Table II. Tie-Line Data at 25° C.

n-Propyl Alcohol, Per Cent			
In hexamethyldisiloxane layer	In water layer	In hexamethyldisiloxane layer	In water layer
0.1	10.0	6.8	47.6
1.2	15.3	9.0	49.7
1.9	22.0	10.8	53.8
2.4	28.8	14.5	57.4
3.0	35.6	18.6[a]	59.3[a]
3.9	38.2	23.5[a]	60.3[a]
4.9[a]	43.7[a]	30.4[a]	59.2[a]

[a] Values determined from Bachman plot of tie-line data by extrapolation and interpolation.

boundary or binodal curve. Figure 2 presents the variation of refractive index of mixtures of the same components as a function of the same binodal curve compositions and Figure 3 is a similar plot of density.

The data for the Bachman (*1*) plot (Figure 4) were obtained by preparing equilibrium liquid phase mixtures of the ternary system, allowing them to separate, and analyzing each layer separately by its density. The amount of each component present in the total mixture was predetermined by weighing and was used as a check on the tie-line data. From a knowledge of the density of each layer the weight per cents were determined using the data in Figure 3.

The isothermal phase diagram (Figure 1) was plotted using the weight per cents of the components determined as described above. Tie lines (Table II) were determined from experimental data and from interpolation and extrapolation of the Bachman plot.

ACKNOWLEDGMENT

The services of Donald Riggs, Myron Lindsey, Kenneth Davis, Leo Bondurant, Wayne Stevenson, Kenneth English, and Kay Fletcher, undergraduate students, in the experimental phases of this investigation are gratefully acknowledged.

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RECEIVED for review August 4, 1958. Accepted November 21, 1958.

Solubility Measurements on the Systems Ammonium, Sodium, and Potassium Perchlorate and Ammonium, Sodium, and Potassium Chloride

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The solubilities of ammonium chloride, potassium chloride, sodium chloride, ammonium perchlorate, potassium perchlorate, and sodium perchlorate at -33°, 0°, 25°, and 50° C. in liquid ammonia have been determined as well as the solubilities of the salt pairs and the ternary mixtures necessary to prepare the quaternary phase diagrams for the two chemical processes:

$$NaClO_4 + NH_4Cl \rightleftarrows NH_4ClO_4 + NaCl \quad (1)$$

$$\text{and } KClO_4 + NH_4Cl \rightleftarrows NH_4ClO_4 + KCl \quad (2)$$

These equilibrium diagrams show the possibility of carrying out the above processes in liquid ammonia.

The research of Grubb, Chittum, and Hunt (*1*), Hunt (*2*), Hunt and Boncyk (*3*), Hunt and Larsen (*4*), Johnson and Krumboltz (*5*), Linhard (*6*), Linhard and Stephan (*7*), Patscheke (*8*), Patscheke and Tanne (*9*), Plank and Hunt (*10*), and Ritchey and Hunt (*11*) indicates that Reactions 1 and 2 may be carried out in liquid ammonia at temperatures ranging from -33° to 50° C. Because sodium chloride and potassium chloride are relatively insoluble, these reactions should go nearly to completion. By controlling the concentrations the type of ammonium perchlorate crystal can be regulated and ammonium perchlorate can be prepared with physical properties suitable for use as an oxidizing agent in solid propellants.

EXPERIMENTAL PROCEDURE

Two types of apparatus were used for measuring the solubilities of the salts in liquid ammonia (Figures 1 and 2). The apparatus shown in Figure 1 could also be used for measuring the vapor pressures of the solutions.

Process A. This apparatus was evacuated and heated to drive out moisture. A weighed amount of salt was placed in the bulb with a glass-covered iron stirrer. The proper amount of salt was previously determined in a trial run. The apparatus was again pumped out to remove air and moisture. Dry ammonia in excess was then condensed on the salt and in the bulb labeled ammonia. If the vapor pressure of the solution is low, no ammonia is condensed in the latter. The apparatus was cooled with dry ice and carbon tetrachloride for the condensation process. With sufficient ammonia in both bulbs, valve 1 was closed and the system evacuated to remove hydrogen.

