[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

A Revision of Some Normal Electrode Potentials

BY JOSEPH SHRAWDER, JR., I. A. COWPERTHWAITE AND V. K. LA MER

In a previous paper,[1] E^0 values from 0 to 50° have been presented for the cell

Pb-Hg (two phase), $PbSO_4(s)$, $H_2SO(m)$, H_2 (1)

Since the potential of the hydrogen electrode is, by definition, zero at all temperatures, the E^0 values of the above cell constitute the normal potentials of the lead two phase amalgam–lead sulfate electrode at the temperatures investigated. By combining these data with published values for other cell combinations, several revised normal electrode potentials have been obtained.

The mercury–mercurous sulfate normal electrode potential may be obtained by combining the E^0 for the above cell with the potential of the cell

Pb-Hg (two phase), $PbSO_4(s)$, $Na_2SO_4(m)$, $Hg_2SO_4(s)$,Hg(l) (2)

measured by Henderson and Stegeman,[2] and Carpenter.[3]

The normal potential of **zinc two phase amalgam** and of **zinc** may be obtained with the aid of the E^0 value given by Cowperthwaite and LaMer,[4] for the cell

Zn-Hg (two phase), $ZnSO_4(m)$, $PbSO_4(s)$, Pb-Hg (two phase) (3)

and the potential of zinc against zinc amalgam as given by Cohen.[5]

The normal potential of **cadmium two-phase amalgam** and of **cadmium** may be found by taking the E^0 value for the cell

Cd-Hg (two phase), $CdSO_4(m)$, $PbSO_4(s)$, Pb-Hg (two phase) (4)

given by La Mer and W. G. Parks,[6] and also the value of the potential of cadmium against cadmium amalgam as given by the same authors.[7]

From the indicated combinations, the following table of revised normal potentials has been constructed.

TABLE I

NORMAL ELECTRODE POTENTIALS AT 25°

	E^0_{298}	$-\Delta F^0_{298}$ per equivalent
Pb-Hg (two phase), $PbSO_4(s)$, SO_4^{--}	+0.3505	8088
Hg, $Hg_2SO_4(s)$, SO_4^{--}	− .6141	−14170
Zn-Hg (two phase), Zn^{++}	+ .7614	17569
Zn, Zn^{++}	+ .7620	17583
Cd-Hg (two phase), Cd^{++}	+ .3519	8120
Cd, Cd^{++}	+ .4024	9285

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[1] Shrawder and Cowperthwaite, THIS JOURNAL, **56**, 2340 (1934).

[2] Henderson and Stegeman, *ibid.*, **40**, 84 (1918).

[3] Carpenter, Thesis, Columbia University, 1934.

[4] Cowperthwaite and La Mer, THIS JOURNAL, **53**, 4333 (1931).

[5] Cohen, *Z. physik. Chem.*, **34**, 612 (1900).

[6] La Mer and Parks, THIS JOURNAL, **53**, 2040 (1931).

[7] Parks and La Mer, *ibid.*, **56**, 90 (1934).

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY AND THE CHEMICAL LABORATORY AT THE GEORGE WASHINGTON UNIVERSITY]

Behavior of the Hydronitrogens and their Derivatives in Liquid Ammonia. X. Equilibria in the System Hydrazine Trinitride–Ammonia[1,2]

BY D. H. HOWARD, JR., AND A. W. BROWNE

Investigation of the ternary system hydrazine–hydrogen trinitride–ammonia and of the three related binary systems, from the viewpoint of the phase rule, was projected many years ago in this Laboratory.[3] The system hydrazine–ammonia has been studied[4] throughout the entire range of composition, while the systems hydrazine–hydrogen trinitride,[5] and hydrogen trinitride–ammonia[1d,1i] have been investigated over ranges covering percentages of hydrogen trinitride from 0% to the percentage of that component present in the respective compounds hydrazine trinitride and ammonium trinitride.[6]

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[1] For the earlier articles of this series see THIS JOURNAL, (a) **33**, 1728, (b) 1734, (c) 1742 (1911); (d) **35**, 649, (e) 672 (1913); (f) **41**, 1769 (1919); (g) **55**, 1968, (h) 3211 (1933); (i) **56**, 2332 (1934).

[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 fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] Ref. 1a, p. 1728.

[4] Friedrichs, *Z. anorg. allgem. Chem.*, **127**, 221 (1923).

[5] (a) Thesis, "Hydronitric Acid and Hydrazine Trinitride," by Harold Eaton Riegger, 1910. A typed copy is on file in the Library of Cornell University, Ithaca, N. Y. (b) Dresser and Browne, THIS JOURNAL, **55**, 1963 (1933).

[6] Work is still to be done upon these two systems over ranges covering higher percentages of hydrogen trinitride; *i. e.*, upon the binary systems hydrazine trinitride–hydrogen trinitride, and ammonium trinitride–hydrogen trinitride.

The scope of the current research has been limited by maintaining a constant equimolecular ratio between the hydrazine and hydrogen trinitride, and thus virtually reducing the system to the category of binary systems. The work was undertaken, however, with a clear realization of the probability that hydrazine trinitride might undergo ammonolysis,[1a,1b] especially at higher temperatures, in liquid ammonia solution, as expressed by the equilibrium

$$N_2H_5N_3 + NH_3 \rightleftharpoons NH_4N_3 + N_2H_4$$

The objectives of the present investigation have therefore comprised not merely (1) the mapping of the pressure–composition, pressure–temperature and solubility curves for the system hydrazine trinitride–ammonia, and (2) the isolation of possible ammonates of hydrazine trinitride, but also (3) the charting of the field throughout which ammonolysis of hydrazine trinitride takes place.

