TRANSLATION

FUSIBILITY DIAGRAMS IN THE SYSTEMS $LiClO_4$ - $Ca(ClO_4)_2$ AND $NaClO_4$ - $Ca(ClO_4)_2$

By

N. V. Krivtsov and A. A. Zinov'yev

FOREIGN TECHNOLOGY DIVISION

AIR FORCE SYSTEMS COMMAND

WRIGHT-PATTERSON AIR FORCE BASE

OHIO

UNEDITED ROUGH DRAFT TRANSLATION

FUSIBILITY DIAGRAMS IN THE SYSTEMS $LiClO_4$ - $Ca(ClO_4)_2$ AND $NaClO_4$ - $Ca(ClO_4)_2$

BY: N. V. Krivtsov and A. A. Zinov'yev

English Pages: 12

SOURCE: Russian Periodical, Zhurnal Neorganicheskoy Khimii, Izdatel'stvo AN SSSR, Vol. 8, Nr. 1, 1963, pp 186-191

S/78-63-8-1

THIS TRANSLATION IS A RENDITION OF THE ORIGINAL FOREIGN TEXT WITHOUT ANY ANALYTICAL OR EDITORIAL COMMENT. STATEMENTS OR THEORIES ADVOCATED OR IMPLIED ARE THOSE OF THE SOURCE AND DO NOT NECESSARILY REFLECT THE POSITION OR OPINION OF THE FOREIGN TECHNOLOGY DIVISION.	PREPARED BY: TRANSLATION DIVISION FOREIGN TECHNOLOGY DIVISION WP-AFB, OHIO.

FUSIBILITY DIAGRAMS IN THE SYSTEMS

$LiClO_4$ - $Ca(ClO_4)_2$ AND $NaClO_4$ - $Ca(ClO_4)_2$

By

N. V. Krivtsov and A. A. Zinov'yev

Acidocomplex compounds formed by perchloric acid are not described in the literature, but there are some indications of the possibility of their existence. Thus, A. A. Zinov'yev and N. A. Shchirova [1] obtained data indicating the existence of perchloroceric acid $H_2[Ce(ClO_4)_6]$, which they did not succeed in isolating. As a result of a study of the triple system NH_4ClO_4 - $NaClO_4$ - H_2O, A. S. Karnaukhov [2] proved that the anhydrous binary salt $7NH_4ClO_4 \cdot NaClO_4$ exists in this sytem.

The investigation of fusibility in systems composed of anhydrous perchlorates is limited to only a few articles in which the absence of binary compounds is shown. A. A. Zinov'yev, L. A. Chudinova, and L. P. Smolina [3] established that the system $NaClO_4$ - $Ba(ClO_4)_2$ is characterized by the presence of only a simple eutectic and by two polymorphic transitions of barium perchlorate. The absence of a binary compound was established by I. A. Zakharova, V. G. Markova and A. A. Zinov'yev [4] in the system $NaClO_4$ - $LiClO_4$. However, in this case they obtained an indication of the existence of solid solutions derived from sodium perchlorate. A study of the system $LiClO_4$ - $KClO_4$ by Markowitz [5] showed that only a simple eutectic and a polymorphic transition of $KClO_4$ exist.

We undertook the study of fusibility in the systems $LiClO_4$ - $Ca(ClO_4)_2$ and $NaClO_4$ - $Ca(ClO_4)_2$.

INITIAL SUBSTANCES AND METHODS OF INVESTIGATION

As is known, lithium perchlorate crystallizes in a rhombic system and has no polymorphism. This is the only metallic perchlorate which melts without decomposition. In the literature there is no single value for the melting point of lithium perchlorate. For example, according to I. A. Zakharova et al. [4], its melting point is 234°, while according to Vorländer and Kaascht [6], lithium perchlorate melts at 247°.

Sodium perchlorate, according to Vorländer and Kaascht [6], has two polymorphic modifications with the transition point of the enantiotropic type being 308°. This transition temperature was confirmed by other researchers. The melting of sodium perchlorate is accompanied by thermal decomposition. Therefore the melting point of sodium perchlorate, like those of the other perchlorates of alkali metals cannot be determined exactly. The melting point of sodium perchlorate lies between 461° and 482°.