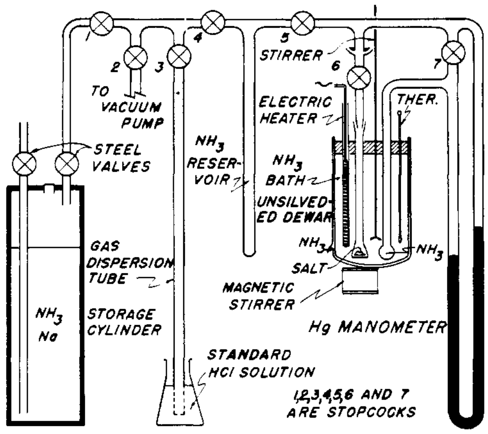


Figure 1. Solubility and vapor pressure apparatus

Table I. Solubilities and Vapor Pressures in Liquid Ammonia

Salt	Temperature, °C. -33	0	25	50
NaCl				
A[a]	3.29	12.60	4.50	1.2
B[c]	0.564	2.16	0.77	0.206
C[d]	754	3118		
KCl				
A	0.191	0.129	0.096	0.075
B	0.0256	0.0172	0.013	0.01
C	759.6	3219		
NH_4Cl				
A	14.69	63.6	130.4	124.0
B	2.75	11.90	24.4	23.2
C	728	2471	3140	
$NaClO_4$				
A	278.3	304.3	318.3	328.0
B	22.7	24.8	26.0	26.75
C	101	161	446	1010
$KClO_4$				
A	39.55	47.46	48.1	48.4
B	2.86	3.42	3.47	3.49
C	716.5	2856		
NH_4ClO_4				
A	221.3	240.5	243.3	254.77
B	18.8	20.0	20.7	21.65
C	146	337	939	1973

A. Grams per 100 grams.
B. Moles per 1000 grams.
C. Vapor pressure in mm. of mercury.

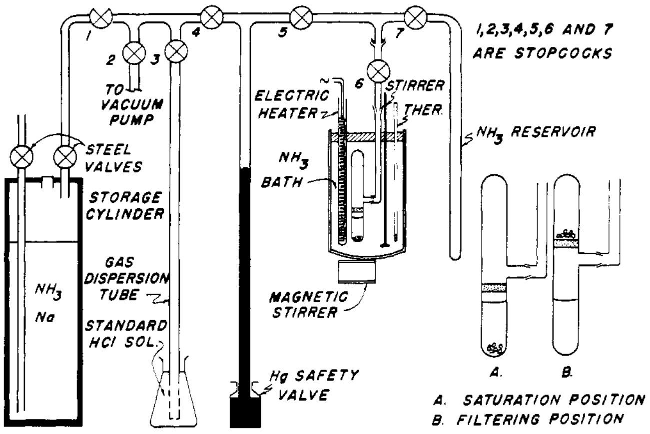
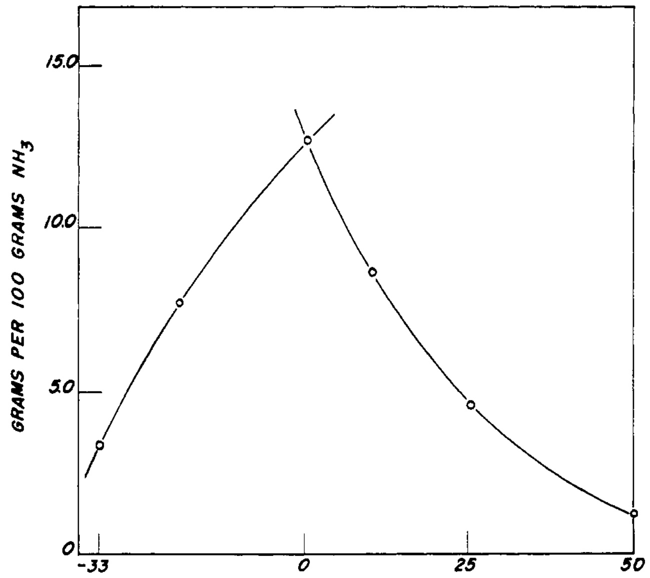


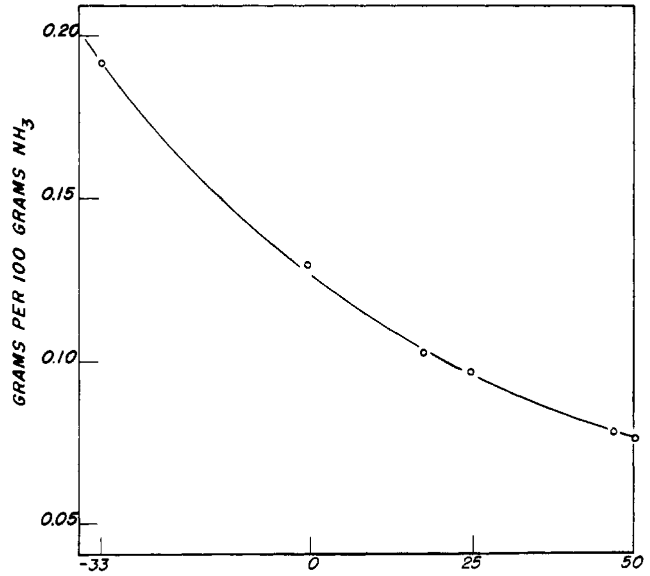
Figure 2. Alternative solubility apparatus

