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PHASE DIAGRAM FOR THE TERNARY SYSTEM $CaCl_2$–KCl–$CaCrO_4$*

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ABSTRACT

The phase diagram for the system $CaCl_2$–KCl–$CaCrO_4$ has been determined using differential thermal analysis in conjunction with X-ray diffraction. $CaCl_2$–KCl–$CaCrO_4$ has been shown to be a stable diagonal section of the Ca,K//Cl, CrO_4 reciprocal ternary system. The 3 binary systems are: $CaCl_2$–KCl which exhibits a congruently melting compound ($CaKCl_3$) melting at 741°C with eutectics at 24.0 mole % KCl (m.p. 615°C) and 74.3 mole % KCl (m.p. 594°C); $CaCl_2$–$CaCrO_4$ which shows a eutectic at 23.4 mole % $CaCrO_4$ (m.p. 660°C); and KCl–$CaCrO_4$ with a eutectic at 24.2 mole % $CaCrO_4$ (m.p. 651°C).

The binary congruently melting compound separates the ternary system into 2 pseudoternary subsystems. A binary eutectic exists in the pseudobinary system $CaKCl_3$–$CaCrO_4$ at 12.9 mole % $CaCrO_4$ (m.p. 672°C). Ternary eutectics exist at 71.8 mole % $CaCl_2$–17.3% KCl–10.9% $CaCrO_4$ (m.p. 575°C) and 23.2 mole % $CaCl_2$–71.2% KCl–5.6% $CaCrO_4$ (m.p. 573°C).

Isotherms are shown for the liquidus surface (primary crystallization) and for the secondary crystallization surface. Isothermal and vertical sections through the phase diagram are also shown.

INTRODUCTION

Thermal cells (voltaic cells employing a molten salt electrolyte) frequently employ a calcium anode and an electrolyte-cathodic depolarizer mixture[4] of LiCl–KCl–$CaCrO_4$. At the elevated internal temperatures (500 to 600°C) attained in thermal cells, the Ca anode will react with the LiCl to form $CaCl_2$[2]. Consequently, the ternary system $CaCl_2$–KCl–$CaCrO_4$ exists and a knowledge of the phase relationships in that system is important to thermal cell technology. $CaCl_2$–KCl–$CaCrO_4$ is a stable diagonal section of the Ca, K//Cl, CrO_4 reciprocal ternary system.

The three binary systems have been previously studied. The phase diagram for KCl–$CaCrO_4$ was reported as part of a general investigation of the LiCl–KCl–

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$CaCrO_4$ ternary system[1]. The phase diagrams for the other 2 binary mixtures, $CaCl_2$–$CaCrO_4$ and $CaCl_2$–KCl, have also recently been reported[3].

EXPERIMENTAL

The samples used in this investigation were reagent grade KCl, vacuum dried for 16 h at 120°C; high-purity $CaCrO_4$ (assay 99.85%) prepared from reagent grade $CaCO_3$ and Na_2CrO_4 using a method previously described[1]; and ultra-pure anhydrous $CaCl_2$ (99.95%) from Research Organic/Inorganic Chemical Corporation, Sun Valley, Calif. The $CaCrO_4$ was vacuum dried at 400°C for 4 h and the $CaCl_2$ was vacuum dried at 120°C for 2 h.

Samples were prepared in a controlled atmosphere "dry room" in which the humidity is maintained at approximately 0.25% RH (~50 ppm H_2O at 22°C) by circulating the room air through beds of molecular sieves. Approximately 3 g of each sample were prepared by weighing the appropriate amounts of each compound, fusing in a platinum crucible at 800°C for 60 min, cooling at room temperature and grinding the solidified mixture into a powder. The powdered sample was then pressed into 2.40 mm diameter pellets weighing ~4 mg. Samples prepared in this manner were stored in a dry, inert atmosphere (<1 ppm H_2O, <1 ppm O_2, and <1 ppm N_2) prior to use. Chemical analysis and X-ray diffraction both indicated that no chemical reactions took place during sample preparation. Data were obtained up to ~40 mole % $CaCrO_4$. Further data cannot be obtained because the $CaCrO_4$ decomposes above this composition at the temperatures of interest.

Phase change data were determined by DTA. All DTA curves were obtained using a Stone differential thermal analysis system, Model DTA-202 coupled with a Hewlett-Packard Model 7100B two-pen strip chart recorder. The sample holder was a Model SH-11BR employing ring-type, Platinel II thermocouples with a ring diameter of 4.0 mm. The pelletized 4 mg salt samples were placed in open platinum pans which fit into the rings. The pans were formed from 0.05 mm thick Pt sheet and weighed approximately 34 mg. Calcined alumina was employed as the reference material. A constant heating rate of 10°C min^{-1} was employed for all samples. Data were obtained only during heating because severe supercooling occurred during the cooling cycles.

