

TABLE I
SOLUBILITY OF CADMIUM SULFATE IN ACETIC ACID
SOLUTIONS. 25°

Rotation time, days	Satd. soln.		Wet solid		Solid ^a Wt. % H ₂ O
	Wt. % HC ₂ H ₃ O ₂	Wt. % CdSO ₄	Wt. % HC ₂ H ₃ O ₂	Wt. % CdSO ₄	
39	71.34	0.11	9.58	70.17	18.90
7	9.78	31.72	1.79	72.09	19.08
7	21.25	19.69	4.00	69.33	18.76
15	20.85	19.87	3.69	70.50	18.61
14	46.34	2.77	6.32	70.69	18.53
29	32.39	10.05	4.91	70.60	18.58
25	75.48	0.06	11.56	68.43	19.16
38	76.35	.05	19.52	60.38	18.90
38	82.92	.01	13.52	67.96	18.80
26	89.77	.01	16.14	66.74	18.61
36	85.13	.02	28.89	60.62	8.24 ^b
64	85.49	.02	32.72	56.61	8.28 ^b
53	90.91	.007	36.33	55.32	7.89 ^b
72	89.52	.007	40.85	50.09	7.88 ^b
63	95.79	.015	28.90	64.29	7.93
20	95.87	.004	27.26	65.87	7.92
24	97.53	.016	23.86	69.42	8.01
24	98.59	.025	18.45	74.81	7.97

^a Calculated for 3CdSO₄·8H₂O, 18.73% H₂O and for CdSO₄·H₂O, 7.96% H₂O.

^b The solid introduced was 3CdSO₄·8H₂O. In the two with 85% acetic acid transition was probably incomplete. The transition point is probably near 85% acetic acid.

A number of determinations were made at 30° in solutions of between 12 and 66% acetic acid. The solubility was practically the same as at 25° throughout the entire range.

Summary

The solubility of the octotrihydrate of cadmium sulfate in mixtures of acetic acid and water decreases rapidly as acetic acid is added and is very small when the solvent is above 55% acetic acid. The octotrihydrate is the stable solid phase when the percentage of acetic acid in the solution is less than 85%.

The composition of the monohydrate of cadmium sulfate has been confirmed.

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Behavior of the Hydronitrogens and their Derivatives in Liquid Ammonia. IX. Equilibria in the System Ammonium Trinitride-Ammonia^{1,2}

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As a preliminary to an extended study and comparison of the structural and genetic relationships that may exist between the various solvated saline hydronitrogens,³ which are probably of the nature of coördination compounds, and their respective nitrogen-chain empirical isomers of the diazene⁴ and monazane series, the present investigation of the binary system ammonium trinitride-ammonia from the viewpoint of the phase rule has been undertaken. In this work the number, composition, stability, and fields of existence of the ammonates of ammonium trinitride have been determined, as well as all inversion and other transition points of the system. While many ammonates of a large variety of

substances have been described previously,⁵ the investigations in nearly all cases have covered but a limited range of temperature and pressure, and the phase relations have been studied only incompletely.

In the current investigation, pressure has been varied from 0 to 4000 mm., temperature from -90 to +30°, and concentration from 0 to 100% ammonia.

Apparatus and Materials

The apparatus (Fig. 1) is of the latest form employed in this Laboratory for the phase rule investigation of binary systems with one volatile component. Ammonia from a steel cylinder (A) is passed through a series of tubes (C) filled with soda-lime and metallic sodium, and is condensed at -78° in a reservoir (D) from which are pumped out the small volumes of non-condensable gases present in the ammonia. This reservoir contains a soluble salt, such as ammonium iodide, the saturated solution of which has a vapor tension of about one atmosphere at room temperature, and serves as a convenient source of highly purified ammonia gas.

(1) For references to Articles I to VII of this series see Howard and Browne, *THIS JOURNAL*, **55**, 1968 (1933). For VIII see *ibid.*, **55**, 3211 (1933).

(2) The current article is based chiefly upon a part of the thesis presented to the Faculty of the Graduate School of Cornell University by David H. Howard, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Dresser and Browne, *THIS JOURNAL*, **55**, 1963 (1933).

(4) These compounds are now under investigation in this Laboratory.

(5) See for example Ephraim, *Ber.*, **52**, 940 (1919); Biltz, *Z. anorg. allgem. Chem.*, **180**, 93 (1923).

A weighed amount of the solid component is sealed into the reaction cell (L), the temperature of which is controlled through a suitable bath (Q), and the pressure in which is registered on the manometer (M). Equilibrium is ensured by thorough stirring of the bath, and by agitation of the cell, accomplished by means of an eccentric (P) and a glass spring (K).

Any desired volume of ammonia, measured and corrected automatically in a water-jacketed buret (G) provided with a Pettersson compensator may be introduced into or withdrawn from the reaction cell (L).

