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THE ALLOTROPY AND SOLUBILITIES IN WATER OF AMMONIUM BROMIDE.

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Introductory.

Wallace,[1] using cooling-curve, dilatometric, and optical methods, observed that ammonium chloride and ammonium bromide undergo enantiotropic transformation at 159° and 109°, respectively. The chloride has recently been more carefully studied by Scheffer.[2] He finds from heating and cooling curves that the transformation takes place between the limits 187° (heating) and 174° (cooling). Determination of the solubility of ammonium chloride in water from 160° to 205° gave two curves intersecting at 184.5°, the transition temperature.

Before Scheffer's paper appeared, we had obtained similar results with the chloride from heating and cooling curves. The same method applied to the bromide had shown the transformation to take place at 143–144° on heating, while for the cooling curves the temperature varied from 119° down to about 107°. An experiment in which the thermometer and salt were sealed in a glass tube with a small amount of water (only the vapor phase, however, being in contact with the bromide) showed a

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[1] *Centralblatt Min. Geol. u. Palaöntol.*, 1910, 33.

[2] *Proc. Akad. Wetenschappen*, 18, 446 (1915); *C. A.*, 10, 411 (1916).

change on cooling at about 130°. The transition temperature for the bromide thus lay between the limits 130° and 143°. The low temperatures reported by Wallace may be due either to an error in the calibration of his thermocouple, or more probably to supercooling, since the transformation in both cases is very sluggish.

The more exact determination of these two transition temperatures was in progress when Scheffer's paper came to our notice. In as much as his work had fixed with sufficient accuracy the transition point of the chloride, we completed only the determination of the transition temperature of the bromide, by measuring the solubilities of the salt in water over a temperature range sufficient to include the transition point.

In making the solubility determinations from 100 to 170°, it was observed that our curve was not a continuation of the one given by the solubility tables, all of which take their data from an article by Eder.[1] Consequently the determinations were carried on down to 0° in order to give a complete solubility curve for ammonium bromide.

The Experimental Method.

The sealed tube method, which has been widely used in the investigation of freezing point or solubility curves of various systems[2] where one of the components has a high vapor pressure, was the only method practicable for the present investigation.

A piece of soft glass tubing about 1 cm. in diameter was constricted and closed at one end (Fig. 1*a*) forming a bulb of about 1 cc. capacity. The volume of the bulb, required in calculating the weight of water in the vapor phase, was determined by weighing the tube empty and filled to the constriction with water. After the tube was carefully dried a small amount of ammonium bromide, which has been recrystallized from distilled water, sublimed *in vacuo* and dried at 110°, was introduced into the bulb and the tube was again weighed. An approximate weight of distilled water was then added, the bulb sealed off at the constriction and finally the two parts were weighed. A short length of glass rod was then fused on to the bulb (Fig. 1*b*) and served to support the bulb in the bath.

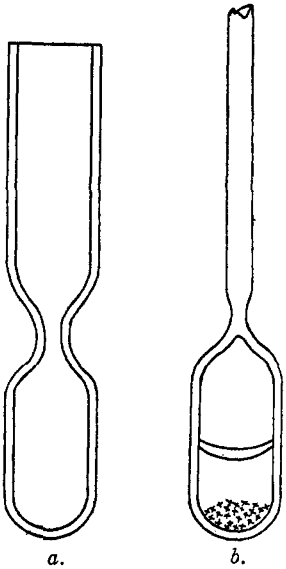

Fig. 1.—(Linear dimensions = actual size.)

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[1] *Ber. K. Akad. Wiss., Wien,* [2] 82, 1284 (1880).

[2] Cf. Étard, *Ann. chim. phys.,* [7] 2, 511 (1894): Kuriloff, *Z. physik. Chem.,* 23, 547 (1897); Hartley, *J. Chem. Soc.,* 89, 1015 (1906); Tyer, THIS JOURNAL, 97, 622 (1910); Kendall, *Ibid.,* 36, 1227 (1914); Smits and Bokhorst, *Z. physik. Chem.,* 89, 374 (1915).

"Crisco" cooking oil, well stirred in a large beaker, was employed as a bath. A Bunsen burner was regulated to maintain a temperature one or two degrees below that desired, and the final temperature was obtained from an elongated electric light bulb partially immersed in the bath. With a switch to operate this light, the temperature of the bath could easily be maintained constant, to within a few hundredths of a degree, at any desired point from that of the room to about 200°. The mercury thermometer used was a standard instrument, graduated to 1/5° C., and calibrated by the Reichsanstalt. A correction was applied for the exposed stem.

The saturation temperature was taken as the mean of determinations made with rising and falling temperatures.[1] For the former, the temperature was first raised sufficiently to completely dissolve the ammonium bromide. By sudden cooling very small crystals were obtained which dissolved sharply when the bulb was placed in the bath and the temperature was gradually raised. The supporting handle of the bulb was constantly tapped, giving the contents an irregular rotary motion, to assist in the rapid attainment of equilibrium. In order to make the disappearance of the crystals, as well as their formation in the following determination, as distinct as possible, the bath was illuminated by a strong electric light placed directly behind it. The crystallization temperature was determined by allowing all but one or two small fragments of the crystals to dissolve. By then allowing the temperature of the bath to fall gradually, the point at which crystallization became noticeable was determined. The difference between the two temperatures determined in this way varied from 0.2° to 0.6°. Their mean, the accuracy of which was within ±0.2°, was taken as the equilibrium temperature for saturation.

