SOME CUPROUS AMMONIA HALIDES

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The work described in the following pages consists essentially in the determination of the compounds existing between the cuprous halides and ammonia within the temperature range of zero and 150° and in the measurement of their temperature pressure curves. With one exception no records of any cuprous-halide ammonia compounds exist, although the analogous silver compounds were among the first to be investigated. The exception referred to is a description by Ritthausen¹ of a compound $\text{Cu}_2\text{Cl}_2\text{NH}_3$ which he obtained by dissolving copper filings in aqueous ammonium chloride. This compound I was unable to obtain either by his or any other method, and in view of the extreme readiness with which similar substances absorb water its formation from aqueous solution seems improbable. As the existence of cuprous fluoride appears to be in doubt no attempt was made to prepare compounds of it.

The method of investigation employed was the usual one. The cuprous halide under examination was saturated with ammonia gas at zero, and its vapor pressure at some constant temperature observed as ammonia was gradually withdrawn from it. By plotting the molecular amounts of ammonia remaining against the pressure observed, curves were obtained which indicate clearly the number and composition of the compounds formed. To measure the temperature pressure curve of any particular compound, then, it was necessary merely to keep withdrawing ammonia at the constant temperature until the desired section of the curve had been reached, and then to vary the temperature and read the corresponding pressures.

The compounds containing the largest quantities of ammonia were prepared by passing thoroughly dried ammonia

¹ J. Pr. Chem., 59, 369.

gas over small quantities of the salts contained in bent tubes which were immersed in a freezing mixture. It was found necessary to take unusual precautions to dry the ammonia, and it was passed through two three-foot tubes filled with lime, as well as four towers of the same material. It is necessary also to pass the ammonia very slowly over the halides, as the heat of reaction is considerable and sometimes the compound fuses and is quite useless for pressure measurements. All the compounds observed absorbed moisture very readily from the air, taking up a considerable amount even upon transference from one vessel to another.

The apparatus used in the measurements consisted of a mercury air pump and a manometer, to which was connected a small glass cell 5 cm long and 1 cm in diameter which contained the compound under examination. About 5 grams of the substance were used at a time. For temperatures up to 70° C. a water bath was used; for higher temperatures an oil bath. An Ostwald thermo-regulator enabled the temperature to be kept constant to within two-tenths of a degree.

Within the range of temperature mentioned, cuprous iodide and cuprous bromide each form two compounds with ammonia; cuprous chloride, however, forms three. The formula of each, together with its color and approximate melting point, is given below.

			M. P.
Cu_2I_2	6NH_3	Light green	105
Cu_2I_2	3NH_3	Dark brown	117
Cu_2Br_2	6NH_3	Green	115
Cu_2Br_2	3NH_3	Brown	135
Cu_2Cl_2	6NH_3	Green	123
Cu_2Cl_2	3NH_3	Light brown	144
Cu_2Cl_2	NH_3	Dark brown	162

Tables 1, 2 and 3 give the pressures in mm of mercury at certain temperatures shown by each of the three halides, as ammonia gas was gradually removed. The results are shown graphically in Figs. 1, 2 and 3.

Fig. 1

Fig. 2

Fig. 3

TABLE I

$\text{Cu}_2\text{I}_2(\text{NH}_3)_x$

Temp. 51.75°

Mols (NH_3)	Pressure.
6.25	771
6.1	768
5.8	766
5.4	767
5.0	768
4.7	765
4.3	767
3.8	769
3.2	768
2.95	767
....	...
2.6	491
2.2	489
1.8	490
1.3	487
0.8	489
0.5	490
0.35	180
0.2	90

TABLE II

$\text{Cu}_2\text{Br}_2(\text{NH}_3)_x$

Temp. 100°C.

Mols (NH_3)	Pressure.
6.0	867
5.1	865
4.2	867
3.2	868
....	...
2.95	472
2.4	360
1.8	352
1.5	353
0.75	352
0.5	100
0.25	62

TABLE III

 $\text{Cu}_2\text{Cl}_2(\text{NH}_3)_x$

Temp. 90° C.

Mols (NH_3)	Pressure.
6.1	783
5.6	780
5.1	779
4.4	781
3.4	778
....	...
2.9	720
2.7	660
2.5	650
2.0	651
1.5	648
1.1	649
....	...
0.9	620
0.8	530
0.65	522
0.45	523
0.3	522
0.2	312
0.1	40

The following tables contain the pressure temperature curves of the seven compounds.

 $\text{Cu}_2\text{I}_26\text{NH}_3$ $\text{Cu}_2\text{I}_23\text{NH}_3$

Temp.	Pressure.	Temp.	Pressure.
18.25	150	17.5	60
38.5	422	20.25	75
47.0	615	41.0	272
52.0	784	45.0	330
56.0	952	48.0	396
58.75	1084	51.75	490
		59.5	742
		65.0	999

$\text{Cu}_2\text{Br}_2(6\text{NH}_3)$		$\text{Cu}_2\text{Br}_2(3\text{NH}_3)$	
Temp.	Pressure.	Temp.	Pressure.
69.0	214	83	200
78.5	347	100	352
90.5	601	110	456
100.0	865	120	620

$\text{Cu}_2\text{Cl}_2(6\text{NH}_3)$		$\text{Cu}_2\text{Cl}_2(3\text{NH}_3)$	
Temp.	Pressure.	Temp.	Pressure.
88	736	67.5	324
93	915	85.0	567
98	1132	92.0	700
110	1650	100.0	845

$\text{Cu}_2\text{Cl}_2\text{NH}_3$	
Temp.	Pressure.
87.0	518
90.0	523
120.0	680
135.5	819

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