EQUILIBRIUM IN THE SYSTEM AMMONIA : MERCURIC CYANIDE

BY S. R. BRINKLEY

Mercuric cyanide is one of a limited number of salts which are exceedingly soluble in ammonia, and lower the vapor pressure of the latter to such an extent that they deliquesce in the vapor at common temperatures when the vapor pressure is comparatively low.[1] Such solutions of salts in ammonia have recently received considerable attention, chiefly on account of the possibility of using them to condense ammonia at relatively low pressures in the absence of water.[2]

In the present article the vapor pressures at $0°$ have been determined for the binary system, ammonia : mercuric cyanide over a range from 370 mm. to about 1600 mm.; and in the ternary system of these two substances and water the solubility curve at the same temperature has been determined.

Vapor Pressures

The method used for determining the vapor pressure was that described by Foote and Brinkely.[3] For the vapor pressure of the saturated solution this method with the variation described by Foote[4] was used.

For the system where the phases were solid and vapor, the method used was first to prepare a solution of the salt in ammonia by passing in the gas at high pressure. The pressure of ammonia was then lowered to 370 mm. and ammonia evaporated to constant weight. Afterwards the higher pressures where these were the only phases, were used. It was found that reliable results were not obtained by the direct passage of ammonia at low pressures over mercuric cyanide, because of the time involved in reaching equilibrium in the solid phase transformation.

The mercuric cyanide was the purest that could be obtained and was recrystallized and dried until it showed no trace of moisture. Analysis showed it to contain no appreciable amount of any other substance.

The determinations were carried out at $0°$ only, since at higher temperatures the vapor pressure of the solution rises very rapidly.[5]

Table I shows the results of the vapor-pressure determinations. Several

[1] Franklin and Kraus, Am. Chem. J., 20, 820 (1898); ibid., 23, 300 (1900).

[2] Foote and Hunter, THIS JOURNAL, 42, 69 (1920). Foote and Brinkley, ibid., 43, 1018 (1921). Davis, Olmstead and Lundstrum, ibid., 43, 1575, 1580 (1921).

[3] Foote and Brinkley, Ref. 2.

[4] Foote. THIS JOURNAL, 43, 1031 (1921).

[5] Bradley and Alexander, ibid., 34, 15 (1912), erroneously reported mercuric cyanide to be among those substances which deliquesce in ammonia gas at ordinary temperatures and a pressure of one atmosphere.

samples were used to eliminate errors as far as possible. Corrections were made in weights for the changed gas content of the absorption tube, and the barometric readings were corrected for temperature. Col. 1 gives the observed vapor pressure of the system whose ammonia content is shown in Cols. 2 and 3. Col. 4 shows the percentage of the pressure of pure ammonia, exhibited by the solutions. The vapor pressure of ammonia at 0° is that determined by Keyes and Brownlee.[6] The data of Cols. 3 and 4 are of no significance when both solid and liquid phases are present and are therefore omitted from the table. Since this system is univariant, both composition of solution and vapor pressure are constant at the temperature of the experiment.

In the first part of the table the system was that in which no liquid phase was present. The composition of the solid was found to be constant over a wide range of pressures of ammonia and, moreover, to agree within experimental limits with that required by the formula, $Hg(CN)_2.2NH_3$. In the second part the data are for the system when varying amounts of solid were present with the saturated solution and vapor. The vapor pressure was found to be constant. The last part of the table shows the data for the unsaturated solution.

TABLE I

VAPOR PRESSURES, AMMONIA:MERCURIC CYANIDE

$T = 0°$ $P_{NH_3} = 3255$ mm.

P	Wt.-% NH_3	Mol.-% NH_3	$\frac{100\,p}{P_{NH_3}}$	P	Wt.-% NH_3	Mol.-% NH_3	$\frac{100\,p}{P_{NH_3}}$
I. Phases: $Hg(CN)_2.2NH_3$ and vapor.				II. Phases: $Hg(CN)_2.2NH_3$, saturated solution vapor			
369	11.75	66.40	..	1053	16.57	...	..
556	11.63	...	..	1071	16.79	...	..
753	11.56	...	..	1067	18.35	...	..
993	11.59	...	..	1073	18.94	...	..
...	...	...	...	1065	19.30	...	..
...	...	...	..	1066	20.21	...	..
		III. Phases: solution and vapor					
1067	20.72[a]	79.34	32.8	1362	23.40	81.92	41.8
1098	20.93	79.71	33.7	1445	24.33	82.66	44.4
1200	21.87	80.57	36.9	1536	25.20	83.36	47.2
1257	22.36	81.02	38.6	1615	26.10	83.80	49.6

[a] Extrapolated value.

