CCLX.—*The Ternary System Carbamide–Ammonium Nitrate–Sodium Nitrate.*

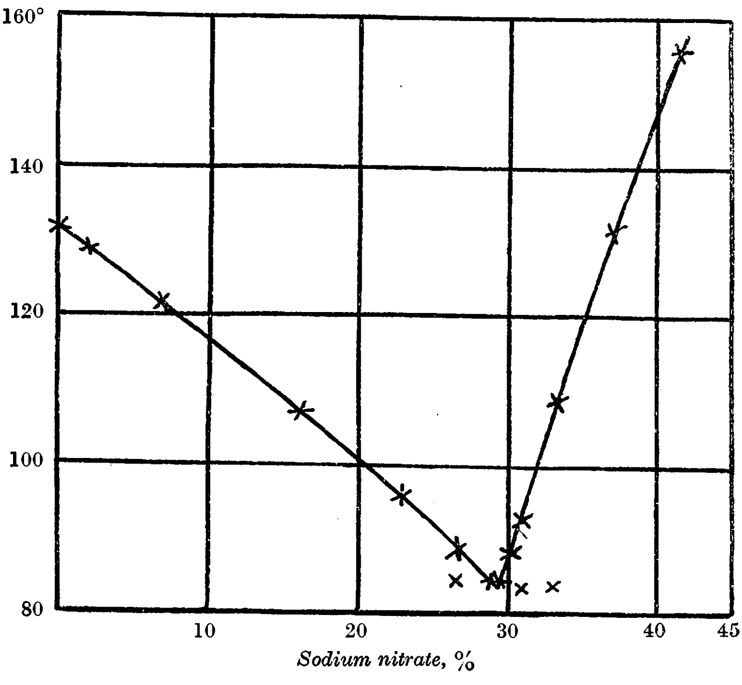
By William John Howells.

In a previous paper (J., 1929, 910) the behaviour of the system carbamide–ammonium nitrate was described, and that of the ternary system carbamide–ammonium nitrate–sodium nitrate is now recorded. A complete study of the system was not possible since carbamide and ammonium nitrate decompose at temperatures well below the m. p. of sodium nitrate.

The relevant binary systems show the following characteristics: (1) Carbamide and ammonium nitrate (Howells, *loc. cit.*) show a eutectic at 44·7° and 47% of carbamide; the transition of regular to rhombohedral ammonium nitrate occurs at 126°. (2) As a mean of the results of Early and Lowry (J., 1922, **121**, 963) and of Perman (*ibid.*, p. 2473), the eutectic of ammonium and sodium nitrates

FIG. 1.

Carbamide + sodium nitrate.

