a highly basic nature are thrown down, while on evaporation gummy, non-crystalline masses are obtained. Perhaps the only basic beryllium compounds which have been prepared in a state of purity are the salts of the type of basic beryllium acetate, $3Be(CH_3COO)_2{\cdot}BeO$ or $Be_4O(CH_3COO)_6$.[16] In contrast with the difficulty of obtaining aquo basic salts of beryllium in a state of purity from water is the relative ease with which many crystalline ammonobasic halides of beryllium can be prepared in liquid ammonia. It is noteworthy though unexpected fact that the very basic compound, $5Be(NH_2)_2{\cdot}BeI_2$, is much more soluble in liquid ammonia at $-40°$ than the less basic $3Be(NH_2)_2{\cdot}BeI_2$.

In conclusion, the author wishes to thank Dr. E. C. Franklin for his interest in this work and for looking over the manuscript prior to publication.

Summary

1. Beryllium dissolves in liquid ammonia solutions of an excess of ammonium chloride and bromide to form normal beryllium halides with ammonia of crystallization. The salts, $BeCl_2{\cdot}4NH_3$, $BeCl_2{\cdot}2NH_3$ and $BeBr_2{\cdot}4NH_3$ have been prepared.

2. Solutions of the normal halides of beryllium in liquid ammonia readily react with metallic beryllium to form ammonobasic halides; $3Be(NH_2)_2{\cdot}BeBr_2{\cdot}4NH_3$, $3Be(NH_2)_2{\cdot}BeBr_2{\cdot}8NH_3$, $3Be(NH_2)_2{\cdot}BeI_2{\cdot}4NH_3$ and $5Be(NH_2)_2{\cdot}BeI_2{\cdot}4NH_3$ have been prepared in crystalline form. There is good evidence for the existence of $2BeBr_2{\cdot}Be(NH_2)_2{\cdot}8NH_3$, although it has not been obtained in crystalline form.

STANFORD UNIVERSITY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ROCHESTER]

THE SOLUBILITY OF SILVER IN MERCURY[1]

BY ARTHUR A. SUNIER AND C. B. HESS

RECEIVED OCTOBER 3, 1927 PUBLISHED MARCH 7, 1928

In connection with work on solutions in this Laboratory, attention was directed to the lack of conclusive data on the solubility of silver in mercury. Many determinations have been made at isolated temperatures[2] but, to our knowledge, Joyner[3] has made the only systematic attempt to investigate this system over a range of temperatures. Yet his work,

---

[16] Parsons, ref. 3, pp. 62–64; Bragg and Morgan, *Proc. Roy. Soc.* (*London*), **104A**, 437 (1923); Morgan and Astbury, *ibid.*, **112A**, 441 (1926).

[1] This paper was presented by one of the authors (C. B. H.) at the 1927 Spring Meeting of the American Chemical Society, held in Richmond, Virginia.

[2] (a) Gouy, *J. phys.*, [3] **4**, 320 (1895); (b) Humphreys, *J. Chem. Soc.*, **69**, 243 (1896); (c) Reinders, *Z. physik. Chem.*, **27**, 285 (1898); (d) Ogg, *ibid.*, **50**, 209 (1905); (e) Eastman and Hildebrand, THIS JOURNAL, **36**, 2020 (1914).

[3] Joyner, *J. Chem. Soc.*, **99**, 195 (1911).

dealing mainly with the ternary system tin–silver–mercury is not accompanied by sufficient control work to weight his results properly on silver and mercury alone.

The present paper is a report of solubility determinations of silver in mercury up to 200°.

Materials

The mercury used was first washed by dropping it five times through a five foot Meyer column containing mercurous nitrate. The dried mercury was then distilled three times from an all-glass apparatus according to the method of Hulett and Minchin.[4] Samples of the purified product yielded no residue when carefully distilled *in vacuo*.

Two samples of silver were used. The first, employed in what are later to be described as Series A, B, C determinations, was U. S. Mint bar of the "999" fineness. Filings of this were obtained with a clean, hard file. Because traces of iron were appearing in the final analyses, a second sample was used in our final (Series D) determinations. This was 1000 fine foil, very kindly supplied us by the Philadelphia Mint. Thin strips of this were used in charging the solubility tubes. Below (Table I) are given the results of analysis of both samples by the authors.

TABLE I

ANALYSIS OF SILVER USED

					Av.
Ag filings, % Ag	99.76	99.72	99.71	99.73	99.73
Ag foil, % Ag	99.97	99.96	99.96	99.96	99.96

Apparatus

The solubility tube (Fig. 1) was made of Pyrex glass. It consists essentially of a sample tube B with projections C for suspending it in the balance case, a capillary filter finely constricted at D, a glass-wool filter E and a lower tube F in which the amalgams were prepared.