Apparatus and Materials

The apparatus figured and described in an earlier article[1c] was employed in the current research. The source of ammonia and the method used for its purification were also identical with those already described.

The hydrazine trinitride was taken from the supply of this material prepared by Dr. A. L. Dresser, and was analyzed by the method used in his work,[5b] with the single modification that the silver trinitride was precipitated from a dilute solution of the original sample, appropriately buffered with sodium acetate and held at 0°. Under these conditions the silver ion is not perceptibly reduced by the hydrazine. This procedure obviates the necessity for distilling the hydronitric acid from the hydrazine salt prior to precipitation by silver nitrate.

Anal. (a) Subs., 0.0278. 0.0264. Calcd. for $N_2H_5N_3$: N_2H_4. 42.69. Found: N_2H_4, 42.93, 42.98. (b) Subs., 0.2141, 0.1539. AgN_3, 0.4240. 0.3046. Calcd. for $N_2H_5N_3$: HN_3, 57.31. Found: HN_3. 56.5. 56.4.

The Pressure–Concentration Isotherms.—Isotherms were investigated at 60, 50, 40, 30, 20. 12.5, 5, 0, −5.4, −9, −13.4, −20, −35 and −50°. Accurately weighed samples of hydrazine trinitride ranging from 0.3243 to 0.2142 g. were employed. The data are presented in Table I and typical curves are plotted in Fig. 1.

TABLE I

PRESSURE–CONCENTRATION DATA IN THE SYSTEM $N_2H_5N_3$–NH_3 (FIG. 1)

Concn., moles NH_3 per mole $N_2H_5N_3$	Press., mm.	Curve (if plotted) phases
	−50.0° Isotherm	
3.96	129	$2N_2H_5N_3 \cdot NH_3$, $NH_4N_3 \cdot 2NH_3$, satd. soln., vapor
4.34	132	
4.61	132	
4.88	134	
4.53	116	Dilute soln., vapor
4.87	129	
5.10	136	
5.38	147	
5.59	154	
5.80	160	
6.19	173	
	−35.0° Isotherm	
3.88	267	$2N_2H_5N_3 \cdot NH_3$, $NH_4N_3 \cdot 2NH_3$, satd. soln., vapor
3.96	268	
4.11	268	
4.16	268	
4.27	268	
4.16	263	$NH_4N_3 \cdot 2NH_3$, satd. soln., vapor
4.24	266	
4.31	269	
4.36	270	
4.38	271	
4.06	241	Dilute soln., vapor
4.18	249	
4.28	257	
4.33	261	
4.50	277	
4.73	297	
4.96	316	
	−20.0° Isotherm	
0.53	329	UV $2N_2H_5N_3 \cdot NH_3$, $NH_4N_3 \cdot 2NH_3$, satd. soln., vapor
.58	450	
.70	470	
.94	476	
1.23	478	
1.44	478	
1.64	479	
1.79	479	
2.05	480	
2.29	482	
2.44	481	
2.58	481	
2.69	481	
2.92	481	
3.04	482	
3.23	481	
3.41	481	
3.55	482	
3.63	485	VW $NH_4N_3 \cdot 2NH_3$, satd. soln., vapor
3.68	488	
3.73	490	
3.25	405	W′WX Dilute soln., vapor
3.40	428	
3.54	454	
3.68	478	
3.75	488	
3.85	507	
	−13.4° Isotherm	
2.64	619	QR $2N_2H_5N_3 \cdot NH_3$, $NH_4N_3 \cdot 2NH_3$, satd. soln., vapor
2.75	620	
2.90	619	
2.97	619	
3.07	619	
3.26	619	

TABLE I (*Continued*)

Concn., moles NH_3 per mole $N_2H_5N_3$	Press., mm.	Curve (if plotted) phases
3.21	608	R'RS $NH_4N_3\cdot 2NH_3$, satd. soln., vapor
3.30	617	
3.35	622	
3.40	625	
3.46	628	
3.51	631	
3.54	633	
3.57	635	
3.35	581	S'ST Dilute soln., vapor
3.44	604	
3.58	634	
3.61	642	
3.70	662	
3.78	680	
3.83	693	
3.98	731	
	−9.0° Isotherm	
2.10	722	$2N_2H_5N_3\cdot NH_3$, $NH_4N_3\cdot 2NH_3$, (NH_4N_3), satd. soln.. vapor
2.31	723	
2.49	724	
2.73	725	
2.87	725	
2.73	697	$NH_4N_3\cdot 2NH_3$, (NH_4N_3), satd. soln., vapor
3.06	732	
3.23	746	
3.38	757	
3.26	700	Dilute soln., vapor
3.39	737	
3.62	801	
3.76	842	
3.96	898	
4.16	954	
	−5.4° Isotherm	
2.38	815	LM $2N_2H_5N_3\cdot NH_3$, NH_4N_3, satd. soln., vapor
2.55	814	
2.72	815	
2.69	803	M'MN NH_4N_3, satd. soln., vapor
2.90	829	
3.08	848	
3.22	862	
3.35	875	
3.49	892	
3.39	858	N'NP Dilute soln., vapor
3.62	934	
3.81	995	
3.99	1064	
	0.0° Isotherm	
0.02	4.5	AB $N_2H_5N_3$, $2N_2H_5N_3\cdot NH_3$, vapor
.05	4.9	
.13	4.6	
.21	5.2	
.28	4.9	
.37	6.3	
.42	6.6	
.47	7.0	
0.50	24	BC $2N_2H_5N_3\cdot NH_3$. vapor
.50	42	
.50	111	
.50	149	
.50	180	
.50	272	
.50	316	
.50	409	
.50	468	
.50	488	
.50	536	
.50	610	
.50	633	
.51	746	
.50	758	
.51	770	
.52	829	
.51	849	
.54	889	
.53	894	
.55	923	CD $2N_2H_5N_3\cdot NH_3$, NH_4N_3, satd. soln., vapor
.57	933	
.59	942	
.63	947	
.69	951	
.79	956	
.96	959	
1.16	956	
1.34	957	
1.52	957	
1.69	958	
1.85	958	
2.02	959	
2.18	959	
2.35	959	
1.39	612	D'DE NH_4N_3, satd. soln.. vapor
1.52	679	
1.70	752	
1.86	810	
2.01	852	
2.15	888	
2.31	926	
2.44	947	
2.53	964	
2.60	977	
2.77	1004	
2.92	1027	
3.07	1048	
3.23	1068	
3.38	1088	
3.32	1048	E'EF Dilute soln., vapor
3.39	1075	
3.45	1101	
3.51	1125	
3.58	1153	
3.71	1205	
3.84	1264	
3.85	1258	
3.99	1315	
4.06	1344	
4.09	1362	

