very rapidly indeed and qualitative observations indicate that no difficulty due to slow absorption would be experienced.

Summary.

1. Vapor pressures at 0°, 10° and 20° have been determined for the two binary systems ammonia:ammonium nitrate, and ammonia:ammonium thiocyanate, and for three mixtures in the ternary system composed of the two salts mentioned and ammonia. The vapor-pressure range investigated was from the saturated solutions to those showing pressures of about 1600 mm.

2. Neither double salts nor solid addition products with ammonia form at 0° and above; but the saturated solutions are in equilibrium with the simple salts.

3. The solubility curves of ammonium nitrate and ammonium thiocyanate in the three-component system have been determined at 0°, 10° and 20°, together with the univariant point at which these curves intersect.

4. The results show that at the temperatures investigated, curves of equal vapor pressure in the ternary system are very nearly straight lines which connect points of equal vapor pressure in the two binary systems.

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

6. At any temperature, the saturated solution containing the two salts approximately in the molecular ratio 1 NH_4NO_3 : 3 NH_4CNS shows the lowest vapor pressure. This solution is therefore most efficient for absorbing ammonia from gas mixtures.

NEW HAVEN, CONN.

EQUILIBRIUM IN THE SYSTEM AMMONIA : WATER : AMMONIUM THIOCYANATE.

By H. W. FOOTE.

In this investigation, as in the preceding article, we have determined (1) the vapor pressures up to about two atmospheres and (2) the solubility relations, in the ternary system, and the corresponding values, so far as necessary, in the three binary systems which enclose it. The temperatures chosen were 10°, 20° and 30°.

The only solid phase at the temperatures of experiment is the thiocyanate. There is consequently no univariant system of the three components, but with excess of the salt, the system is divariant and at a given temperature a series of saturated solutions exists, which is limited by the saturated solution of the thiocyanate in water on the one side, and in ammonia, on the other. Like the preceding system, all the unsaturated solutions containing the three components are trivariant, and

at a given temperature, with a fixed ratio between the water and salt, the vapor pressure may be varied.

The vapor pressures required in the binary system ammonia:water have already been partly determined by Perman.[1] Our results meet his curves and are continued at higher pressures. The system ammonia: ammonium thiocyanate is discussed in the preceding article, and only the vapor pressures at 30° above one atmosphere have had to be determined here.   The system water:ammonium thiocyanate had little interest in the present case and no vapor-pressure determinations were made.   For most purposes, the values, which are all small, can be calculated with sufficient accuracy from the results of Tammann[2] at a higher temperature, as the ratio of the vapor pressure of solution to vapor pressure of water is very nearly independent of temperature.

Vapor Pressures.

The method and apparatus used in these determinations were essentially the same as in the preceding article. There was one source of error, however, in the present case which did not exist before, for which a correction was introduced when necessary. This was due to the vapor pressure of water in the solutions. It is evident that if dry ammonia is passed through a solution of thiocyanate and water, the latter evaporates if its vapor pressure is appreciable. To avoid this difficulty, a guard tube was placed in front of the weighed absorption tube, containing water and salt in the same proportions as in the tube. If both solutions are saturated with ammonia at any pressure, the solution in the weighed tube will not change in composition by passing more ammonia at the same pressure. Since ammonia, containing some water vapor from the guard tube, condenses in the absorption tube, before equilibrium sets in, the increase in weight is not entirely due to ammonia. Similarly, if the pressure on a saturated solution is reduced, there is a slight loss in water. These sources of error are negligible in most cases (affecting the composition of the solution less than 0.1%) but in the dilute aqueous solutions, particularly at 30°, they become appreciable. A correction in this region was therefore introduced, based on the partial pressures of ammonia and water. These can be calculated with sufficient accuracy for the purpose from Tammann's results on the vapor pressure lowering produced by thiocyanate and from Perman's results on the partial pressure of water vapor in aqueous solutions of ammonia.

The results of the vapor-pressure determinations are given in the following tables. Two or more samples were used in determining each vapor-pressure curve. For the ternary system at 20°, four different ratios between water and salt were chosen. At the other two tempera-

[1] Perman. *J. Chem. Soc.*, **83**, 1168 (1903).

[2] Tammann, *Mem. Acad. Peters*, [7] **35**, (1887).

TABLE I.

Vapor pressures.
ammonia : water.