For stirring the amalgams a long, vertical rod pivoted at its center was used. The lower end of this rod had two projecting posts so spaced that the two eyes of the tubes could be slipped over them. The upper end of the rod was slotted and attached to the arm of an automobile windshield cleaner. When in operation a pendulum-like motion was imparted to the solubility tubes on the lower end of the rod of such an amplitude as to completely transfer the amalgams from one end of the tubes to the other.

The thermostat, a ten-gallon copper tank heavily lagged, contained cylinder oil which had a flash point of 275°. After three months' use this oil did not smoke appreciably at 180° and showed no evidences of carbonization or lowering of the flash point. Four double paddle stirrers

---

[4] Hulett and Minchin, *Phys. Rev.*, 21, 388 (1905).

(1000 r.p.m.) kept the oil in violent agitation. Heat was supplied by four 500-watt immersion heaters. Thermal balance at any temperature was obtained by the use of two circular nichrome heating elements of variable resistance immersed in the bath near the top and bottom. The mercury thermo-regulator operated a 40-watt elongated bulb. Beckmann thermometers permanently placed in the bath showed a deviation of much less than 0.1° over a period of eight hours.

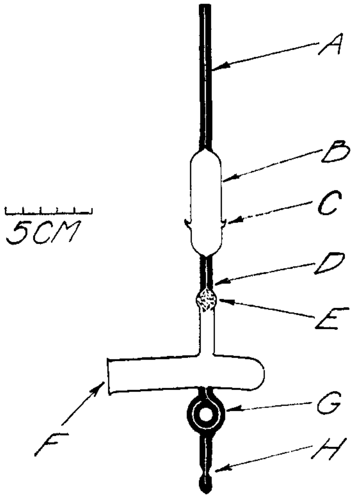


Fig. 1.

Temperatures were read from a mercury thermometer especially standardized for this investigation by the Physical Laboratory of the Taylor Instrument Companies. At the conclusion of the solubility work, this thermometer was compared against one recently standardized for us by the Bureau of Standards.

The amalgam samples were vacuum distilled from an all-glass apparatus previous to analysis. A Cenco pump produced a vacuum of 0.003 mm. Pressures were read from a McLeod gage capable of being read to 0.001 mm.

Experimental Procedure

About 7 cc. of pure mercury and excess silver were put into the Tube F (Fig. 1), which was then sealed off. Capillary A was connected to a Cenco pump and the amalgam boiled out, when the tube was sealed off from the pump and A bent into an eye. A fine wire was attached at G and the constricted capillary H file marked. The eyes on the tubes enabled them to be slipped onto the stirrer posts, the whole device then being firmly clamped in the thermostat.

For a determination of the solubility at a certain temperature, saturation in every case was attained from the low and then from the high temperature side. In the former case the shaker with four tubes was started and the bath raised to the desired temperature, which usually required about an hour. After thermal balance was established at this temperature, the tubes were shaken for an additional period of three hours and then sampled.

For the corresponding high side determination, four tubes were inserted in the hot-bath, the temperature was raised about 20°, held there for an hour or more and then allowed to drop back to the determination temperature. This preheating, occupying from three to five hours, was succeeded by the usual three hour shaking at constant temperature and sampling.

The remarkable agreement between these two measurements at every temperature was sufficient evidence that equilibrium was being attained.

When the amalgams were ready to be sampled, the shaker was stopped and a tube slipped off, keeping it at all times below the oil surface. The counterweighted eye A was then released and the wire on G firmly held, when the tube inverted under the oil. Carefully drawing up the wire until the tip H just protruded (Fig. 2), the exposed capillary was wiped dry and broken under clean rubber tubing. Atmospheric pressure forced the amalgam through the glass wool filter E into the lower tube. After filtration the tubes were removed from the bath, dried and cooled. Sample tube B was cut off, suspended in the balance case and weighed. The amalgam samples were then transferred to the distillation tubes and boiled out prior to distillation. All glassware with which the cooled amalgam came in contact was treated later in the analysis with nitric acid.

The tubes containing the amalgams were sealed to the distillation apparatus and the system was evacuated. The temperature was gradually raised to about 200°, distillation requiring about two hours. The residues were then flamed in the vacuum to the softening point of Pyrex. Separate control distillations established the fact that these residues consisted approximately of 1 atom of mercury to 50 of silver.

Tubes and contents were then transferred to beakers and treated with 10 cc. of concentrated nitric acid. After boiling, the solutions were diluted, the tubes removed and the silver was precipitated with dilute hydrochloric acid. Digestion until the volumes were well below 50 cc. was followed by filtration, re-solution of the silver chloride with ammonia, and a second precipitation and digestion to small volume. Porcelain crucibles with unglazed porous bottoms were used in the weighing.