TABLE I (*Continued*)

Concn., moles NH_3 per mole $N_2H_5N_3$	Press., mm.	Curve (if plotted) phases
	+5.0° Isotherm	
1.70	1097	GH $2N_2H_5N_3\cdot NH_3$, NH_4N_3, satd. soln., vapor
1.86	1098	
1.97	1098	
2.09	1097	
2.14	1097	
2.17	1098	
2.15	1076	H'HJ NH_4N_3, satd. soln., vapor
2.26	1109	
2.34	1128	
2.48	1164	
2.61	1195	
2.76	1222	
2.88	1245	
3.00	1266	
3.16	1289	
3.04	1175	J'JK Dilute soln., vapor
3.12	1209	
3.23	1265	
3.35	1325	
3.46	1371	
3.56	1422	
3.69	1478	
3.80	1538	
	+12.5° Isotherm	
1.16	1288	$2N_2H_5N_3\cdot NH_3$, NH_4N_3, satd. soln., vapor
1.38	1291	
1.57	1292	
1.68	1293	
1.80	1238	NH_4N_3, satd. soln., vapor
1.88	1280	
2.03	1349	
2.20	1418	
2.37	1479	
2.55	1535	
2.72	1584	
2.84	1615	
2.99	1649	
3.13	1672	
3.06	1579	Dilute soln., vapor
3.18	1656	
3.31	1745	
3.40	1799	
3.50	1860	
	+20.0° Isotherm	
0.52	988	$2N_2H_5N_3\cdot NH_3$, vapor
.54	1135	
.57	1328	
.65	1403	$2N_2H_5N_3\cdot NH_3$, NH_4N_3, satd. soln., vapor
.73	1434	
.85	1454	
1.00	1460	
1.13	1464	
1.26	1464	
1.39	1466	
1.52	1467	
1.42	1276	NH_4N_3, satd. soln., vapor
1.51	1363	
1.59	1441	
1.68	1512	
1.80	1600	
1.99	1718	
2.17	1820	
2.39	1919	
2.58	1997	
2.74	2050	
2.93	2108	
2.97	2050	Dilute soln., vapor
3.04	2110	
3.11	2165	
3.17	2215	
3.23	2270	
3.28	2312	
3.38	2387	
	+30.0° Isotherm	
0.74	1581	$2N_2H_5N_3\cdot NH_3$, NH_4N_3, satd. soln., vapor
.88	1599	
1.04	1609	
1.22	1614	
1.08	1216	NH_4N_3, satd. soln., vapor
1.18	1401	
1.26	1528	
1.33	1630	
1.39	1726	
1.46	1840	
1.55	1940	
1.66	2088	
1.76	2190	
1.86	2280	
1.97	2369	
2.08	2447	
2.22	2536	
2.43	2665	
2.63	2771	
2.74	2822	
2.83	2800	Dilute soln., vapor
2.92	2904	
3.01	3007	
3.13	3158	
	+40.0° Isotherm	
0.67	1532	$2N_2H_5N_3\cdot NH_3$, NH_4N_3. satd. soln., vapor
.78	1563	
.80	1561	
.89	1574	
.95	1578	
1.00	1580	
0.97	1347	NH_4N_3, satd. soln., vapor
1.00	1460	
1.05	1611	
1.06	1663	
1.11	1739	
1.16	1821	
1.18	1938	
1.25	2090	
1.32	2218	

TABLE I (*Concluded*)

Concn.. moles NH_3 per mole $N_2H_5N_3$	Press., mm.	Curve (if plotted) phases
	+50.0° Isotherm	
0.51	941	$2N_2H_5N_3 \cdot NH_3$, vapor
.53	1090	
.58	1191	$2N_2H_5N_3 \cdot NH_3$, NH_4N_3, satd. soln., vapor
.64	1225	
.74	1251	
.76	1022	
.78	1185	
.81	1259	
.83	1336	NH_4N_3, satd. soln., vapor
.87	1484	
.90	1650	
.94	1834	
1.01	2001	
	+60.0° Isotherm	
0.12	7.6	
.19	29	
.22	41	
.29	79	
.43	261	NH_4N_3, satd. soln., vapor
.50	399	
.55	556	
.63	848	
.70	1177	
.77	1508	
.84	1806	
.89	2130	

From these data it is obvious that one solvate only of hydrazine trinitride is capable of existence. This is the hemiammonate, $2N_2H_5N_3 \cdot NH_3$, a white, crystalline solid which exhibits extreme hygroscopicity on exposure to the air. In the absence of moisture, however, it is very stable, and, in equilibrium with solid hydrazine trinitride, has a surprisingly low vapor tension with respect to ammonia, as shown by the curves AB (Fig. 1) and AB (Fig. 2). Because of its low vapor tension, the hemiammonate may be prepared without difficulty by condensing liquid ammonia upon solid hydrazine trinitride, permitting the solution to evaporate to dryness, and warming to room temperature.