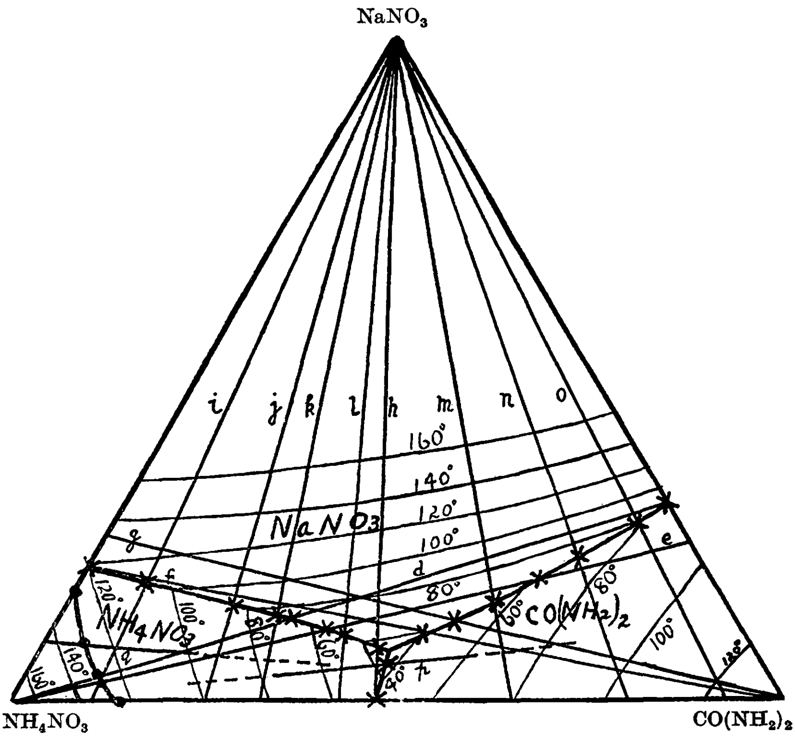


may be placed at 120·9° and 20·3% of sodium nitrate, and the transition point of the former is at 126° (see above). (3) The thermal diagram of the system carbamide–sodium nitrate is shown in Fig. 1; it exhibits a eutectic point at 83·9° and 29·5% of sodium nitrate, but no compound formation.

The Ternary System.—Details of the experimental work involved were as previously described (*loc. cit.*). The compositions of the 14 ternary mixtures investigated are indicated in the tables of freezing points. The thermal equilibrium curves corresponding to these various systems are shown as projections on an equilateral triangle in the general equilibrium diagram (Fig. 2), which indicates the solid phases separating and the phase reactions involved. The minimum points on the curves are denoted by crosses, and transition points by dots. Isothermal lines are shown at intervals of 20°.

A few curves require special mention. The left-hand branch of Curve *d* (right-hand in Fig. 2) is slightly convex, rising to a maximum at 95°; the solid phase is sodium nitrate. A sharp minimum occurs

FIG. 2.



at 69° and 58% of ammonium nitrate; at this point the solid phases sodium nitrate and ammonium nitrate are precipitated. The ammonium nitrate branch shows a transition point at 126·5°.

Curve *e* consists of three main branches. The middle branch, where the solid phase is sodium nitrate, is slightly convex, showing a maximum at 66·3°. Two sharp minima occur at 63° and 57°, corresponding to 22·3% and 53% of ammonium nitrate, respectively. The third branch has a transition point at 126·5°. The convex branches in Curves *d* and *e* do not indicate the formation of compounds, since their projections run to the ammonium nitrate corner (Fig. 2), and not parallel to the base of the triangle.

Curve *f* consists of two main branches, and shows a sharp minimum at 40° and 46·3% of carbamide. The left-hand branch shows a break at 108° and 7·5% of carbamide. Up to this point the curve runs—for practical purposes—along a ternary eutectic curve.

The other curves are of the usual two-branch type. Only essential portions of systems *p* and *q* have been studied. Similarly to Curves *a*, *b*, *d*, and *e*, Curves *i* and *q* show transition points at 126·5° and 126·7°, respectively.

There are three main areas in the diagram. In the largest, the solid phase precipitated is sodium nitrate. The ammonium nitrate area is sub-divided into two distinct sections by a monovariant boundary line where the two solid phases, regular and rhombohedral ammonium nitrate, are precipitated. The transition of rhombohedral to α-rhombic ammonium nitrate at 83° was not observed : apparently the latter modification is not readily formed in the presence of carbamide (compare the system ammonium nitrate–water; Millican, Joseph, and Lowry, J., 1922, **121**, 959).

The ternary eutectic point of the system occurs at 37·1°, and a composition of about 45% carbamide, 47·5% ammonium nitrate, and 7·5% sodium nitrate. The temperature given is the mean of a series of ternary eutectic arrests observed.

Analysis of one solid phase. The left-hand branches of Curves *f* and *g* show a somewhat sudden change in gradient, and in order to examine this more closely, the solid phase was analysed at a few appropriate points on the largest saturation surface. It was practically impossible to drain the solid phase free from the viscous mother-liquor, so the analysis was done indirectly by analysing the mother-liquor remaining after precipitation. When the temperature was allowed to fall very slowly the minute crystals settled fairly readily to the bottom of the tube. Portions of the initial melt and of the final almost clear mother-liquor were treated in the same way. Since the other two components were decomposed and volatilised at high temperatures, the sodium nitrate present was estimated by conversion into sulphate.