Hydrogen was produced by drying the ammonia with sodium. Hydrogen is insoluble in ammonia. Valve 3 was kept closed. Then valves 5 and 7 were closed and the dry ice bath changed to an ammonia bath for -33° C. determinations, an ice and water bath for 0° C. and a water bath for 25° and 50° C. determinations. The temperature was carefully regulated by means of a heater, stirrer, and thermometer as shown. When the system comes to equilibrium as proved by a constant vapor pressure, the vapor pressure is read. Then with valves 1, 2, 3, and 4 closed and 5 and 6 open, ammonia was con-

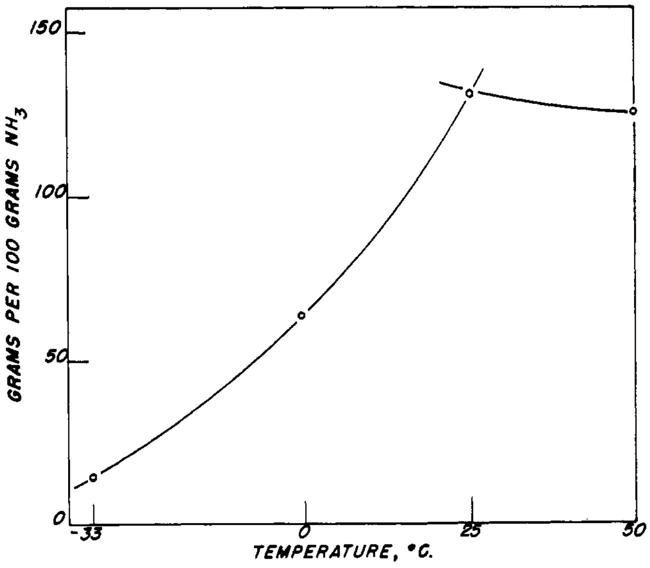
Solubility Diagrams



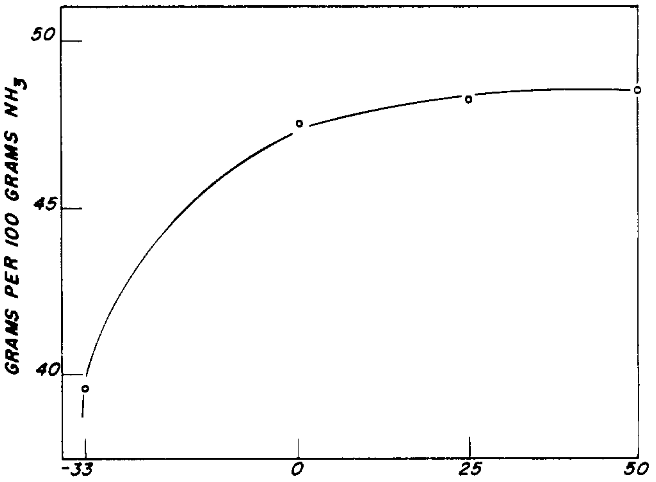
Sodium chloride in ammonia



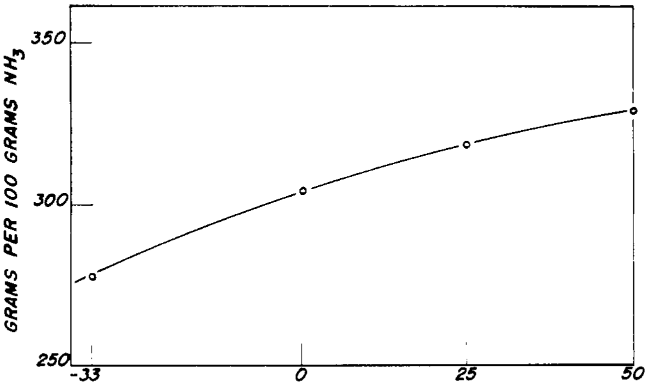
Potassium chloride in ammonia



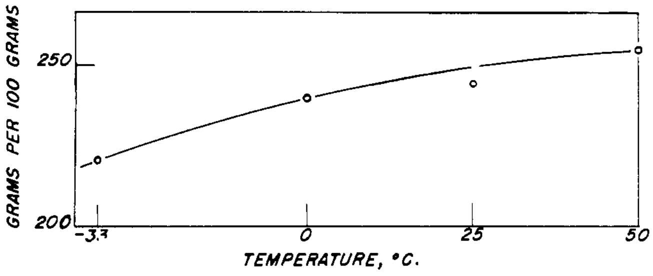
Ammonium chloride in ammonia



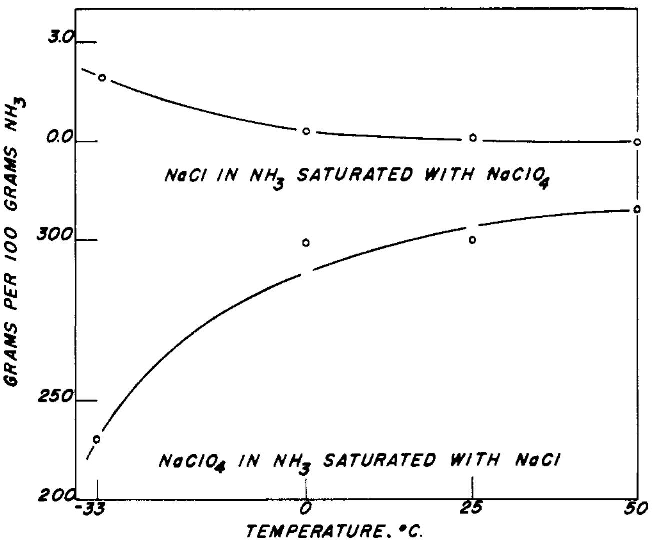
