Equilibrium in the System:
Potassium Chlorate, Potassium Nitrate and Water at 25°C.

By

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According to Herbette,[1] two kinds of crystals separate when a mixed solution of potassium chlorate and nitrate is evaporated. The one is monoclinic and contains both salts, and the other is rhombic and consists of the pure nitrate. Thus, whilst potassium nitrate may take an unstable form isomorphous with the ordinary form of the chlorate, there seems to be no second form of the latter isomorphous with the stable form of the former.

From the above cited fact, a systematic investigation of the system consisting of potassium chlorate, potassium nitrate, and water was desirable to add an example of a special type to the literature of the heterogeneous equilibrium of salts and water, the author took up the problem to study it from the standpoint of the phase rule.

As the materials, potassium chlorate and nitrate of the Jap. Pharm. purified by thrice recrystallisation, and ordinary distilled water were used.

The experiments were carried out in the following way : Mixtures of salts in different proportions were put each in an Erlenmeyer flask of a capacity of about 30 cc. with a well ground stopper, which was made to rotate in a thermostat at 25·0°C, for about two days and nights. When equilibrium was attained, the flask was allowed to

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[1] M. J. Herbette, C.R., **143.** 128–130, (1906).

stand still in the same thermostat until the suspended matter had completely subsided, then a proper portion of the mother liquor was taken out by a pipette, through a short glass tube with purified cotton wool and attached to the pipette by a rubber tubing, to a weighing bottle and subjected to analysis.

To prepare the residue for analysis, it was pressed down between folded filter paper to remove as much as possible of the adhering mother liquor, then a part of it, previously weighed, was redissolved in water to a definite volume.

The methods of analysis used were as follows: Exactly 10 cc. of the solution, in a beaker, was diluted with about 30 cc. of water, treated with 40 cc. of a 10 per cent. solution of ferrous sulphate, heated with constant stirring till it began to boil, and kept at that temperature for about fifteen minutes. Aqueous ammonia which was absolutely free from chlorine was added into this solution to remove ferric salt. It was gently boiled until the excess of ammonia was expelled, then the precipitate was filtered and washed five times with hot water. The filtrate was used for the determination of the chlorine according to Volhard's method, improved by V. Rothmund and A. Burgstaller.[1] Potassium was determined as potassium sulphate by means of sulphuric acid, as directed in Treadwell-Hall's "Analytical Chemistry"[2]

Results.

The results are given in the following table :—

TABLE I.

	Composition of solution in gram percentages.		Composition of residue[3] in gram percentages.	
No.	$KClO_3$	KNO_3	$KClO_3$	KNO_3
1	7·745	...	...	...
2	7·65	0·68	94·44	0·81
3	7·07	1·55	93·95	1·90
4	6·52	3·59	93·37	2·83
5	5·76	7·12	93·65	4·85
6	5·10	12·81	91·44	6·80

1 V. Rothmund and A. Burgstaller: Z. anorg. Chem., **63.** 330, (1909).
2 Treadwell-Hall: Analytical Chemistry. Vol. II, 41.
3 The residue was slightly wet with the mother liquor.

7	4·39	18·97	88·85	9·11
8	3·90	27·14	86·05	11·90
9	3·90	27·12	50·65	43·63
10	3·90	27·14	19·13	76·96
11	3·90	27·16	9·54	86·96
12	3·61	27·21	0·17	95·98
13	1·63	27·57	0·33	95·18
14	...	27·24	...	...

The following table was calculated from the last, using the following formula to represent the compositions of the solutions and residues :

$$100m H_2O \ x KClO_3 \ (100-x) KNO_3$$

and in the table, a function of m, $N = \dfrac{100m}{100+m}$, was calculated to represent the amount of water.

TABLE II.

| | Solution. | | Residue. | | |
No.	N	x	N	x	Formula of the residue found graphically.
1	44·76	100·00	...	...	$KClO_3$
2	42·25	90·29	0·34	98·97	$K(ClO_3, NO_3)$
3	41·00	79·01	0·29	97·62	,,
4	36·00	60·00	0·26	86·47	,,
5	29·17	40·01	0·10	94·11	,,
6	21·30	24·73	0·12	91·73	,,
7	16·00	16·03	0·14	88·95	,,
8	11·30	10·59	0·14	85·63	,,
9	11·32	10·59	0·37	48·92	$K(ClO_3, NO_3) + KNO_3$
10	11·30	10·59	0·24	17·01	,, ,,
11	11·53	10·84	0·21	8·30	,, ,,
12	11·39	9·85	0·22	0·14	KNO_3
13	12·08	4·64	0·26	0·29	,,
14	13·03	0·00	...	...	,,