A few samples of selected composition were analyzed using X-ray diffraction. The X-ray diffraction results were used in the identification of possible compounds formed as a result of interaction between the starting materials.

RESULTS

$CaCl_2$–$CaCrO_4$ binary system

The phase diagram for this system has been previously reported[3] and is shown in Fig. 1. This diagram shows a simple eutectic system with a eutectic composition of 23.4 mole % $CaCrO_4$ which melts at 660°C.

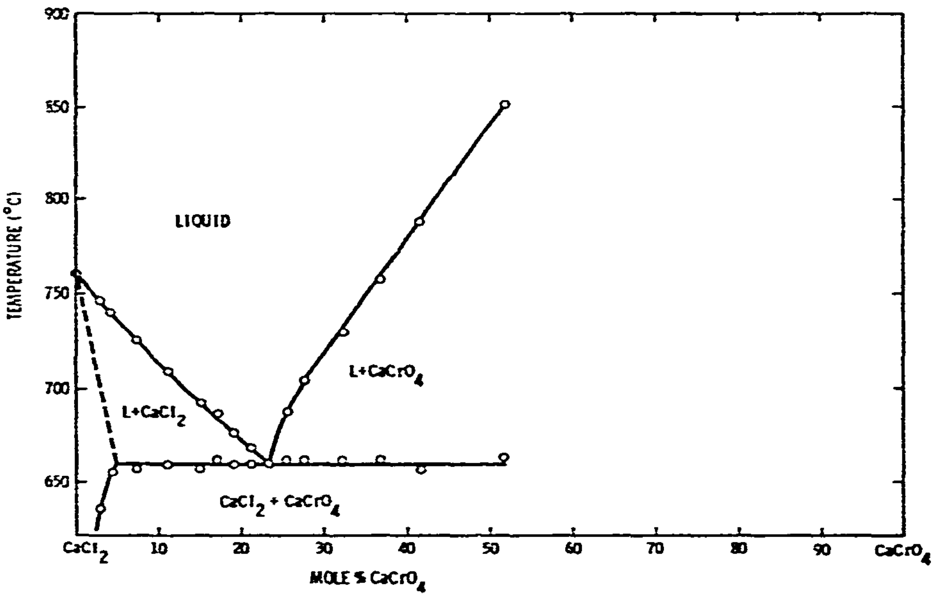


Fig. 1. $CaCl_2$–$CaCrO_4$ binary phase diagram.

KCl–$CaCrO_4$ binary system

KCl and $CaCrO_4$ also form a simple eutectic of composition 24.2 mole % $CaCrO_4$, which melts at 651 °C. The phase diagram, as previously reported[1], is shown in Fig. 2.

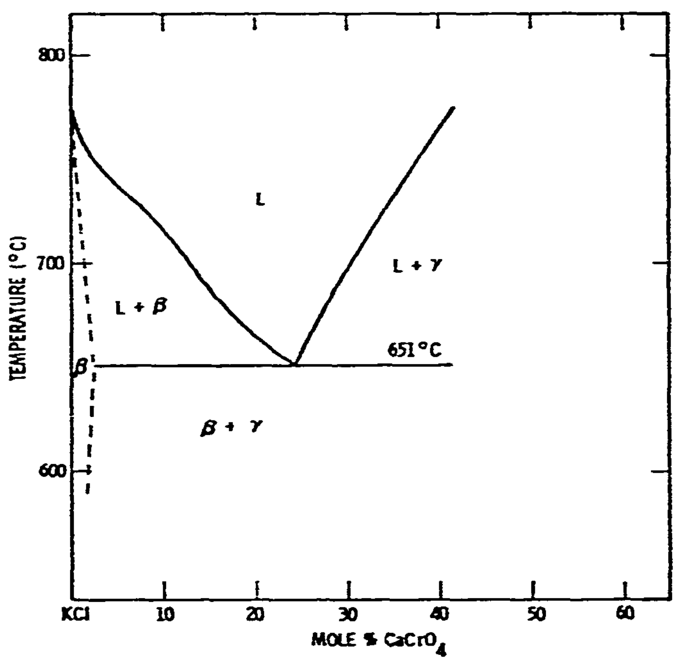


Fig. 2. KCl–CaCrO$_4$ binary phase diagram.