Calcium perchlorate is very inadequately described in the literature. Vorländer and Kaascht, who were the first to determine the transition temperatures of alkali-metal perchlorates and of the perchlorates of silver, barium and thallium, reported nothing concerning the polymorphism of calcium perchlorate. But in the article by A. A. Zinov'yev and L. I. Chudinova [7] there was an indication of a polymorphic transition of calcium perchlorate at 340°.

Perchlorates of lithium, sodium, and calcium were prepared on the reaction of dilute perchloric acid and the carbonates of the corresponding metals. The crystalline hydrates obtained from the solutions were repeatedly recrystallized out of water, until the required degree of purity was reached, and then the crystalline hydrates were dehydrated by heating at 150-200° in a vacuum at 1-2 mm Hg.

Analyses of the perchlorate-ion content were performed by using nitron (1, 2, 4-diphenylendoanilodihydrotriazol) as the precipitating agent [8]. All of the perchlorates were, within the limits of accuracy of the analysis, 100% and did not contain even traces of chlorides.

The fusibility was studied by the visual-polythermic and the thermographic methods (on a Kurnakov pyrometer). The device for visual-polythermic determination of the melting point (or temperature of incipient crystallization) did not differ in principle from the device used for that purpose in an earlier article [4]. The mixing of the fusion took place automatically in a hermetically sealed vessel. The upper end of the mixer, which was made of iron, was placed inside a magnetic induction coil, to which electrical pulses were fed at definite intervals.

The temperature was measured by a Chromel-Alumel thermocouple and by an M-81 millivolt ammeter. The thermocouple was calibrated according to the melting points of tin, lead, aluminum, $K_2Cr_2O_7$, KNO_3, and the boiling point of water. The rate of heating or cooling of the furnace was regulated by an autotransformer and amounted to 2-3 degrees per minute.

The boundaries of the solid-phase fields were determined from the cooling curves of completely fused mixtures.

In those cases where the temperature of complete fusion of the perchlorate mixture was higher than the temperature of incipient decomposition (higher than 370°), the mixtures were held at 350° for 5 to 6 hours, and then the cooling curves were recorded on a pyrometer. The absence of decomposition of perchlorates during such holding was proved by a controlled weighing upon completion of the measurements.

RESULTS OF EXPERIMENTS

Phase transitions of perchlorates were studied by the thermographic method and by visual observations of the change in the substances during heating.

It was confirmed that lithium perchlorate has no polymorphic transition, and it was discovered that it melts without decomposition at 249 ± 2°. The temperature of rapid decomposition of lithium perchlorate lies at approximately 470°.

The data obtained confirm the presence of a polymorphic transition at 308° in the case of sodium perchlorate. The melting point with partial decomposition simultaneously occurring (not more than 1%) is 482 ± 4°, while the temperature of rapid decomposition of sodium perchlorate is approximately 570°.

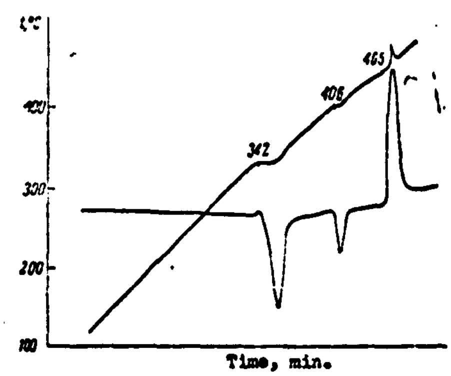

Fig. 1. Thermogram of calcium perchlorate.

Figure 1 shows a thermogram of calcium perchlorate. It shows the presence of two endothermic effects (at 342 and 406°) and one exothermic effect at 465°.

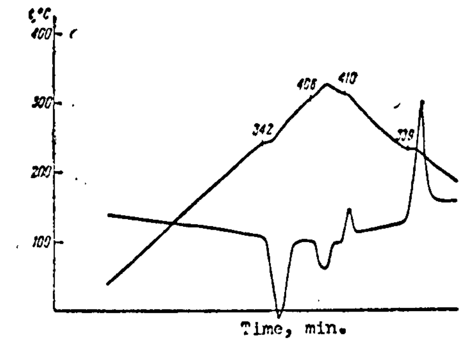

Fig. 2. Thermogram of calcium perchlorate recorded during heating and subsequent cooling of the sample.

Both endothermic effects are reproduced on the cooling branch of the thermogram in Fig 2. It was visually established that these effects relate to a transformation of calcium perchlorate in the solid state. In an earlier article [7] the effect at 406° was erroneously related to melting.

