feel, however, that the evidence points to the first explanation analogous to that of Sidgwick (*loc. cit.*, p. 199) for excessive hydration by polymerized water molecules.

Undoubtedly the system krypton-boron trifluoride will show stabler compounds and the system xenon-boron trifluoride still stabler. Investigations of these systems are already under way and will be reported as soon as possible.

Summary

Study of the system boron trifluoride-argon has shown that:

1. The freezing point of any mixture increases with increase in pressure up to a certain value and is in general little affected by any further pressure increase, indicating an equilibrium $A + xBF_3 \rightleftharpoons A\cdot xBF_3$ or $A\cdot xBF_3 + yBF_3 \rightleftharpoons A\cdot(x + y)BF_3$.

2. A graph of the freezing points *versus* composition exhibits maxima and minima, the maxima corresponding to the ratios $A\cdot BF_3$, $A\cdot 2BF_3$, $A\cdot 3BF_3$, $A\cdot 6BF_3$, $A\cdot 8BF_3$ and $A\cdot 16BF_3$, indicating compound formation. These compounds are unstable and dissociate above their melting points. From the shape of the curve the ratio $A\cdot 2BF_3$ appears to be the stablest.

3. The freezing points of the argon-boron trifluoride mixtures of compositions approximating that of the maxima and minima were sharp and immediately complete while intermediate compositions melted over a range of temperatures. This is typical of systems in which compounds are formed.

4. At pressures in the neighborhood of 35 atmospheres, a second liquid layer appears which is probably best explained as retrograde immiscibility.

CLEVELAND, OHIO RECEIVED JUNE 19, 1935

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Critical Phenomena of the System Argon-Boron Trifluoride[1]

BY HAROLD SIMMONS BOOTH AND KARL STUART WILLSON

In view of the fact that thermal analysis of the system argon-boron trifluoride[2] showed maxima indicating compound formation, it was thought interesting to see whether or not this tendency would result in abnormalities in the critical phenomena.

The gases were purified and samples prepared as previously described.[2] Temperatures were measured by the Leeds and Northrup Micromax potentiometer using a two-junction copper-constantan thermocouple with ice as reference point. The couple was calibrated at the ice and carbon dioxide snow point and the calibration curve drawn through these points guided by the theoretical curve. Temperatures are subject to a maximum error of ±0.4°.

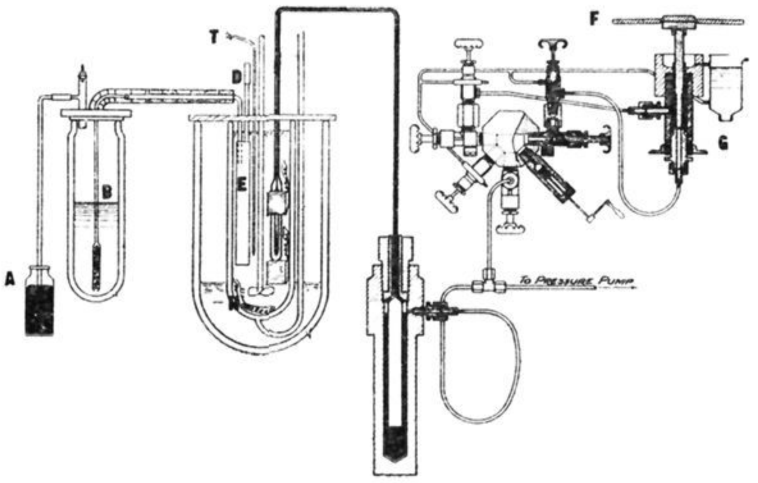

Fig. 1.—Critical apparatus.

The thermostat (Fig. 1) consisted of a pint Dewar flask set in a gallon Dewar. The temperature of the thermostat was controlled in either of two ways. For temperatures down to −85°, alcohol was used as the bath liquid and cooling was effected by placing liquid nitrogen in the outer Dewar. The rate of cooling of the bath was controlled by the depth of the liquid nitrogen in the outer bath and also by adjustment of the vacuum of the inner Dewar. The control contacts on the recording potentiometer were adjusted to close the relay heating circuit and warm the bath by means of the coil (H) when the bath cooled below the desired temperature. By adjusting the rate of cooling and the heating circuit, the bath temperature could be held within the limits of sensitivity of the recorder (±0.2°) for determination of the critical constants of the mixtures. For critical constants of pure boron trifluoride, manual control and observation of a calibrated mercury thermometer permitted an accuracy of ±0.05°.