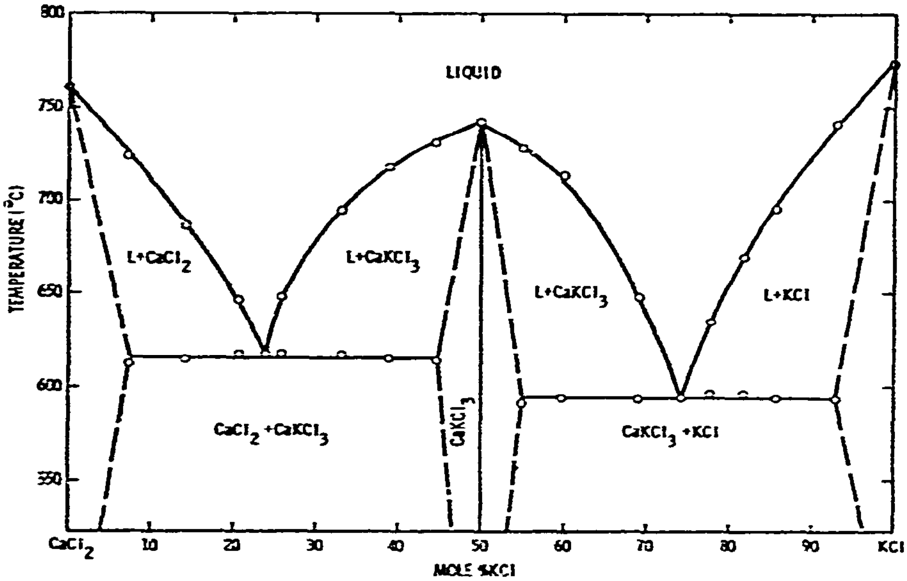


Fig. 3. $CaCl_2$–KCl binary phase diagram.

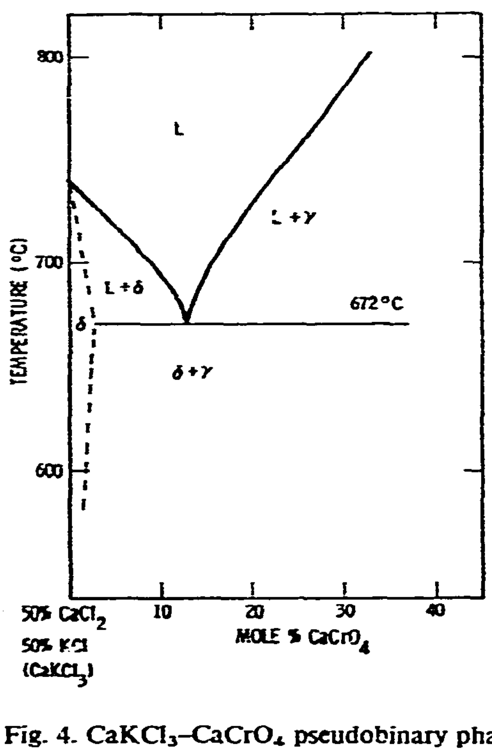


Fig. 4. $CaKCl_3$–$CaCrO_4$ pseudobinary phase diagram.

$CaCl_2$–KCl binary system

This binary system has been recently studied[3] and the resulting phase diagram is shown in Fig. 3. This system exhibits a congruently melting compound ($CaKCl_3$) with a melting point of 741 °C. There are two eutectics: one at 24.0 mole % KCl (m.p. 615 °C) and the other at 74.3 mole % KCl (m.p. 594 °C).

$CaKCl_3$–$CaCrO_4$ pseudobinary system

The pseudobinary system consisting of the congruently melting double salt $CaKCl_3$ and $CaCrO_4$ has been investigated as part of this work. The resulting diagram is shown in Fig. 4. It is seen that a pseudoeutectic exists at 12.8 mole % $CaCrO_4$ with a melting point of 672 °C.

$CaCl_2$–KCl–$CaCrO_4$ ternary system

The complete set of DTA data obtained for the $CaCl_2$–KCl–$CaCrO_4$ ternary system is shown in Table 1. The data are listed as crystallization temperatures. This means that any one phase will be partially or totally in the solid state below the temperature shown and will be totally in the liquid state above that temperature. A few representative DTA curves are shown in Fig. 5. The particular compositions for which curves are shown were selected to show a variety of types of phase conditions. Curve (a) shows the solidus at 573 °C with the δ phase ($CaKCl_3$) being liquid above that temperature. Beginning at 617 °C (secondary crystallization temperature) the β phase (KCl) is entirely liquid, and finally at 659 °C, the liquidus line is reached where the third phase (γ or $CaCrO_4$) is also liquid. Curve (b) is for a composition in which the three phases which exist in the solidus are α($CaCl_2$), γ($CaCrO_4$),

