CXIX.—*The Binary System Carbamide–Ammonium Nitrate. Molecular Association in each Component.*

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CARBAMIDE is known to form compounds with certain nitrates, *e.g.*, silver and mercuric, and one of the objects of this research was to determine whether it combined with ammonium nitrate. Also, attempts are described to determine (*a*) the molecular depression of the freezing point for carbamide and for ammonium nitrate, and (*b*) the state of molecular association of certain compounds when dissolved in these two substances in the molten state.

EXPERIMENTAL.

The materials used were of a high degree of purity, and were powdered and dried carefully—generally in a water-oven, and for several days in the case of ammonium nitrate—before use. When not in use, they were kept over fused calcium chloride in a desiccator.

The freezing-point apparatus was of the usual kind. The outer jacket, a cylindrical glass jar, was wrapped in cotton-wool at the bottom, and the inner tube was a hard-glass test-tube (6″ × 1″) provided with a tightly fitting cork which carried a solid glass stirrer and two thermometers, one of which (a standard) dipped into the melt. The other thermometer, together with a third, outside the apparatus, enabled the correction for exposed stem to be made in two parts.

About 30 g. of pure dry ammonium nitrate were weighed into the hard-glass test-tube, which was tightly corked and heated in an oil-bath; as soon as the nitrate had melted, the tube was refitted with the thermometers and stirrer, left in the bath for a minute, then wiped and quickly placed in its jacket. The molten nitrate was stirred until crystals appeared throughout its bulk, whereupon the temperature rose slightly but rapidly to a stationary maximum, which was taken as the freezing point. The temperatures on both auxiliary thermometers were read immediately. In all cases, the mean of four such determinations was taken as the true freezing point.

A weighed quantity of carbamide was now introduced into the molten ammonium nitrate, and the freezing point redetermined. After two lots of carbamide had been added, a fresh quantity of nitrate was used. Subsequently, the freezing points were determined of pure carbamide and of its mixtures with weighed amounts of ammonium nitrate. The two molten liquids are miscible in all proportions. Very concentrated solutions exhibited no rise in temperature at their crystallisation point, so the temperature at which crystals appeared throughout the melt was taken as the freezing point; the reading was facilitated by placing a luminous flame behind the apparatus. With a few of the concentrated solutions, observations of a eutectic arrest were made.

As Saunders (J., 1922, **121**, 698) has shown that at 200° pure dry ammonium nitrate evolves 20 c.c. of gas per 50 g. per hour, the temperature in the present work was rarely taken above 180°: the slight decomposition occurring, which was greater with mixtures, was negligible in all cases. The same is true for carbamide and its mixtures.

The results are in Table I, and are shown graphically in the figure.

TABLE I.

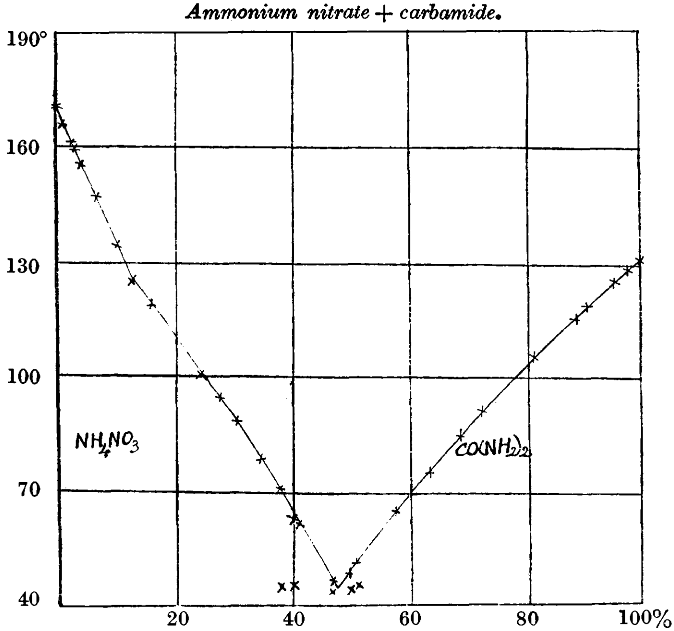
Freezing Points of Ammonium Nitrate and Carbamide Mixtures.

Carbamide, %.	F. p.	Carbamide, %.	F. p.	Carbamide, %.	F. p.	Carbamide, %.	F. p.
0	169·6°	15·08	120·8°	41·14	60·4°	80·24	106·2°
1·09	165·3	15·80	119·2	46·10	45·2 (*c*)	88·82	115·7
2·33	160·8	24·26	100·5	48·99	47·28(*d*)	90·1	118·1
2·65	159·7	27·36	93·9	49·95	51·0 (*e*)	95·56	125·65
3·47	156·7	29·90	87·9	57·5	65·2	95·61	126·1
5·87	148·3	33·90	77·9	63·6	76·0	97·93	129·0
9·77	135·5	37·30	71·3 (*a*)	68·07	85·2	98·83	130·2
12·19	126·0	40·00	61·38(*b*)	72·3	91·2	100·0	132·1

Eutectic arrests observed at points marked *a*, *b*, *c*, *d*, and *e* were at 45·1°, 44·45°, 44·85°, 44·05°, and 44·9°, respectively, the mean being 44·67°.

FIG. 1.

Ammonium nitrate + carbamide.



Carbamide, %.

The freezing-point curve for the binary system consists of two limbs, giving a definite eutectic point, and there is no indication of the formation of a double compound. The eutectic point is at

44·7°, and the eutectic mixture contains 47% of carbamide, or 54·18 mols.%. This temperature is in close agreement with the mean of the eutectic arrests.