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[1] From a part of a thesis submitted by K. S. Willson to the Graduate Faculty of Western Reserve University, May, 1935, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Booth and Willson, THIS JOURNAL, **57**, 2273 (1935).

To secure rapid cooling and for controlling the bath at the lower temperatures, liquid nitrogen was forced into the evaporator (E) by closing the outlet from the reservoir (B) at (A). By adjusting a screw clamp at (D) a very slow cooling rate could be secured and then the temperature maintained constant by the heater (H) operated by the relay control circuit. For these lower temperatures commercial butane served as the bath liquid.

The experimental procedure used in determining the critical constants was similar to that employed and described in detail by Booth and Carter.[3] Pressures were measured by the dead weight gage described by Booth and Swinehart.[4]

Experimental Results.—The tables and figures present the critical data. The points listed are those at which the first liquid appeared, when approached from the gaseous region.

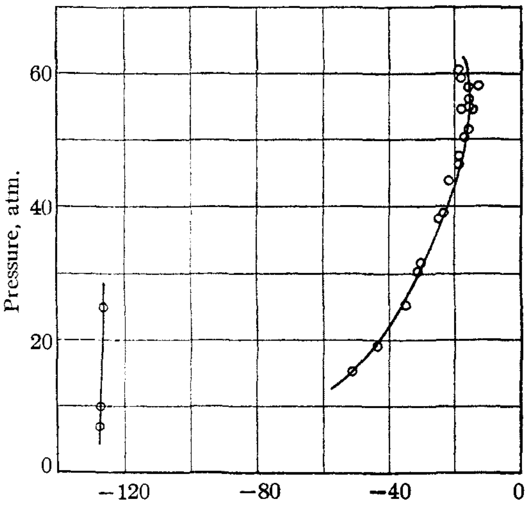

Fig. 2.—10 mole % argon.

The freezing points[2] are also plotted although the scale used does not represent adequately the experimental details found.

TABLE I

CRITICAL CONSTANTS OF THE PURE GASES

	P_c, atm.	T_c, °C.
BF_3	49.3 ± 0.1 (49.2 ± 0.1	−11.8 ± 0.05 −12.25 ± 0.03°)[5]
Argon	47.7 ± 0.1 (48.0	−120.6 ± 0.5 −122.4)[6]

TABLE II

CRITICAL PHENOMENA OF MIXTURES

The points listed are those at which the first liquid appeared when approached from the gaseous region.