Fig. 1 shows these results graphically. The nearly vertical straight line shows the variable vapor pressure under which the solid $Hg(CN)_2.$-$2NH_3$ can exist. The slight deviation from the vertical is due to experimental error. The horizontal line shows constant vapor pressure of the saturated solution in the univariant system, where there are three phases. The proportions between the solid and solution change as the amount of

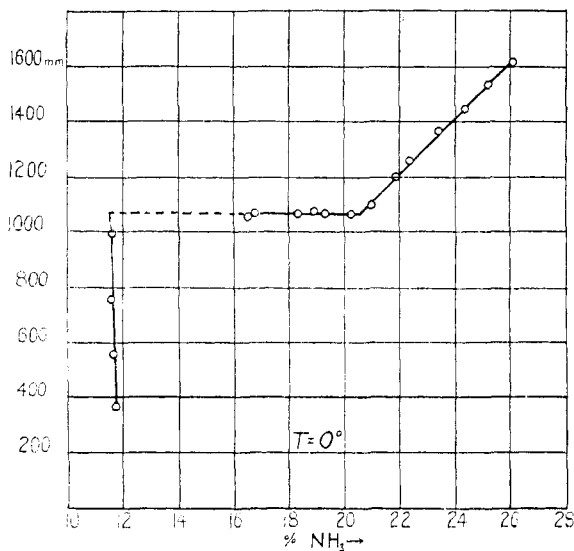[6] Keyes and Brownlee, THIS JOURNAL, **40**, 35 (1918).

Fig. 1.

ammonia in the system increases. The ascending line shows the vapor pressures of the unsaturated solution. The point of intersection of the horizontal line and the vapor-pressure curve of the solution gives the composition of the saturated solution.

Solubility

The vapor-pressure method was not suitable for determining the possible existence of other solid addition products, since at the low pressures involved there was considerable doubt of having reached equilibrium in the solid phase transformation, even after long passage of ammonia.

Recourse was therefore had to a solubility method for the investigation of this field. The aqueous solution of ammonia and mercuric cyanide was admirably adapted for this purpose, since in the dilute solutions very low partial pressures of ammonia could be obtained. If no solid hydrated addition product between mercuric cyanide and water could exist at 0°, the solid separating from solution would necessarily have the same composition as if it were in equilibrium with dry ammonia at this temperature, and a pressure of ammonia gas equal to its partial pressure in the aqueous solution. The solubility curve at 0° for the ternary system ammonia : mercuric cyanide: water was therefore determined.

These determinations were carried out in glass-stopped bottles which were shaken in an ordinary solubility tank. In all cases the solutions were prepared at higher temperatures, taking care that the last trace of

solid was in solution. They were then brought to equilibrium at 0° by long shaking in the solubility tank.

The samples for analysis were withdrawn through a tube containing a plug of glass wool into a weighed specimen tube. The precautions previously described[3] were used to minimize errors. Ammonia was determined in the usual way by adding a measured excess of standard hydrochloric acid and titrating the excess by means of standard ammonia solution, using congo red as indicator. Previous determinations had shown that the presence of mercuric cyanide did not affect the accuracy of the method. Mercuric cyanide was determined by precipitating mercuric sulfide in hydrochloric acid solution with hydrogen sulfide, and drying to constant weight at 110°, previous tests having shown this to give accurate results.

The composition of the solid phase was determined by Schreinemakers' method[7] of residues. The solubility results are given in Table II. The solubility of mercuric cyanide in pure liquid ammonia was obtained by extrapolation from the vapor-pressure data.