In the absence of a better method, the ammonium nitrate was estimated by boiling with an excess of standard potassium hydroxide solution. Any of the latter which was decomposed by the carbamide present was converted into an equivalent amount of carbonate, so that titration of the excess alkali with standard sulphuric acid gave the percentage of ammonium nitrate present; the end-point with methyl-orange was not sharp, however. The carbamide was estimated by difference. The following results were obtained :

		Initially.		Finally.	
(a)	$NaNO_3$	24·92%		16·39%	
	NH_4NO_3	52·07%	Ratio 2·26 : 1	58·03%	Ratio 2·27 : 1
	$CO(NH_2)_2$	23·01%		25·58%	
(b)	$NaNO_3$	24·97%		16·99%	
	NH_4NO_3	44·81%	Ratio 1·48 : 1	49·88%	Ratio 1·51 : 1
	$CO(NH_2)_2$	30·22%		33·13%	

Allowing for error in the estimation of ammonium nitrate (a small error is magnified many times in the final results), and for the attendant error in the estimation of carbamide, it appears that the proportion of ammonium nitrate to carbamide remains constant during separation of the solid phase. It follows that the solid phase is sodium nitrate. (For the theoretical basis—which is geometrical —of this argument, see Bancroft, *J. Physical Chem.*, 1902, **6**, 178; Carveth, *ibid.*, 1898, **2**, 209.)

Freezing Points of Various Mixtures.

(i) *Carbamide and sodium nitrate.*

$NaNO_3$, %.	F. p.	$NaNO_3$, %.	F. p.	$NaNO_3$, %.	F. p.	$NaNO_3$, %.	F. p.
0	132·0°	23·22	95·8°	29·49	84·3°	33·20	109·0° (*d*)
2·19	128·3	27·00	88·8(*a*)	30·50	88·4	36·69	131·7
6·90	121·4	29·00	84·1(*b*)	31·01	92·5(*c*)	41·30	156·0
16·35	106·8						

Eutectic arrests observed at points marked (*a*), (*b*), (*c*), and (*d*) were at 84·9°, 84·5°, 83·6°, and 84·2°, respectively; mean 84·3°.

(ii) (*Carbamide + sodium nitrate*) *eutectic and ammonium nitrate.*

NH_4NO_3, %.	F. p.	NH_4NO_3, %.	F. p.	NH_4NO_3, %.	F. p.	NH_4NO_3, %.	F. p.
0	83·9°	21·13	94·7°	60·23	74·0°	90·28	137·2°
2·17	84·4	26·02	94·0	64·86	83·6	91·20	139·5
3·37	85·4	37·90	89·7(*a*)	69·86	94·4	93·84	148·7
5·66	87·9	45·49	85·5(*b*)	81·50	116·5	95·13	153·0
14·16	94·5	50·05	79·5	82·98	118·5	95·69	154·0
20·03	95·0	56·14	71·6(*c*)	86·87	126·0		

Ternary eutectic arrests observed at points marked (*a*), (*b*), and (*c*) were at 36·5°, 37·2°, and 37·2°, respectively.

(iii) (*Carbamide* + 24% *sodium nitrate*) *mixture and ammonium nitrate.*

NH_4NO_3, %.	F. p.	NH_4NO_3, %.	F. p.	NH_4NO_3, %.	F. p.	NH_4NO_3, %.	F. p.
0	94·5°	26·01	64·2°	50·97	58·1°	87·69	127·6°
7·79	85·4	28·20	64·7	56·39	63·0	89·63	134·3
14·84	75·3	35·03	66·3	61·86	74·9	93·57	146·8
18·29	70·3	39·99	65·4(*a*)	70·81	94·2	97·15	158·5
20·25	67·8	46·94	62·0	80·57	113·7	100	169·5
23·09	63·4						

A ternary eutectic arrest observed at the point marked (*a*) was at 37·0°.