Press., atm.	Temp., °C.	Press., atm.	Temp., °C.	Press., atm.	Temp., °C.
Mol % argon		30.0	Sample A	49.7	
10.0	Sample A	30.0	B	20.8	−64.6[a]
10.0	B	14.1	−54.9 A	27.1	58.7
9.9	C	22.7	41.7 A	34.9	53.4
15.3	−51.6 A	24.3	45.8 A	39.8	50.6
19.2	44.4 A	32.0	38.6 B	45.6	48.6
25.4	35.6 A	32.9	34.6 A	51.2	46.6
30.4	31.7 A	34.3	39.5 A	53.2	45.9
30.5	30.4 C	37.4	31.9 A	59.9	44.2
38.0	25.6 A	40.4	33.1 B	70.1	43.0
39.0	24.0 C	45.7	29.5 A	77.8	42.9
40.4	22.5 B	49.0	28.5 A	59.9	Mol % argon
43.8	22.5 A	50.4	28.3 B	16.3	−70.3
46.4	19.5 C	54.1	26.7 B	17.4	67.7
50.4	17.9 B	57.8	25.1 B	19.1	64.4
50.5	16.9 C	59.8	24.4 B	23.2	61.2
54.5	15.1 B	63.8	24.0 B	28.7	59.4
54.7	18.9 A	67.4	23.5 B	30.8	57.9
55.0	16.2 C	71.1	23.4 B	42.1	53.1
58.0	16.6 A	73.6	23.8 B	42.8	51.4
58.2	13.9 B	77.2	25.0 B	43.0	50.5
59.3	18.9 A	80.3	28.7 B	46.7	49.5
60.6	20.0 A	85.4	31.4 B	49.4	50.0
20.7	Sample A	89.5	35.7 B	50.9	49.0
20.2	B	91.6	38.0 B	55.2	48.4
12.8	−55.2 A	93.0	38.8 B	60.0	47.7
19.0	45.8 A	101.8	46.0 B	63.0	46.3
22.7	42.4 A	102.5	50.8 B	70.7	45.5
30.0	36.6 A	107.6	56.6 B	79.5	44.6
32.4	35.4 A	108.3	61.2 B	90.9	46.9
34.1	34.6 A	109.0	66.0 B	97.4	48.7
36.5	33.1 A	39.9	Sample A	90.0	Mol % argon
39.8	30.8 A	40.0	B	20.4	−115 (approx.)
40.3	28.3 B	12.1	−59.6 A	40.5	94.3
44.4	25.7 B	14.4	56.6 A	48.9	94.2
47.1	−24.4 B	18.6	52.8 A	50.5	95.0
51.7	23.0 B	22.5	48.7 A	50.5	94.0
54.0	21.9 B	33.5	44.4 A	50.5	92.8
57.7	20.6 B	34.1	44.4 A	54.2	92.8
59.7	20.5 B	38.8	44.3 A	54.5	94.2
63.4	20.0 B	41.8	41.5 A	58.4	95.5
67.1	20.0 B	51.3	38.0 A	58.4	93.7
68.8	20.5 B	62.3	32.3 B	59.8	92.8
70.2	21.8 B	70.8	31.3 B	59.8	92.8
70.3	21.8 B	80.9	32.0 B	62.8	96.7
75.3	25.2 B	91.0	37.7 B	63.3	95.7
76.9	25.8 B	94.3	41.6 B	67.5	93.5
80.8	28.7 B	98.5	46.0 B	68.5	95.4
82.4	30.8 B	101.6	50.5 B	70.0	93.5
87.2	34.3 B	103.8	55.2 B	79.3	105.0
87.6	34.4 B	105.8	59.8 B		
91.6	37.3 B	107.2	64.3 B		
95.0	46.0 B	107.9	72.3 B		

[a] Since this sample was not carried to the point where increase in pressure causes lowering of the maximum temperature of liquefaction, the values of T_m and P_m could not be plotted.

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(3) Booth and Carter, *J. Phys. Chem.*, **34**, 2801 (1930).

(4) Booth and Swinehart, THIS JOURNAL, **57**, 1337 (1935).

(5) Booth and Carter, *J. Phys. Chem.*, **36**, 1359 (1932).

(6) Crommelin, *Comm. Phys. Lab. Univ. Leyden*, **115**, **118a** 1910).

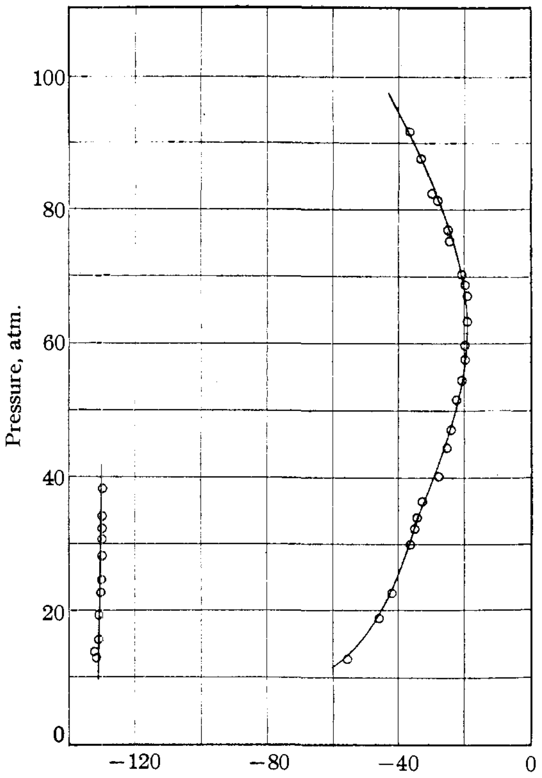

Fig. 3.—20 Mole % argon.

