

*Citation:*

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The two above equations pass now into one :

$$\log \frac{1-x_1'}{x_1'} = \frac{q_1}{RT_e} \beta'(1-2x_1') \dots \dots \dots (18)$$

In this complementary composition we have a distinct criterion, whether or no it is allowed to put  $\alpha'_1 = \alpha'_2$  (i. e.  $r = 0$ ). Further the equation (18) furnishes a simple means, when  $r$  may really be put  $= 0$ , for calculating the quantity  $\beta'$  from the composition  $x_1'$  of the solid phase at the eutectic point.

If we find e.g.  $x_1' = 0,1$ , we may find by means of  $T_e = 500$ ,  $q_1 = 2400$ .

$$\log 9 = \frac{2400}{1000} \beta' \times 0,8,$$

hence :

$$\beta' = \frac{25}{48} \log 9 = 1,14.$$

If  $x'$  had been 0,01, we should have found with the same values of  $T_e$  and  $q_1$  :

$$\log 99 = \frac{12}{5} \beta' \times 0,98,$$

hence .

$$\beta' = \frac{125}{294} \log 99 = 1,95.$$

It is seen, that a slight increase of  $\beta'$  is able to depress the composition  $x_1'$  of the solid phase at the eutectic point very strongly. This is of course in connection with the enormously strong decrease of the relation  $\frac{x'}{x}$  with increasing  $\beta'$ . This relation was e.g. for  $T = T_1$

and great  $\beta'$  represented by  $\left(\frac{x'}{x}\right)_0 = e^{-\frac{\alpha'}{RT_1}}$  (see § 3), which converges very quickly to 0.

**Chemistry.** — “*The phenomena of solidification and transformation in the systems  $NH_4NO_3$ ,  $AgNO_3$  and  $KNO_3$ ,  $AgNO_3$ .*” By Professor H. W. BAKHUIS ROOZEBOOM.

(Communicated in the meeting of September 26, 1903.)

Of the nitrates of univalent metals, those of Li, Na, Ag,  $NH_4$ , K, Tl have been studied more in detail as to their mutual relations. It has already been shown that the nitrates of the first three are very prone to yield mixed crystals and the same takes place with the last three.  $LiNO_3$  and also  $NaNO_3$  do not seem to form with the

nitrate of the last group any mixed crystals at all or else only to a small extent and in any case they do not enter into chemical combination.

As regards the relation of  $\text{AgNO}_3$  to the nitrates of the second group, the only system examined up to the present (by VAN EYK) was that consisting of  $\text{AgNO}_3 + \text{TlNO}_3$  in which a compound in the proportion 1:1, was formed. To complete our knowledge in this direction, the systems  $\text{NH}_4\text{NO}_3 + \text{AgNO}_3$  and  $\text{KNO}_3 + \text{AgNO}_3$  have been investigated by ZAWIDZKI and Ussow and the results are comprised in the Figures 1 and 2.