TABLE 1

DTA DTA FOR PHASE DIAGRAM FOR $CaCl_2$–KCl–$CaCrO_4$ SYSTEM

Mole %			*Crystallization temperature (°C)*			
$CaCl_2$	*KCl*	*$CaCrO_4$*	*α ($CaCl_2$)*	*β (KCl)*	*γ ($CaCrO_4$)*	*δ ($CaKCl_3$)*
96.4	—	3.6	744		646	
89.1	7.4	3.5	683		621	575
82.2	14.4	3.4	652		596	575
75.5	21.1	3.4	623		575	603
69.2	27.5	3.3	601		575	662
63.2	33.6	3.2	575		602	692
57.4	39.5	3.1	575		636	712
51.9	45.0	3.1	575		661	724
48.5	48.5	3.0			672	727
41.5	55.6	2.9		573	651	718
36.6	60.5	2.9		573	630	694
31.9	65.3	2.8		573	607	661

(Table continued on p. 118).

TABLE 1 (*continued*)

Mole %			*Crystallization temperature (°C)*			
$CaCl_2$	KCl	$CaCrO_4$	α ($CaCl_2$)	β (KCl)	γ ($CaCrO_4$)	δ ($CaKCl_3$)
27.4	69.8	2.8		573	584	618
23.0	74.3	2.7		597	575	573
18.8	78.5	2.7		646	580	573
14.8	82.6	2.6		680	584	573
10.9	86.5	2.6		705	590	573
7.2	90.3	2.5		727	598	573
3.5	94.0	2.5		742	619	573
—	97.6	2.4		749	652	
92.7	—	7.3	726		660	
85.4	7.5	7.1	678		615	575
78.4	14.6	7.0	636		598	575
71.8	21.4	6.8	606		575	621
65.5	27.9	6.6	575		592	661
59.5	34.0	6.5	575		632	687
53.7	40.0	6.3	575		661	704
46.9	46.9	6.2			672	714
42.9	51.0	6.1		573	670	706
37.8	56.2	6.0		573	655	692
32.9	61.2	5.9		573	634	670
28.2	66.0	5.8		573	605	627
23.2	71.2	5.6		573	573	573
19.4	75.1	5.5		624	587	573
15.2	79.4	5.4		658	603	573
11.2	83.5	5.3		686	615	573
7.3	87.5	5.2		710	627	573
3.6	91.3	5.1		727	641	753
—	95.0	5.0		737	652	
88.9	—	11.1	709		660	
81.5	7.6	10.9	660		624	573
74.6	14.8	10.6	623		605	575
67.9	21.7	10.4	575		605	621
61.7	28.2	10.1	575		641	659
55.6	34.5	9.9	575		663	683
49.8	40.5	9.7			668	692
45.2	45.3	9.5			672	697
39.1	51.7	9.2		573	668	689
34.0	56.9	9.1		573	661	674
29.1	62.0	8.9		573	635	641
24.5	66.8	8.7		573	632	598
20.0	71.5	8.5		603	623	573
15.7	75.9	8.4		638	621	573
11.6	80.2	8.2		667	631	573
7.6	84.4	8.1		693	638	573
3.7	88.4	7.9		712	646	573
—	92.2	7.8		727	652	573
84.9	—	15.1	692		660	
77.6	7.7	14.7	643		632	575
70.6	15.0	14.4	610		643	575
64.0	22.0	14.0	575		650	634

TABLE 1 (*continued*)

Mole %			Crystallization temperature (°C)			
$CaCl_2$	KCl	$CaCrO_4$	α ($CaCl_2$)	β (KCl)	γ ($CaCrO_4$)	δ ($CaKCl_3$)
57.7	28.6	13.7	575		658	656
51.7	35.0	13.3	575		666	665
45.9	41.0	13.1			672	672
43.6	43.5	12.9				672
35.2	52.3	12.5		573	670	663
30.1	57.6	12.3		573	669	650
25.3	62.7	12.0		573	667	623
20.7	67.6	11.7		600	659	573
16.2	72.3	11.5		617	650	573
11.9	76.8	11.3		640	630	573
7.8	81.1	11.1		674	638	573
3.8	85.3	10.9		695	647	573
—	89.3	10.7		712	652	
80.8	—	19.2	668		660	
73.5	7.8	18.7	625		656	575
66.6	15.2	18.2	601		677	575
59.9	22.3	17.8	575		692	634
53.6	29.0	17.4	575		700	657
47.6	35.5	16.9	565		708	670
41.8	41.7	16.5			715	672
36.4	47.4	16.2		573	711	666
31.2	53.0	15.8		573	704	652
26.1	58.4	15.5		573	695	626
21.3	63.5	15.2		573	685	573
16.7	68.4	14.9		614	677	573
12.3	73.1	14.6		628	661	573
8.0	77.7	14.3		661	638	573
3.9	82.1	14.0		683	646	573
—	86.3	13.7		694	652	
76.6	—	23.4	660		660	
69.3	7.9	22.8	624		686	575
62.4	15.5	22.1	575		705	605
55.8	22.6	21.6	575		717	635
49.4	29.5	21.1	575		726	658
39.8	39.8	20.4			732	672
37.8	42.1	20.1		564	731	670
32.3	48.0	19.7		573	729	661
27.1	53.7	19.2		573	723	641
22.1	59.1	18.8		573	715	605
17.3	64.3	18.4		603	705	573
12.7	69.3	18.0		628	692	573
8.3	74.0	17.7		638	668	573
4.1	78.6	17.3		668	647	573
—	83.0	17.0		677	652	
72.3	—	27.7	660		704	
65.0	8.1	26.9	621		722	575
58.0	15.7	26.3	575		734	596