TABLE II

SOLUBILITY. AMMONIA:MERCURIC CYANIDE:WATER
$T = 0°$

Solution		Residue		Solid phase
Wt.-% $Hg(CN)_2$	Wt.-% NH_3	Wt.-% $Hg(CN)_2$	Wt.-% NH_3	
6.31	None	Not analyzed		$Hg(CN)_2$
8.46	.43	89.22	.05	
11.66	1.09	92.58	.55	$Hg(CN)_2 + Hg(CN)_2.NH_3$
11.69	1.06	89.24	2.66	
9.40	2.06	83.95	5.74	
9.44	2.74	84.05	5.82	
10.32	4.08	85.11	6.14	
15.43	6.82	85.31	6.04	$Hg(CN)_2.NH_3$
17.51	7.67	87.65	6.24	
19.31	8.25	84.69	6.36	
24.68	9.40	84.37	6.48	
25.41	9.50	81.75	9.33	
25.41	9.55	79.92	9.71	$Hg(CN)_2.2NH_3 + Hg(CN)_2.NH_3$
25.52	9.50	80.92	10.34	
24.04	11.23	79.00	11.58	
23.40	12.59	77.73	11.84	
24.46	16.87	76.80	12.56	
43.57	22.09	84.04	12.31	$Hg(CN)_2.2NH_3$
66.10	21.51	86.03	12.11	
79.30[a]	20.70	...	...	

[a] Extrapolated from v. p.

[7] Schreinemakers, Z. physik. Chem., **55**, 73 (1906).

The solubility curve is shown in Fig. 2. Along the curve AB mercuric cyanide is the solid phase, along the curve BC the solid is of the composition $Hg(CN)_2.NH_3$, and along the curve CD the solid is $Hg(CN)_2.-2NH_3$. At the univariant point B the two solids $Hg(CN)_2$ and $Hg(CN)_2.-NH_3$ are in equilibrium with a solution of fixed composition for fixed temperature; and at the univariant point C, the solid phases are $Hg(CN)_2.NH_3$ and $Hg(CN)_2.2NH_3$.

The addition product $Hg(CN)_2.2NH_3$ was described by Franklin and Kraus[8] as obtained when a solution of mercuric cyanide in liquid ammonia was allowed to evaporate.
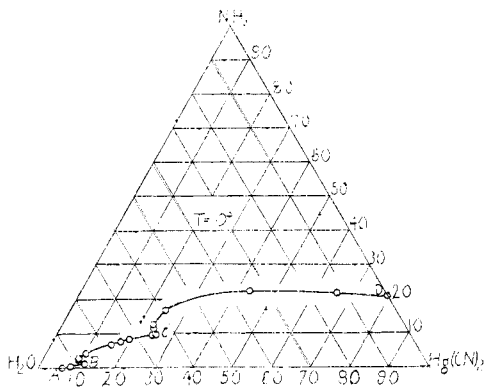
Varet[9] mentioned the existence of the two addition products and also of two hydrated addition products of the composition $Hg(CN)_2.NH_3.^1/_2H_2O$; and $Hg(CN)_2.2NH_3.^1/_2H_2O$.

Fig. 2.

The conditions under which he worked were not well defined. Moreover the physical appearances of the hydrated and unhydrated products as described by him are essentially the same. Since these addition products rapidly lose ammonia when exposed to the air, it would obviously be difficult to obtain them completely free from solution without some decomposition. The amount of water required to satisfy the above formulas is very small and could readily be explained as due to failure to free his solids completely from solution.

In this investigation no hydrated products were obtained even from the most dilute solutions. It is evident that at 0° the two addition products described are the only ones capable of separating in the solid phase from the solution; and therefore are the only solid addition products capable of existence.

Discussion of Results

Reference to Table I shows that the vapor pressures of the solutions of different composition vary greatly from those required by Raoult's law. In Cols. 3 and 4, respectively, the molecular percentage of ammonia and the relation $100 \, p/P_{NH_3}$ are shown. According to Raoult's law these values should be identical.

Foote and Hunter[2] for the system ammonia:ammonium thiocyanate,

[8] Franklin and Kraus, This Journal, 29, 49 (1907).