In addition to the usual calibrations of buret, manometer and thermometer, several others are necessary for the purpose of determining the amount of ammonia in the vapor phase, and by difference between this and the total amount of ammonia in the system, the amount in the condensed phases. By introducing successive small amounts of ammonia into the empty, evacuated cell, held at 0°, and observing the corresponding pressures, the amounts of ammonia in the vapor phase at any pressure up to that of liquid ammonia is determined. The volume of the cell, which is always immersed to constant depth, is ascertained prior to attachment to the apparatus, by calibration with water. When liquid or solid phases are present, their volume is estimated as accurately as possible, and subtracted from the total cell volume. Calibration curves for temperatures other than 0° are calculated for a volume of ammonia equal to that of the cell.

The ammonium trinitride was prepared by the method of Frost, Cothran and Browne⁶ and was purified by sublimation in a sealed tube at 130°.

Pressure-Concentration Isotherms

The 0, -15, -20, -35, -50 and -78.3° isotherms were investigated.⁷ Accurately weighed samples of ammonium trinitride ranging from 0.9592 to 0.0260 g. were employed. At every temperature except 0°, considerable difficulty was experienced in the attainment of stable equilibrium, owing to a strong tendency toward the formation of supersaturated solutions and metastable solids. This was overcome by bringing the system for a short time to the temperature of either solid carbon dioxide or liquid air.

The quest of higher solvates was the principal incentive to investigation of the isotherms at -50 and -78.3°. At these temperatures the system appeared to be labile with respect to the diammonate. The pentammonate was not obtained at -50, and even at -78.3° was formed only after the system had previously been cooled to the temperature of liquid air.

The data concerning the isotherms are recorded

(6) Frost, Cothran and Browne, *THIS JOURNAL*, **55**, 3516 (1933).

(7) In a preliminary investigation of the 0 and -33° isotherms a diammonate of ammonium trinitride with inversion temperature at -9° was identified by Browne and Houlehan [*THIS JOURNAL*, **35**, 649 (1913)].

in Tables I to VI, and typical curves are plotted in Fig. 2.

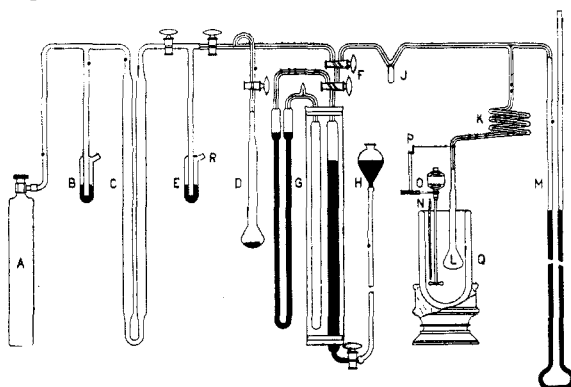


Fig. 1.—Apparatus for determining equilibria in the system ammonium trinitride-ammonia.

The isotherm at 0° (Fig. 2) indicates the non-existence of solvates at this temperature. The isotherms at -15, -20, -35 and -50°

TABLE I
PRESSURE-CONCENTRATION DATA IN THE SYSTEM
NH₄N₃-NH₃, 0° ISOTHERM

Concn., moles NH ₃ per mole NH ₄ N ₃	Press., mm.	Curve (Fig. 2)
4.27	1668	
4.17	1625	DC
4.07	1580	(dil. soln., vapor)
3.96	1531	
3.91	1509	
3.86	1488	
3.81	1488	
3.70	1488	
3.50	1488	
3.30	1488	
3.07	1488	
2.83	1488	
2.58	1488	
2.34	1488	
2.09	1488	
1.87	1488	CB
1.61	1488	
1.37	1488	(NH ₄ N ₃ , satd. soln., vapor)
1.13	1488	
0.89	1488	
.65	1488	
.42	1486	
.22	1485	
.08	1482	
.06	1479	
.02	1466	
.00	1431	
.00	1260	BA
.00	1096	(NH ₄ N ₃ , vapor)
.00	709	
.00	342	
.00	2.6	

prove the existence of one solvate only, the diammonate, $\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$. That at -78.3° identi-