(*Table continued on p. 120*).

TABLE 1 (*continued*)

Mole %			Crystallization temperature (°C)			
$CaCl_2$	KCl	$CaCrO_4$	α ($CaCl_2$)	β (KCl)	γ ($CaCrO_4$)	δ ($CaKCl_3$)
51.4	23.0	25.6	575		745	648
45.1	29.9	25.0	575		750	663
39.2	36.4	24.4			752	672
37.9	37.9	24.2			753	672
33.5	42.7	23.8			752	666
28.0	48.7	23.3		573	750	653
22.9	54.4	22.7		573	744	616
17.9	59.9	22.2		592	735	573
13.1	65.1	21.8		614	722	573
8.6	70.1	21.3		632	697	573
4.2	74.9	20.9		648	673	573
—	79.5	20.5		663	652	
67.8	—	32.2	660		731	
60.5	8.2	31.3	620		745	575
53.6	15.9	30.5	575		761	612
47.0	23.3	29.7	575		770	642
40.7	30.3	29.0	575		774	661
35.8	35.8	28.4			775	672
29.1	43.3	27.6		573	772	657
23.7	49.4	26.9		573	765	628
18.5	55.2	26.3		573	756	573
13.6	60.7	25.7		606	744	573
8.9	65.9	25.2		628	731	573
4.3	71.0	24.7		643	702	573
—	75.8	24.2		652	652	
63.2	—	36.8	660		759	
55.9	8.3	35.8	616		773	575
49.0	16.2	34.8	575		784	614
42.4	23.7	33.9	575		792	650
36.2	30.7	33.1			799	670
33.6	33.6	32.8			801	672
30.2	37.5	32.3		561	798	670
24.6	43.9	31.5		573	794	642
19.2	50.1	30.7		573	788	603
14.1	55.9	30.0		599	777	573
9.2	61.5	29.3		625	752	573
4.5	66.8	28.7		643	724	573
—	71.9	28.1		652	684	
58.4	—	41.6	660		788	
51.1	8.5	40.4	607		802	575
44.2	16.5	39.3	575		809	632
37.7	24.0	38.3	575		813	659
31.5	31.2	37.3			815	672
25.6	38.0	36.4		573	813	653
20.0	44.5	35.5		573	811	624
14.6	50.8	34.6		596	804	573
9.5	56.7	33.8		619	792	573
4.6	62.3	33.1		640	761	573
—	67.7	32.3		652	714	

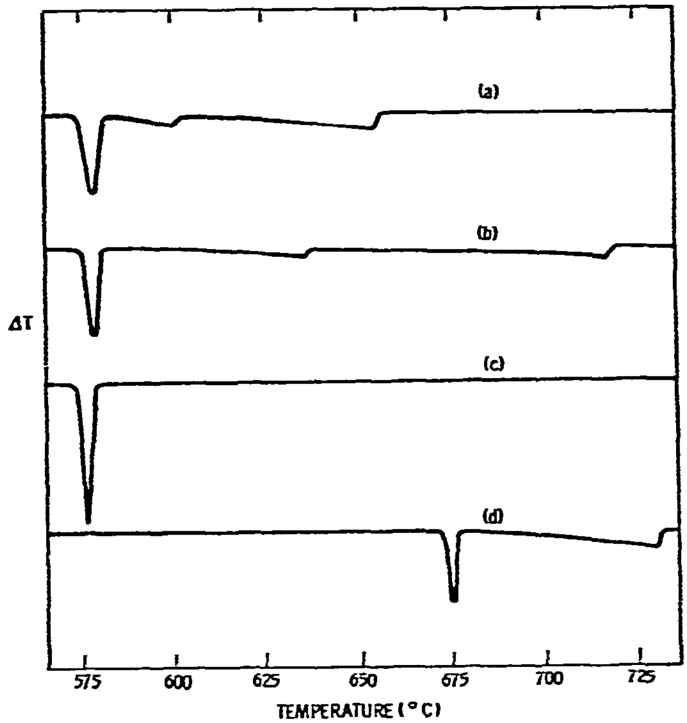


Fig. 5. Typical DTA curves for the system $CaCl_2$–KCl–$CaCrO_4$. (a) 20.7% $CaCl_2$–67.6% KCl–11.7% $CaCrO_4$; (b) 55.8% $CaCl_2$–22.6% KCl–21.6% $CaCrO_4$; (c) 23.2% $CaCl_2$–71.2% KCl–5.6% $CaCrO_4$; (d) 39.8% $CaCl_2$–39.8% KCl–20.4% $CaCrO_4$.