Thus we may assume that endothermic effects are associated with two polymorphic transitions of calcium perchlorate, for which, consequently, there exist three polymorphic modifications. In another article [3] three polymorphic modifications were also discovered for barium perchlorate.

The exothermic effect at 465° in the thermogram in Fig. 1 is associated with the thermal decomposition of calcium perchlorate. The slow evolution of oxygen already begins at 400°.

THE SYSTEM $LiCO_4$ - $Ca(ClO_4)_2$

The results of a study of this system are presented in Tables 1 and 2 and in Fig. 3. The diagram in Fig. 3 shows the presence of two transition points P'_1 and P'_2 and respectively two horizontal lines P'_1 P'_2 and P'_2P_2 corresponding to the two polymorphic transitions of calcium perchlorate which occur at 342 and 406°.

Polymorphism is confirmed by the fact that in the thermograms mixtures of lithium and calcium perchlorates the intensities of the heat effects at 342 and 406° increase with an increase in the amount of calcium perchlorate in the mixture.

The eutectic mixture melts at 228° and has a composition of 76.9 equiv. % $Li_2(ClO_4)_2$ and 23.1 equiv. % $Ca(ClO_4)_2$.

TABLE 1

Temperature of Incipient Crystallization in the System

$LiClO_4 - Ca(ClO_4)_2$

Amount of $Li_2(ClO_4)_2$ in the fusion, equiv.%	Temperature of incipient crystallization °C	Amount of $Li_2(ClO_4)_2$ in the fusion, equiv.%	Temperature of incipient crystallization °C
100,0	250	68,9	254
97,5	249	67,1	264
91,7	246	63,4	269
87,0	242	61,6	278
84,8	241	55,4	295
82,5	238	52,3	304
80,2	234	49,5	312
78,2	229	47,3	318
77,9	233	43,6	324
77,3	232	43,2	327
76,4	233	40,9	331
74,7	235	37,4	343
73,9	241	35,6	356
72,9	243	33,4	374
70,8	248		

We did not discover any transitions in the system below the eutectic line. Above 370° mixtures of all compositions begin to decompose, thus indicating the lower thermal stability of perchlorate mixtures as compared with the stability of pure components. For this reason no line of primary crystallization above 370° could be ascertained.

TABLE 2

Results of Thermographic Study of the System $LiClO_4$ – $Ca(ClO_4)_2$

Amount of $Li_2(ClO_4)_2$ in the fusion, equiv. %	Melting point of eutectic mixture	Temperature of polymorphic transition $\beta \rightarrow \gamma$, °C	Temperature of polymorphic transition $\alpha \rightarrow \beta$, °C
100,0	—	—	—
95,8	228	—	—
92,3	225	—	—
88,3	228	—	—
78,5	226	—	—
73,9	230	—	—
69,5	227	—	—
68,4	225	—	—
60,7	228	—	—
57,7	226	—	—
46,6	222	—	—
42,7	222	—	—
34,7	228	342	—
25,7	226	342	410
18,8	228	341	406
14,7	226	344	406
12,5	226	342	408
10,1	226	341	408
0,0	—	342	[illegible]

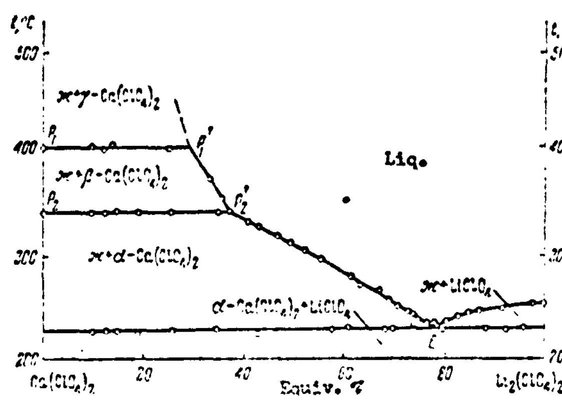

Fig. 3. Fusibility diagram of the system. $Li_2(ClO_4)_2$ – $Ca(ClO_4)_2$.