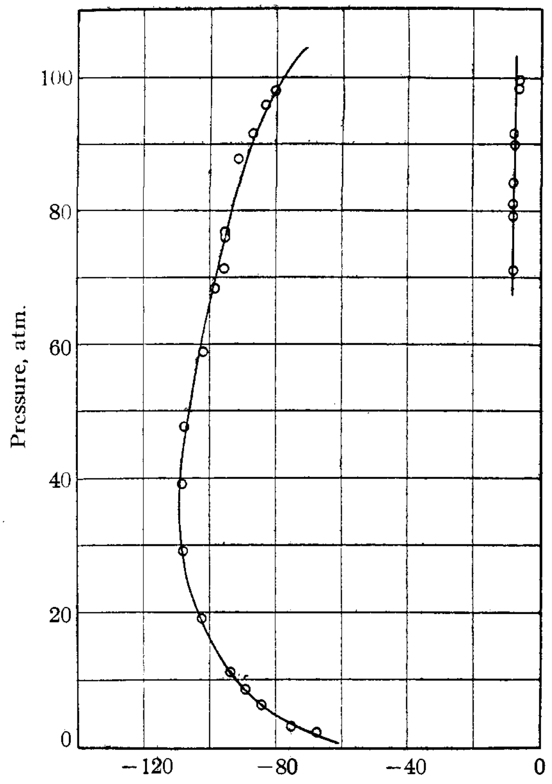

Fig. 5.—40 Mole % argon.

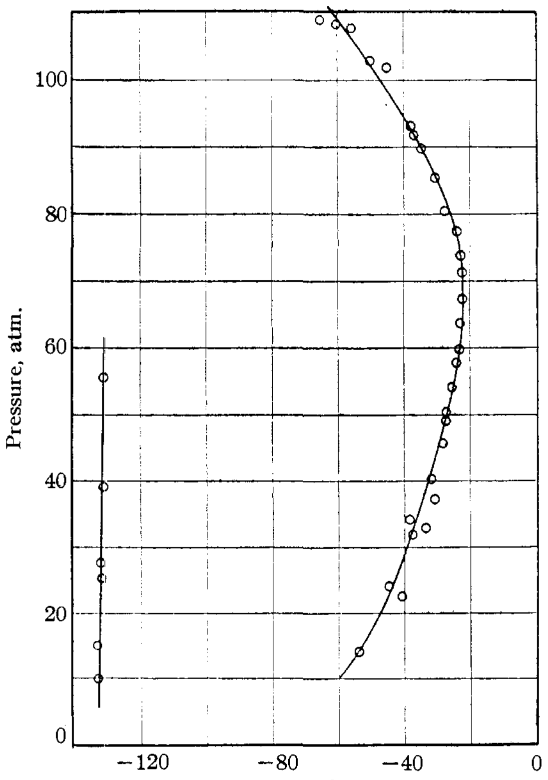

Fig. 4.—30 Mole % argon.

TABLE III

MAXIMUM TEMPERATURE OF LIQUEFACTION AND CORRESPONDING PRESSURE

Bracketed figures are interpolated from Fig. 10.

Mole % argon	T_m, °C.	P_m, atm.
0	−11.8	49.3
10	15	57
20	20	63
30	24	70
40	30	75
50	(36)	(78)
60	45	75
70	(58)	(71)
80	(75)	(65)
90	96	(57)
100	120.6	47.7

Discussion of Results

As commonly reported in the studies of critical phenomena of two component mixtures retrograde condensation was observed and also what may be described as a new phenomenon, retrograde immiscibility. This latter phenomenon is described in the previous paper.

In the range from 0 to 60% argon, the curve T (Fig. 9) giving the maximum temperature of liquefaction is only slightly distorted from the normal curve. On reflection this is not surprising in view of the fact that the critical region lies about 110° above the temperature at which the compounds A·xBF$_3$ dissociate.

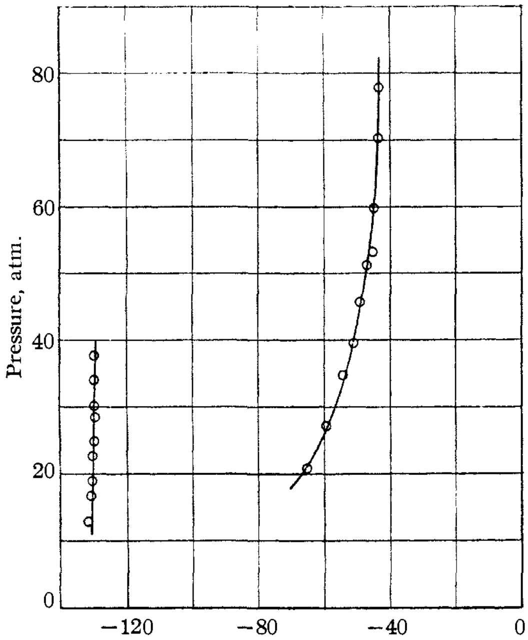

Fig. 6.—50 Mole % argon.

