double salt that forms from water between —11° and 80°. No anhydrous salt has been described, though Meyerhoffer[1] mentions briefly that he obtained one.

In our work mixtures of the single salts were treated with alcohol just as in the previous case. Glass rods were used in the bottles to assist in reaching equilibrium. In analyzing solutions, only copper was determined (by titration with thiosulfate as before) as the amount of ammonium chloride dissolved was very small, and the solubility relations are sufficiently clear from the data found for cupric chloride alone. The residues were very fine and always included a small amount of alcohol. In the table, the composition of the dry residue is given except in the last two results, where the alcohol formed a compound.

The following results were obtained:

TABLE III.—SOLUBILITY OF AMMONIUM-CUPRIC CHLORIDES IN ABSOLUTE ALCOHOL AT 25°.

No.	Per cent. $CuCl_2$ in solution.	Per cent. $CuCl_2$ in residue.	Per cent. NH_4Cl in residue.	Per cent. alcohol in residue.	Residue contains
1	4.65	10.70	89.30	...	NH_4Cl and $NH_4Cl.CuCl_2$
2	4.74	63.54	36.46	...	
3	6.45	71.45	28.55	...	$NH_4Cl.CuCl_2$
4	12.90	72.33	27.67	...	
Cal. for $NH_4Cl.CuCl_2$		71.53	28.47	...	
5	34.92	72.54	24.56	2.90	$NH_4Cl.CuCl_2$ and $CuCl_2.C_2H_5OH$
6	34.50	74.04	8.09	17.87	

The single 1 : 1 salt is the only one formed. It is entirely different in type from the hydrated double salt but corresponds to the potassium cupric compound, which it also resembles in color.

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EQUILIBRIUM IN THE SYSTEM: LEAD NITRATE AND PYRIDINE.

BY JAMES H. WALTON, JR., AND ROY C. JUDD.

Received May 3, 1911.

Pyridine occupies in many ways a unique position among organic solvents. Not only does it dissolve many organic compounds—such as the fats, oils and certain of the carbohydrates—but it also exercises a solvent action on a large variety of inorganic compounds. Moreover, just as water unites with many of these inorganic compounds as water of crystallization, so many of them take up pyridine of crystallization. With pyridine, types of solubility curves have been obtained which are analogous in every way to those resulting from solubility determinations when water was used as a solvent.

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[1] *Z. phys. Chem.*, 3, 340 (1889).

Tombeck[1] has made certain solubility determinations with pyridine, but by far the greater part of the work on this subject has been carried out by Kahlenberg[2] and his students, who have investigated the solubility in pyridine of the nitrate, chloride, bromide and iodide of silver, and also of mercuric chloride. The following research forms a part of an extensive investigation which is still being carried on in this laboratory.

It has been known for some time that lead nitrate is soluble in pyridine. In 1897 Schmujlow[3] described the compound $Pb(NO_3)_2.3C_5H_5N$. In 1898 Pincussohn[4] working with precipitates thrown down by the addition of water to solutions of lead nitrate in pyridine made and described $Pb(NO_3)_2.2C_5H_5N$ and $Pb(NO_3)_2.C_5H_5N.HNO_3$. The object of this investigation was to establish the solubility curve of lead nitrate in pyridine and to ascertain what compounds are in equilibrium with the saturated pyridine-lead nitrate solution at the various temperatures.

Materials Used.—The lead nitrate, which was obtained from Merck, was recrystallized and thoroughly dried. The pyridine was also obtained from Merck. It was first dried over fused potassium hydroxide, then boiled with potassium permanganate and distilled off. The distillate was then boiled with barium oxide for five hours,[5] using a reflux condenser. This distillate was then redistilled from fresh barium oxide, the portion coming over between 114° and 115° being used in the investigation. This purified pyridine was kept in glass-stoppered bottles which were capped with thin sheet rubber.

The thermometers used were graduated to one-tenth of a degree, and the temperature could easily be estimated to one one-hundredth of a degree. They were standardized by comparing them with an instrument which had been checked by the Bureau of Standards. Below 0° a toluene thermometer was used.

Methods of Analysis.

Gravimetric.—For the estimation of the lead in the pyridine solution, two methods were available: gravimetric, weighing the lead as lead sulfate, and volumetric by means of the well-known ammonium molybdate titration.

The gravimetric method was first employed and was carried out as follows: The solution of lead nitrate in pyridine was placed in a casserole, about 50 cc. of water were added, then 5 cc. of concentrated nitric acid (sp. gr. 1.42). The solution was then boiled, and after cooling 3 cc. of sul-

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[1] *Ann. chim. phys.*, [7] 21, 433 (1900).

[2] *J. Physic. Chem.*, 12, 283 (1908); *Ibid.*, 13, 421 (1909); *Ibid.*, 14, 189 (1910).

[3] *Z. anorg. Chem.*, 12, 1 (1897).

[4] *Ibid.*, 14, 379 (1898).

