TABLE I

EXPERIMENTAL HEAT CAPACITIES OF GASEOUS CYCLOPENTANE, CYCLOHEXANE AND METHYLCYCLOHEXANE

Calories per degree per mole

Substance	Press., atm.	T, °K.	C_p	$C_p - C_p°$	$C_p°$
Cyclopentane	1	353	24.74 ± 0.2	0.36	24.38
		372	26.16 ± .2	.31	25.85
		395	28.29 ± .3	.26	28.03
		424	30.40 ± .3	.21	30.19
		463	33.32 ± .3	.16	33.16
		503	36.14 ± .4	.12	36.02
		539	38.36 ± .4	.10	38.26
	0.6	353	24.67 ± .3	.22	24.45
Cyclohexane	1	384	34.59 ± .3	.38	34.21
		428	38.94 ± .4	.27	38.67
		460	41.9 ± .4	.22	41.7
		495	45.5 ± .5	.18	45.3
		521	47.2 ± .5	.15	47.0
		544	49.4 ± .5	.13	49.3
	0.46	384	34.31 ± .3	.17	34.14
	0.30	384	34.35 ± .3	.11	34.24
Methylcyclohexane	1	398	44.58 ± .4	.45	44.13
		439	49.00 ± .5	.38	48.62
		480	53.48 ± .5	.24	53.24
		527	58.06 ± .6	.18	57.82

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Summary

The heat capacities of gaseous cyclopentane, cyclohexane and methylcyclohexane have been measured from slightly above the boiling point to about 250°. A few measurements made at reduced pressures indicated that the heat capacities of the ideal gas are given to good approximation by the Berthelot correction.

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[CONTRIBUTION FROM THE BAILEY CHEMICAL LABORATORY, UNIVERSITY OF KANSAS]

Amphiprotic Substances. II.[1] The System Formamide–Ammonia

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The fact that amides of the carboxylic acids stand at a point intermediate between ammonia and carboxylic acids in the Brönsted scale of acidities has already been discussed. Likewise, experimental evidence for the basic properties of these amides in anhydrous acetic acid and for their acidic properties in liquid ammonia has been cited. Compound formation was shown to take place in the systems acetamide–ammonia and acetamide–acetic acid. The systems formamide–acetic acid, formamide–formic acid, formamide–*n*-butyric acid, and formamide–water also have been studied.[2] The system formamide–ammonia remained, however, to be investigated. The investigation of this system was therefore undertaken as the second step in the present series of experiments.

Experimental

Materials.—The formamide was obtained from the Eastman Kodak Co. It was dried by allowing it to stand over drierite for one week, and was purified by distillation under vacuum, a middle fraction boiling from 107 to 109° under 15 mm. pressure being retained. The substance thus obtained melted at 2.2 ± 0.2°, in good agreement with the values of 2.0 to 2.55° given in the literature.[3]

The ammonia used was synthetic anhydrous ammonia

TABLE I

S	T	S	T
(a) Solid phase, $HCONH_2$			
0	2.2	35.5	−36.3
1.9	1.0	39.7	−44.0
5.7	−2.3	44.0	−50.9
7.3	−3.7	46.8	−55.2
11.5	−8.5	49.2	−62.5
14.0	−10.4	49.9	−75.1*
15.9	−12.0	50.3	−67.7
22.6	−19.8	51.1	−75.4*
30.3	−29.8	52.1	−72.7
33.5	−33.9	53.4	−74.0
(b) Solid phase, $NH_3 \cdot HCONH_2$			
53.5	−75.1	65.1	−83.0
54.9	−75.5	67.3	−90.5*
56.6	−76.0		−85.4
58.9	−77.6	68.5	−86.6
60.8	−77.6	69.6	−89.5
(c) Solid phase, $2NH_3 \cdot HCONH_2$?			
71.1	−91.9	77.5	−97.5*
71.6	−91.5		−95.0
	−94.0*	77.9	−94.8
73.5	−92.3	79.2	−96.0
75.4	−93.0		
(d) Solid phase, NH_3			
80.2	−94.0	91.9	−83.2
82.2	−91.4	94.3	−80.9
83.4	−90.6	100.0	−77.5
86.9	−85.8		

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(1) The first paper in this series: Sisler, Davidson, Stoenner and Lyon, THIS JOURNAL, **66**, 1888 (1944).