[9] Varet, Bull. soc. chim., [3] 6, 220 (1891); Compt. rend., 109, 903 (1889), and 112, 313 (1891).

and Foote and Brinkley[2] for the system ammonia:ammonium nitrate concluded that the great deviation was due partly to the formation of addition products in solution, and partly to electrolytic dissociation. Since mercuric cyanide is not appreciably ionized in ammonia solution[10] and since solid addition products have been shown to exist at $0°$, the divergence here may to a very large extent be attributed to compound formation. On this basis the average composition of the compound in solution may be calculated by the Callendar formula used in the above mentioned articles: $\dfrac{p_0 - p}{p_0} = \dfrac{n}{N - an + n}$. Here p_0 and p represent the vapor pressures of ammonia from the pure solvent and the solution respectively; N the molecules of solvent; n the molecules of solute; and a the number of molecules of solvent combined with one molecule of solute. In Table III the values of a have been calculated for several mercuric cyanide solutions.

TABLE III

MOLECULES OF SOLVENT (a) COMBINED WITH SOLUTE

$T = 0°$

Mol. per cent. of ammonia	a	Mol. per cent. of ammonia	a
83.80	4.18	81.02	3.64
82.66	3.97	79.34	3.35

Comparison with the results of Foote and Brinkley[2] shows that in the extent of compound formation with ammonia the salts stand in the following order: ammonium thiocyanate, mercuric cyanide, ammonium nitrate. This is shown by the fact that for solutions of the same molecular concentration the abnormality in the depression of the vapor pressure is greatest for ammonium thiocyanate and least for ammonium nitrate.

By interpolation from the data of Davis, Olmstead, and Lundstrum[2] and conversion to molecular percentages, it is found that at $0°$ the solution of lithium nitrate in ammonia shows a vapor pressure of 290 mm., when the molecular percentage of ammonia is 69.03. For the same concentration the ammonium thiocyanate solution shows a pressure of 270 mm.,[3] and the ammonium nitrate solution 665.[3] The values of a for these solutions are: ammonium thiocyanate, $a = 2.14$; lithium nitrate, $a = 2.12$; ammonium nitrate, $a = 1.97$, as derived from the vapor-pressure data. The solutions in which the vapor-pressure lowering is greatest, show the compound formation to the greatest extent.

The molar solubility of mercuric cyanide in ammonia is not as great as in the case of the other salts mentioned, and the vapor pressure of the saturated solution is considerably higher than for any of these. The rate of absorption of ammonia by mercuric cyanide is also slower and a much greater time is necessary for reaching equilibrium. Hence it probably

[10] Franklin and Kraus. *Am. Chem. J.*, **23**, 277 (1900); THIS JOURNAL, **27**, 197 (1905).

would not be as satisfactory an absorbent for ammonia for practical use as those described by Foote and Hunter,[2] Foote and Brinkley[2] and Davis, Olmstead and Lundstrum.[2]

Summary

1.   The vapor-pressure curve at 0° for the system ammonia:mercuric cyanide has been determined from 369 to 1615 mm.

2.   The solubility curve of the ternary system ammonia:mercuric cyanide:water has been determined at 0°.

3.   The vapor pressures of the solutions are far below those required by Raoult's law.

4.   The solid addition products, $Hg(CN)_2.NH_3$ and $Hg(CN)_2.2NH_3$, have been isolated and have been shown to be the only ones formed at 0°.

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THE CONSTITUTION OF METALLIC SUBSTANCES

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I.   Introduction

Recent advances in our knowledge of the structure of the atoms and of crystalline substances have made it possible to render a fairly satisfactory account of the constitution of salts and of many non-metallic compounds. The constitution of metallic elements and metallic compounds, however, remains almost as obscure as heretofore.   Indeed, few writers have ventured to hazard a guess as to the nature of these interesting substances.

Approximately 80% of the known elements are metallic in the free state, and all compounds between distinctly metallic elements are metallic. In addition, many compounds between metallic and non-metallic elements are likewise metallic.   The metals thus include a large number of important substances.   The study of metallic substances has received little attention, particularly from the chemical point of view.   It is only recently that methods have been developed as a result of which we now have information relative to the composition of metallic compounds.   Even now, many simple systems have not been systematically studied, while the more complex systems have scarcely been touched upon except in a few instances.   The physical and chemical properties of metallic compounds are little known even from a qualitative standpoint.   Data relative to the energy changes accompanying the formation of metallic compounds are very meager.   It is apparent that at the present time the metals constitute a great field which remains practically undeveloped.

Before proceeding to a discussion of the constitution of metallic sub-