considerable part of the current. It is significant that the temperature region in which the change from uni-ionic to bi-ionic conduction occurs is the same as the temperature region in which the slope of the conductance curve (log k *vs.* $1/T$) doubles its value.

In the temperature range 558 to 655° the fraction carried by the chloride ion appears to decrease with increasing temperature. This is thought to be a polarization effect.

[Contribution from the Missouri School of Mines and Metallurgy]

THE SOLUBILITY OF ALUMINUM BROMIDE IN CARBON DISULFIDE

By H. H. Kaveler and C. J. Monroe

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Carbon disulfide as a solvent of inorganic salts was first studied by Arctowski,[1] who found the mercury halides slightly soluble, but the common inorganic salts insoluble. Kohler[2] found that aluminum bromide and iodide are rather soluble. Qualitative data of various investigators on the solubilities of various salts in this solvent have been compiled by Walden.[3]

As aluminum bromide dissolves in carbon disulfide to the extent that various inorganic salts dissolve in water, quantitative determinations of its solubilities at various temperatures were made.

Preparation of the Reagents

The carbon disulfide was purified by the method of Sidot,[4] with modifications of Arctowski, as follows. Commercial carbon disulfide was shaken with mercury until the surface of the metal was no longer tarnished and was then distilled from anhydrous calcium chloride. It was kept in contact with phosphorus pentoxide until ready for use, when it was decanted into a dry flask containing a little paraffin, from which it was distilled out of contact with air. The product, which had a sweet, pleasant odor, was used immediately.

Aluminum bromide was prepared from the purest commercial aluminum and c. p. bromine purified by distilling from chromic acid and from potassium hydroxide and potassium bromide.

As the extreme solubility of the salt made it desirable to prepare as much as 700 g. at one time, a somewhat different apparatus than that of Kohler, Richards,[5] and others was used, as shown in Fig. 1.

A combustion tube (c), of 12 mm. diameter and 1 meter length, resting in an electric furnace (E), was fused onto a train of three 750cc. distilling flasks. It was charged

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[1] Arctowski, *Z. anorg. Chem.*, **6**, 267, 404 (1894).

[2] Kohler, This Journal, **22**, 387 (1900).

[3] Walden, "Electrochemie Nichtwassrigen Lösungen," **1924**, p. 480–481.

[4] Sidot, *Compt. rend.*, **69**, 1303 (1869).

[5] Richards, This Journal, **42**, 2222 (1920).

with 100 g. of the metal, cut into small strips, and was heated to 400°, at which temperature a stream of dry hydrogen saturated with bromine was passed over the hot aluminum. The product was most rapidly formed when a reaction between the hydrogen and bromine to form hydrogen bromide proceeded with the production of flashes of light, the hot metal being a good catalyst for this reaction, which normally proceeds at a higher temperature.

When about 80% of the metal was used up, the introduction of bromine was stopped. The salt, carried by the escaping gas into the first flask, was then refluxed in a slow stream of hydrogen and distilled, at a pressure of about 15 mm., into the second, and then the third flask. The product is a white, highly crystalline compound. Its melting point has been reported to be 97.1°.[6]

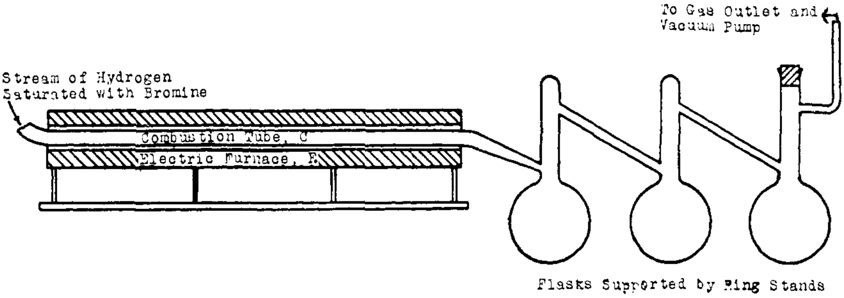

Fig. 1.—Arrangement for preparing quantities of aluminum bromide.

Determination of the Solubility

After sealing off the third distilling flask from the others, the desired amount of disulfide was added to the bromide while dry hydrogen was passed into the side neck. The sample tube was inserted and the flask shaken in a thermostat. At temperatures below 70°, an hour was found to be sufficient time for equilibrium to be attained. At higher temperatures, more than twelve hours was allowed for establishment of equilibrium, due to a polymorphic transformation of the solute.

Below 30°, an ordinary glass tube served as a delivery tube for taking samples. Since at higher temperatures the highly concentrated solutions would deposit crystals when forced into a sampling tube cooler than the bath, a delivery tube had to be used which could be kept at the temperature of the thermostat. A glass sampling tube was wound with nichrome wire and sealed inside of a larger tube to prevent the wire from coming in contact with the solution (see Fig. 2). This was calibrated, under the conditions at which it was to be used, with the aid of a small thermometer suspended inside the delivery tube, a temperature–current curve being obtained. With this device samples at the high temperatures could be taken with the same accuracy as at the low temperatures.