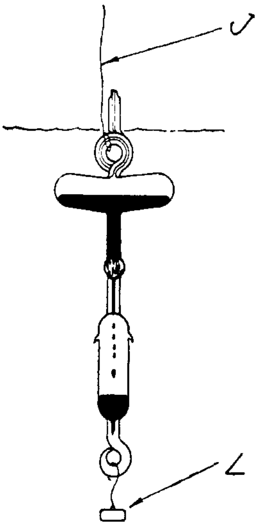


Fig. 2.

Before adopting the above method of analysis, much control work was done on the methods available. The first investigated was that of Joyner,[3] devised to provide for the appreciable solubility of silver chloride in mercuric nitrate solutions.[5] The standard blowpipe method was also studied, using cupels of dental investment compound. In Table II are given results using each method for the analysis of 400 mg. of silver dissolved in 5 cc. of mercury. In Joyner's method the amalgam is dissolved directly in nitric acid; in the other two, distillation was first carried out.

TABLE II

COMPARISON OF ANALYTICAL METHODS

Method	Joyner	Blowpipe	Present paper
% Ag recovered	99.38	98.8	99.78
	99.03	99.4	99.66
	98.45	99.9	99.78
	98.94	..	99.69
Av.	98.95	99.0	99.73

To test the whole experimental arrangement, four tubes were made up containing weighed amounts of silver and mercury and carried through the entire procedure outlined above, including shaking in the bath for three hours and sampling; in Table III are given the results.

TABLE III

ANALYSIS OF AMALGAMS OF KNOWN CONCENTRATION

Atomic % of silver taken	0.847	0.869	0.854	0.697
Atomic % of silver found	0.845	0.867	0.851	0.694

---

[5] Buttle and Hewitt, *J. Chem. Soc.*, **93**, 1405 (1908).

Results

In all four series of determinations were made. The first two (A and B) were distinctly preliminary and included much of the control work given above. The results were of the same order of magnitude as our final values, except that in the measurements from the high temperature side the method of stirring then in use was not producing equilibrium. The shaking device above described was then installed.

TABLE IV

SOLUBILITY OF SILVER IN MERCURY

(Complete Data for Two Temperatures)

Detn.		Temp., °C.	Ag at start g.	Wt. of amalgam, g.	Wt. of AgCl, g.	Atomic % sol.
17-D			0.6	94.128	0.1962	0.291
18-D	Low Side	80.2	.6	90.009	.1838	.285
19-D			.6	79.541	.1623	.285
20-D			.6	97.826	.1993	.285
21-D			.5	85.310	.1730	.283
22-D	High Side	80.2	.5	99.137	.2018	.285
24-D			.5	97.910	.2000	.285
					Av.	.286
13-D			.6	93.414	.2760	.413
14-D	Low Side	98.2	.6	84.176	.2494	.414
15-D			.6	67.723	.1985	.409
16-D			.6	93.020	.2737	.411
10-D			.6	97.158	.2840	.408
11-D	High Side	98.2	.6	100.827	.2953	.408
12-D			.6	96.770	.2846	.411
					Av.	.411

TABLE V

SOLUBILITY OF SILVER IN MERCURY

(Summary of Experimental Data)

No. of detns.	Temp., °C.	Atomic % sol.	Av. dev. from mean (p.p.t.)
17–22, 24 D	80.2	0.286	3.5
10–16 D	98.2	.411	4.9
10–12, 14–17 C	121.9	.612	1.6
15–19, 21 C	144.5	.849	1.2
1, 3, 4, 6–8 D	160.6	1.057	7.6
25–27, 29–32 D	177.9	1.346[a]	2.2
34–40 D	198.9	1.746[a]	5.2

[a] At these higher temperatures it was feared that the large precipitate of AgCl obtained in the analysis might have contained mother liquor or salt in the precipitation from the small volumes necessary in working at the lower temperatures. Mr. G. H. Reed, working in this Laboratory, repeated the measurements above 180° using greater care in the washing and drying of the AgCl. His results were about 0.03 atomic per cent. lower than ours. They are