In liquid ammonia, however, the hemiammonate undergoes ammonolysis, to an extent that varies directly with temperature and with concentration of ammonia. At 0° (Fig. 1), for example, the compound is stable toward ammonia along BC until a pressure of 960 mm. is reached. Along CD ammonolysis takes place progressively in accordance with the equation presented in an earlier paragraph. As a result of this ammonolysis, the ratio of hydrazine to hydrogen trinitride is no longer constant in each phase in which these compounds are present, as would be the case if the compound hydrazine trinitride were not decomposed. The system, which up to this point was of binary character, becomes ternary, and four phases co-exist along CD. These are solid hemiammonate, solid ammonium trinitride, saturated solution, and vapor.

This solution is saturated with respect to each of the two solids, and the ratio of ammonia to hydrazine and to hydrogen trinitride remains constant in this phase. As ammonia is added to the system the amount of solid hemiammonate decreases, while that of solid ammonium trinitride increases, to preserve this ratio. At D, the hemiammonate has dissolved completely. Along DE, the three remaining phases, solid ammonium trinitride, saturated solution, and vapor are in equilibrium, and the ternary system becomes bivariant. As ammonia is added, the solution, while remaining saturated toward ammonium trinitride, becomes progressively more dilute toward the hemiammonate (*i. e.*, toward hydrazine trinitride), and consequently the pressure increases. At E, the solid ammonium trinitride is completely dissolved, and along EF the dilute solution and vapor constitute a system that may be regarded as binary, in view of the circumstance that hydrazine and hydrogen trinitride are again present in equimolecular ratio in the single condensed phase.

This rationale of the system finds confirmation in the observations of its behavior in the metastable state. As ammonia is withdrawn along ED, a metastable prolongation of this curve to D′ may be realized. Only one solid, ammonium trinitride, is present under these conditions. A sudden, spontaneous separation of a second solid phase, the hemiammonate, is invariably observed to occur, with coincident rise of pressure to that of the four-phase system (CD).

Another manifestation of metastable equilibrium is portrayed along EE′, where the binary system becomes metastable with respect to the ternary system, or, in other words, the solution becomes supersaturated toward ammonium trinitride.

As a consequence of the low vapor tension of the hemiammonate the vertical curve OA, representing equilibria between solid anammonous hydrazine trinitride and vapor is very short, and no actual points have been located experimen-

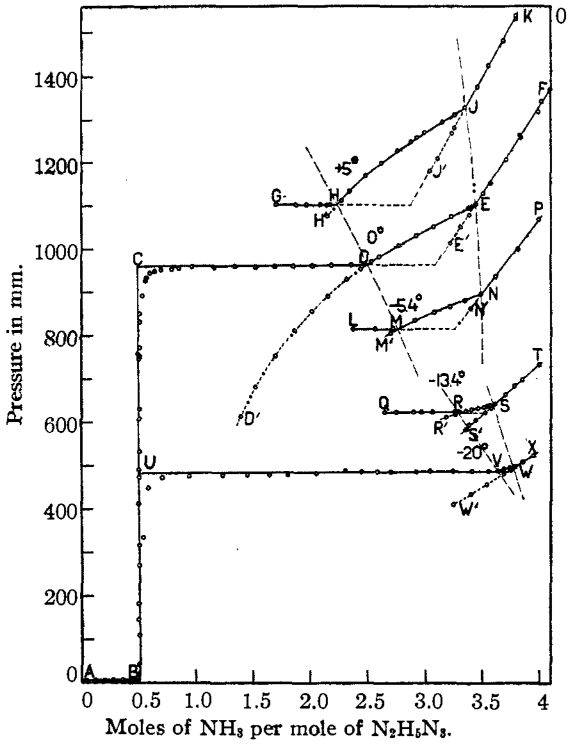

Fig. 1.—Pressure-concentration isotherms of the system hydrazine trinitride-ammonia.

Legend	Phases present	Order of system
	−20° Isotherm	
UV	$2N_2H_5N_3 \cdot NH_3$, $NH_4N_3 \cdot 2NH_3$, satd. soln., vapor	Ternary
VW	$NH_4N_3 \cdot 2NH_3$, satd. soln., vapor	Ternary
W'W	Supersatd. soln., vapor	Binary
WX	Dilute soln., vapor	Binary
	−13.4° Isotherm	
QR	$2N_2H_5N_3 \cdot NH_3$, $NH_4N_3 \cdot 2NH_3$, satd. soln., vapor	Ternary
R'R	$NH_4N_3 \cdot 2NH_3$, satd. soln., vapor (metastable)	Ternary
RS	$NH_4N_3 \cdot 2NH_3$, satd. soln., vapor	Ternary
S'S	Supersatd. soln., vapor	Binary
ST	Dilute soln., vapor	Binary
	−5.4° Isotherm	
LM	$2N_2H_5N_3 \cdot NH_3$, NH_4N_3, satd. soln., vapor	Ternary
M'M	NH_4N_3, satd. soln., vapor (metastable)	Ternary
MN	NH_4N_3, satd. soln., vapor	Ternary
N'M	Supersatd. soln., vapor	Binary
NP	Dilute soln., vapor	Binary
	0° Isotherm	
OA	$N_2H_5N_3$, vapor	Binary
AB	$N_2H_5N_3$, $2N_2H_5N_3 \cdot NH_3$, vapor	Binary
BC	$2N_2H_5N_3 \cdot NH_3$, vapor	Binary
CD	$2N_2H_5N_3 \cdot NH_3$, NH_4N_3, satd. soln., vapor	Ternary
D'D	NH_4N_3, satd. soln., vapor (metastable)	Ternary
DE	NH_4N_3, satd. soln., vapor	Ternary
E'E	Supersatd. soln., vapor	Binary
EF	Dilute soln., vapor	Binary
	+5° Isotherm	
GH	$2N_2H_5N_3 \cdot NH_3$, NH_4N_3, satd. soln., vapor	Ternary
H'H	NH_4N_3, satd. soln., vapor (metastable)	Ternary
HJ	NH_4N_3, satd. soln., vapor	Ternary
J'J	Supersatd. soln., vapor	Binary
JK	Dilute soln., vapor	Binary