(iv) (*Ammonium nitrate* + *sodium nitrate*) *eutectic and carbamide.*

$CO(NH_2)_2$, %.	F. p.	$CO(NH_2)_2$, %.	F. p.	$CO(NH_2)_2$, %.	F. p.	$CO(NH_2)_2$, %.	F. p.
2·88	115·9°	17·97	97·0°	31·42	76·6°(*a*)	55·77	60·4°
5·01	112·0	20·86	93·5	32·95	74·5	67·36	83·0
5·46	111·1	22·76	91·7	35·56	68·7	70·96	89·0
8·00	107·4	25·20	87·4	37·97	64·0	74·40	95·0
10·31	105·6	26·10	86·6	41·07	56·1	77·40	99·8
12·79	103·0	27·46	83·5	44·93	42·7(*b*)	80·60	104·9
14·80	101·0	30·05	79·4	51·48	51·3	100	132·0

Ternary eutectic arrests at points marked (*a*) and (*b*) were at 37·3° and 37·5°, respectively.

(v) (*Ammonium nitrate and* 25% *sodium nitrate*) *mixture and carbamide.*

$CO(NH_2)_2$, %.	F. p.	$CO(NH_2)_2$, %.	F. p.	$CO(NH_2)_2$, %.	F. p.	$CO(NH_2)_2$, %.	F. p.
0	131·7°	31·01	95·2°	38·92	78·2°	52·11	51·4°
4·66	127·6	32·94	91·8	45·08	62·6	53·23	52·9
14·98	118·0	35·10	87·0	48·01	51·4	54·93	56·6
23·00	107·7	36·82	82·9	49·97	46·1	58·01	63·6
28·05	100·5						

(vi) (*Ammonium nitrate and carbamide*) *eutectic and sodium nitrate.*

$NaNO_3$, %.	F. p.	$NaNO_3$, %.	F. p.	$NaNO_3$, %.	F. p.	$NaNO_3$, %.	F. p.
0	44·7°	10·50	47·6°(*b*)	16·1	82·6°	22·37	114·7°
3·93	39·9	11·92	54·9	18·51	96·9	23·00	116·0
7·07	39·1	12·99	61·6	18·96	98·7	25·05	125·4
8·79	39·8(*a*)	13·99	68·7	19·98	103·2	30·40	145·1

Ternary eutectic arrests observed at points marked (*a*) and (*b*) were at 37·6° and 37·2°, respectively.

(vii) (*Ammonium nitrate and* 10% *carbamide*) *mixture and sodium nitrate.*

$NaNO_3$, %.	F. p.	$NaNO_3$, %.	F. p.	$NaNO_3$, %.	F. p.	$NaNO_3$, %.	F. p.
0	135·0°	7·68	120·4°	18·51	106·8°	24·88	130·8°
1·17	131·0	10·12	116·5	19·50	110·1	30·00	148·0
2·05	128·9	15·08	110·1	22·14	121·3	32·28	154·3
4·08	124·8	16·81	108·6				

(viii) (*Ammonium nitrate and* 25% *carbamide*) *mixture and sodium nitrate.*

$NaNO_3$, %.	F. p.	$NaNO_3$, %.	F. p.	$NaNO_3$, %.	F. p.	$NaNO_3$, %.	F. p.
0	99°	13·45	85·4°	16·55	95·9°	21·01	115·6°
4·39	94·9	14·39	85·3	17·88	102·1	25·19	131·4
9·94	89·5	15·01	88·1				

(ix) (*Ammonium nitrate and 32% carbamide) mixture and sodium nitrate.*

$NaNO_3$, %.	F. p.	$NaNO_3$, %.	F. p.	$NaNO_3$, %.	F. p.	$NaNO_3$, %.	F. p.
0	83·0°	11·43	72·9°	16·41	92·7°	25·24	130·6°
4·92	77·9	12·79	73·6	19·89	108·7	29·49	145·2
7·12	75·9	13·57	76·6				