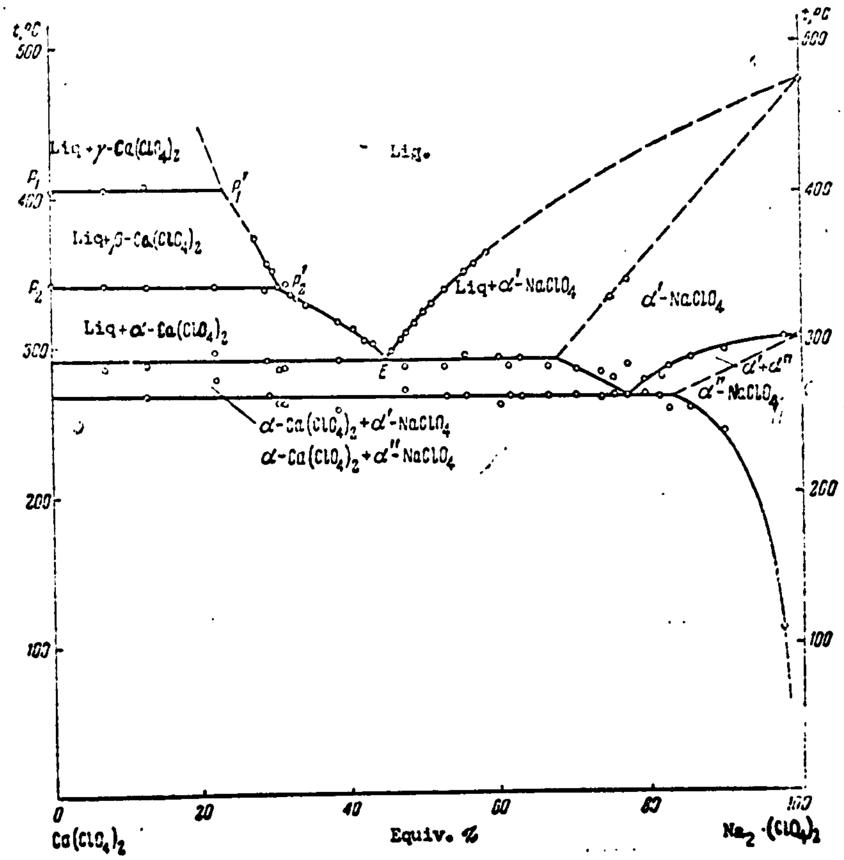

Fig. 4. Fusibility diagram of the system $Na_2(ClO_4)_2$ — $Ca(ClO_4)_2$.

TABLE 3

Temperature of Incipient Crystallization in the System

$NaClO_4$ — $Ca(ClO_4)_2$

Amount of $Na_2(ClO_4)_2$ in the fusion, equiv. %	Temperature of incipient crystallization °C	Amount of $Na_2(ClO_4)_2$ in the fusion, equiv. %	Temperature of incipient crystallization °C
100,0	482	45,6	298
58,6	364	44,7	295
56,7	358	43,2	304
55,8	352	42,2	306
52,8	340	40,6	315
51,0	330	38,4	319
50,0	324	34,2	330
49,7	323	33,1	335
48,6	317	33,0	334
48,2	314	32,4	336
48,1	312	31,4	344
47,6	311	29,9	353
47,1	308	28,8	357
46,9	306	27,3	375
46,1	301		

TABLE 4

Results of Thermographic Study of the System $NaClO_4$ – $Ca(ClO_4)_2$

Amount of $Na_2(ClO_4)_2$ in the fusion equiv. %	Temperature of incipient melting of mixtures, °C	Trans. temperature of solid solutions °C	Temperature of polymorphic trans. $\beta \rightarrow \gamma$, °C	Temp. of polymorphic trans. $\alpha \rightarrow \beta$, °C
100,0	482	308 (polymorphous trans.)	—	—
97,7	—	113; 308	—	—
89,8	—	244; 298	—	—
85,5	—	260; 293	—	—
82,6	—	258; 288	—	—
81,9	—	258; 280	—	—
81,6	—	270; 279	—	—
79,6	288	260	—	—
76,6	334; 279	260	—	—
74,8	345; 280	269	—	—
73,5	284	266	-	—
72,1	284	270	—	—
66,6	289	279	—	—
62,7	295	268	—	—
61,8	294	267	—	—
60,8	288	269	—	—
59,9	294	262	—	—
55,4	295	268	—	—
52,8	288	268	—	—
45,4	288	273	—	—
38,3	293	258	—	—
31,7	287	263	—	—
30,4	287	266	343	—
28,9	293	270	340	—
22,0	299	289	342	406
12,8	290	270	342	410
5,2	287	—	342	406
0,0			342	406

THE SYSTEM $NaClO_4$ – $Ca(ClO_4)_2$

The results of the study of this system are presented in Tables 3 and 4 and in the diagram in Fig. 4.