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[6] The melting point of aluminum bromide has been reported (a) as 97.1° by Kendall, Crittenden and Miller, THIS JOURNAL, **45**, 963 (1923), and (b) as 90.5° by Biltz and Voigt, *Z. anorg. Chem.*, **126**, 39 (1922).

A convenient aspirator was made from two 500cc. leveling bottles, filled with mercury, the raising or lowering of one causing pressure to be applied or withdrawn quickly, while the same dry air is kept in contact with the solutions.

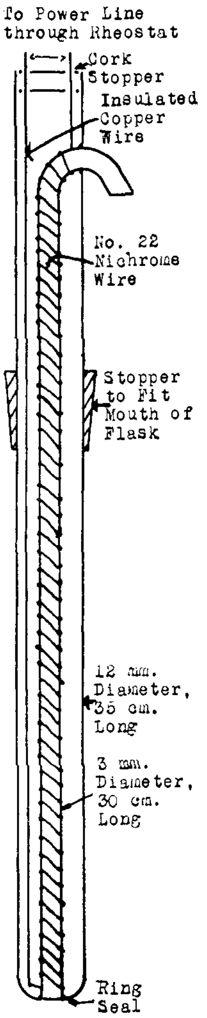

Fig. 2.—Device for sampling saturated solutions at constant temperatures.

The end of the delivery tube was placed in a bell jar filled with dry air to prevent fuming during the taking of a sample.

As aluminum bromide dissolves in carbon disulfide with the absorption of heat, and in water with the evolution of a large quantity of heat, addition of water to a sample, preliminary to analysis for bromide by the Volhard method, resulted in local, violent reaction, even when the temperature was far below zero. Addition of a third liquid, as ethyl alcohol, which forms with the first two a one-phase region, resulted in the violence of the reaction being reduced to such an extent that the method could have been used, although a small amount of hydrogen bromide was still lost. It was found that the complex $AlBr_3 \cdot 2C_6H_5NO_2$ was readily formed below 20°,[7] and that it reacted with water very quietly, with no loss of hydrogen bromide, so the following method of analysis was adopted.

(1) The weighing bottle containing the weighed sample was set into 100 cc. of water in a 600cc. beaker and 15–25 cc. of pure, anhydrous nitrobenzene added to the sample. (2) Four hundred cc. of water, cooled to about 10°, was poured into the beaker. (3) With the weighing bottle covered with water, the mixture in it was stirred until all the aluminum bromide had reacted to form the complex. (4) The bottle was tipped, allowing water to run in slowly, the white, gummy complex going into solution with a hissing noise. (5) After stirring, the aqueous solution was decanted into a volumetric flask. (6) The residual emulsion of nitrobenzene, carbon disulfide and water, which retains some of the salt, was washed with water until the emulsion broke, when no detectable amount of bromide remained with the organic liquids. (7) The volume of the combined aqueous solution was made up to a standard liter, an aliquot part taken and titrated for bromide

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[7] This compound, along with others of the benzene series, was reported by Menschutkin; see Seidell, "Solubilities of Inorganic and Organic Compounds," D. Van Nostrand Co., New York, **1919**, pp. 21–24.

by the Volhard method, and the percentage of aluminum bromide in the original sample calculated.

Using this method of analysis, as much as 80 g. of the anhydrous salt were put into solution without difficulty.

TABLE I

RESULTS OF ANALYSES (SEE FIG. 3)

Temp., °C.	Wt. of sample, g.	Wt. % of $AlBr_3$	Mole % (av.) of $AlBr_3$
0.1	25.943	41.8	
	14.238	41.5	17.0
8.4	14.374	49.1	
	17.895	49.0	21.6
15.0	12.105	55.4	
	17.720	54.7	25.8
20.0	14.979	58.7	
	15.545	58.9	28.9
25.0	10.309	62.8	
	16.165	62.5	32.3
30.0	23.615	66.6	
	12.874	66.7	36.2
50.1	10.687	80.9	54.5
60.0	13.257	86.5	
	15.536	86.2	64.4
70.0	18.955	90.5	73.1
71.0	6.915	91.0	
	29.569	91.1	74.2
76.0	10.363	93.5	79.1
81.0	7.717	94.5	83.3
85.0	81.639	96.2	87.8

Discussion of Results

The exceptionally high solubility of this salt in carbon disulfide is in accordance with several rules[8] derived from a study of solutions of electrolytes in other solvents.

TABLE II

SOLUBILITIES IN CARBON DISULFIDE

Salt	M. p., °C.	Heat of fusion, cal./mole[a]	Soly. in CS_2 in mole % at 25
KCl	772	6450	Insoluble (0.002)
KBr	748	(3040)	Insoluble
KI	(about 748)	(3820)	Insoluble
AgCl	455	3500	Insoluble
AgBr	430	2370	Insoluble
$HgCl_2$	265	5490	0.0147
$HgBr_2$	235	5010	0.0489
HgI_2	250	3280	0.0638
$AlCl_3$	195	(3450)	Slightly soluble
AlI_3	191	(4280)	Rather soluble
SnI_4	145.3	4180	Rather soluble
$AlBr_3$	97.1	2790	32.3

[a] The heats of fusion in parentheses were calculated, the others and the melting points were taken from standard tables. The salts are arranged in the order of their solubilities.

