EQUILIBRIA IN THE SYSTEM: $Ca(ClO_3)_2 + 2\,KCl \rightleftarrows 2\,KClO_3 + CaCl_2$ at 15° and 45°C.

By Yukichi OSAKA and Hideo NISHIO.[1]

Received April 26, 1930. Published June 28, 1930.

In the old process for manufacture of potassium chlorate, chlorine is passed into milk of lime and then potassium chloride is added to the solution thus formed to produce potassium chlorate by double decomposition. The reactions involved in this process are represented by the equations:

$$6Ca(OH)_2+6Cl_2=Ca(ClO_3)_2+5CaCl_2+6H_2O, \quad \ldots\ldots\ldots\ldots(1)$$

$$2KCl+Ca(ClO_3)_2=2KClO_3+CaCl_2. \quad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

We have studied the equilibria of the second reaction at $15.0°\pm0.1°$ and $45.0°\pm0.1°$C. One of us, Nishio, by whom the experiments were being carried out, had to leave the Laboratory and so we report here very briefly the results so far obtained.

The materials used were carefully purified and the method was the ordinary one.[2]

The compositions of the liquid phases are expressed according to the general formula:

$$100mH_2O,\ x\text{K},\ (100-x)\,(\tfrac{1}{2}\text{Ca}),\ y\text{Cl},\ (100-y)ClO_3.$$

The results are given in Tables 1 and 2 and graphically in Figs. 1 and 2.

The data with asterisk were calculated from the values interpolated from the data found in the International Critical Tables, Vol. IV.

As seen from the diagrams, potassium chlorate and calcium chloride are the stable pair in these temperatures, and this fact is fundamentally important for the process of manufacture of potassium chlorate.

The solution obtained by the reaction (1) is expressed by

$$100mH_2O,\ 100\,(\tfrac{1}{2}\text{Ca}),\ 83.3\text{Cl},\ 16.7ClO_3,$$

---

(1) This report has been already published by one of us under his former name Hideo Takesuye in the Report of the Imperial Industrial Laboratory in Osaka where the work was carried out.

(2) For the details, see the Report, above cited, Vol. **10** (1929), No. 11.

Table 1.

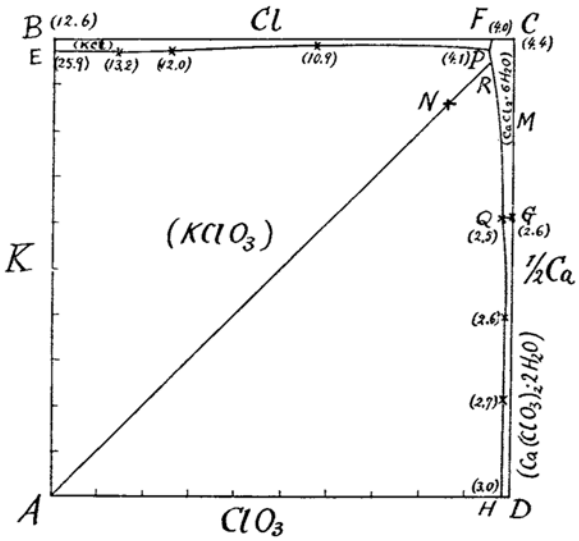
Temperature: 15.0°C.

No.	x	y	m	Residue.
1	100	100	12.6*	KCl
2	100	0	111 *	$KClO_3$
3	0	100	4.4*	$CaCl_2.6H_2O$
4	0	0	—	$Ca(ClO_3).2H_2O$
5	100	97.09	25.68	$KCl+KClO_3$
6	85.39	97.05	13.23	,, + ,,
7	74.26	97.20	12.04	,, + ,,
8	42.33	97.97	10.90	,, + ,,
9	17.28	98.20	7.14	,, + ,,
10	4.71	100.	4.02	,, $+CaCl_2.6H_2O$
11	0	61.17	2.56	$CaCl_2.6H_2O+Ca(ClO_3)_2.2H_2O$
12	3.40	85.77	3.91	,, $+KClO_3$
13	1.27	0	2.99	$KClO_3+Ca(ClO_3)_2.2H_2O$
14	1.08	21.59	2.88	,, + ,,
15	1.09	39.64	2.57	,, + ,,
16	5.01	97.55	4.10	$KCl+KClO_3+CaCl_2.6H_2O$
17	2.01	60.88	2.46	$KClO_3+Ca(ClO_3)_2.2H_2O+CaCl_2.6H_2O$

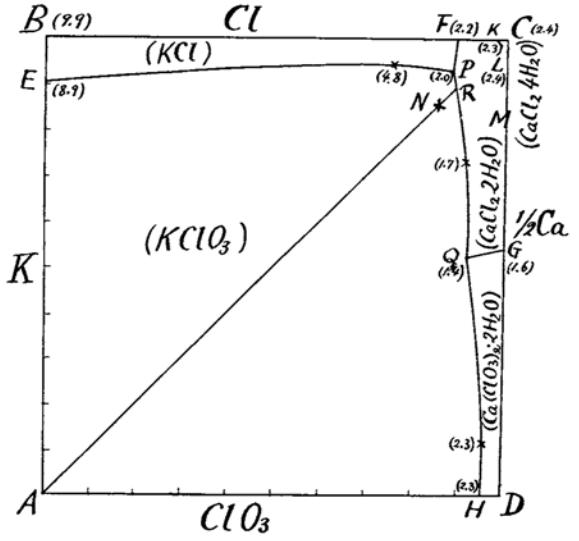
Table 2.

Temperature: 45.0°C.

No.	x	y	m	Residue.
1	100	100	9.9*	KCl
2	100	0	40.5*	$KClO_3$
3	0	100	2.4*	$CaCl_2.4H_2O$
4	0	0	—	$Ca(ClO_3)_2.2H_2O$
5	100	90.43	8.94	$KCl+KClO_3$
6	24.72	94.81	4.85	,, + ,,
7	10.61	100	2.17	,, $+CaCl_2.2H_2O$
8	1.63	100	2.35	$CaCl_2.2H_2O+CaCl_2.4H_2O$
9	0	98.57	2.33	,, + ,,
10	0	54.22	1.56	,, $+Ca(ClO_3)_2.2H_2O$
11	8.47	73.07	1.69	$KClO_3+CaCl_2.2H_2O$
12	4.53	0	2.28	,, $+Ca(ClO_3)_2.2H_2O$
13	4.27	11.50	2.27	,, + ,,
14	11.70	92.99	1.99	$KCl+KClO_3+CaCl_2.2H_2O$
15	8.13	52.38	1.42	$KClO_3+Ca(ClO_3)_2.2H_2O+CaCl_2.2H_2O$



Temperature: 15.0°C.
Fig. 1.



Temperature: 45.0°C.
Fig. 2.

---

and represented by the point M in the diagrams. When potassium chloride equivalent to the chlorate is added, the solution before separation of any solid phase is expressed by

$$100mH_2O,\ 14.3K,\ 85.7(\tfrac{1}{2}Ca),\ 85.7\ Cl,\ 14.3ClO_3,$$

and represented by the point N in the diagrams.

The straight line drawn from A through N meets the curve PQ at R. The line NR represents the change of the composition of the solution as potassium chlorate crystallizes out, and when it reaches R, calcium chloride begins to crystallize out together with potassium chlorate.

When the two diagrams are compared, it may be concluded that the lower the temperature the more potassium chlorate crystallizes out before the deposition of calcium chloride.

The Imperial Industrial Laboratory,
Osaka.