TABLE II
PRESSURE-CONCENTRATION DATA IN THE SYSTEM
 $\text{NH}_4\text{N}_3\text{-NH}_3$, -15° ISOTHERM

Concn., moles NH_3 per mole NH_4N_3	Press., mm.	Curve (not plotted)		
5.23	1043			4.49
5.09	1014	(dil. soln., vapor)		4.33
4.91	976			3.99
4.71	933			3.73
4.52	892			3.68
4.35	861			3.54
4.14	862			3.19
3.94	862			2.85
3.73	861			2.47
3.52	861	($\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$, satd. soln., vapor)		2.37
3.30	860			2.29
3.10	860			2.15
2.89	858			2.08
2.71	856			1.99
2.50	857			2.04
2.30	846			2.05
2.11	831			2.07
2.00	853	($\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$, vapor)		2.04
2.03	800			1.98
2.00	775			1.77
1.96	709			1.63
1.87	710			1.46
1.65	712			1.29
1.39	710			1.15
1.24	710	($\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$, NH_4N_3 , vapor)		1.01
1.08	710			0.97
0.99	709			.87
.89	710			.72
.64	709			.51
.49	710			.19
.18	708			.04
				.00
				.00
				.00
				.06
				.13
				.47
				.67
				1.25
				1.68
				1.99
				2.45
				2.91
				3.35
				3.78
				4.08

TABLE III
PRESSURE-CONCENTRATION DATA IN THE SYSTEM
 $\text{NH}_4\text{N}_3\text{-NH}_3$, -20° ISOTHERM

Concn., moles NH_3 per mole NH_4N_3	Press., mm.	Curve (Fig. 2)
5.80	932	
5.54	897	NM
5.34	860	
5.22	846	(dil. soln., vapor)
5.07	820	
4.83	778	
4.66	745	
4.52	719	
4.35	690	MLL'
4.31	678	
4.17	650	(supersatd. soln., vapor)
4.02	619	
3.99	611	
3.89	590	
3.80	570	

fies two ammonates, $\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$ and $\text{NH}_4\text{N}_3 \cdot 5\text{NH}_3$. Both the diammonate and the pentammonate of ammonium trinitride were obtained as white, crystalline solids.

It is to be noted that at -20° metastable solutions (dilute, ML; saturated, LK; supersaturated, LL') of anammonous ammonium trinitride, and at -78.3° , (dilute, YY'; saturated, Y'Y'') of the diammonate have been obtained. In fact, the curve Y'Y'' has been followed in one experiment to the point of its intersection with the prolongation of UV, and then downward along this vertical line.

At -15 , -20 , and -35° isothermal results indicating the possibility of a lower ammonate than the diammonate were obtained. Independent experiments conducted (by Friedrichs and by Howard), many years apart, led to the conclusion that this was the monammonate. Its

TABLE IV
PRESSURE-CONCENTRATION DATA IN THE SYSTEM
 $\text{NH}_4\text{N}_3\text{-NH}_3$, -35° ISOTHERM

Concn., moles NH_3 per mole NH_4N_3	Press., mm.	Curve (not plotted)
5.60	442	(Dil. soln., vapor)
5.77	427	
5.51	408	
5.32	392	(Supersatd. soln., vapor)
5.08	371	
4.81	346	
5.13	394	
4.77	394	
4.61	394	
4.33	394	($\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$, satd. soln., vapor)
4.11	394	
3.80	393	
3.48	394	
3.27	392	
3.00	392	
2.73	391	
2.38	389	
2.21	388	
2.04	371	
2.03	326	($\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$, vapor)
1.97	274	
2.01	252	
1.98	202	
1.90	193	
1.72	192	
1.63	192	
1.33	192	
1.07	191	($\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$, NH_4N_3 , vapor)
0.92	193	
.78	192	
.70	191	
.46	193	
.27	191	
.14	192	

solubility, temperature of inversion to the anammonous salt, and vapor pressure both in equilibrium with anammonous salt and with saturated solution, seemed to be identical with the corresponding values for the diammonate. Evidence of the existence of the supposed monammonate was obtained only when ammonia was being added to the system starting with the anammonous salt and never when ammonia was being withdrawn from the system starting with a dilute solution. In the latter case, the only solvate ob-

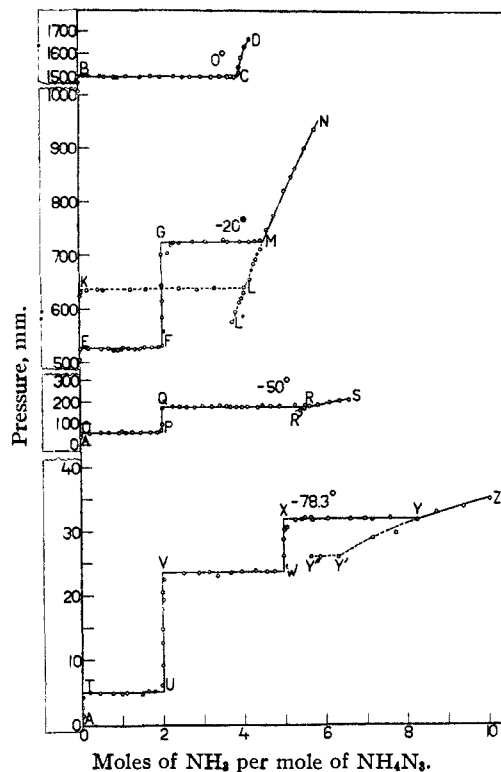


Fig. 2.—Pressure-concentration isotherms of the system ammonium trinitride-ammonia.