Potassium perchlorate in ammonia

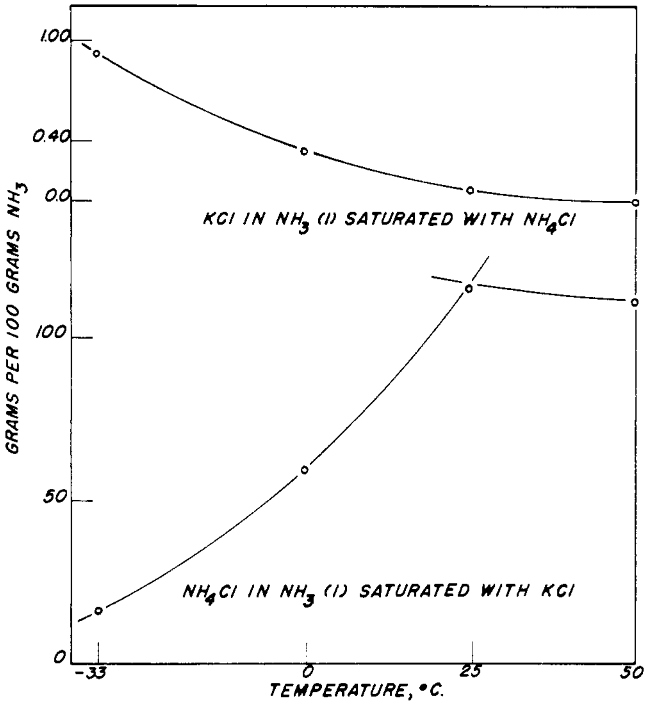


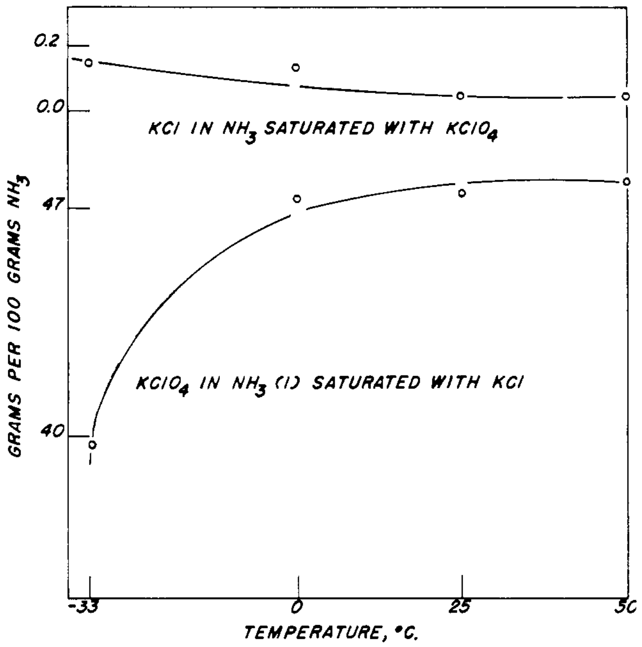
Sodium perchlorate in ammonia

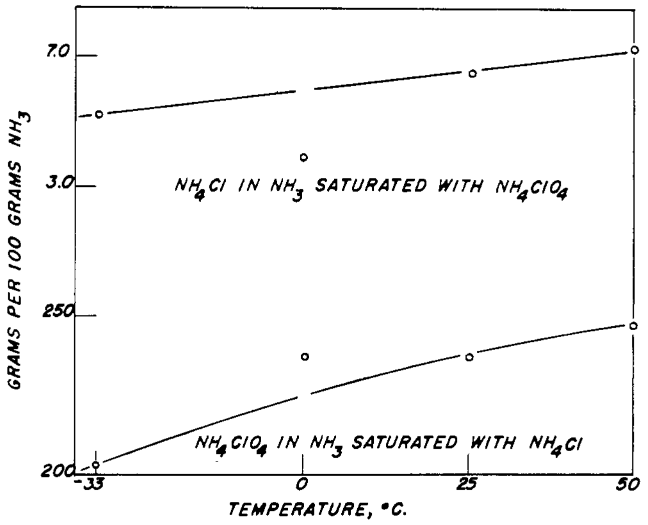


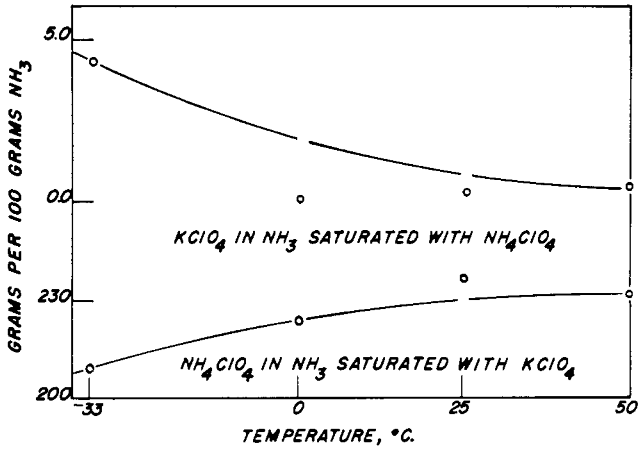
Ammonium perchlorate in ammonia

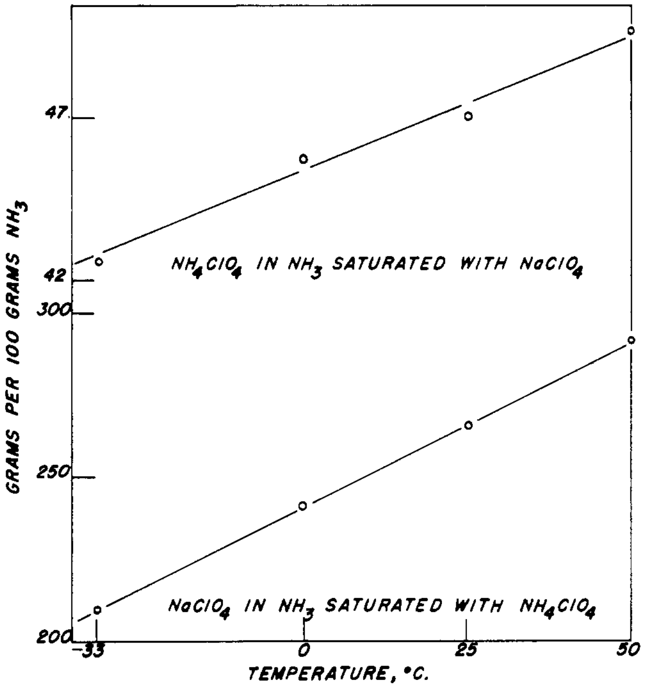


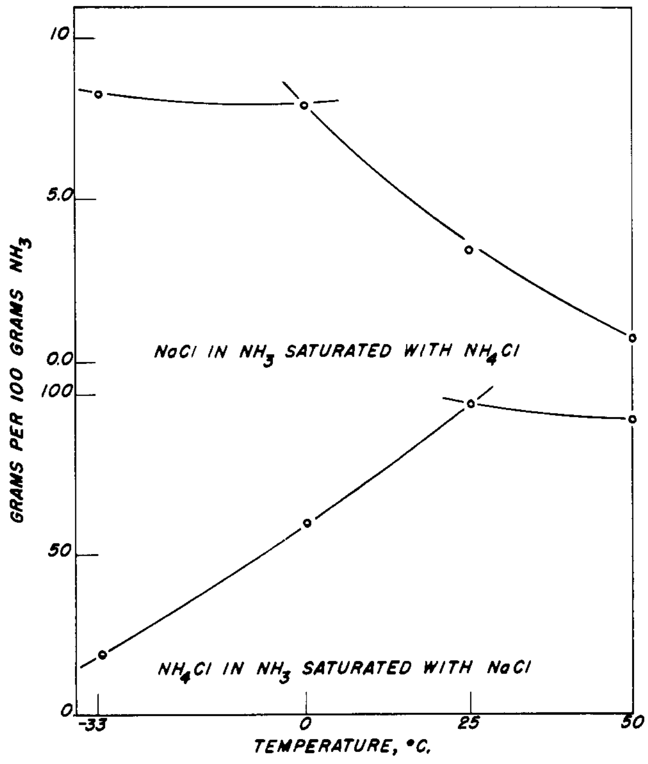












Solubility Diagrams ←

densed from the solution into the tube marked ammonia reservoir. With valve 5 closed the system again came to temperature and pressure equilibrium for another reading. Meanwhile valves 3 and 4 were opened and the ammonia was absorbed in standard acid. The ammonia was determined by titrating the excess acid with standard base. This procedure was repeated until the vapor pressure no longer decreases, and then until five or six points were located with a constant vapor pressure. The solution was saturated or had