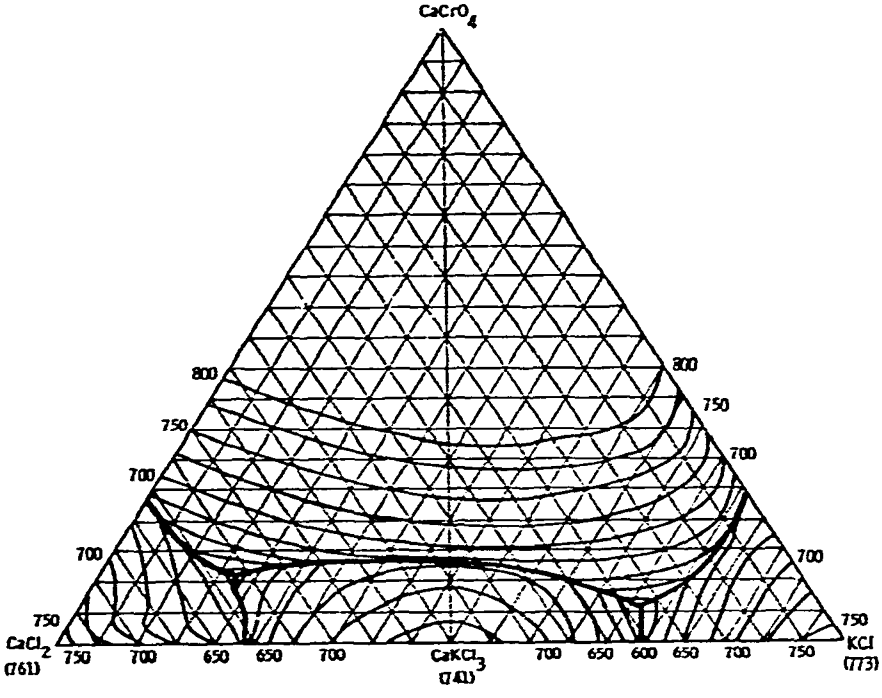


Fig. 6. An isothermal representation of the liquidus surface for the $CaCl_2$–KCl–$CaCrO_4$ system.

and $\delta(CaKCl_3)$. As the sample is heated, temperatures are reached where the α, δ, and γ phases, in that order, go into the liquid state. Curve (c) is for a ternary eutectic where the β, γ, and δ phases all go from solid to liquid at 573°C. Curve (d) is for a composition of equimolar amounts of $CaCl_2$ and KCl. Therefore, only the γ and δ phases are present, with the δ phase going into the liquid state at 672°C and the liquidus temperature being 732°C.

The overall phase diagram for the $CaCl_2$–KCl–$CaCrO_4$ system is shown with the isothermal representation of the liquidus surface in Fig. 6. The pseudobinary system $CaKCl_3$–$CaCrO_4$ divides the overall ternary system into 2 pseudoternary subsystems, $CaCl_2$–$CaKCl_3$–$CaCrO_4$ and KCl–$CaKCl_3$–$CaCrO_4$. It is seen that each subsystem contains 3 binary eutectics and 1 ternary eutectic.

In Fig. 7 the three-phase lines connecting the 2 ternary eutectics with the 3 binary and 1 pseudobinary eutectics are shown. The arrows represent the direction