Temp., °C.	Curve	Phases
0	AB	NH_4N_3 , vapor
	BC	NH_4N_3 , satd. soln., vapor
	CD	Dilute soln., vapor
	DE	NH_4N_3 , vapor
-20	AE	NH_4N_3 , vapor
	EF	NH_4N_3 , $\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$, vapor
	FG	$\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$, vapor
	GM	$\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$, satd. soln., vapor
	MN	Dilute soln., vapor
	KL	NH_4N_3 , satd. soln., vapor (metastable)
	L'LM	Supersatd. soln., vapor (metastable)
-50	AO	NH_4N_3 , vapor
	OP	NH_4N_3 , $\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$, vapor
	PQ	$\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$, vapor
	QR	$\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$, satd. soln., vapor
	RS	Dilute soln., vapor
	R'R	Supersatd. soln., vapor (metastable)
-78.3	AT	NH_4N_3 , vapor
	TU	NH_4N_3 , $\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$, vapor
	UV	$\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$, vapor
	VW	$\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$, $\text{NH}_4\text{N}_3 \cdot 5\text{NH}_3$, vapor
	WX	$\text{NH}_4\text{N}_3 \cdot 5\text{NH}_3$, vapor
	XY	$\text{NH}_4\text{N}_3 \cdot 5\text{NH}_3$, satd. soln., vapor
	YZ	Dilute soln., vapor
	Y'Y'	$\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$, satd. soln., vapor (metastable)
Y''Y''	Supersatd. soln., vapor	

TABLE V
PRESSURE-CONCENTRATION DATA IN THE SYSTEM
 $\text{NH}_4\text{N}_3\text{-NH}_3$, -50° ISOTHERM

Concn., moles NH_3 per mole NH_4N_3	Press., mm.	Curve (Fig. 2)			
6.54	206	SR	8.23	32.0	YY'
6.36	202	(Dil. soln.,	7.75	30.4	(supersatd.
6.11	195	vapor)	7.11	29.0	soln., vapor)
5.88	188		6.30	26.0	Y''Y'
5.65	181	RR'	5.88	26.2	($\text{NH}_4\text{N}_3\cdot 2\text{NH}_3$,
5.43	172	(supersatd.	5.71	26.0	satd. soln.,
5.34	168	soln., vapor)	7.75	32.5	vapor)
5.42	184		7.57	32.2	YX
5.19	184		7.11	31.8	($\text{NH}_4\text{N}_3\cdot 5\text{NH}_3$,
4.94	184		6.98	32.0	satd. soln.,
4.70	184		6.61	31.9	vapor)
4.47	184		6.36	32.2	
4.32	182		6.05	32.0	
4.10	182		5.71	32.3	
3.99	182	RQ	5.70	31.7	
3.91	183	($\text{NH}_4\text{N}_3\cdot 2\text{NH}_3$,	5.49	32.1	
3.72	182	satd. soln.,	5.40	31.9	
3.59	184	vapor)	5.17	31.7	
3.38	185		5.03	30.4	
3.18	184		4.99	30.3	XW
3.01	184		4.98	28.9	($\text{NH}_4\text{N}_3\cdot 5\text{NH}_3$,
2.88	184		4.91	25.9	vapor)
2.56	181		4.97	26.1	
2.41	181		4.75	23.6	
2.24	182		4.53	23.8	
2.08	180		4.18	23.9	
2.03	176	QP	3.97	23.6	WV
2.02	97	($\text{NH}_4\text{N}_3\cdot 2\text{NH}_3$,	3.72	23.3	($\text{NH}_4\text{N}_3\cdot 5\text{NH}_3$,
2.00	62	vapor)	3.30	22.7	$\text{NH}_4\text{N}_3\cdot 2\text{NH}_3$,
1.92	60		3.08	23.6	vapor)
1.73	61		2.92	23.4	
1.49	60		2.50	23.4	
1.25	60	PO	2.09	22.5	
1.09	60	($\text{NH}_4\text{N}_3\cdot 2\text{NH}_3$,	2.02	21.1	
1.01	61	NH_4N_3 ,	2.01	19.4	VU
0.98	60	vapor)	2.00	17.8	($\text{NH}_4\text{N}_3\cdot 2\text{NH}_3$,
.70	60		1.97	14.8	vapor)
.43	61		1.96	12.5	
.14	60		1.96	9.0	
.08	60		1.95	6.4	
.03	59	OA	1.78	5.4	
.00	0	(NH_4N_3 , vapor)	1.60	5.3	UT
			1.48	4.9	($\text{NH}_4\text{N}_3\cdot 2\text{NH}_3$,
			1.08	5.0	NH_4N_3 ,
			0.95	5.0	vapor)
			.70	5.0	
			.42	5.1	
			.08	5.1	
			.00	4.4	TA
			.00	2.5	(NH_4N_3 , vapor)
			.00	1.5	