[5] Wilcox: *J. Phys. Chem.*, 14, 576 (1910).

furic acid (sp. gr. 1.84) were added to convert the lead to the sulfate. The pyridine and nitric acid were now expelled by evaporating to the fumes of sulfuric acid, water and alcohol were then added to the cold solution and the lead sulfate filtered on a Gooch crucible, then washed, dried and weighed in the usual manner.

The gravimetric method was unsatisfactory for two reasons: in the first place, the lead when precipitated from the solution containing pyridine came down as a dark colored slimy precipitate which was difficult to filter, and which crept up on the side of the casserole so badly that mechanical loss was almost inevitable. In the second place the gravimetric method was too slow. It was necessary to stir the lead nitrate-pyridine mixture until a state of equilibrium had been reached. This could be ascertained by taking and analyzing samples of the solution from time to time. Upon analyzing two consecutive samples and obtaining the same results it could safely be assumed that the solution was saturated with respect to the lead nitrate. Obviously such a method for analyzing the pyridine solution required a method of analysis which was not only accurate but rapid as well, and the gravimetric method did not fulfil the second requirement.

The Volumetric Method.—A solution of ammonium molybdate was prepared and standardized by weighing out samples of pure lead nitrate, converting them to the sulfate by heating with concentrated sulfuric acid, dissolving the sulfate in ammonium acetate and titrating in the usual way using tannic acid as an indicator. One cubic centimeter of this solution was equivalent to 0.01300 gram of lead nitrate.

Before the volumetric method could be used it was necessary to see whether or not a solution of ammonium acetate containing lead nitrate and some pyridine gave the same value when titrated with molybdate solution as an ammonium acetate solution containing lead sulfate instead of the nitrate, and no pyridine.

To test this point samples of pure lead nitrate were dissolved in ammonium acetate solutions, pyridine added, and the titration carried out by means of ammonium molybdate as in the standardization with lead sulfate. The following table shows the results of these experiments:

Experiment.	Wt. of $Pb(NO_3)_2$ taken.	Wt. of $Pb(NO_3)_2$ found.	Volume of the solution.
1	0.2196	0.2197	100 cc.
2	0.2196	0.2194	100 cc.
3	0.2196	0.2196	100 cc.

In each of these determinations 3 cc. of pyridine were added to the solution, which was then boiled until the odor of pyridine could no longer be observed.

The above experiments show that the lead may be titrated when present in the solution as lead nitrate and moreover that the presence of a small amount of pyridine does not influence this determination.

In the subsequent volumetric determination of lead the method just described was closely followed.

The Meyerhoffer and Sanders apparatus was used in making the solubility determinations. The particular form consisted of a hard glass test tube ten inches long and two inches in diameter immersed in a constant temperature bath. The tube was fitted with a stirrer which turned in a mercury seal (Fig. 1), thus preventing the loss of solvent by evaporation or the admission of moisture from the air. To take a sample the weighing tube A was introduced into the larger tube through a hole in the stopper. After coming to the temperature of the bath the stirrer was stopped, the end of the small tube B, which was covered with a piece of closely-woven muslin, was dipped below the surface of the pyridine and filled by applying suction at C. A was then removed, stoppered, weighed and the contents analyzed.

In working at 0° the thermostat was filled with finely crushed ice and water. Below that temperature freezing mixtures were used. From 0° to 50° water alone was used, the temperature of the bath below 25° being kept lower than that of the room by means of a spiral tube through which water at the temperature of 5° was allowed to flow. From 50° to 90° the water in the bath was covered with a layer of paraffin —above that temperature paraffin alone was used.

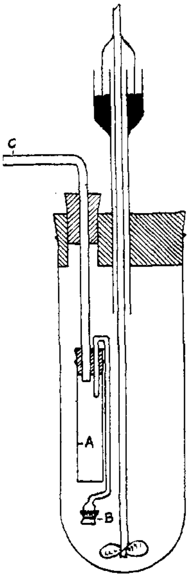

Fig. 1.

The results obtained in the solubility determinations are given in the following table, in which the solubility is expressed in grams of lead nitrate soluble in 100 grams of pyridine. Each figure given is the mean of at least two determinations lying well within the limits of experimental error. The results are shown graphically in Fig. 2, temperatures being charted as abscissas and amounts of lead nitrate, in grams soluble in 100 grams of pyridine, being represented as ordinates.

Analysis of the Solid Phase.—From an inspection of the curve it was evident that in the range of temperature through which these experiments were conducted three solid phases must exist. Analysis of the solids in equilibrium with the pyridine solution were carried out as follows:

The solid in equilibrium at ordinary temperature was filtered off, dried by pressing with filter paper and the percentage of lead determined. The average of several determinations gave 59.11 per cent. $Pb(NO_3)_2$,

EQUILIBRIUM BETWEEN SATURATED SOLUTION AND SOLID.