tally. When as small an amount as 1 mg. of ammonia was introduced into the system containing the solid *in vacuo* the resultant pressure exceeded the decomposition pressure of the hemiammonate, and a point along AB was obtained after equilibrium had been reached.

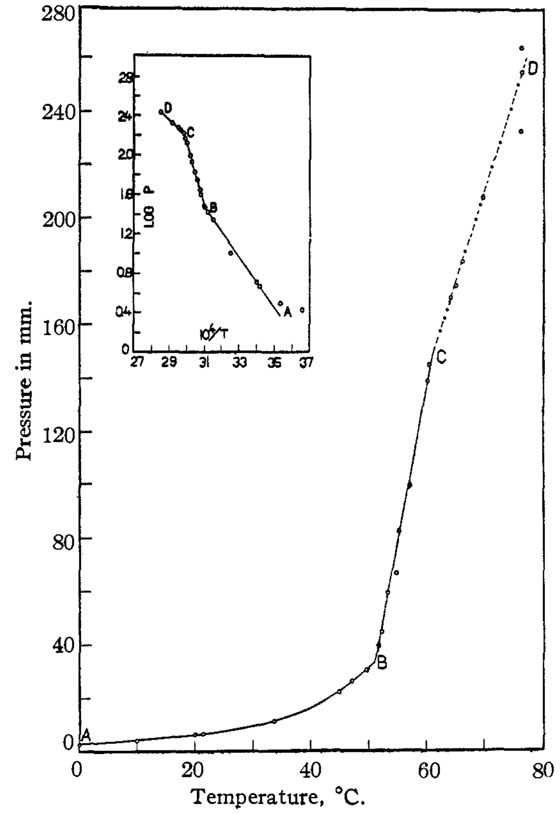

Fig. 2.—Pressure-temperature curves of the system hydrazine trinitride-ammonia.

Legend	Phases present	Order of system
AB	$N_2H_5N_3$, $2N_2H_5N_3 \cdot NH_3$, vapor	Binary
BC	$N_2H_5N_3$, NH_4N_3, satd. soln., vapor	Ternary
CD	NH_4N_3, satd. soln., vapor (bivariant)	Ternary

The isotherms at +5 and −5.4° are similar as regards phases present along analogous portions of the curves, with that at 0°. Those at temperatures below −9°, the inversion temperature of ammonium trinitride diammonate to anammonous salt, however, differ in that the diammonate takes the place of anammonous salt. This accounts for the intersection of the dotted lines WS (part of the solubility curve for ammonium trinitride diammonate) and JEN (part of the solubility curve of ammonium trinitride) (Fig. 1) at a temperature[7] somewhat below −9°, and also for the break in the curves NOP and EHK (Fig. 3). The corresponding intersection of the dotted lines VR and HDM (Fig. 1), and breaks in NQR and EFG (Fig. 3), may be similarly explained by the presence of the diammonate at temperatures below its inversion point.

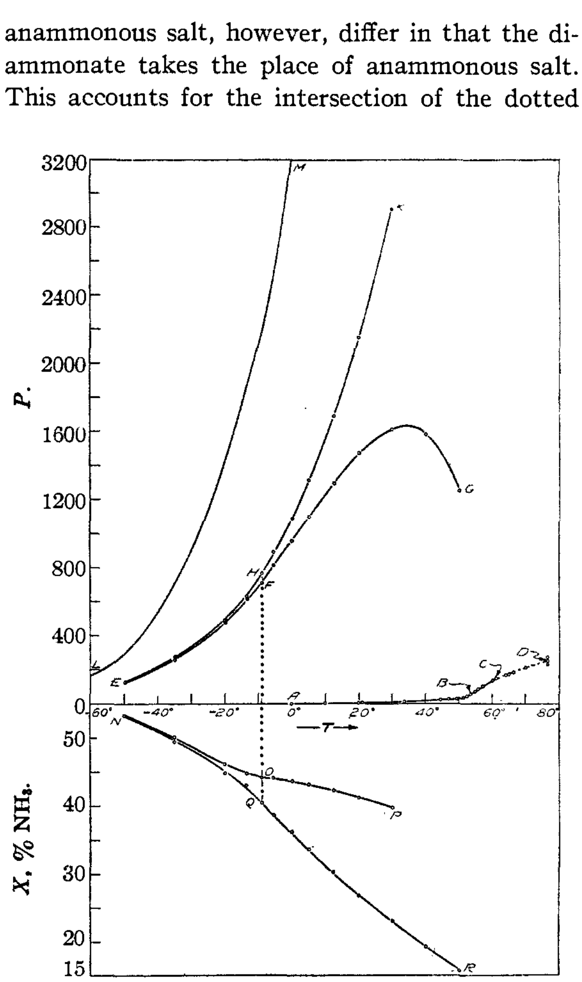

Fig. 3.—Pressure–temperature and temperature–concentration curves of the system hydrazine trinitride–ammonia.