TABLE VI
PRESSURE-CONCENTRATION DATA FOR THE SYSTEM
 $\text{NH}_4\text{N}_3\text{-NH}_3$, -78.3° ISOTHERM

Concn., moles NH_3 per mole NH_4N_3	Press., mm.	Curve (Fig. 2)
11.16	36.9	ZY
10.58	35.6	(dil. soln.,
10.04	35.1	vapor)
9.38	34.0	
8.77	33.1	

tained was the diammonate, and even if ammonia were withdrawn until there was only a small amount of the diammonate left, upon subsequent successive additions of ammonia, the same path was retraced to dilute solution. These

equilibria were attained quite rapidly. However, if ammonia were added to the entirely unsolvated ammonium trinitride, and the system cooled to effect solvation, a break in the curve indicating a monammonate was obtained.

Later investigation showed that this break did not always occur at the precise point where the solid phase contained 1 mole of ammonia per mole of the salt, but might be realized at various points between 0 and 2 moles of ammonia. Furthermore, the equilibria corresponding to saturated solution of monammonate, if held for a very long time, would finally shift to those corresponding to the equilibria between anammonous salt, diammonate and vapor. Such a shift might occur over forty-eight hours after the system had come to apparent equilibrium, with pressure constant within one millimeter throughout this period. Evidently the crystals of the anammonous salt had become encrusted with a protective layer of the diammonate, which served greatly to retard further ammoniation. Therefore, subsequent addition of ammonia prematurely yielded saturated solution of the diammonate, producing a break in the curve at a composition lower in ammonia than that of the diammonate. The validity of this explanation was further attested by the fact that when the original crystals of anammonous salt were exceedingly fine, having been obtained in less than two minutes by evaporation to dryness of a dilute solution of the salt, the shift in equilibrium noted above was much more rapid.

From these considerations, the conclusion was finally reached that the monammonate is probably non-existent. The breaks repeatedly obtained in the immediate neighborhood of 1 mole of ammonia were evidently fortuitous. Moreover, the identity of the values for the inversion point, vapor tensions, and solubilities of the supposed monammonate with those of the diammonate seems to preclude further investigation except along isothermal lines.

Pressure-Temperature Curves

Pressure-temperature curves were determined for systems consisting of (a) diammonate, anammonous salt, and vapor; (b) pentammonate, diammonate, and vapor; and (c) saturated solution, solid, and vapor. The samples of ammonium trinitride used were the same as those employed in the investigation of the isotherms. Once a

system with the desired phases was obtained, by the procedure outlined above, equilibrium was readily attained at any temperature within the field of existence of the ammonate under investigation.

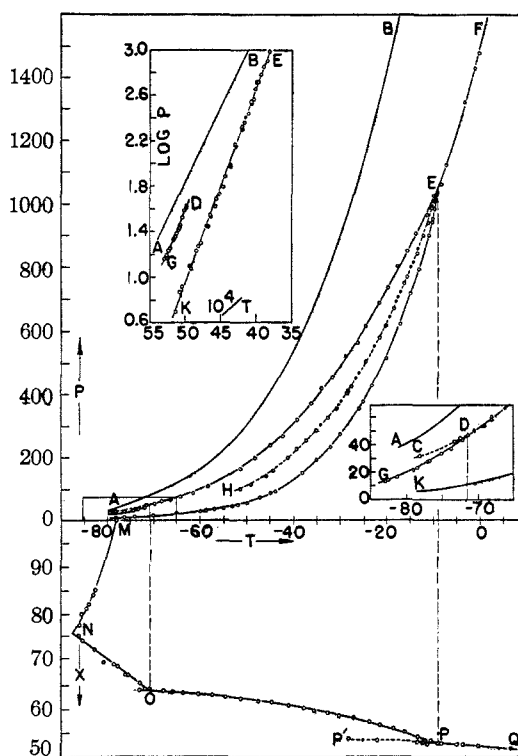


Fig. 3.—Pressure-temperature and temperature-concentration curves of the system ammonium trinitride-ammonia.