The left-hand limb of the curve shows a definite break at 126°, corresponding to the transition of the regular to the rhombohedral form of ammonium nitrate at 125°, but seems to pass smoothly through the transition point at 83°. It thus appears that the lower portion of this limb was obtained under metastable conditions.

Molecular Association in Ammonium Nitrate and in Carbamide.

The depression of the freezing point caused by the addition of dextrose, ammonium nitrate, and acetamide to carbamide (about 25 g.) was determined at three different concentrations in each case, and the corresponding molecular depressions were calculated; the results are in Table II (*a*), Δ being the observed depression.

TABLE II.

(*a*) Carbamide mixtures.

Substance added.	G. per 100 g. carbamide.	Δ.	Mol. depression.	*M*, calc.	*M*, obs.
$C_6H_{12}O_6$	2·024	2·42°	215	180	
	4·680	5·32	205	,,	
	6·450	7·20	201	,,	
NH_4NO_3	1·184	1·9	128	80	134
	2·114	3·1	117	,,	140
	2·880	4·0	111	,,	145
$CH_3·CO·NH_2$	0·800	1·07	79	59	161
	1·550	1·92	73	,,	166
	2·144	2·55	70	,,	169

(*b*) Ammonium nitrate mixtures.

Substance added.	G. per 100 g. NH_4NO_3.	Δ.	Mol. depression.	*M*, calc.	*M*, obs.
$CO(NH_2)_2$	2·386	8·8°	221	60	
,,	6·240	21·3	205	,,	
$CH_3·CO·NH_2$	2·362	8·22	205·3	59	63·5
,,	5·571	17·42	185	,,	65·4
$Ca(NO_3)_2$	2·060	3·34	266	164	141
[1] KNO_3	4·04	3·3	82·5	101	
,,	10·50	8·4	80·8	,,	
[2] H_2O	2·05	23·0	202	18	18·3
[3] $LiNO_3$	2·76	8·8	220	69	69
[4] $NaNO_3$	3·40	8·3	207·5	85	90·5
,,	8·84	20·0	192·3	,,	90·6
[5] NH_4Cl	5·60	12·9	123	53·5	89·2

[1] Perman and Howells, J., 1923, **123**, 2129.
[2] Millican, Joseph, and Lowry, J., 1922, **121**, 959.
[3] Perman and Harrison, J., 1924, **125**, 1709.
[4] Early and Lowry, J., 1922, **121**, 963.
[5] Perman, *ibid.*, p. 2473.

The figures obtained for dextrose at the concentrations indicated are in fair agreement with Blagden's law, but since the concordance is not exact, the values 215, 205, and 201 have, in turn, been adopted as the value of the molecular depression " constant " in deriving the calculated molecular weights at the three concentrations of the other two substances. The results show that ammonium nitrate and acetamide exhibit molecular association when dissolved in carbamide, and that their degrees of association increase slightly with increase in concentration, approaching the values 2 and 3 respectively at the concentrations involved. (Amides as a class show strong association in many solvents.)

Determinations of the freezing points were made when carbamide, acetamide, and calcium nitrate were added separately to about 30 g. of ammonium nitrate. (Dextrose was at once charred when added to the molten salt, and naphthalene, triphenylmethane, and diethylmalonylurea proved to be too sparingly soluble.) The results are in Table II (*b*), together with those for five other substances as calculated from published data.

The values of the molecular depressions for carbamide, lithium nitrate, and water are in close agreement, especially when they refer to approximately equal molecular concentrations; hence carbamide and lithium nitrate probably have their normal molecular weights, water being possibly slightly associated rather than dissociated. Consequently, 221 and 205 have been adopted as the values of the molecular depression " constants " for ammonium nitrate according as calculations are made at one or other of the two molecular concentrations concerned.

The figures in the last column indicate that acetamide is slightly associated, but not nearly to the same extent as when dissolved in molten carbamide. Sodium nitrate appears to be slightly associated. On the other hand, ammonium chloride is strongly associated in molten ammonium nitrate.

The molecular depression due to calcium nitrate, *viz.*, 266, was calculated from the depression of the freezing point caused by a concentration of 0·0126 mol. per 100 g. of ammonium nitrate. At this concentration carbamide produces a depression of 2·9° (value obtained from the curve) corresponding to a molecular depression of 229; hence, if carbamide is " normal " in ammonium nitrate solution, the observed molecular weight for calcium nitrate is 141, indicating some dissociation.

The abnormal results obtained with potassium nitrate are interesting, but the sub-normal molecular depression of the freezing point may be due, not only to molecular association of the solute (compare sodium nitrate, above), but also, at least in part, to the separation of mixed crystals, which Perman and Howells (J., 1923, **123**, 2128) have shown to exist.

It is intended to investigate the molecular depressions caused by the addition of rubidium, cæsium, and thallous nitrates to ammonium nitrate, since these metals and ammonium belong to a series of "isomorphous elements."

Summary.

1. The equilibrium curve for the binary system ammonium nitrate–carbamide consists of two limbs, and exhibits a eutectic point at 44·7° and 47% of carbamide. The ammonium nitrate exhibits a transition point at 126°. The two substances do not form a compound at the temperatures involved in these experiments.

2. For dilute solutions, the molecular depression per 100 g. of carbamide is approximately 215. Ammonium nitrate and acetamide are strongly associated in molten carbamide.

3. For dilute solutions in molten ammonium nitrate, the molecular depression is about 221 per 100 g. Carbamide, lithium nitrate, and water are all normal, or nearly so, in this solvent, but sodium nitrate and acetamide are slightly associated. Potassium nitrate causes a sub-normal depression of the freezing point, partly, at least, because it separates with the solvent in the form of mixed crystals. Calcium nitrate is slightly dissociated and ammonium chloride strongly associated in molten ammonium nitrate.

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