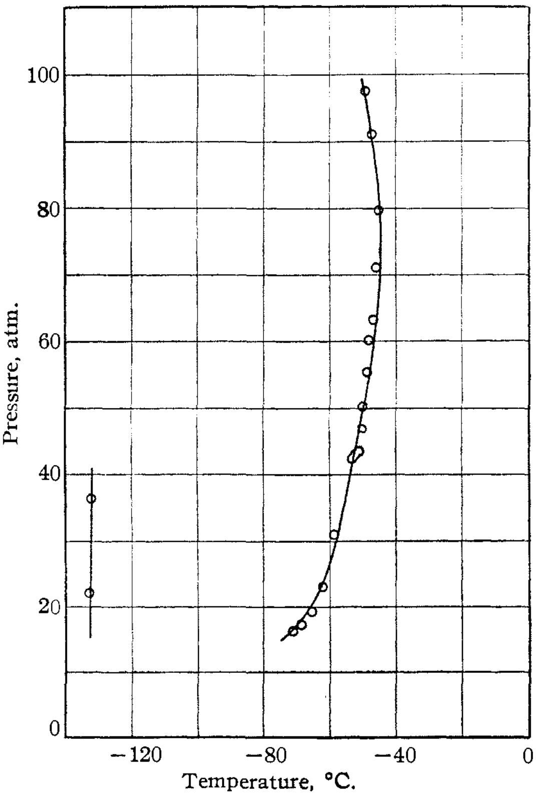

Fig. 7.—60 Mole % argon.

The maximum temperature of liquefaction T_m decreases along a smooth curve as the argon percentage is increased. The pressure P_m corresponding to T_m increases as the argon percentage increases to 50% and then decreases. The erratic points in the highest pressure regions on some of the curves are due to the liquid rising into the capillary tube and preventing adequate stirring.

The regions surrounding the critical point of a mixture have been little studied and merit an accurate investigation, but could not be studied in this work due to the low temperatures involved which caused the mercury to freeze in the capillary tubes. In the high argon samples, great difficulty in getting accurate critical data was encountered due to the small amount of liquid formed even over a wide temperature and pressure variation. Thus, the conditions under which the first trace of liquid appeared were difficult to determine, and an additional complication arose due to the liquid adhering to the walls of the cell and the stirrer, instead of falling to the bottom of the cell. The plot of the 90% argon sample shows the lack of reproducibility of the points and gives only a general idea of the critical data in that region.

Appearance of a second liquid layer in the freezing point curves for high pressures suggests pos-

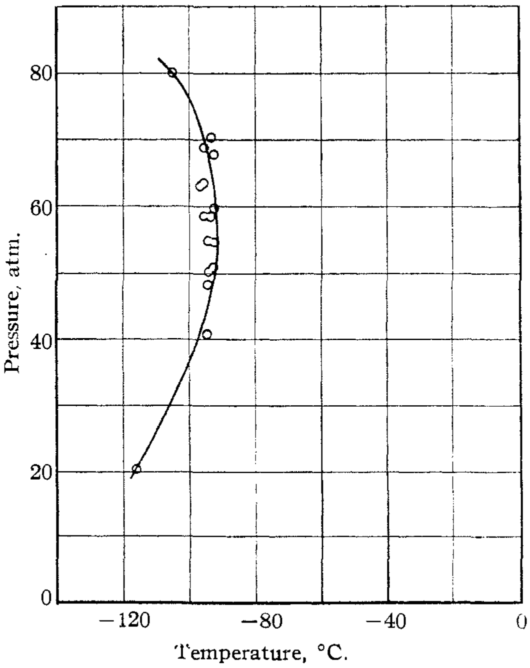

Fig. 8.—90 Mole % argon.

sible abnormalities in the high pressure, low temperature part of the critical curves but experimental difficulties precluded an investigation of this region.