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(2) English and Turner, *J. Chem. Soc.*, **107**, 774 (1915).

(3) *E. g.* English and Turner, ref. 2; Lowry and Cutter, *J. Chem. Soc.*, **125**, 1469 (1933); Taylor and Davis, *J. Phys. Chem.*, **32**, 1469 (1928).

obtained from E. I. du Pont de Nemours and Co. and having a stated purity of 99.95%. Its freezing point was found to be −77.5 ± 0.4°, in accord with values between −77.7 and −77.8° found in the literature.[4]

Method.—The system was studied by means of the freezing point method, the freezing points being determined by means of cooling curves recorded by a Leeds and Northrup Micromax recorder.[5] The cell used was identical with the one described in previous papers from this Laboratory.[5] Data obtained by this method are believed to be correct to ±1.5°. All points recorded were determined at least twice.

Data obtained for the system are listed in Table I and recorded graphically in Fig. 1. *S* denotes the mole per cent. of ammonia and *T* the equilibrium temperature. Because of the high vapor pressure of ammonia, direct analysis of the various solid phases was not considered practicable. Data marked with an asterisk indicate metastable equilibria.

Discussion of Results

It is evident from the course of the curve in Fig. 1 that formamide and ammonia form a solid addition compound in which the mole ratio is 1:1 and a second compound in which the mole ratio is probably 1:2. Neither compound melts congruently, but the 1:1 compound was obtained in metastable equilibrium with a solution of the same composition at a temperature of −75°. The composition and melting point of the second compound cannot be determined precisely from the curve; a short extrapolation indicates, however, that the mole ratio is 1:2 and that the melting point is around −90 to −91°.

The 1:1 compound undergoes dissociation to formamide and solution at a temperature just below its melting point. The second compound undergoes dissociation into the 1:1 compound and solution at a temperature between −91 and −92°. A eutectic point with ammonia occurs at a composition of 79 mole per cent. of ammonia and a temperature of −96°.

By analogy with the sodium salts of formamide formed in liquid ammonia solution[6] we may consider the 1:1 compound to be an ammonium aquo-ammono formate of the formula, $HCONH[NH_4]$. One is tempted to interpret the formation of a 1:2 compound as taking place through the interaction of the second proton on the amide group with an ammonia molecule. There is no direct experimental basis for this interpretation, however; in fact, it is not at all impossible that the second ammonia be joined by the sharing of its electron pair with the carbon atom on the formamide. This carbon atom is electron deficient as a result of the electron withdrawal by the oxygen atom.

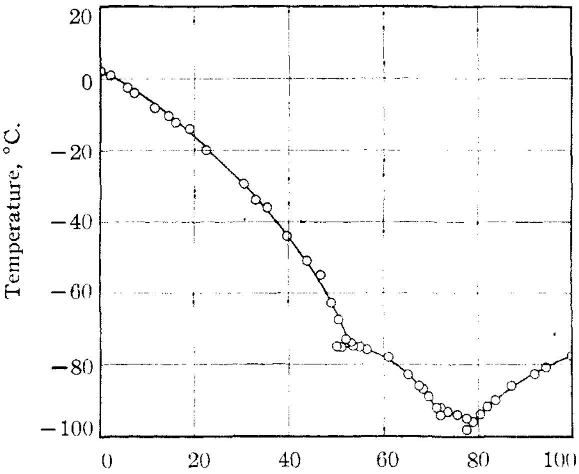

Fig. 1.

Summary

1. The temperature–concentration curve for the system formamide–ammonia has been determined throughout the entire concentration range.

2. The existence of two new compounds, $HCONH_2 \cdot NH_3$ and $HCONH_2 \cdot 2NH_3$ (?), has been demonstrated. The name ammonium aquo-ammono formate has been suggested for the former.

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[4] Elliott, *J. Phys. Chem.*, **28**, 611 (1924).

[5] Davidson, Sisler and Stoenner, THIS JOURNAL, **66**, 779 (1944).

[6] Franklin, "The Nitrogen System of Compounds," Reinhold Publishing Corp., New York, N. Y., 1931, Chapter XXIX.