Curve	Phases
AB	Liquid ammonia, vapor
CD	$\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$, satd. soln., vapor (metastable)
DE	$\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$, satd. soln., vapor
GD	$\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$, $\text{NH}_4\text{N}_3 \cdot 5\text{NH}_3$, vapor
D	$\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$, $\text{NH}_4\text{N}_3 \cdot 5\text{NH}_3$, satd. soln., vapor
HE	NH_4N_3 , satd. soln., vapor (metastable)
EF	NH_4N_3 , satd. soln., vapor
KE	NH_4N_3 , $\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$, vapor
E	NH_4N_3 , $\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$, satd. soln., vapor
MN	NH_3 (solid), satd. soln., vapor
NO	$\text{NH}_4\text{N}_3 \cdot 5\text{NH}_3$, satd. soln., vapor
OP	$\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$, satd. soln., vapor
P'P	NH_4N_3 , satd. soln., vapor (metastable)
PQ	NH_4N_3 , satd. soln., vapor
N	NH_3 (solid), $\text{NH}_4\text{N}_3 \cdot 5\text{NH}_3$, satd. soln., vapor
O	$\text{NH}_4\text{N}_3 \cdot 5\text{NH}_3$, $\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$, satd. soln., vapor
P	$\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$, NH_4N_3 , satd. soln., vapor

The data are presented in Tables VII to IX, and plotted in Fig. 3. The empirical equation expressing the logarithmic curve for the system diammonate, anammonous salt, and vapor is

$$\log P = -(1733/T) + 9.568$$

That for the system pentammonate, diammonate, and vapor is

$$\log P = -(1606/T) + 9.636$$

Inversion of the diammonate to the anammonous salt is found to occur at -9° ; that of the pentammonate to the diammonate, at -71° .

TABLE VII

PRESSURE-TEMPERATURE DATA OF THE SYSTEM
 $\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3 - \text{NH}_4\text{N}_3 - \text{NH}_3$ (CURVE KE, FIG. 3)

Temp., °C.	Press., mm. obs.	Press., mm. calcd.	Diff., mm.
-78.3	5.0	4.6	0.4
-76.3	7.0	5.7	1.3
-74.3	8.3	7.0	1.3
-70.0	12.6	10.7	1.9
-69.8	12.0	10.9	1.1
-66.1	16.5	15.3	1.2
-65.0	19.3	17.2	2.1
-63.1	21.3	20.3	0.8
-60.3	27.0	26.4	.6
-60.0	27.2	26.9	.3
-58.0	33.5	32.1	1.4
-57.3	35.0	34.1	0.9
-55.0	42.1	41.5	.6
-53.2	48.0	44.2	3.8
-52.0	54.8	53.0	1.8
-50.0	61.8	64.7	-2.9
-47.0	76.7	79.1	-2.4
-45.0	92.6	92.3	0.3
-44.0	96.3	99.5	-3.2
-40.0	135	134	1.0
-38.0	153	156	-3.0
-35.0	194	192	2.0
-32.0	233	237	-4.0
-30.0	272	272	0.0
-26.0	347	355	-8.0
-25.0	379	379	0.0
-23.0	425	430	-5.0
-20.0	522	520	2.0
-17.0	624	627	3.0
-13.0	796	796	0.0
-10.0	956	951	5.0

TABLE VIII

PRESSURE-TEMPERATURE DATA OF THE SYSTEM
 $\text{NH}_4\text{N}_3 \cdot 5\text{NH}_3 - \text{NH}_4\text{N}_3 \cdot 2\text{NH}_3 - \text{NH}_3$ (CURVE GD, FIG. 3)

Temp., °C.	Press., mm. obs.	Press., mm. calcd.	Diff., mm.
-83.3	14.8	14.8	0.0
-82.7	15.8	15.7	.1
-81.5	18.1	17.7	.4
-79.2	22.9	22.3	.6
-78.4	24.2	24.1	.1
-77.0	27.3	27.7	-.4
-76.8	28.3	28.1	.2
-75.0	33.7	33.4	.3
-73.5	38.4	38.4	.0
-72.0	36.4	44.1	-.8

TABLE IX

PRESSURE-TEMPERATURE DATA OF THE SATURATED
 SOLUTION OF NH_4N_3 IN LIQUID AMMONIA

(Curve CDE, Fig. 3) Temp., °C.	Press., mm.	(Curve HEF, Fig. 3) Temp., °C.	Press., mm.
-78.0	30.8	-51.7	105
-73.15	42.1	-49.6	121
-71.7	48.5	-46.4	146
-69.6	53.7	-44.3	169
-68.0	60.2	-41.2	204
-66.4	67.1	-39.2	230
-64.3	77.4	-35.0	292
-61.16	92.2	-32.9	328
-58.0	115	-30.9	365
-54.8	140	-28.4	419
-51.7	166	-27.8	430
-48.5	198	-24.8	503
-45.4	242	-21.7	589
-42.25	279	-18.6	678
-39.2	323	-15.5	784
-36.1	374	-13.6	852
-34.0	423	-11.3	942
-31.9	456	- 9.3	1024
-28.8	524	- 8.3	1072
-26.8	568	- 7.25	1125
-24.75	617	- 5.2	1223
-21.65	690	- 3.05	1329
-19.6	743	- 1.0	1441
-17.5	807	0.0	1490
-15.45	861	+ 2.0	1610
-13.4	914	+ 4.0	1733
-11.35	974	+ 6.0	1873
- 9.3	1031	+ 8.0	2011
		+10.0	2168
		+12.0	2333
		+14.0	2491
		+16.0	2661
		+18.0	2856
		+20.0	3053
		+22.0	3255
		+24.0	3477
		+26.0	3702
		+28.0	3946

Temperature-Concentration Curves

The solubility data for the system under investigation are listed in Table X, and plotted in Fig. 3.