T, 10°.		T = 20°.		T, 30°.	
P.	% NH₃.	P.	% NH₃.	P.	% NH₃.
410	32.66	762	34.69	776	29.45
568	36.96	960	38.04	923	31.76
772	40.96	1181	41.10	1106	34.26
964	44.34	1377	43.52	1298	36.59
1182	47.69	1542	45.42	1536	39.12
1388	50.58				
1547	52.69				

TABLE II.^{a}

Vapor pressures.
Ammonia : ammonium thiocyanate.
T = 30°

P........................	761	939	1167	1337	1523
% NH₃.................	28.89	31.22	33.88	35.70	37.38

^{a} The values, expressed in molecular percentages, at 10° and 20°, are given in the preceding article, Table II. At 30°, the values up to a pressure of 685 mm. have been determined by Foote and Hunter (THIS JOURNAL, **42**, 69 (1920)).

TABLE III.

Vapor pressures.
Ammonia : water : ammonium thiocyanate.
T = 10°.
H₂O : NH₄CNS = 1 : 1 (by weight).

P......	97	177	344	554	766	978	1175	1358	1526
% NH₃.	16.64	23.24	30.44	35.90	39.68	42.98	45.64	47.84	49.74

TABLE IV.

Vapor pressures.
Ammonia : water : ammonium thiocyanate.
T = 20°
Proportion H₂O:NH₄CNS by weight.

10 : 3		7 : 6		1 : 2		2 : 12.67	
P.	% NH₃.	P	% NH₃.	P.	% NH₃.	P.	% NH₃.
64	9.37	66	8.47	77	9.53	159	17.51
137	14.89	107	13.10	154	16.79	268	22.74
235	20.63	198	19.24	270	22.78	421	27.51
395	26.58	394	26.71	447	28.37	564	30.69
565	30.90	593	31.44	614	31.83	667	32.43
757	34.52	773	34.55	775	34.63	769	34.09
950	37.47	928	36.76	970	37.61	898	36.20
1168	40.33	1107	38.99	1188	40.20	1031	37.91
1368	42.67	1291	41.13	1370	42.11	1136	39.15
1550	44.62	1451	42.83			1266	40.56
		1559	43.89			1377	41.65
						1463	42.51

tures, it was considered necessary to use only one ternary mixture. The vapor pressure is so nearly independent of small changes in the ratio of thiocyanate to water, that to save space in the tables involving the three components, we have assumed that the ratio remains constant throughout a series. In the actual determinations at low pressures the ratios varied slightly from those given, due to condensation or evaporation of water.

TABLE V.

Vapor pressures.

Ammonia : water : ammonium thiocyanate.

$T = 30°$

$H_2O : NH_4CNS = 1 : 1$ (by weight.)

P...............	252	371	550	755	956	1167	1381	1530
% NH_3..........	16.67	20.98	25.34	29.20	32.02	34.52	36.72	38.10

In order to present the results in a more comparable form, they have been plotted and the vapor pressures have been interpolated at 5% intervals, beginning at 20% of ammonia. Lower percentages of ammonia are not obtainable with the thiocyanate—ammonia solutions on account of saturation. The results are given in Table VI.

TABLE VI.

Vapor Pressures (Interpolated).

Col. 1 = System ammonia:water.

Col. 2 = System ammonia:water:ammonium thiocyanate. Ratio of water to thiocyanate = 1:1 by weight.

Col. 3 = System ammonia:ammonium thiocyanate.

	$T = 10°$.			$T = 20°$.			$T = 30°$.		
% NH_3.	(1).	(2).	(3).	(1).	(2).	(3).	(I).	(2).	(3).
20	144[1]	128	....	235[1]	208	....	373[1]	338	317
25	226[1]	207	208	360[1]	335	335	561[1]	530	510
30	346[1]	332	335	535[1]	520	563	817[1]	805	823
35	493	510	530	770	798	815	1160	1200	1265
40	712	775	818	1096	1184	1208	1620	....	....
45	1003	1130	1193	1496	....	....	....	....	....
50	1345	1545	....	....	....	....	....	....	....

[1] Perman, *loc. cit.*

Solubility.

As the only solid phase in the systems under consideration is ammonium thiocyanate, which forms no addition products with ammonia or water at the temperatures adopted, the problem consisted merely of determining the composition of solutions in equilibrium with this salt with varying proportions of water and ammonia. The limits of the curve are the solubility in water and in ammonia. The method used in the determinations is the same as in the preceding article. Water was always determined by difference and is omitted in the tables.

TABLE VII.

Solubility.   Solid phase, NH₄CNS.

Ammonia : water : ammonium thiocyanate.