excess salt in equilibrium with the saturated solution. Then the final ammonia was removed by heating and quantitatively determined. By plotting vapor pressure against ammonia present the saturation point was determined.

Process B. When the alternative apparatus (Figure 2) was used, dried salt was sealed in bulb *A* and it was connected in

Table II. Triple Points for Ternary Mixtures

	K^+	NH_4^+	ClO_4	Cl	Temp., °C.
		KCl-NH_4Cl-NH_4ClO_4			
A	0.206	12.3	11.3	1.18	-33
B	1.65			9.4	
A	0.03	20.12	19.43	0.72	0
B	0.15			3.57	
A	0.349	20.4	19.3	1.39	25
B	1.69			6.71	
A	0.01	21.73	20.32	1.42	50
B	0.05			6.53	
		KCl-$KClO_4$-NH_4ClO_4			
A	0.25	10.65	10.55	0.29	-33
B	2.1			2.68	
A	0.01	18.83	18.56	.28	0
B	0.05			1.5	
A	0.165	18.27	18.26	0.167	25
B	0.9			0.906	
A	0.070	18.57	16.99	1.65	50
B	0.375			8.85	
	Na^+	NH_4^+	ClO_4^-	Cl^-	Temp., °C.
		$NaCl$-NH_4Cl-NH_4ClO_4			
A	0.78	12.39	11.1	2.1	-33
B	5.9			15.8	
A	0.32	20.51	19.95	0.88	0
B	1.54			4.22	
A	0.76	19.15	18.5	1.4	25
B	3.84			7.0	
A	0.58	23.9	23.0	1.49	50
B	2.36			6.08	
		$NaCl$-$NaClO_4$-NH_4ClO_4			
A	17.4	3.06	20.46	0.0 -	-33
B		15.0		0.00 -	
A	19.45	4.1	23.33	0.086	0
B		17.4		0.366	
A	19.4	3.53	22.93	0.0 -	25
B		15.4		0.00 -	
A	25.1	4.74	29.84	0.0 -	50
B		15.9		0.0 -	

A. Moles per 1000 grams.
B. Per cent based on 100% cations and 100% anions.

the vacuum train in position *A*. When the salt had all dissolved at the given temperature, ammonia was bled from the system until salt crystals were visible in the solution. The cell was then inverted in the bath, position *B*, and the solution filtered through the sintered glass plate. The porosity of the plate is determined by the salt used. After filtration, the ammonia was all removed and determined as in Process A and then the cell is opened and the salt removed and analyzed.