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[8] Hildebrand, "Solubility," The Chemical Catalog Company, Inc., New York, **1924**, p. 166.

(*a*) Aluminum bromide is unique in that it has a melting point and a heat of fusion much lower than the same values for almost any inorganic salt. (Some salts have lower melting points, but much higher heats of fusion; others have lower heats of fusion but much higher melting points.) Table II shows that the solubilities of salts in carbon disulfide are in accordance with the rule of greater molal solubility the lower the melting point and heat of fusion.

(*b*) Solvation tends to increase solubility. The color of the saturated solutions varied from a red at low temperature to an almost opaque black at 85°, possibly due to molecules of $x\mathrm{AlBr}_3y\mathrm{CS}_2$ being formed.

(*c*) The solubilities of the various salts in Table II are roughly in accordance with the rule that equal polarity of solvent and solute tends to increase solubility, although aluminum chloride, which has about the same polarity as aluminum bromide, is insoluble in carbon disulfide.

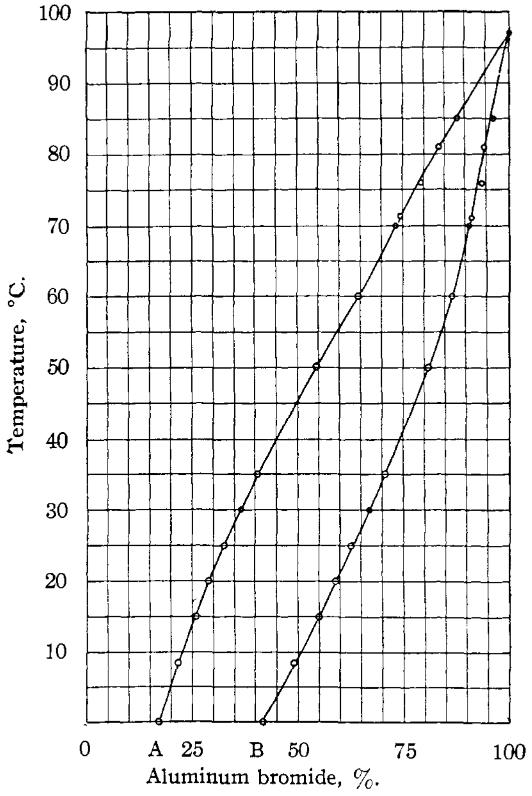
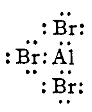


Fig. 3.—Curve A, mole %; curve B, weight %.

(*d*) On the basis of the Lewis theory,[9] the electronic structure of aluminum bromide is



$$\begin{array}{l} \quad :\ddot{\mathrm{Br}}: \\ :\ddot{\underset{\cdot\cdot}{\mathrm{Br}}}:\ddot{\underset{\cdot\cdot}{\mathrm{Al}}} \\ \quad :\underset{\cdot\cdot}{\mathrm{Br}}: \end{array}$$

The Al atom, not having the maximum number of electrons, may obtain a pair from a bromine atom of another molecule, with resultant polymerization and increased solubility (Kohler,[2] by the boiling point rise method, found the salt had the formula $\mathrm{Al}_2\mathrm{Br}_6$ in carbon disulfide), or may obtain the desired electrons from an atom of sulfur, with resultant solvation and increased solubility (see rule b), in accordance with the rule that the existence, in one of the components, of an atom without the maximum number of surrounding electrons or atoms promotes the solubility.

[9] Lewis, This Journal, **38**, 762 (1916).

The ideal solubility[10] of aluminum bromide is 38 mole % at 20°, and 88 mole % at 85°, calculated using the approximate Raoult's law equation

$$\log N = -(L_f/4.58)\ (1/T - 1/T_m)$$

The experimental data show a negative deviation from this law at low temperature and almost perfect agreement at high temperature, typical of the behavior of many binary systems.[11]

The solubility-temperature curve shows a change of slope between 70 and 71°, indicating the existence of two crystalline modifications of the solute, confirming the thermal method report[6a] on a polymorphic transformation at 70.1°.

The Conductivity of CS_2–$AlBr_3$ Solutions

Dilute solutions were found to have conductivities more than a thousand times that of pure carbon disulfide, although the solvent, due to its low dielectric constant, is a poor ionizing agent.

Summary

1. A method for the synthesis of quantities of aluminum bromide is described.

2. A method for sampling saturated solutions at constant temperature is described.

3. A new method for the analysis of anhydrous aluminum bromide has been found.

4. Quantitative data on the solubility of the salt in carbon disulfide have been obtained.

5. Solutions of aluminum bromide in carbon disulfide have been found to be appreciably conducting.

6. The existence of polymorphic forms of aluminum bromide has been confirmed by the solubility method.

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[10] Ref. 8, p. 158.

[11] Ref. 8, p. 40–58.