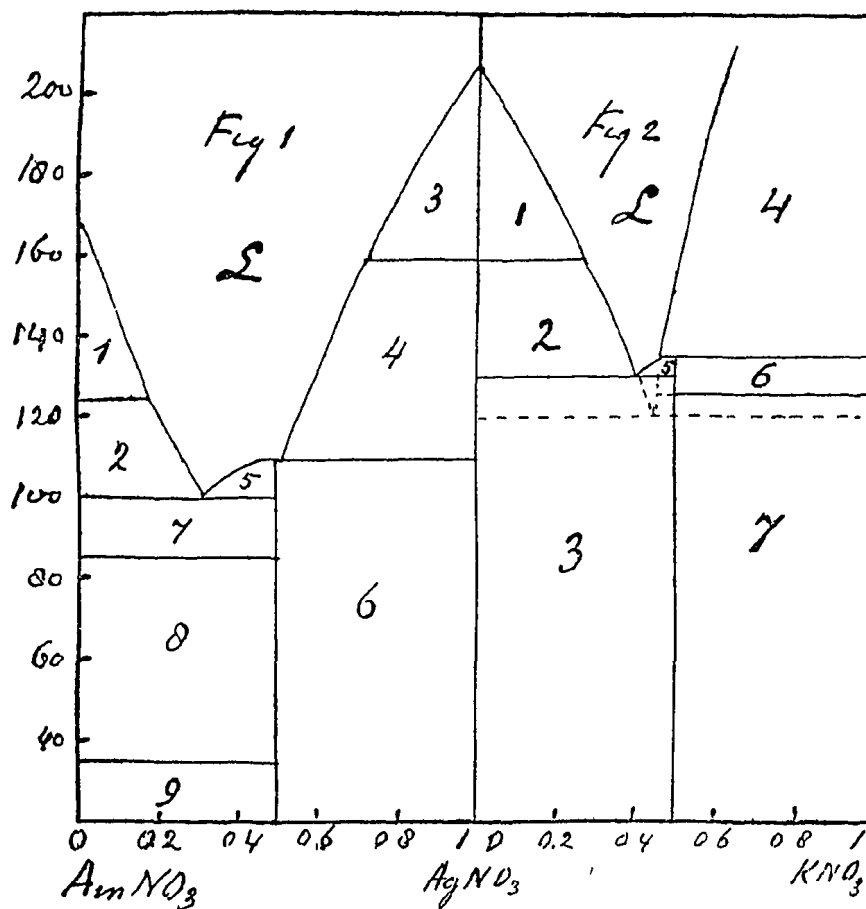


Fig. 1 and 2.

The first system is interesting on account of the fact that with  $\text{NH}_4\text{NO}_3$ , four and with  $\text{AgNO}_3$ , two solid phases succeed each other which, starting from the melting-point, we will designate by Am 1—4 and Ag 1—2.

It now appears that in the case of mixtures of the two salts the

transition point of  $\text{AgNO}_3$  and the first transition point of  $\text{NH}_4\text{NO}_3$  falls in the region where these mixtures are still partially liquid; the two lower transition points of  $\text{NH}_4\text{NO}_3$ , however, are situated in the region where everything has already become solidified.

Owing to this, the deposition of  $\text{AgNO}_3$  from melted mixtures rich in silver takes place according to two lines which meet each other at  $160^\circ$ ; the solidification of  $\text{NH}_4\text{NO}_3$  from mixtures rich in this salt, also takes place along two lines which meet each other at  $125^\circ$ . Neither transition point is modified by the mixing process, from which we may conclude that the salts are deposited in a pure condition and do not yield mixed crystals.

From the intermediate concentrations, however, a compound  $\text{D} = \text{NH}_4\text{NO}_3 \cdot \text{AgNO}_3$  is deposited with a pure melting point at  $109.6^\circ$ . Its melting-point-line extends towards the  $\text{Ag}$ -side only up to 52 Mol. %, towards the  $\text{NH}_4$ -side up to 30 %  $\text{Ag}$ . Consequently, all mixtures of 50—100 %  $\text{Ag}$  solidify at  $109.6$  to conglomerates of  $\text{D} + \text{Ag}_2$  and all mixtures of 0—50 %  $\text{Ag}$  at  $101.5$  to conglomerates of  $\text{Am}_2 + \text{D}$ .

The latter, on further cooling, undergo a new transformation at  $85^\circ$  and  $35^\circ$  owing to the reversion of  $\text{Am}_2$  into  $\text{Am}_3$  and then into  $\text{Am}_4$ . As both take place in the different mixtures at the same temperature at which reversion of the pure  $\text{AmNO}_3$  takes place, this proves that no mixed crystals occur between this salt and the double salt.

If now we express the liquid mixtures by  $\text{L}$  we have in Fig. 1 the following regions.