The solid phases in equilibrium with saturated solution and vapor along the various branches of the curve are respectively as follows: along MN, ammonia; NO, pentammonate; OP, diammonate; PQ, and its metastable prolongation, PP', anammonous ammonium trinitride. The eutectic, N, is located at -87° and 76% ammonia. The two other quadruple points, O and P, are located at -71 and -9° . These correspond to the inversion points D and E shown on the pressure-temperature curve.

TABLE X
TEMPERATURE-CONCENTRATION OR SOLUBILITY DATA OF
THE SYSTEM $\text{NH}_4\text{N}_3\text{-NH}_3$

Temp., °C.	Soly. in % NH_3	Curve (Fig. 3)
-77.7	100.0	
-82.5	85.02	
-83.0	83.97	MN
-83.8	82.21	(Solid NH_3 ,
-84.4	81.20	satd. soln.,
-85.2	79.52	vapor)
-86.0	77.60	
-86.1	75.48	
-85.4	74.51	
-82.9	72.42	
-80.9	70.80	
-78.5	69.61	NO
-78.0	69.02	(Solid
-76.8	68.20	$\text{NH}_4\text{N}_3 \cdot 5\text{NH}_3$,
-76.0	67.59	satd. soln.,
-75.4	67.09	vapor)
-73.0	65.62	
-72.0	64.29	
-73.15	64.30	
-71.4	64.14	
-68.0	63.96	
-65.8	63.77	
-63.8	63.57	
-60.5	63.27	
-57.25	63.01	
-54.7	62.67	
-51.3	62.27	
-47.4	61.77	
-44.85	61.29	
-41.2	60.81	OP
-37.7	60.24	(Solid
-35.65	59.84	$\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$,
-32.7	59.26	satd. soln.,
-30.25	58.71	vapor)
-27.1	58.18	
-24.0	57.34	
-21.35	56.72	
-18.65	55.98	
-16.3	55.22	
-13.4	54.41	
-12.5	54.15	
-11.3	53.83	
-10.7	53.58	
-10.2	53.44	
-9.4	53.18	
-28.4	53.84	
-20.2	53.54	
-13.6	53.14	P'PQ
-9.0	53.00	(NH_4N_3 , satd.
-8.9	52.97	soln., vapor)
-8.4	52.85	
-5.0	52.70	
-0.4	52.40	
+6.9	51.90	

three variables, pressure, temperature and concentration, are represented as increasing along the three axes. The percentage of ammonia increases from left to right as indicated by the arrow. The area inclosed by the letters ABRC represents the co-existence of solid anammonous salt, saturated solution and vapor. Along AB, at -9° , inversion of the diammonate into anammonous salt takes place. Accordingly, the "dry" area AEFD contains the loci for equilibria with solid anammonous salt, solid diammonate, and vapor; while the "wet" area DGHIB contains those with solid diammonate, saturated solution, and vapor. The "cliff" along DF between these

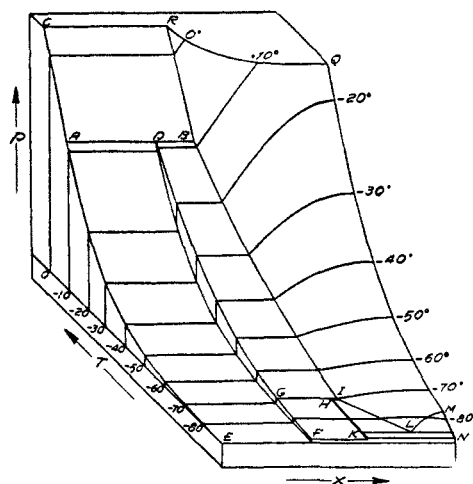


Fig. 4.—Model of the system ammonium trinitride-ammonia on Cavalier's projection.

two areas represents the field of existence of solid diammonate and vapor. Along HI, at -71° , inversion of the pentammonate into the diammonate takes place. GFKH is the "dry" field of existence of solid diammonate, solid pentammonate, and vapor. Along HK is another "cliff," of solid pentammonate and vapor. HKLI contains solid pentammonate, saturated solution, and vapor; and LNM, solid ammonia "ice," saturated solution, and vapor. L, at -87° , is the eutectic point. RBILMQ is, of course, the field of existence of dilute solution and vapor. QM is the vapor tension curve of pure liquid ammonia, and MN that of pure solid ammonia. M, at -77.7° , is the triple point in the one component system, ammonia.