The above results are graphically shown in Fig. 1, in a square diagram, measuring water (N) on the vertical side and molar percentages of the chlorate (x) on the horizontal side.
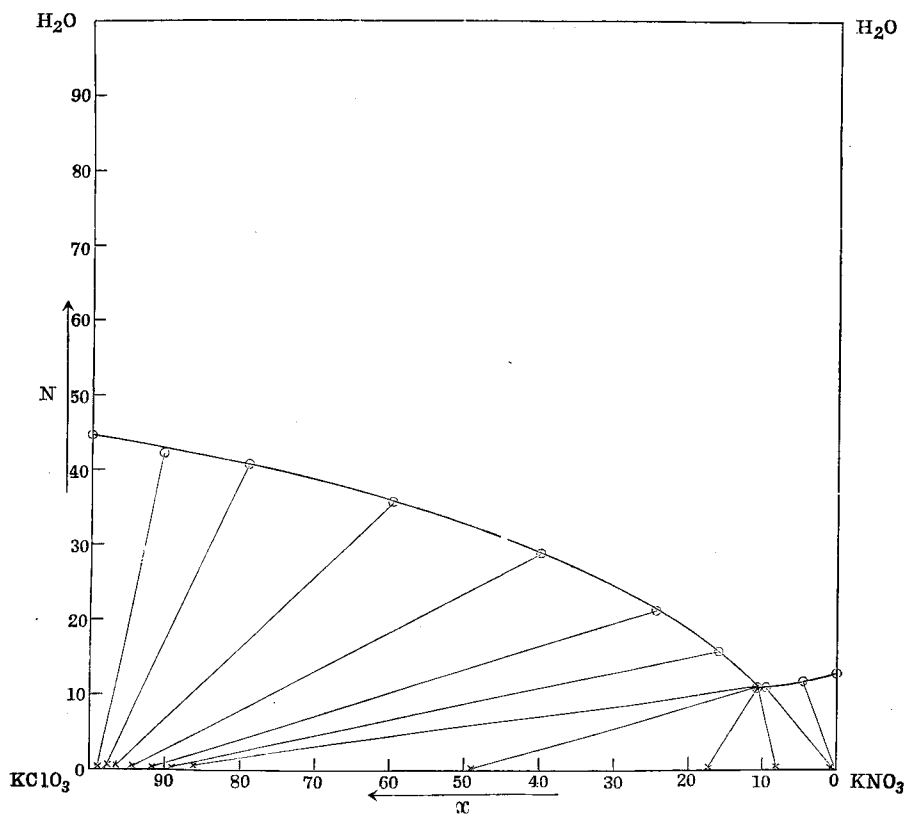
Fig. I.

The following table was calculated from Table I, using the following formulae to represent the molar percentages of the salts in the solutions and residues:

$$x\text{KNO}_3 \ (100-x)\text{KClO}_3 \quad \text{Solution,}$$
$$y\text{KNO}_3 \ (100-y)\text{KClO}_3 \quad \text{Residue.}$$

TABLE III.

No.	Solution. x	Residue. y
I	0·00	0·00
2	9·71	1·03
3	20·99	2·38

4	40·00	3·53
5	59·99	5·89
6	75·27	8·27
7	83·97	11·05
8	89·41	14·37
9	89·41	51·08
10	89·41	82·99
11	89·16	91·70
12	90·15	99·86
13	95·36	99·71
14	100·00	100·00

The above results are graphically shown in Fig. 2, in a square diagram, measuring molar percentages of the nitrate in the solutions (x) on the vertical side and those in the residues (y) on the horizontal side.
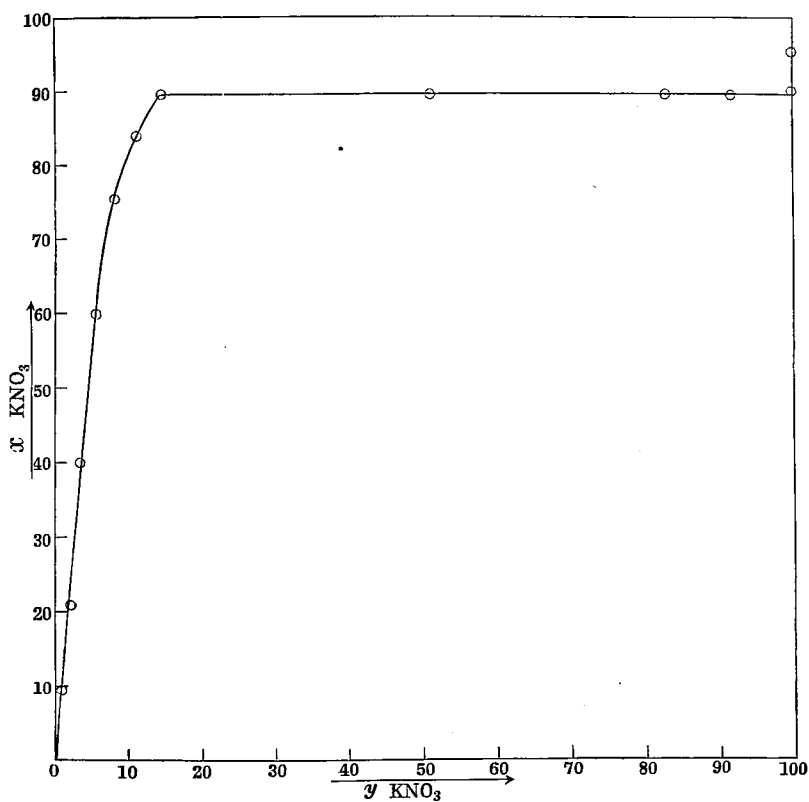

Fig. 2.

The crystalline form of the solid solution is monoclinic. From this fact it may be presumed that this mixed crystal is of the same kind as the crystal which was obtained by Herbette[1] by evaporation of a solution containing 15 grams of chlorate and 100 grams of nitrate. As the monoclinic crystals, separated by Herbette, contained 65 per cent. of the chlorate, the molar percentage of the nitrate in them is calculated as 39·47, but the mixed crystals obtained in the present investigation contains as the maximum only 14·37 of potassium nitrate in molar percentage (Fig. 2). This difference may be principally due to the difference of temperature.

Summary.

The equilibrium of a system consisting of potassium chlorate, potassium nitrate, and water was studied at 25·0°C.

The solubility of potassium chlorate was determined to be 7·745 grams per 100 grams solution or 8·395 grams in 100 grams water, and that of the potassium nitrate to be 27·24 grams per 100 grams solution or 37·44 grams in 100 grams water.

At 25°C. potassium chlorate takes up potassium nitrate to form a solid solution to an extent of 14·37 in molar percentage, while the nitrate takes up none of the chlorate.

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[1] *Loc. cit.*, 128–130.