Legend	Phases present	Order of system
LM	Liquid NH_3, vapor	Unitary
EH	$NH_4N_3\cdot 2NH_3$, satd. soln., vapor	Ternary
HK	NH_4N_3, satd. soln., vapor	Ternary
EF	$2N_2H_5N_3\cdot NH_3$, $NH_4N_3\cdot 2NH_3$, satd. soln., vapor	Ternary
FG	$2N_2H_5N_3\cdot NH_3$, NH_4N_3, satd. soln., vapor	Ternary
AB	$N_2H_5N_3$, $2N_2H_5N_3\cdot NH_3$, vapor	Binary
BC	$N_2H_5N_3$, NH_4N_3, satd. soln., vapor	Ternary
CD	NH_4N_3, satd. soln., vapor (bivariant)	Ternary
NO	$NH_4N_3\cdot 2NH_3$, satd. soln., vapor	Ternary
OP	NH_4N_3, satd. soln.. vapor	Ternary
NQ	$2N_2H_5N_3\cdot NH_3$, $NH_4N_3\cdot 2NH_3$, satd. soln.. vapor	Ternary
QR	$2N_2H_5N_3\cdot NH_3$, NH_4N_3, satd. soln., vapor	Ternary

Against the possible contention that these phenomena may be ascribed to the influence of an ammonate of hydrazine trinitride higher than the hemiammonate, may be cited the data plotted on the −20° isotherm (Curve UV, Fig. 1), which were sought for the express purpose of settling this question.

The isotherm at 60° differs from all others in that it lies above the inversion temperature of the hemiammonate.

Pressure–Temperature Curves

Upon a sample of hydrazine trinitride weighing 0.3242 g. an amount of liquid ammonia sufficient to dissolve it at 0° was condensed. Ammonia was then withdrawn until its concentration in the condensed phases was slightly lower than 0.5 mole per mole of the salt. Vapor pressure determinations for this system, which was composed of hydrazine trinitride, hemiammonate and vapor, were made from 0° to the inversion temperature of the solvate, or to somewhat above 50°. Pressure–temperature data for systems containing other phases than these have been read from the isotherms.

The data are recorded in Tables II and III, and plotted in Figs. 2 and 3.

Table II

Pressure–Temperature Data of the System $2N_2H_5N_3\cdot NH_3$–$N_2H_5N_3$–NH_3 (Curve AB, Figs. 2 and 3)

Temp., °C.	Pressure, mm. Observed	Pressure, mm. Calcd.	Difference, mm.
0.0	2.7	1.0	+1.7
10.0	3.2	2.3	+0.9
20.1	5.4	4.7	+ .7
21.2	5.7	5.1	+ .6
33.8	11.2	11.8	− .6
44.7	22.4	23.1	− .7
47.0	26.8	26.4	+ .4
49.6	30.6	30.8	− .2

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(7) The inversion temperature of ammonium trinitride diammonate to the anammonous salt has already been investigated.[10] The fact that this temperature was found to be lower than −9° in the present investigation is due to the presence of hydrazine trinitride, which acts as an impurity in the system It has been observed that the inversion point of any solvate may be depressed by the presence of a foreign substance in the melt. For example, the inversion point of sodium sulfate decahydrate may be lowered several degrees by the addition of an appropriate amount of sucrose.

TABLE III

PRESSURE–TEMPERATURE DATA OF THE SYSTEM $N_2H_5N_3$–NH_3 (FIGS. 2 AND 3)

Temp., °C.	Press., mm.	Curve (phases)
51.4	38.9	BC $N_2H_5N_3$, NH_4N_3, satd. soln., vapor
52.2	44.8	
53.4	59.9	
55.6	83.8	
54.8	67.9	
57.1	100	
60.2	139	
60.6	146	
63.8	171	CD NH_4N_3, satd. soln., vapor
64.7	175	
66.3	184	
70.0	209	
76.3	255	
76.3	265	
76.3	233	
−50.0	133	EF $2N_2H_5N_3 \cdot NH_3$, $NH_4N_3 \cdot 2NH_3$, satd. soln., vapor
−35.0	267	
−20.0	480	
−13.4	621	
− 9.0	725	FG $2N_2H_5N_3 \cdot NH_3$, NH_4N_3, satd. soln., vapor
− 5.4	815	
0.0	960	
5.0	1098	
12.5	1293	
20.0	1470	
30.0	1614	
40.0	1580	
50.0	1255	
−50.0	133	EH $NH_4N_3 \cdot 2NH_3$, satd. soln., vapor
−35.0	271	
−20.0	490	
−13.4	634	
− 9.0	767	HK NH_4N_3, satd. soln., vapor
− 5.4	888	
0.0	1090	
5.0	1317	
12.5	1688	
20.0	2155	
30.0	2900	

The empirical equation expressing the logarithmic curve for the system hydrazine trinitride, hemiammonate and vapor is

$$\log P = -(2620/T) + 9.61$$

It is to be noted that at temperatures above the inversion point of the hemiammonate (B, Figs. 2 and 3) all constituents of the system become appreciably volatile, especially when the concentration of ammonia is low. Therefore the data plotted on Curves BC and CD (Figs. 2 and 3) are not of as high a degree of certitude as those observed at lower temperatures. Moreover, the curve CD is merely one of an indefinite number of similar curves, extending outward from C (the melting point of hydrazine trinitride in this system), in a direction dependent upon the concentration of ammonia in the system. Fusion of the hydrazine trinitride increases the degree of freedom of the system by one. One point on each of two such curves is shown near D. The point above D was obtained by addition, and that below D by withdrawal of ammonia from the system.

Temperature–Concentration Curves.—The data listed in Table IV and plotted in Fig. 3 were obtained during the isothermal investigation of the system.