Calculation of the Weight of Water in the Vapor Phase.

At temperatures below 60°, where the volume of the gas space is of the order of 1 cc., as in the present case, no correction for the weight of water in the vapor phase was needed. Above 60°, the correction becomes appreciable and at higher temperatures failure to take this factor into consideration may readily introduce an error of 1% or more in the calculation of the composition of the liquid phase.

The volume of each bulb being known, the fraction of the volume occupied by the liquid at the saturation temperature was "estimated" and from this estimated volume and the total weight of the solution, an approximation of its density was obtained. The density estimations at slightly different temperatures were averaged, as were also the temperatures themselves, and the results plotted. In as much as these densities, along with the density of saturated ammonium bromide solution at 15°,[2]

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[1] Cf. Hartley, *Loc. cit.*

[2] Eder, *Ibid.*

fall on a fairly smooth curve, the approximation was considered sufficiently close for the purpose. The densities used were:

t.	15°	113°	137°	158°
d.	1.29	1.66	1.71	1.76

The density of the saturated solution read from this curve was then employed to calculate the volume of the liquid phase in any given case and, by subtracting from the total volume of the bulb,[1] the volume of the gas space was obtained.

The vapor pressure of the solution was taken to be the same fraction of the vapor pressure of water, at a given temperature, as the molar fraction of water in the system. This again is only a rough approximation, but sufficiently accurate for the purpose.

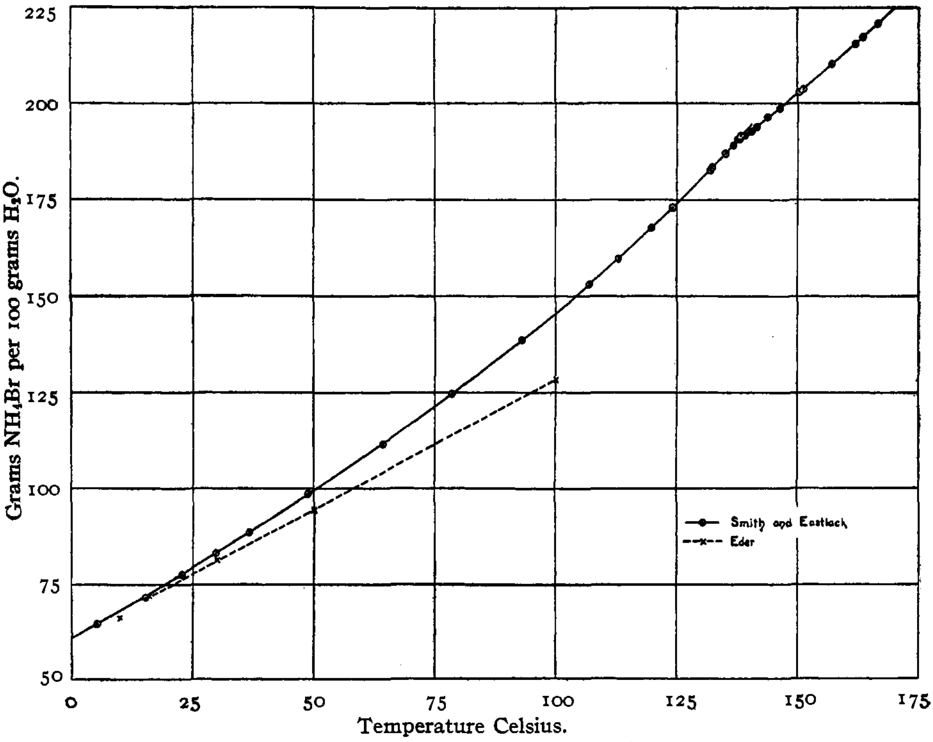

Fig. 2.—The solubilities of ammonium bromide in water.

The weight of water vapor was calculated from its volume and partial pressure as thus obtained, and was subtracted from the total weight of water in the bulb before the composition of the liquid phase was calculated.

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[1] The increase in volume of the bulb due to the expansion of the glass was estimated to be negligibly small.

The correction thus applied varied from zero at low temperatures to 0.0019 g. at one of the higher temperatures, out of a total weight of 0.1 to 0.2 g. of water.

Experimental Results.

The results of the determinations of the solubility of ammonium bromide in water are given in Table I.

TABLE I.—SOLUBILITIES OF NH_4Br IN H_2O—OBSERVATIONS.