T, 10°.		T, 20°.		T, 30°.	
NH₃. %.	NH₄CNS. %.	NH₃. %.	NH₄CNS. %.	NH₃. %.	NH₄CNS. %.
None	58.23	None	62.54	None	66.26
3.49	59.40	3.53	63.57	2.85	67.28
6.86	61.03	6.23	64.99	5.79	68.30
9.22	62.61	8.57	66.20	8.38	69.48
12.33	65.29	11.19	67.57	12.18	71.84
14.53	66.67	12.54	69.06	14.46	74.00
17.12	69.50	15.65	71.89	17.04	76.63
19.78	72.84	18.07	74.15	20.01	79.99
22.70	77.30	21.35	78.65		

All vapor pressures and solubilities determined at 20° have been plotted as in the preceding article and are shown in Fig. 1.   In the curve showing vapor pressures of ammonia and water, the seven results at low pressures
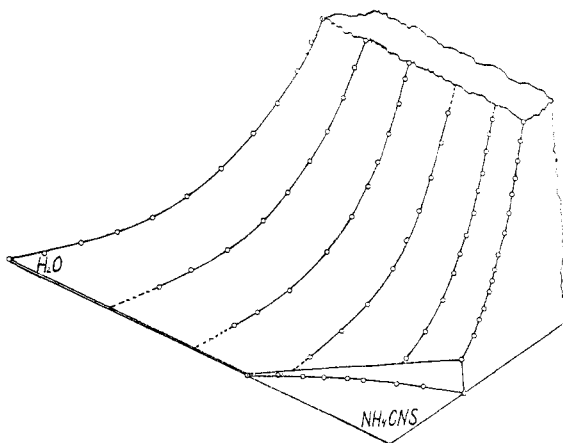

Fig. 1.

are taken from Perman.[1]   The vapor-pressure curve of ammonia and ammonium thiocyanate is taken from the preceding article.   Diagrams showing the results at 10° and 30° are similar in type and are therefore omitted.

Discussion of the Results.

The vapor pressures which have been determined are of course, total pressures of water vapor and ammonia, but the partial pressure of ammonia is so much in excess of the pressure of water vapor (except in very dilute aqueous solution, where the total pressure is very small) that the total pressures do not differ materially from the partial pressures of

[1] *Loc. cit.*

ammonia. The same simple relation exists between the vapor pressure of solutions in the binary and ternary systems that was found in the preceding article; that is, curves of equal vapor pressure in the ternary system are very nearly straight lines which connect points of equal vapor pressure in the binary systems ammonia:water, and ammonia:ammonium thiocyanate. Tables VIII to X give the compositions of solutions for a series of equal vapor pressures. They were obtained by interpolating the results on vapor pressure given previously. Col. 1 shows the vapor pressures exhibited by solutions containing the percentage of ammonia expressed in the other columns. The second and last columns give the results for the binary systems.

TABLE VIII.

COMPOSITION OF SOLUTIONS SHOWING EQUAL VAPOR PRESSURES.

T, 10°.

P.	H_2O % NH_3.	$H_2O:NH_4CNS = 1:1$ % NH_3.	NH_4CNS % NH_3.
300	28.60	29.00	28.90
500	35.25	34.70	34.35
700	39.70	38.55	38.20
900	43.20	41.85	41.25
1100	46.55	44.80	43.85
1300	49.45	47.20	46.15
1500	52.05	49.50	48.30

TABLE IX.

COMPOSITION OF SOLUTIONS SHOWING EQUAL VAPOR PRESSURES.

T, 20°.

		Ratio of H_2O to CNS.				
P.	H_2O % NH_3.	10:3 % NH_3.	7:6 % NH_3.	1:2 % NH_3.	2:12.67 % NH_3.	NH_4CNS % NH_3.
300	22.75	23.45	23.70	24.00	23.90	23.95
500	29.20	29.40	29.40	29.70	29.30	29.10
700	33.70	33.50	33.45	33.45	33.05	32.80
900	37.15	36.80	36.35	36.75	36.10	35.90
1100	40.10	39.50	38.95	39.25	38.80	38.55
1300	42.60	41.90	41.25	41.40	40.95	40.85
1500	44.90	44.05	43.30	43.20	42.90	42.65

TABLE X.

COMPOSITION OF SOLUTIONS SHOWING EQUAL VAPOR PRESSURES.

T, 30°.

P.	H_2O % NH_3.	$H_2O:CNS = 1:1$ % NH_3.	NH_4CNS % NH_3.
300	17.50	18.80	. . . . .
500	23.55	24.30	24.50
700	27.95	28.20	28.10
900	31.30	31.25	30.75
1100	34.15	33.85	33.05
1300	36.60	35.90	35.20
1500	38.70	37.85	37.15