Above 380° mixtures of all compositions undergo decomposition. Therefore the liquidus curve is investigated only up to this temperature. The eutectic mixture melts at 293° and has a composition of 44.9 equiv. % $Na_2(ClO_4)_2$ and 55.1 equiv. % $Ca(ClO_4)_2$.

In the diagram in Fig. 4 in the region of compositions rich in calcium perchlorate there are two transition points P_1' and P_2' and two

..rizontal lines P_1P_1' and P_2P_2' corresponding to them, which correspond to the transition points of the polymorphic modifications of calcium perchlorate at 342° and 406° respectively. This is confirmed by the fact that the duration of the pauses in the thermograms becomes greater at these temperatures with an increase in the amount of calcium perchlorate in the fusions.

Consequently, in the hypoeutectic region pure calcium perchlorate crystallizes in three crystalline modifications, each of which exists in a corresponding temperature range.

In the hypereutectic region of concentrations a solid solution derived from a high-temperature modification of sodium perchlorate crystallizes. This solution undergoes a eutectoid transition with the formation of a second solid solution.

The eutectoid point lies at a temperature of 270° and has a composition of approximately 29 equiv. % $Na_2(ClO_4)_2$ and 71 equiv. % $Ca(ClO_4)_2$.

Thus, in the system $NaClO_4 - Ca(ClO_4)_2$, in addition to the liquid phase, the following solid phases may also exist:

γ - $Ca(ClO_4)_2$, exists above 406°.

β - $Ca(ClO_4)_2$, exists within the temperature range 342-406°.

α - $Ca(ClO_4)_2$, exists below 342°.

The solid phase α' derived from sodium perchlorate.

The solid phase α'' derived from sodium perchlorate.

CONCLUSIONS

1. The systems $LiClO_4 - Ca(ClO_4)_2$ and $NaClO_4 - Ca(ClO_4)_2$ are studied. The fusibility diagram in both systems is characterized by a simple eutectic and by polymorphic transitions of the components.

2. We did not succeed in forming compounds in these systems. In the system $NaClO_4 - Ca(ClO_4)_2$ in the region rich in sodium perchlorate, the existence of two solid solutions is proved.

3. On the basis of a thermographic study of calcium perchlorate and a study of systems derived from it we obtained data indicating the presence of three polymorphic modifications of calcium perchlorate with transition points at 342 and 406°.

REFERENCES

1. A. A. Zinov'yev and N. A. Shchirova. Zh. neorgan. khimii, 5, 540 (1960).

2. A. S. Karnaukhov and I. G. Druzhinin. Doklad. AN SSSR, 84, 963 (1952).

3. A. A. Zinov'yev, L. A. Chudinova and L. P. Smolina. Zh. neorgan. khimii, 1, 1850 (1956).

4. I. A. Zakharova, V. G. Markova and A. A. Zinov'yev. Zh. neorgan. khimii, 5, 914 (1960).

5. M. M. Markowitz, D. A. Boryta and R. F. Harris. J. Phys. Chem., 65, 261 (1961).

6. D. Vorländer and E. Kaascht. Ber., 56, 1157 (1923).

7. A. A. Zinov'yev and L. I. Chudinova. Zh. neorgan. khimii, 1, 1722 (1956).

8. O. Loebich. Z. analyt., 68, 34 (1926).

N. S. Kurnakov Insitute of General and Inorganic Chemistry of the Academy of Sciences of the USSR.

Received on March 20, 1962.

DISTRIBUTION LIST

DEPARTMENT OF DEFENSE	Nr. Copies	MAJOR AIR COMMANDS	Nr. Copies
		AFSC	
		SCFDD	1
		DDC	25
		TDBTL	5
HEADQUARTERS USAF		TDBDP	2
		AEDC (AEY)	1
AFCIN-3D2	1	AFWL (WLF)	1
ARL (ARB)	1	ASD (ASYIM)	2
		ESD (ESY)	1

OTHER AGENCIES	
CIA	1
NSA	6
DIA	6
AID	2
OTS	2
AEC	2
PWS	1
NASA	1
ARMY (FSTC)	3
NAVY	3
NAFEC	1
RAND	1
AFCRL (CRXLR)	1
PGE	12