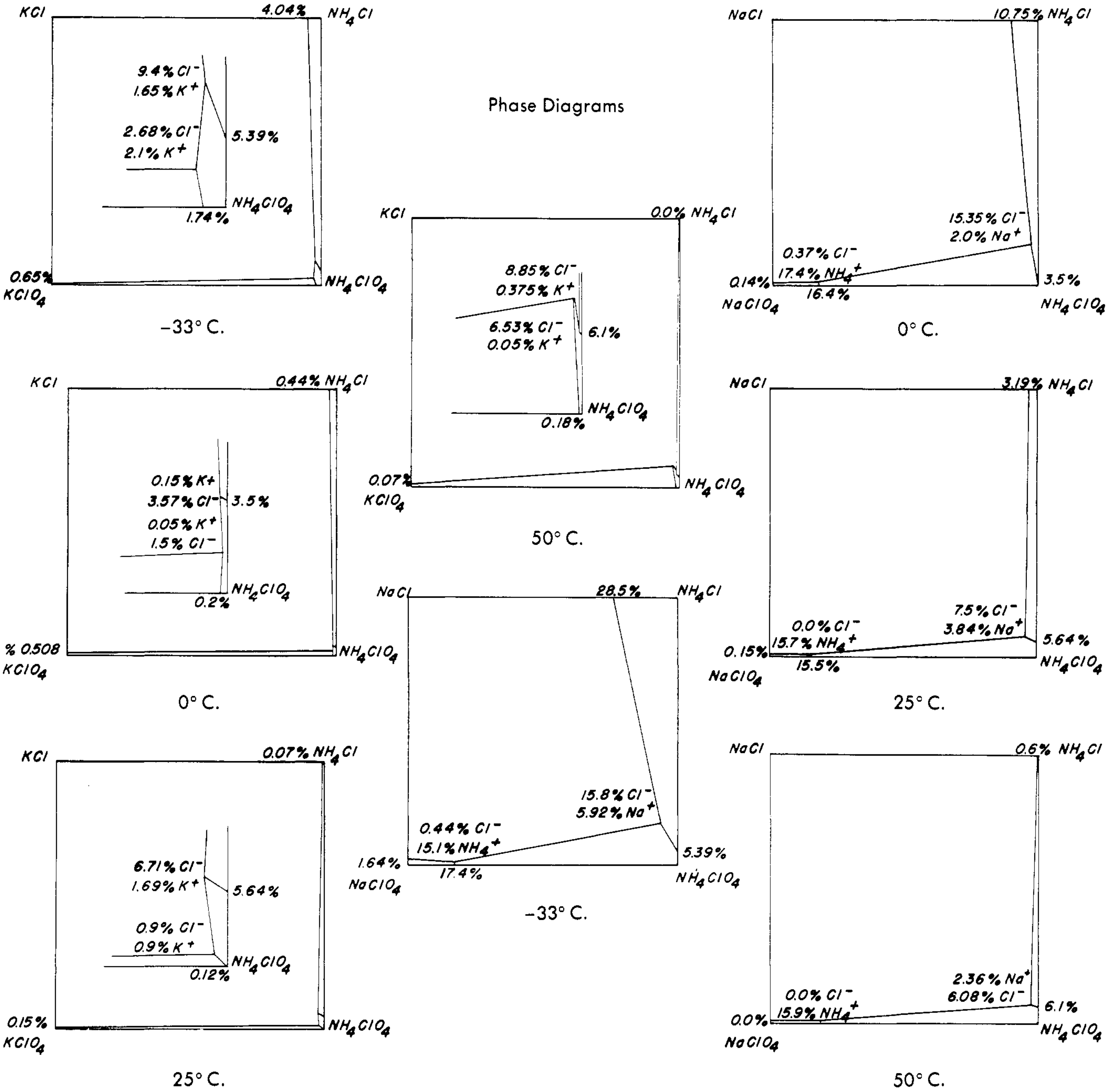
This procedure was reversed by measuring the amount of ammonia necessary to dissolve all the salt at a fixed temperature, but it is tedious and time consuming. If the vapor pressures were high, Process B had the disadvantage that all free gas space had to be determined and the amount of ammonia in it calculated and subtracted from the total ammonia to get the amount of ammonia in solution. For this reason the volume of gas space was kept to a minimum after the first or second trial.