Temp., °C.	181.8	193.3	212.7
Solubility, atomic %	1.365	1.573	1.953

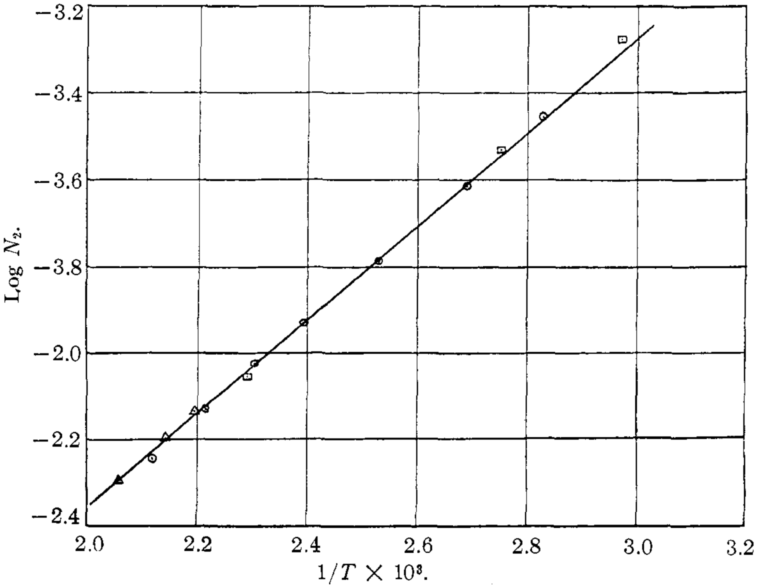
Table VI

Solubility of Silver in Mercury at Rounded Temperatures
(From Log N vs. $1/T$ Plot)

Temp., °C.	100 N (from curve)	100 N (calcd.)	Error, p.p.t.
80.0	0.288	0.286	7
100.0	.419	.419	0
120.0	.587	.587	0
140.0	.797	.797	0
160.0	1.053	1.050	3
180.0	1.356	1.350	4
200.0	1.708	1.700	4

Of the 56 final determinations only eight have been omitted. Of these six were due to poor filtering, oil in tubes, or bumping in distillation. Two determinations only were rejected because their deviation from the mean was more than 4 times the average deviation for that temperature.

All solubilities are given in atomic per cent. (atoms of silver per 100 total atoms).



□, Joyner; △, Reed, ⊙, Authors.

Fig. 3.—Solubility of silver in mercury.

Discussion of Results

In Fig. 3 the results are plotted as log N vs. $1/T$. The values of Joyner and Reed have been distinguished from those of the present authors. Very satisfactory agreement is found in the various results.

This agreement is particularly of interest since Joyner used thermostatting periods of a fortnight in the preparation of his amalgams. He also used a pipet for sampling, an instrument which in the hands of others has often led to fictitious solubility data.

Joyner's data show, in some cases, an experimental error of 200 p.p.t. Much of this is undoubtedly due to his method of sampling.

A large scale plot was carefully constructed and used in determining the equation for the straight line which results. The equation which has been found to hold satisfactorily is $\log_{10} N = -1074.2(1/T) + 0.501$. The rounded solubility values in Table VI were obtained from this large plot. The calculated values in Table VI are those obtained using the above equation; the agreement is seen to be quite satisfactory.

In the analysis of the amalgams, it was found that distillation at 0.1 mm. and 200° yielded a residue of the approximate composition Ag_3Hg_4. As has been mentioned above, increasing the vacuum to 0.003 mm. and using flame temperatures, a residue composed of about 1 atom of Hg to 50 of Ag was obtained. There is every reason to believe that with a further decrease in pressure in distillation, results found by weighing the residues as silver would be fully as accurate as most wet methods for the determination of silver in the presence of mercury.

The authors wish to thank Professor Willard R. Line of the University of Rochester for his help in the analytical phase of the work.

Summary

1. A method of preparing and analyzing silver amalgams has been described which yields results uniformly only 2 p.p.t. low.

2. A tube has been developed of general applicability to solubility work, which permits of sampling without removal of the equilibrium mixture from the thermostat or the introduction of sampling devices.

3. This tube has been used to determine the solubility of silver in mercury up to 200°, over fifty determinations having been made.

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF OREGON]

THE ADSORPTION OF ORGANIC COMPOUNDS ON HYDROUS OXIDES AND FULLER'S EARTH

BY DONALD P. GRETTIE WITH ROGER J. WILLIAMS

RECEIVED OCTOBER 13, 1927 PUBLISHED MARCH 7, 1928

Adsorbents have not infrequently been used in the separation of materials of biological importance from extracts of tissues containing them. They have been used in this Laboratory for work of this nature where attempts are being made to isolate a "bios" from yeast extracts. The desire to use adsorbents as intelligently as possible made it desirable to have data on the adsorption of various organic compounds by different adsorbents under comparable conditions. The particular question which appeared most interesting to us was whether the adsorption of various compounds would take place in accordance with the acidic and basic properties of the adsorbent and adsorbate, and to what extent one might expect the adsorption to be specific and unpredictable.

Because data of this sort were not available the work here reported was done. This consisted in a study of the adsorption from solution