CCCCXLVI.—*Binary Systems comprising Carbamide with Certain Metallic Nitrates.*

By William John Howells.

In two previous papers (J., 1929, 910 ; 1930, 2010) the systems carbamide–ammonium nitrate and carbamide–sodium nitrate were described. The present paper records the behaviour of carbamide with several other metallic nitrates. The experimental details were as in the first paper (above).

The compositions of the binary mixtures investigated are given in Table I. Measurements far beyond the melting point of carbamide were not possible on account of its decomposition. The thermal equilibrium diagrams of the systems have the following characteristics :

(1) *Carbamide and lithium nitrate.* Owing to the extreme deliquescence of the nitrate, a slow current of warm dry air was led into the freezing-point apparatus while the determinations were in progress. The thermal diagram has three branches, and exhibits two eutectic points—at 71° and 98·5°, and 18·8% and 50%, respectively, of lithium nitrate. The middle branch shows a maximum at 126° and approximately 36·5% of nitrate (= $33\frac{1}{3}$ mols. %) : this indicates the formation of a compound,

$$LiNO_3,2CO(NH_2)_2,$$

stable at its m. p., 126°. At the first eutectic point the solid phases are carbamide and the compound; at the second, lithium nitrate and the compound.

When the melt is cooled slowly it is possible to follow the freezing point curves of the two compounds to temperatures well below the eutectic points on account of the sluggishness with which the compound crystallises. Sudden cooling favours its crystallisation : a similar behaviour was observed by Philip in the binary system phenol-α-naphthylamine (J., 1903, **83**, 814).

(2) *Carbamide and calcium nitrate.* On account of the extreme

deliquescence of the salt, the same precautions were necessary as with lithium nitrate. The thermal diagram shows a eutectic point at 88° and 21% of nitrate, and a convex branch rising to a sharp maximum at 151·5° and 40·5% of nitrate (20 mols. %), indicating the formation of a compound, $Ca(NO_3)_2,4CO(NH_2)_2$, stable at it smelting point, 151·5°. This compound has been mentioned by previous workers, but not its melting point. It was not possible to investigate the system beyond 47·2% of calcium nitrate owing to cloudiness of the melt and to the difficulty with which the nitrate dissolved.

(3) *Carbamide and potassium nitrate.* These show a thermal diagram of the usual two-branched type; it exhibits a eutectic point at 109·5° and 24·5% of nitrate. The right-hand limb shows a slight break at 129°, corresponding to the transition of rhombohedral to rhombic potassium nitrate at 129°.

The compositions of the eutectic mixtures for the ammonium, sodium, and potassium nitrate systems (those in which combination occurs are not considered) conform to Vanstone's generalisation (J., 1913, **103**, 1826), *viz.*, the greater the divergence in the melting points of the two components, the greater the molecular percentage of the lower-melting component in the eutectic mixture:

Component.	M. p.	Carbamide, mols. %.
NH_4NO_3	169·6°	54·18
$NaNO_3$	308	77·2
KNO_3	333	83·9

TABLE I.

(1) *Carbamide and lithium nitrate.*

$LiNO_3$, %.	F. p.	$LiNO_3$, %.	F. p.	$LiNO_3$, %.	F. p.	$LiNO_3$, %.	F. p.
0	132·0°	14·53	90·1°	29·56	117·5°	48·63 (*h*)	104·1°
2·78	126·7	19·52	74·0 (*a*)	32·60	122·5	50·38	100·6 (*d*)
4·67	122·3	19·83	64·1 (*f*)	35·92	125·9	52·85	121·3 (*e*)
7·93	113·9	22·98	44·7 (*g*)	39·39	123·7	54·10	127·9
10·79	105·0	25·68	106·8 (*b*)	42·25	122·0	57·07	146·4
11·31	102·9	27·89	113·5 (*c*)	46·36	113·2		

Eutectic arrests observed at points marked (*a*), (*b*), (*c*), (*d*), and (*e*) were at 70·7°, 71·1°, 71·2°, 98·6°, and 98·5°, respectively. The determinations marked (*f*) and (*g*) were made by cooling the melt slowly, and correspond to the prolongation of the carbamide curve. At the concentration marked (*h*), slow cooling gave a f. p. at 81·6°

(2) *Carbamide and calcium nitrate.*

$Ca(NO_3)_2$, %.	F. p.	$Ca(NO_3)_2$, %.	F. p.	$Ca(NO_3)_2$, %.	F. p.	$Ca(NO_3)_2$, %.	F. p.
0	132·2°	12·62	111·7°	24·00	102·4°(*a*)	40·13	151·3°
3·90	127·0	18·04	100·5	26·88	117·7 (*b*)	44·02	147·2
5·25	125·1	20·04	90·7	27·58	119·9	45·60	144·6
7·45	121·6	23·18	96·3	34·55	143·1	47·20	142·2

Eutectic arrests observed at points marked (*a*) and (*b*) were at 87·7° and 88·8°, respectively.