TABLE IV

TEMPERATURE–CONCENTRATION OR SOLUBILITY DATA OF THE SYSTEM $N_2H_5N_3$–NH_3

Temp., °C.	Soly. in % NH_3	Curves and phases (Fig. 3)
−50.0	53.29	NO $NH_4N_3 \cdot 2NH_3$, satd. soln., vapor
−35.0	50.05	
−20.0	46.03	
−13.4	44.86	
− 9.0	44.26	OP NH_4N_3, satd. soln., vapor
− 5.4	44.12	
0.0	43.68	
5.0	43.09	
12.5	42.27	
20.0	41.20	
30.0	39.76	
−50.0	53.29	NQ $2N_2H_5N_3 \cdot NH_3$, $NH_4N_3 \cdot 2NH_3$, satd. soln., vapor
−35.0	49.38	
−20.0	44.67	
−13.4	43.09	
− 9.0	40.49	QR $2N_2H_5N_3 \cdot NH_3$, NH_4N_3, satd. soln., vapor
− 5.4	38.66	
0.0	36.36	
5.0	33.69	
12.5	30.23	
20.0	26.75	
30.0	23.05	
40.0	19.24	
50.0	15.68	

General Considerations

A three-dimensional view of the system by Cavalier's projection is shown in Fig. 4. The vertical area ABC represents the binary system, solid hydrazine trinitride and vapor; ACDE, the binary system, hydrazine trinitride, its hemiammonate, and vapor; EDFGHE, the binary system hydrazine trinitride hemiammonate, and vapor. The field enclosed by EHGIKE is that of the ternary system hemiammonate, ammonium trinitride, saturated solution, and vapor; GFLI, the ternary system, hemiammonate, ammonium trinitride diammonate, saturated solution, and vapor; NEKIMPQ, the ternary system, ammonium trinitride, saturated solution, and vapor; ILM, the ternary system, ammonium trinitride diammonate, saturated solution, and vapor; PMLRS, the binary system, dilute solution and vapor.

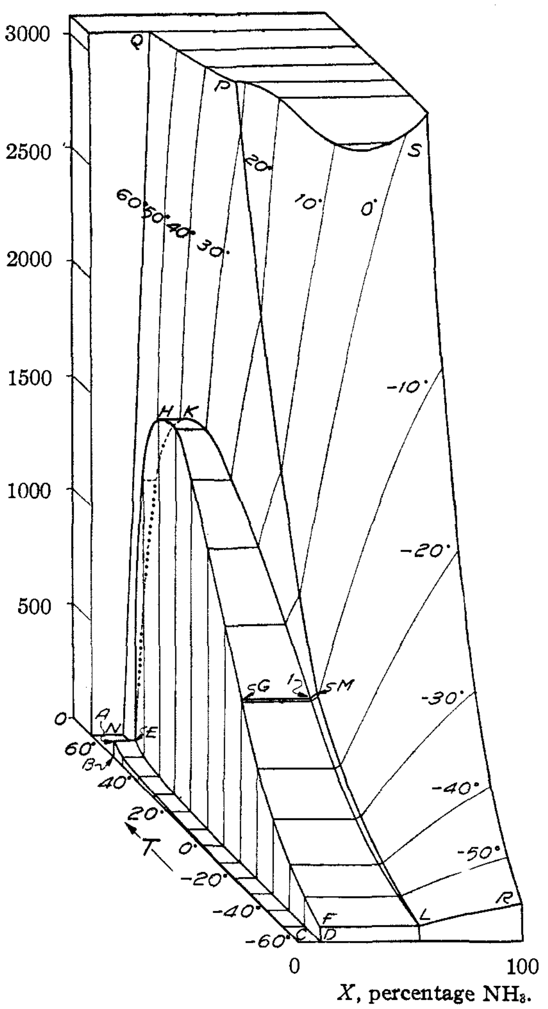

Fig. 4.—Three-dimensional view of the system hydrazine trinitride–ammonia by Cavalier's projection.

Legend	Phases present	Order of system
ABC	$N_2H_5N_3$, vapor	Binary
ACDE	$N_2H_5N_3$, $2N_2H_5N_3 \cdot NH_3$, vapor	Binary
EDFGHE	$2N_2H_5N_3 \cdot NH_3$, vapor	Binary
EHGIKE	$2N_2H_5N_3 \cdot NH_3$, NH_4N_3, satd. soln., vapor	Ternary
GFLI	$2N_2H_5N_3 \cdot NH_3$, $NH_4N_3 \cdot 2NH_3$, satd. soln., vapor	Ternary
NEKIMPQ	NH_4N_3, satd. soln., vapor	Ternary
ILM	$NH_4N_3 \cdot 2NH_3$, satd. soln., vapor	Ternary
PMLRS	Dilute soln., vapor	Binary

Identification of the solid phase or phases present at any time throughout the investigation was easily effected by a combination of observation and inference. The separation of ammonium trinitride or its diammonate during the isothermal studies was attended by a continuous fall in pressure as more and more separated, which would not have been the case had hydrazine trinitride or any of its ammonates separated. The appearance of each solid corresponded to its description in earlier articles.[1d,1i] Furthermore, when a system thought to contain ammonium trinitride was heated above 75.4°, the melting point of hydrazine trinitride,[5b] the solid persisted. Since this temperature is well above that of the inversion of the hemiammonate of hydrazine trinitride (*vide supra*), the only solid now capable of existence is ammonium trinitride. Moreover, upon withdrawal of ammonia from the vapor phase, the solid ammonium trinitride was observed to go into solution as ammonia distilled from the liquid phase. Breaks in the pressure–temperature and temperature–concentration curves just below −9°, as discussed above, indicated clearly whether the diammonate of ammonium trinitride or the anammonous salt had separated. Separation of hydrazine trinitride hemiammonate in the presence of solid ammonium trinitride or its solid diammonate has already been discussed. Below the inversion point of the hemiammonate, the presence of anammonous hydrazine trinitride was observed only when insufficient ammonia was present to convert it entirely to the hemiammonate. Addition at room temperature of such amounts of ammonia to the anammonous salt resulted in the evolution of heat, a swelling of the salt, and a rapid absorption of ammonia. Since the condensed phases remained "dry," and since isothermal additions of ammonia up to 0.5 mole of ammonia in the condensed phases per mole of hydrazine trinitride failed to cause any increase in the equilibrium pressure, there was no doubt as to the reality of the ammonation of the salt.