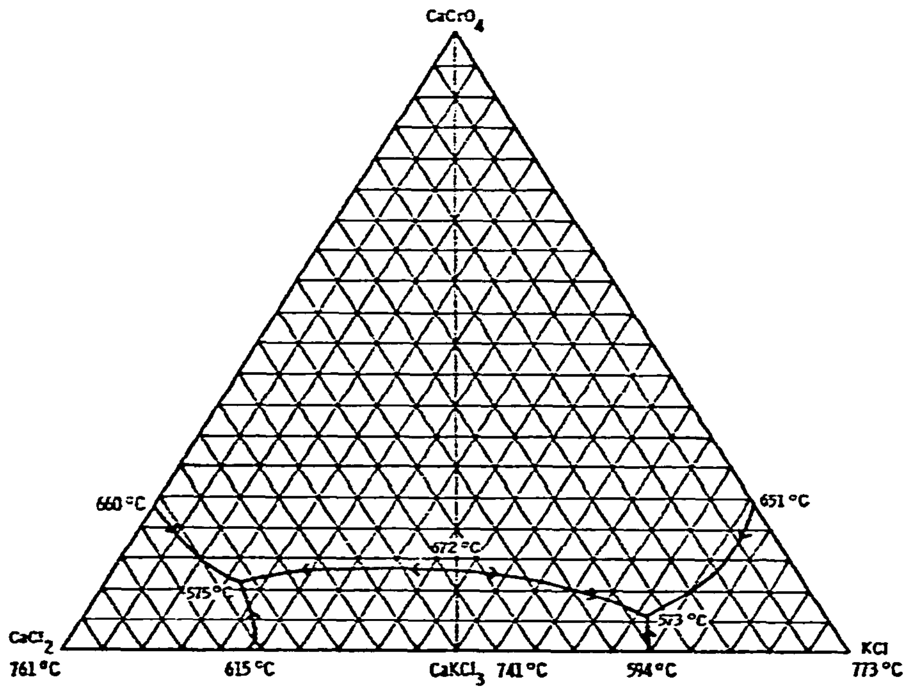


Fig. 7. The Three-Phase Lines for the $CaCl_2$–KCl–$CaCrO_4$ system.

of falling temperature. The 2 ternary eutectics exist at 71.8 mole % $CaCl_2$–17.3% KCl–10.9% $CaCrO_4$ (m.p. 575°C) and 23.2 mole % $CaCl_2$–71.2% KCl–5.6% $CaCrO_4$ (m.p. 573°C). These data, along with data for the binary and pseudobinary eutectics, are summarized in Table 2.

An isothermal representation of the secondary crystallization points is shown in Fig. 8. At temperatures above the surface shown in this figure, but below the liquidus surface (Fig. 6), there will be a liquid phase and one solid phase. The particular solid phase present will depend on the composition of the mixture.

TABLE 2

SUMMARY OF DATA FOR THE $CaCl_2$–KCl–$CaCrO_4$ PHASE DIAGRAM

System	*Significant point*
$CaCl_2$–KCl	Eutectic at 24.0 mole % KCl, m.p. 615 °C
	Eutectic at 74 3 mole % KCl, m.p. 594 °C
	Compound at 50.0 mole % KCl, m.p. 741 °C
KCl–$CaCrO_4$	Eutectic at 24.2 mole % $CaCrO_4$, m.p. 651 °C
$CaCl_2$–$CaCrO_4$	Eutectic at 23.4 mole % $CaCrO_4$, m.p. 660 °C
$CaKCl_3$–$CaCrO_4$	Pseudoeutectic at 12.8 mole % $CaCrO_4$, m.p. 672 °C
$CaCl_2$–KCl–$CaCrO_4$	Eutectic at 71.8 mole % $CaCl_2$–17.3% KCl–10.9% $CaCrO_4$, m.p. 575 °C
	Eutectic at 23.2 mole % $CaCl_2$–71.2% KCl–5.6% $CaCrO_4$, m.p. 573 °C