General Considerations

A three-dimensional view of the system by Cavalier's projection is shown in Fig. 4. The

In the case of most salts, solvation of the cation occurs in general more readily than that of

the anion. The comparatively few instances of the hydration of an ammonium salt, however, may be taken as illustrations of anionic solvation,⁸ since coordination through the ammonium ion is improbable. Ammonation of ammonium salts, especially at lower temperatures, occurs far more frequently than hydration. Unless this ammonation can be attributed to a coordination of simple or associated ammonia molecules through the ammonium ion, it seems inevitable that it must be ascribed to solvation of the anion.

In the system ammonium trinitride-ammonia the diammonate is believed to exhibit anionic solvation. Whether coordination takes place through hydrogen or through nitrogen atoms, however, is a question to which the final answer cannot as yet be given. The pentammonate, on the other hand, with its inversion temperature at -71° , probably does not show exclusively anionic ammonation, but may rather be identical with the diammonate, except that each of the three ammonia molecules has undergone dimeriza-

(8) Sidgwick, "The Electronic Theory of Valency," Oxford University Press, 1929, p. 194.

tion.⁹ This is equivalent to an assumption that one molecule of ammonia is coordinated with the ammonium ion, and that four molecules, or two diammonol molecules, with the trinitride ion. The formula of the pentammonate may on this basis be written $[\text{NH}_3\cdot\text{NH}_4]^+ [\text{N}_3\cdot 2(\text{NH}_3)_2]^-$.

Summary

Pressure-temperature-concentration relationships of the system ammonium trinitride-ammonia have been investigated over ranges from 0 to 4000 mm., -90 to $+30^\circ$, and 0 to 100% ammonia. Two solvates, *ammonium trinitride diammonate*, $\text{NH}_4\text{N}_3\cdot 2\text{NH}_3$, and *ammonium trinitride pentammonate*, $\text{NH}_4\text{N}_3\cdot 5\text{NH}_3$, both of which are white crystalline solids, have been obtained. The diammonate undergoes inversion into an ammonious salt at -9° ; the pentammonate undergoes inversion into the diammonate at -71° . The eutectic is located at -87° and 76% ammonia.

(9) In all probability liquid ammonia, like water, is associated, and contains such molecular species as NH_3 , *ammonol*, $(\text{NH}_3)_2$, *diammonol*, and $(\text{NH}_3)_3$, *triammonol*, analogous to *hydrol*, *dihydrol* and *trihydrol*.

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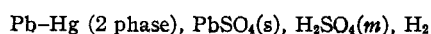
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Activity Coefficients of Sulfuric Acid at Temperatures from 0 to 50° ¹

BY JOSEPH SHRAWDER, JR., AND IRVING A. COWPERTHWAIT

Galvanic cells involving sulfuric acid have been studied by a number of investigators.² With few exceptions the investigations have been confined to the use of the mercury-mercurous sulfate electrode. While this electrode is reversible to sulfate ion and functions nicely in relatively concentrated solutions, the solubility of mercurous sulfate is such³ as to prohibit its use in solutions more dilute than approximately 0.005 molal. For the evaluation of E^0 it is desirable that measurements be obtained to a lower concentration.

The cell



(1) This paper is from a dissertation presented by Joseph Shrawder, Jr., to the Faculty of Pure Science of Columbia University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) (a) Brønsted, *Z. physik. Chem.*, **68**, 693 (1909); (b) Edgar, Thesis, Massachusetts Institute of Technology, 1912; (c) Lewis and Lacy, *THIS JOURNAL*, **36**, 804 (1914); (d) Randall and Cushman, *ibid.*, **40**, 393 (1918); (e) Baumstark, Dissertation, Catholic University of America, 1932.

(3) Harned and Sturgis, *THIS JOURNAL*, **47**, 945 (1925).

is well designed to provide the required measurements in the dilute range. The solubility of lead sulfate, 43.5 mg. per liter in pure water at 20° ,⁴ is sufficiently low in dilute acid to obviate any large correction from this source.

Previous attempts to measure the potential of the above cell have been made by Lewis and Brighton,⁵ Vosburgh and Craig,⁶ and Baumstark.^{2e} Of these, only Baumstark was able to secure reproducible results, the other workers reporting deviations of the order of 0.01 volt.

In the present work the electromotive force of this cell has been measured from 0 to 50° over the concentration range 0.02 to 0.001 *m*.

The methods which have been commonly employed for the extrapolation of electromotive force data to infinite dilution vary from simple graphical extrapolations, on the one hand, through a variety

(4) Purdum and Rutherford, *ibid.*, **55**, 3221 (1933).

(5) Lewis and Brighton, *ibid.*, **39**, 1906 (1917).

(6) Vosburgh and Craig, *ibid.*, **51**, 2009 (1929).