(3) *Carbamide and potassium nitrate.*

KNO_3, %.	F. p.	KNO_3, %.	F. p.	KNO_3, %.	F. p.	KNO_3, %.	F. p.
0	132·2°	14·75	115·6°	27·79	120·1°	34·26	141·8°
2·52	128·9	21·79	110·9	29·61	124·9 (*c*)	36·90	151·6
5·50	125·2	24·60	110·1 (*a*)	31·09	129·8		
8·93	121·2	26·25	114·1 (*b*)	32·64	136·1		

Eutectic arrests observed at points marked (*a*), (*b*), and (*c*) were at 109·8°, 109·7°, and 109·1°, respectively.

Molecular Association of Nitrates in Carbamide.—In addition to the above determinations, measurements of the freezing points were made when silver and thallous nitrates were added separately to about 20 g. of carbamide. With the former, the melt became slightly violet in colour, so it was not possible to proceed beyond the concentration indicated in Table II.

TABLE II.

Substance added.	G. per 100 g. of carbamide.	Δ.	Mol. depn.	*M*, obs.	Assoc. factor.
Dextrose	4·680	5·32°	205°	—	—
NH_4NO_3	2·114	3·1	117	140	1·75
	2·880	4·0	111	148	1·85
	10·988	14·0	102	161	2·01
$NaNO_3$	2·235	3·7	141	124	1·46
	5·091	8·0	134	130	1·53
	7·411	10·6	122	143	1·68
KNO_3	2·588	3·3	129	161	1·59
	5·820	7·0	121	171	1·69
	9·802	11·0	113	183	1·81
$TlNO_3$	5·006	2·8	149	367	1·38
	11·277	5·7	135	405	1·52
	20·783	9·8	126	434	1·63
$LiNO_3$	2·864	5·3	128	111	(1·61)
	4·897	9·7	137	103	
	8·618	18·1	145	98	
	12·756	29·1	157	90	(1·30)
$AgNO_3$	4·535	5·2	195	179	(1·05)
	8·320	10·2	208	168	
	13·380	17·8	226	154	(0·91)
$Ca(NO_3)_2$	4·056	5·2	210	160	(0·98)
	5·491	7·1	212	159	
	8·055	10·6	216	156	
	14·439	20·5	233	144	(0·88)

The figures for the first three substances are from the two previous papers already mentioned. The first concentration given for each compound, except lithium nitrate, is approximately of the same molar concentration in each case, *viz.*, 0·026 mol. in 100 g. of carbamide. A lower concentration might involve an appreciable error in the f. p. depression owing to the slight, but unavoidable, decomposition of carbamide.

The effective molecular weights observed are calculated on the assumption that dextrose has the "normal" molecular weight in molten carbamide.

Solutes which combine with the solvent being omitted, the association factors, or degrees of complexity, exceed unity in all cases. Yet, in all probability, the molten solutions concerned conduct an electric current. Ions are doubtless present—ions active from the standpoint of electrical conductivity, but whose depression of the freezing-point effect and osmotic effect are masked by the presence of complex solute molecules. It may be, too, that a considerable proportion of the ions are osmotically inactive. It is clear that the cryoscopic method does not give the real, but only the effective, or average, association factors of these metallic nitrates in carbamide.

The association factors for the nitrates of ammonium, sodium, potassium, and thallium increase with increasing concentration, as might be expected from the law of mass action. On the other hand, the molecular depressions for the nitrates of lithium, calcium, and silver increase with increasing concentration because these solutes combine with the solvent, and so reduce the amount of active solvent present in the melt. Thus, these addition compounds exist as definite compounds in the solution.

Lithium in many of its compounds resembles silver and calcium more closely than it does sodium and potassium. Lithium nitrate, like calcium nitrate, forms hydrates, and since it forms a compound with carbamide it behaves like the nitrates of calcium and silver.

If the value 205 is accepted as the approximate molecular-depression constant for molten carbamide, the thermodynamical equation $\Delta = 0{\cdot}02T^2/L$ leads to the value 16·0 calories for the latent heat of fusion of carbamide. Application of Trouton's rule as applied by Walden to substances at their melting point, *viz.*, ML/T = constant = 13·5 for unassociated substances, shows that M, the molecular weight of carbamide, is 342. This may be far too high a value, but it indicates that carbamide is associated. Associated substances are usually chemically very active. This possibly accounts for the very many stable compounds that carbamide forms with neutral substances.

Summary.

The thermal diagram for the system carbamide–lithium nitrate indicates the formation of a compound $LiNO_3,2CO(NH_2)_2$, stable at its m. p., 126°; that for carbamide–calcium nitrate shows the formation of $Ca(NO_3)_2,4CO(NH_2)_2$, also stable at its m. p., 151·5°; and that for carbamide–potassium nitrate exhibits a eutectic point

at 109·5° and 24·5% nitrate. The right-hand limb shows a transition point at 129°.

The nitrates of ammonium, sodium, potassium, and thallium show molecular association in molten carbamide. They do not—at least, under the conditions involved—form compounds with carbamide.

LANPARK RD., PONTYPRIDD. [*Received, October* 31*st*, 1931.]