Weight NH_4Br.	Weight H_2O.	Vol. of bulb, cc.	Weight H_2O vapor (calc.). gram.	Ratio. weight $\frac{NH_4Br}{H_2O \text{ (liquid)}}$.	Molar fraction. NH_4Br.	Temp. of satn.
0.1774	0.2750	..	..	0.6452	0.1061	5.3
0.1570	0.2188	..	..	0.7174	0.1166	15.2
0.1978	0.2549	..	..	0.7762	0.1250	22.7
0.1714	0.2062	..	..	0.8312	0.1326	29.8
0.1987	0.2247	..	..	0.8845	0.1399	36.7
0.2327	0.2361	..	..	0.9856	0.1535	48.9
0.2529	0.2268	0.80	0.0001	1.115	0.1702	64.4
0.1788	0.1437	1.12	0.0002	1.247	0.1865	78.6
0.3162	0.2286	1.10	0.0003	1.386	0.2031	93.0
0.2423	0.1591	1.39	0.0007	1.530	0.2195	107.0
0.3162	0.1993	2.12	0.0012	1.596	0.2270	113.0
0.2991	0.1791	1.14	0.0007	1.677	0.2355	119.9
0.3036	0.1762	1.0	0.0007	1.730	0.2414	124.1
0.2629	0.1445	0.72	0.0005	1.826	0.2514	132.0
0.2072	0.1137	0.81	0.0007	1.833	0.2522	132.3
0.2293	0.1234	0.84	0.0008	1.870	0.2560	135.0
0.3967	0.2105	0.87	0.0007	1.891	0.2580	136.7
0.2322	0.1235	0.77	0.0007	1.891	0.2580	136.9
0.2066	0.1092	0.79	0.0008	1.906	0.2595	137.6
0.3197	0.1685	0.93	0.0009	1.907	0.2597	137.9
0.3666*	0.1921	0.90	0.0008	1.916	0.2606	138.2
0.3666	0.1921	0.90	0.0008	1.916	0.2606	139.1
0.3624	0.1889	1.02	0.0010	1.929	0.2619	140.4
0.2971	0.1541	0.85	0.0009	1.939	0.2629	141.5
0.2718	0.1394	0.92	0.0010	1.963	0.2655	143.7
0.3657	0.1852	1.10	0.0013	1.988	0.2677	146.2
0.3512	0.1742	0.94	0.0012	2.030	0.2718	150.4
0.3716	0.1835	0.93	0.0011	2.037	0.2726	151.1
0.3111	0.1495	1.0	0.0015	2.102	0.2788	157.0
0.2913	0.1835	1.13	0.0019	2.155	0.2838	161.9
0.3960	0.1839	1.0	0.0016	2.172	0.2854	163.4
0.4221	0.1926	0.95	0.0016	2.210	0.2890	166.6

* Same tube as one below. Point on metastable portion of curve. See below.

The points obtained lie on two smooth curves which intersect at 137.3° ± 0.3° (Fig. 2). For convenience of reference the solubilities of ammonium bromide at rounded temperatures up to 100°, as read from the carefully smoothed curve plotted on a large scale, are listed in Table II.

TABLE II.—SOLUBILITIES OF NH_4Br IN H_2O TO 100° AT ROUNDED TEMPERATURES.

Temp. ° C.	G. NH_4Br per 100 g. H_2O.	Molar fraction. NH_4Br.	Temp. ° C.	G. NH_4Br per 100 g. H_2O.	Molar fraction. NH_4Br.
0	60.6	0.1004	40	91.1	0.1437
5	64.3	0.1058	45	95.2	0.1491
10	68.0	0.1112	50	99.2	0.1546
15	71.7	0.1165	60	107.8	0.1656
20	75.5	0.1220	70	116.8	0.1768
25	79.3	0.1274	80	126.0	0.1881
30	83.2	0.1328	90	135.6	0.1996
35	87.1	0.1383	100	145.6	0.2111

In one instance (Experiment marked * Table I) a point on the metastable portion of the lower solubility curve was obtained. This was accomplished by placing the cold tube in the bath maintained at the temperature predicted by prolongation of the lower curve and the known composition of the contents of the bulb. In this manner it was possible to completely dissolve the crystals at a temperature nearly 1° below that at which the same sample, when in the form stable at that temperature, was found to dissolve. In order to determine the saturation temperature for the stable form, the temperature of the bath was raised a degree or so above the transition point and the solid was allowed to stand several minutes in contact with the solution (without shaking). On lowering the temperature slightly and determining the saturation temperature in the usual manner the point on the equilibrium curve was obtained.

The solubilities from 0 to 100° do not agree with those given by Eder. To show the amount of the discrepancy, his values are plotted with our own results in Fig. 2. He gives no description of his method of determining the solubility.

Summary.

Heating and cooling curves showed the transition point of ammonium bromide to lie between 130° and 143°. The solubilities in water from 0 to 170° were determined by the closed tube method. A well defined break in the solubility curve occurs at 137.3°, the transition temperature. The solubility measurements from 0 to 100° do not agree with the only ones heretofore available in the literature.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE PRACTICAL INSTALLATION OF THE DOUBLE COMBINATION POTENTIOMETER.

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The advantages of multiple thermoelements for use in calorimetry, and the design and installation of suitable potentiometers for these and