, since the solubility determinations have been carried out at two different temperatures, viz., $15°$ and $25°$. Thorne finds that his results conform to the equation

$$\frac{1}{c} \cdot \log_{10} \frac{s_0}{s} = k$$

where c is the concentration of sodium chloride present in solution, s is the corresponding solubility of ethyl ether, s_0 is the solubility of ether in pure water, and k is a constant for a given temperature, having the value 0.0555 at $15°$ and 0.0536 at $25°$. As a matter of fact, the solubility of ether in pure water is anomalous, but the equation holds fairly

[1] Compare Rothmund, Z. Elektrochem., 14, 532 (1908); Z. physik. Chem., 69, 523 (1909).

[2] Dawson, J. Soc. Chem. Ind., 39, 151T (1920).

[3] Thorne, J. Chem. Soc., 119, 262 (1921).