One of the interesting features of the current investigation has been the determination and plotting of definite boundaries between the fields of solvation and solvolysis, or between the fields of existence of solvates and their solvolytic products, or, in this particular case, between binary and ternary systems. For example, the two curves EHGF and PML (Fig. 4) enclose the four ternary systems (two univariant, and two bivariant) studied. It is believed that the procedure adopted in this work might well be applied to the investigation of numerous other systems, containing hydrates, ammonates or other solvates, either pure or mixed.

Summary

Pressure–temperature–concentration relations of the binary system, hydrazine trinitride–ammonia, and of other parts of the ternary system hydrazine–hydrogen trinitride–ammonia, have been investigated over ranges from 0 to 3200 mm., −50 to +80°, and 0 to 100% ammonia.

Hydrazine trinitride hemiammonate, $2N_2H_5N_3 \cdot NH_3$, the only solvate of the hydrazine salt found, is an extremely deliquescent, stable, white, crystalline solid, with vapor tension of ammonia of 5 mm. at 20°, and inversion point somewhat above 50°. In liquid ammonia it undergoes ammonolysis to an extent that varies directly with temperature and with concentration of ammonia

$$2N_2H_5N_3 \cdot NH_3 + NH_3 \rightleftharpoons 2NH_4N_3 + 2N_2H_4 \text{ (above } -9°)$$
$$2N_2H_5N_3 \cdot NH_3 + 5NH_3 \rightleftharpoons 2(NH_4N_3 \cdot 2NH_3) + 2N_2H_4 \text{(below } -9°)$$

Definite boundaries between the fields of solvation and solvolysis have been determined and plotted.

ITHACA, N. Y. RECEIVED AUGUST 16, 1934

[CONTRIBUTION FROM THE FERTILIZER INVESTIGATIONS UNIT, BUREAU OF CHEMISTRY AND SOILS, UNITED STATES DEPARTMENT OF AGRICULTURE]

The Solubility of Hydrogen in Liquid Ammonia at 25, 50, 75 and 100° and at Pressures to 1000 Atmospheres

BY R. WIEBE AND T. H. TREMEARNE

The investigation leading to this report is a continuation of the work in this Laboratory on the ammonia–hydrogen–nitrogen system. Larson and Black[1] measured the solubility of a 3:1 hydrogen-nitrogen mixture in liquid ammonia through a temperature range of −25.2 to +22.0° and at pressures of 50, 100 and 150 atmospheres. Wiebe and Tremearne[2] determined the solubility of nitrogen in liquid ammonia at 25° and at pressures to 1000 atmospheres. The solubility apparatus and procedure have been described in the preceding paper. The method had previously been checked by making a few determinations of the solubility of nitrogen in water. The results were in very good agreement with those obtained by the bubbling method.[3]

The hydrogen contained 0.1% of nitrogen and the synthetic ammonia 0.02% of water. A new 1500 atmosphere piston gage designed by J. R. Dilley of this Laboratory was used. This gage was calibrated against the 200 atmosphere gage previously described.[4] The latter was in turn compared with the piston gage of the Bureau of Standards.[5] For several pressures the maximum variation in the calculated effective area of the 200 atmosphere piston was less than two parts in 10,000 and for the 1500 atmosphere gage the variation was less than one part in 10,000.

At 100° the machine steel (0.15–0.25% C) used for the construction of the high pressure needle valves[6] became porous at the higher pressures. The ammonia–hydrogen mixture passed freely through the steel walls of the valves in numerous places.[7] A fine-grained chrome–vanadium steel (S. A. E. 6145) was secured from the Washington Navy Yard at the recommendation of Mr. L. Jordan of the Bureau of Standards and gave complete satisfaction as a material for making the valves.

Discussion of Results

The results are plotted in Fig. 1. Pressures are given in international atmospheres, the local acceleration of gravity being 980.049. The solubility evidently increases decidedly with

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(1) Larson and Black, *Ind. Eng. Chem.*, **17**, 715 (1925).

(2) R. Wiebe and T. H. Tremearne, THIS JOURNAL, **55**, 975 (1933).

(3) R. Wiebe, V. L. Gaddy and Conrad Heins, Jr., *Ind. Eng. Chem.*, **24**, 927 (1932), Table II.

(4) E. P. Bartlett, H. L. Cupples and T. H. Tremearne, THIS JOURNAL, **50**, 1275 (1928).

(5) C. H. Meyers and R. S. Jessup, *Bureau of Standards J. of Res.*, **6**, 1061 (1931).

(6) J. R. Dilley and W. L. Edwards, U. S. Dept. of Agriculture Circular No. 61; "Fixed Nitrogen," Edited by Harry A. Curtis, Chapter X, American Chemical Society Monograph Series, The Chemical Catalog Co., Inc., New York, 1932.

(7) For work on the action of hydrogen on various steels see, *e. g.*, Inglis and Andrews, *Engineering*, **136**, 613 (1933).