Temperature, 0° C.	Grams $Pb(NO_3)_2$ in 100 grams of pyridine.	Temperature, 0° C.	Grams $Pb(NO_3)_2$ in 100 grams of pyridine.
$Pb(NO_3)_2.4\ C_5H_5N$		$Pb(NO_3)_2.3\ C_5H_5N$	
—19.4	2.93	59.52	36.70
—14.5	2.14	70.00	47.29
—10.00	1.90	80.00	61.60
0.00	3.54	89.93	90.21
5.4	3.93	94.94	128.06
8.7	5.39		
14.72	6.13	$3Pb(NO_3)_2.2C_5H_5N$	
19.97	6.78	99.89	143.36
24.75	8.56	104.90	152.00
30.03	10.98	109.90	163.80
34.97	13.20		
40.03	16.94		
45.00	22.03		
49.97	29.37		

which corresponds to the compound $Pb(NO_3)_2.4C_5H_5N$ which contains 51.16 per cent. lead nitrate.

The solid phases at higher temperatures were removed from the liquid and dried in a bath kept at the temperature at which they were separated

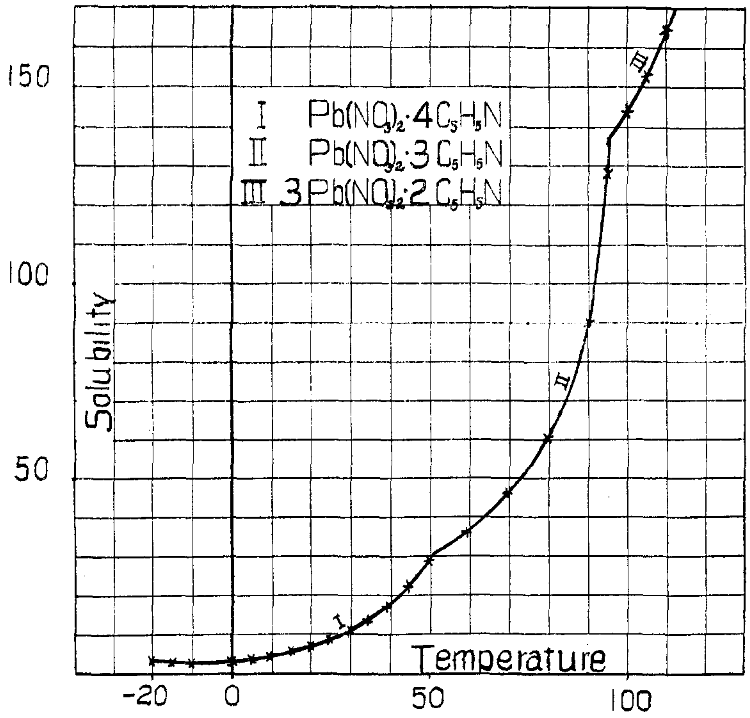

Fig. 2.

from the liquid. The solid phase between 60° and 95° was found to contain 58.93 per cent. of lead nitrate. The compound $Pb(NO_3)_2.3C_5H_5N$ contains 58.98 per cent. lead nitrate. This is the compound discovered and described by Schmujlow in 1897. Above 95° a compound was found which contained 86.2 per cent. of lead nitrate. This is evidently $3Pb(NO_3)_2.2C_5H_5N$, which contains 86.27 per cent. of lead nitrate.

The transition points may be obtained from the curve. At 51° there is a transition point between $Pb(NO_3)_2.4C_5H_5N$ and $Pb(NO_3)_2.3C_5H_5N$. At 96° there is a transition point between $Pb(NO_3)_2.3C_5H_5N$ and $3Pb(NO_3)_2.2C_5H_5N$.

Summary.

In the foregoing investigation the solubility curve of lead nitrate and pyridine has been established between —19.4 and 110°. The results show that for this range of temperature there are three distinct crystalline compounds of lead nitrate and pyridine in equilibrium with the solution. The three compounds are: $Pb(NO_3)_2.4C_5H_5N$; $Pb(NO_3)_2.3C_5H_5N$; and $3Pb(NO_3)_2.2C_5H_5N$. Of these $Pb(NO_3)_2.4C_5H_5N$ and $3Pb(NO_3)_2.2C_5H_5N$ have hitherto been unknown.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY. No. 192.]

THE WEIGHT OF A FALLING DROP AND THE LAWS OF TATE

VII. THE DROP WEIGHTS OF SOME OF THE LOWER ESTERS, AND THE SURFACE TENSIONS AND MOLECULAR WEIGHTS CALCULATED FROM THEM.

BY J. LIVINGSTON R. MORGAN AND FREDERICK W. SCHWARTZ.

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The object of this research was the further testing of the Morgan drop weight apparatus, for the purpose of (1) applying to additional substances the new definition of normal molecular weight in the liquid state; and (2) the direct comparison of the values of surface tension, as found from drop weight, with those from the capillary rise. The main difficulty encountered thus far in the comparison of drop weight results with those from capilliary rise has been the fact that no one agreeing value in many cases could be found from the work of the various observers of capillary rise, their results varying widely. In order that any such variation might be avoided in the capillary rise results used in this research, those liquids, the lower esters, were selected, eight of which have been carefully studied by Ramsay and Aston,[1] each from observations at three tem-

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[1] *Z. physik. Chem.*, 15, 98 (1894).