(x) (*Ammonium nitrate and 42% carbamide) mixture and sodium nitrate.*

$NaNO_3$, %.	F. p.	$NaNO_3$, %.	F. p.	$NaNO_3$, %.	F. p.	$NaNO_3$, %.	F. p.
0	59·0°	11·97	60·0°	15·54	83·2°	21·00	110·5°
5·37	55·0	12·65	63·4	16·53	89·2	22·47	116·7
9·02	52·1	14·12	74·3	19·00	101·9	27·01	134·9
11·19	53·2						

(xi) (*Ammonium nitrate and 65% carbamide) mixture and sodium nitrate.*

$NaNO_3$, %.	F. p.	$NaNO_3$, %.	F. p.	$NaNO_3$, %.	F. p.	$NaNO_3$, %.	F. p
0	79·0°	12·68	59·7°	18·89	78·6°	23·44	105·2°
4·14	73·3	14·06	59·3	21·03	91·8	25·02	113·2
5·94	70·8	15·02	57·6(*a*)	21·98	97·8	27·22	124·0
8·92	66·1	16·17	57·5	22·96	102·8	31·36	141·7
11·61	62·9	17·11	64·6				

A ternary eutectic arrest observed at the point marked (*a*) was at 36·4°.

(xii) (*Ammonium nitrate and 80% carbamide) mixture and sodium nitrate.*

$NaNO_3$, %.	F. p.	$NaNO_3$, %.	F. p.	$NaNO_3$, %.	F. p.	$NaNO_3$, %.	F. p.
0	105·0°	14·98	82·3°	22·01	73·2°	27·02	106·1°
3·06	100·5	15·65	81·5	23·21	80·9	29·13	118·0
6·81	94·8	18·10	76·5	24·76	92·4	31·19	128·9
11·14	88·5	20·98	71·7				

(xiii) (*Ammonium nitrate and 94% carbamide) mixture and sodium nitrate.*

$NaNO_3$, %.	F. p.	$NaNO_3$, %.	F. p.	$NaNO_3$, %.	F. p.	$NaNO_3$, %.	F. p.
0	124·0°	23·93	87·4°	28·13	86·0°	30·65	104·7°
7·34	114·5	26·06	81·8	28·95	92·9	31·66	111·6
13·45	104·7	27·00	80·9	29·88	97·9	33·02	120·4
18·40	96·0						

(xiv) (*Carbamide and 11% sodium nitrate) mixture and ammonium nitrate.*

NH_4NO_3, %	43·81	45·50	47·66	49·92	55·99	57·73
F. p.	48·6°	45·7°	41·4°	42·0°	55·6°	59·2°

(xv) (*Ammonium nitrate and 9% sodium nitrate*) *mixture and carbamide.*

$CO(NH_2)_2$, %	0	1·53	3·32	5·02	7·93	11·49
F. p.	147·0°	140·8°	134·5°	128·6°	122·0°	115·1°

Summary.

The general equilibrium diagram of the system consists of three main areas, or saturation surfaces. The solid phase precipitated on the largest area is sodium nitrate.

A number of the curves show transition points at about 126°, corresponding to the transition of regular to rhombohedral ammonium nitrate. Consequently, the ammonium nitrate area is subdivided into two. The transition of rhombohedral to α-rhombic ammonium nitrate, at 83°, was not observed.

The ternary eutectic point of the system is at 37·1°, and a composition of 45% carbamide, 47·5% ammonium nitrate, and 7·5% sodium nitrate. The corresponding molecular percentages, *viz.*, 52·4, 41·5, and 6·1, respectively, are in the inverse order of the melting points of the components.

MUNICIPAL SECONDARY SCHOOL,
QUAKERS' YARD.

[*Received, July* 16*th*, 1930.]