The results at 20° are plotted in the diagram, Fig. 2. The points of equal vapor pressure in the two binary systems are connected by straight

lines.   The diagram shows to what extent the results obtained diverge from the linear relation.   The greatest divergence is shown at low pressures.
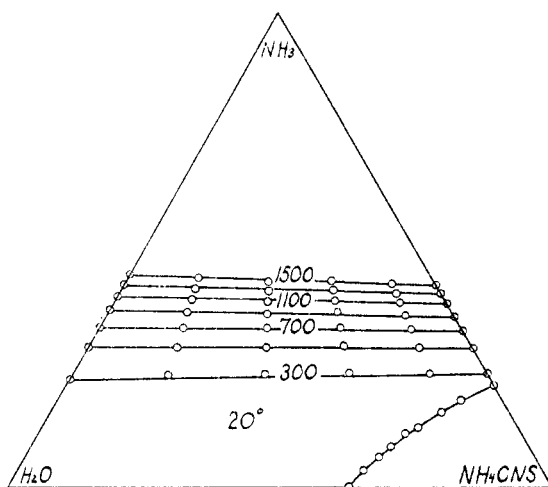

Fig. 2.

This linear relation of the vapor pressures suggests very strongly that the thiocyanate does not form a hydrate in the ammoniacal solutions. If such a hydrate were formed, it is to be expected that it would have a greater or less tendency than its components to form addition products with ammonia in solution and the vapor-pressure curve should diverge accordingly from the linear relation.

The ratio of the vapor pressure of a solution to the vapor pressure of ammonia, p/P_{NH_3}, rises with temperature where normally the ratio should remain constant.   This is shown in Table XI in which this ratio has been calculated for a number of results taken from Table VI.   The values for the vapor pressure of ammonia are taken from Keyes and Brownlee.[1]   This increase in the ratio is undoubtedly due to the breaking down of the ammonia addition products in solution as the temperature rises

TABLE XI.

Showing increase of p/P_{NH_3} with temperature.

Col. 1.   System ammonia : water.

Col. 2.   System ammonia : water : thiocyanate. H_2O : NH_4CNS = 1 : 1 by weight.

Col. 3.   System ammonia : ammonium thiocyanate.

	1.			2.			3.	
% NH₃.	10°.	20°.	30°.	10°.	20°.	30°.	10°.	20°.	30°.
25	0.049	0.056	0.064	0.044	0.052	0.060	0.045	0.052	0.058
35	0.106	0.119	0.132	0.110	0.123	0.136	0.114	0.126	0.144

[1] Keyes and Brownlee, THIS JOURNAL, **40**, 25 (1918).

The effects on the lowering of the vapor pressure of ammonia by thiocyanate and by water have been considered elsewhere[1] and need not be discussed here. It may be noted, however, that equal weights of water and of thiocyanate have approximately equal effect on lowering the vapor pressure of ammonia. For equal numbers of molecules, therefore, thiocyanate has much the greater effect, indicating greater complex formation in solution.

Summary.

1. Vapor pressures at $10°$, $20°$ and $30°$ have been determined (up to approximately 2 atmospheres) in the system ammonia : water : ammonium thiocyanate.

2. The solubility curves of ammonium thiocyanate in this system have been determined at the same temperatures.

3. The results show that at the temperatures investigated, curves of equal vapor pressure in the ternary system are very nearly straight lines which connect points of equal vapor pressure in the two binary systems.

NEW HAVEN, CONN.

NATURAL SYSTEMS FOR THE CLASSIFICATION OF ISOTOPES, AND THE ATOMIC WEIGHTS OF PURE ATOMIC SPECIES AS RELATED TO NUCLEAR STABILITY.

BY WILLIAM D. HARKINS.

1. The Isotopic Number.

Up to the present time no general systems for the classification of isotopes have been proposed,[2] though atomic species have been listed

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[1] Foote and Hunter, *loc. cit.*; Perman, *loc. cit.*

[2] However, the listing of isotopes according to their f values, as in Figs. 4 and 5 and Table I, THIS JOURNAL, **42**, 1956–97 (1920), where the f, which is $1/2$ the isotopic number, is a term in the Harkins-Wilson atomic weight equation, practically introduced this scheme of classification.

The idea of ordinal or atomic numbers for the elements was first developed by Rydberg in 1896, and was further developed by the remarkable experiments of Moseley in 1913. In the latter year Soddy and Fajans found that some of the radio-active elements exist in isotopic forms. This made it apparent that *to designate an isotope it is necessary to give the values of two variables*, the atomic number and one other variable. The simpler form of the Harkins-Wilson atomic weight equation, $W = P = 2 M + 2f$, specified this variable as f, which varies from—$1/2$ for hydrogen and 0 for most of the light atoms of even atomic number, up to 27 for uranium. The first plot of this equation was presented by Durrant, in 1917, and the values of f for all of the known elements were published by the writer in 1920. Since f for the complex atoms has all of the half values between 0 and 27, it is evident that by multiplying the f values by 2 they will be changed into whole numbers varying from 1 to 54, and that is what has been done in this paper. In a recent paper (*Phil. Mag.*, **41**, 281–5 (1921)), received after the present paper