In the case of the salt pairs the amount of each salt was weighed in the alternative apparatus. After equilibrium was attained, the solution had to be analyzed. Chlorides were determined using dichlorofluorescein as an indicator and titrating

Table III. Solubilities of Mixed Salts in Liquid Ammonia

	Salt Pair NaCl-NH$_4$Cl		
	NaCl	NH$_4$Cl	Temp., °C.
A	8.31	19.08	-33
B	1.42	3.57	
C	28.5		
A	7.93	60.3	0
B	1.36	11.3	
C	10.75		
A	3.38	96.85	25
B	0.597	18.1	
C	3.19		
A	0.6	92.0	50
B	0.103	17.2	
C	0.6		
	Salt Pair NaCl-NaClO$_4$		
	NaCl	NaClO$_4$	
A	1.88	236	-33
B	0.322	19.25	
C	1.64		
A	0.20	298.4	0
B	0.0343	24.4	
C	0.14		
A	0.222	299	25
B	0.038	24.4	
C	0.155		
A	0.0 –	310.0	50
B	0.0 –	25.3	
C	0.00 –		
	Salt Pair NH$_4$ClO$_4$-NaClO$_4$		
	NH$_4$ClO$_4$	NaClO$_4$	
A	42.5	210.3	-33
B	3.61	17.1	
C	17.4		
A	45.7	241.7	0
B	3.89	19.75	
C	16.4		
A	47.0	267.0	25
B	4.00	21.8	
C	15.5		
A	49.6	292.2	50
B	4.22	23.8	
C	15.1		
	Salt Pair NH$_4$Cl-NH$_4$ClO$_4$		
	NH$_4$Cl	NH$_4$ClO$_4$	
A	5.26	203	-33
B	0.9875	17.3	
C	5.39		
A	3.92	237.3	0
B	0.734	20.2	
C	3.5		
	Salt Pair NH$_4$Cl-NH$_4$ClO$_4$		
	NH$_4$Cl	NH$_4$ClO$_4$	Temp., °C.
A	6.425	236.5	25
B	1.205	20.18	
C	5.64		
A	7.20	245.5	50
B	1.35	20.8	
C	6.1		
	Salt Pair KCl-NH$_4$Cl		
	KCl	NH$_4$Cl	
A	0.96	16.28	-33
B	0.128	3.05	
C	4.04		
A	0.37	60.0	0
B	0.05	11.2	
C	0.44		
A	0.12	115.6	25
B	0.016	21.7	
C	0.07		
A	0.0 –	110.0	50
B	0.00 –	20.8	
C	0.0 –		
	Salt Pair KCl-KClO^4		
	KCl	KClO$_4$	
A	0.14	39.77	-33
B	0.0187	2.87	
C	0.65		
A	0.13	47.23	0
B	0.017	3.42	
C	0.51		
A	0.04	47.2	25
B	0.0054	3.42	
C	0.15		
A	0.02	47.4	50
B	0.0027	3.42	
C	0.07		
	Salt Pair KClO$_4$-NH$_4$ClO$_4$		
	KClO$_4$	NH$_4$ClO$_4$	
A	4.36	209	-33
B	0.315	17.8	
C	1.74		
A	0.06	222.8	0
B	0.004	19.0	
C	0.02		
A	0.37	243.4	25
B	0.026	20.7	
C	0.012		
A	0.50	230.9	50
B	0.036	19.65	
C	0.18		

A. Grams per 100 grams.
B. Moles per 1000 grams.
C. Mole per cent.



Phase Diagrams

with silver nitrate. Ammonium ion was determined by the standard Kjeldahl procedure.

Some of the salts form ammoniates at the various temperatures.

RESULTS

The solubilities are listed in Tables I, II, and III and shown in the solubility diagrams. The reproducibility of the determinations is illustrated by sodium chloride at 25° C. as 4.575, 4.59, 4.46 and 4.38 grams per 100 grams of ammonia. The averages of the three best determinations are given. The phase equilibria are shown in the phase diagrams. The experimental results are in close agreement with the literature data. Three significant points are found: (1) Ammonium chloride and sodium chloride as well as ammonium chloride and potassium chloride are both more soluble in the mixtures of salts than alone at the same temperature. This may be explained by complex ion formation. It is not in keeping with common ion effect. (2) Some salts have a maximum solubility with temperature. (3) The equilibrium diagrams indicate that the purest ammonium perchlorate can be obtained from potassium perchlorate at 0° C.

ACKNOWLEDGMENT

The authors express their appreciation to Harold W. Ritchey and the Thiokol Chemical Corp. for sponsoring this research.

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RECEIVED for review January 27, 1958. Accepted November 24, 1958.