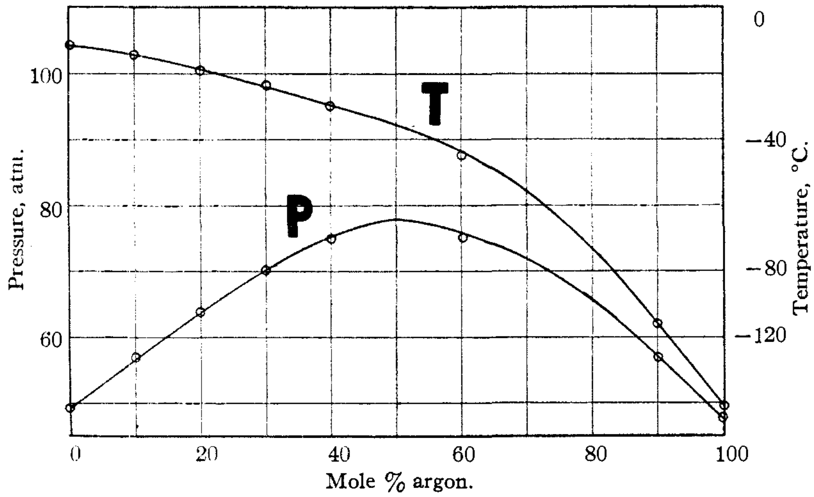

Fig. 9.—Maximum temperature of liquefaction and corresponding pressure.

Summary

The critical phenomena of the system boron trifluoride–argon exhibited the usual retrograde condensation and a new phenomenon best described as retrograde immiscibility at the low temperature, high pressure range.

The compounds formed by the gases at their melting point are practically completely dissociated at the "critical temperature region" which is about 100° higher, and so affect the curve of the maximum temperature of liquefaction only very slightly.

CLEVELAND, OHIO

RECEIVED JUNE 19, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Temperature Coefficients in the Acid Hydration of Sodium Pyrophosphate

BY SAMUEL J. KIEHL AND EDWARD CLAUSSEN, JR.

Introduction

Normal sodium pyrophosphate in aqueous or alkaline solution on long standing at room temperature or even at the boiling point does not change to orthophosphate.[1,2] In acid solution, however, this change takes place, and its rate is dependent upon the concentration both of pyrophosphate and of the acid, used as the so-called catalyst, and the temperature.[3] The rate of change to the orthophosphate in the presence of hydrochloric acid has been measured at 45°,[3] and under very special conditions at 20 and 40° by Muus,[4] who also mentioned work at 100° although no data were presented. In general data at higher temperatures are meager.[5]

In the literature many procedures for measuring the rate of this and similar reactions are published, among which have been methods based upon gravimetric analysis, change of concentration of hydrogen ions, conductivity, colorimetry, nephelometry and volumetric analysis. For purposes of this investigation, however, a modification of the method devised earlier[2] was found to be most convenient. The unchanged pyrophosphate was determined gravimetrically in the presence of orthophosphate which was formed and the velocities at 30, 45, 60, 75 and 90° were secured. From data thus obtained temperature coefficients at fifteen-degree intervals were determined.

Preparation of Materials and Apparatus

The normal sodium pyrophosphate, the disodium orthophosphate and the hydrochloric acid were prepared as described previously.[3]

In the preparation of the zinc acetate reagent used in the analysis both the zinc acetate and the acetic acid were carefully purified to eliminate possible traces of heavy metals—especially iron and lead whose pyrophosphates would interfere in subsequent operations. The final solution of the zinc acetate reagent contained a 0.2 molar zinc acetate with sufficient acetic acid to give a *p*H value of 3.3.

A magnesia mixture without ammonia was prepared by dissolving 50 g. of $MgCl_2 \cdot 6H_2O$, 100 g. of NH_4Cl, and 5 cc. of 13 *M* HCl in one liter of water.

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(1) Rose, *Ann.*, **76**, 2 (1850).

(2) Kiehl and Coats, THIS JOURNAL, **49**, 2180 (1927).

(3) Kiehl and Hansen, *ibid.*, **48**, 2802 (1926).

(4) Muus, *Z. physik. Chem.*, **A159**, (4) 268 (1932).

(5) Abbott, THIS JOURNAL, **31**, 763 (1909), studied the conversion of pyrophosphoric acid itself at 75 and 100°.