1	$\text{Am}_1 + \text{L}$	7	$\text{Am}_2 + \text{D}$	3	$\text{L} + \text{Ag}_1$
2	$\text{Am}_2 + \text{L}$	8	$\text{Am}_3 + \text{D}$	4	$\text{L} + \text{Ag}_2$
5	$\text{D} + \text{L}$	9	$\text{Am}_4 + \text{D}$	6	$\text{D} + \text{Ag}_2$

The system  $\text{AgNO}_3 + \text{KNO}_3$  is simpler in so far that  $\text{KNO}_3$  has only got one transition temperature at  $126^\circ$ .

The transition point of  $\text{AgNO}_3$  again falls within the partially liquid region and the solidification of the mixtures rich in  $\text{Ag}$  therefore, again takes place according to two lines which meet each other at  $160^\circ$ . Under normal conditions, the transition point of  $\text{KNO}_3$  falls within the solid region, consequently there is only one melting point line for the first form of the  $\text{KNO}_3 : \text{K}_1$ ; in the figure this line is represented only from  $210^\circ$  to lower temperatures; it must be imagined to extend to the  $\text{KNO}_3$  axis at its melting point of  $338^\circ$ .

From the intermediate concentrations there is also deposited a double salt  $\text{D} = \text{KNO}_3 \cdot \text{AgNO}_3$ , but its melting-point-line only extends from

131° and 38 %  $\text{KNO}_3$  to 134°.5 and 45 %  $\text{KNO}_3$ ,

Consequently, there exists no pure melting point but D is transformed on heating to 134°.5 into  $\text{KNO}_3$  solid + solution of 45 %.

All mixtures of 0—50  $\text{KNO}_3$  solidify at 131° to  $\text{Ag}_2 + \text{D}$ , all mixtures of 50—100  $\text{KNO}_3$  at 134°.5 to conglomerates of  $\text{D} + \text{K}_1$ . The first named remain unchanged on further cooling. The last named ought to change at 126° into  $\text{D} + \text{K}_2$  but this takes place with great difficulty.

The double salt is also not readily formed. If it does not make its appearance, the melting-point-line for  $\text{K}_1$  runs through to 126°, and below this  $\text{K}_1$  is converted into  $\text{K}_2$  much more readily than in the solid conglomerates. The melting-line of  $\text{K}_2$  runs through to 120° at 42 %  $\text{KNO}_3$  where it meets the prolongation of the melting line of  $\text{Ag}_2$ . If D does not appear, all liquid mixtures solidify at 120° to a conglomerate of  $\text{Ag}_2 + \text{K}_2$ .

The following zones comprised between the full lines represent stable conditions

1	$\text{Ag}_1 + \text{L}$	4	$\text{L} + \text{K}_1$
2	$\text{Ag}_2 + \text{L}$	5	$\text{L} + \text{D}$
3	$\text{Ag}_2 + \text{D}$	6	$\text{D} + \text{K}_1$
		7	$\text{D} + \text{K}_2$

All metastable boundaries are indicated by dotted lines. The regions concerned may be easily deduced from the figure.

From the above it follows that at the ordinary temperature, only the simple salts in the forms which are stable at that temperature and also the double salts 1 : 1 can occur as stable conditions; this agrees with what RETGERS has previously found for the products of crystallisation from aqueous solutions at 15°.

**Chemistry.** — “*The transformation of benzidine*”. By Prof. A. F. HOLLEMAN and J. POTTER VAN LOON.

(Communicated in the meeting of September 26, 1903).

In the report of the meeting of this section of Nov. 29, '02 there will be found a preliminary communication as to the experiments conducted in my laboratory by Dr. J. POTTER VAN LOON, who has since brought his research to a close. His results are briefly described below.

The method by which he succeeded in obtaining benzidine and hydrazobenzene in a perfectly pure condition has already been given in the preliminary communication. In connection with this it may be mentioned that hydrazobenzene was separated as a snow-white