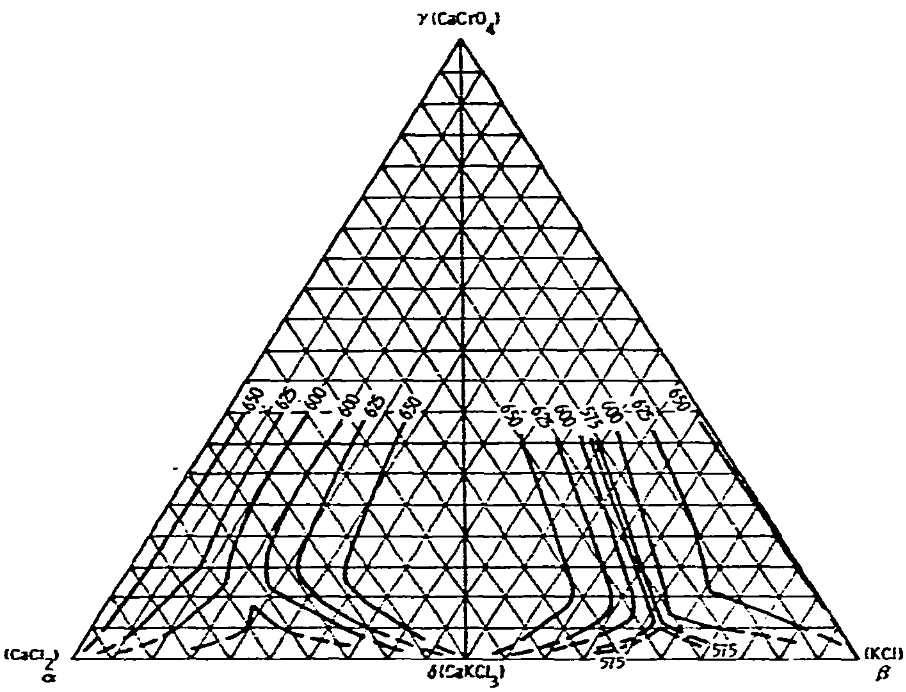


Fig. 8. An isothermal representation of the secondary crystallization surface for the $CaCl_2$–KCl–$CaCrO_4$ system.

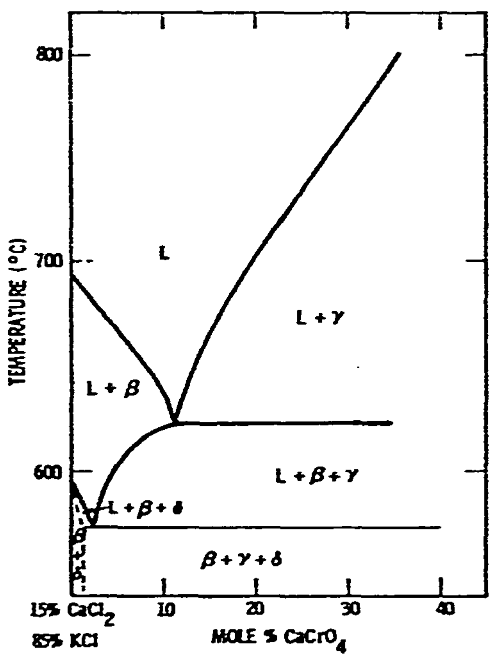
The fact that the 4 phases mentioned are the only phases present was verified by X-ray studies. Five mixtures of $CaCl_2$, KCl, and $CaCrO_4$ were selected from different parts of the phase diagram and analyzed by X-ray diffraction. The results, as shown in Table 3, indicated the existence of only $CaCl_2$, KCl, $CaCrO_4$, and $CaKCl_3$.

A more complete understanding of a ternary phase diagram can be obtained from an examination of sections through the diagram. Figures 9 and 10 are vertical sections in which the $CaCl_2$ to KCl mole ratio is held constant. The section in Fig. 9 ($CaCl_2$ to KCl ratio equal to 15/85) intersects the three-phase line connecting the

TABLE 3

X-RAY DIFFRACTION RESULTS FOR SEVERAL $CaCl_2$–KCl–$CaCrO_4$ MIXTURES

Sample composition (mole %)			*Phases identified by X-ray diffraction*
$CaCl_2$	*KCl*	*$CaCrO_4$*	
50.0	50.0	—	$CaKCl_3$
46.9	46.9	6.2	$CaKCl_3$ $CaCrO_4$ (very weak)
53.6	29.0	17.4	$CaKCl_3$ $CaCl_2$ $CaCrO_4$
21.3	63.5	15.2	$CaKCl_3$ KCl $CaCrO_4$
37.9	37.9	24.2	$CaKCl_3$ $CaCrO_4$



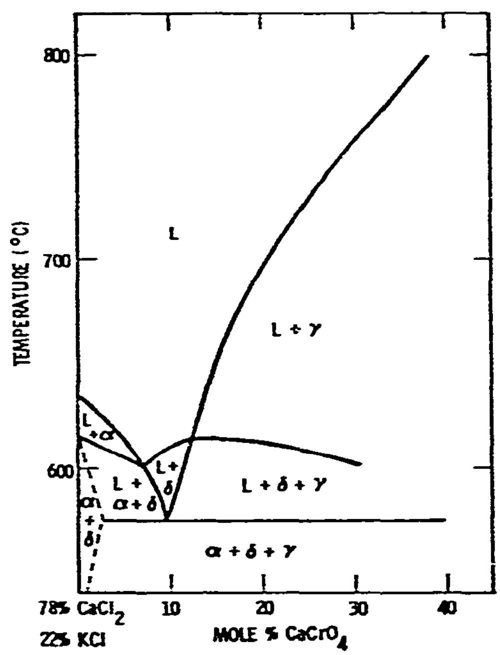


Fig. 9. A vertical section through the $CaCl_2$–KCl–$CaCrO_4$ phase diagram ($CaCl_2$ to KCl mole ratio constant at 15/85).

Fig. 10. A vertical section through the $CaCl_2$–KCl–$CaCrO_4$ phase diagram ($CaCl_2$ to KCl mole ratio constant at 78/22).

KCl–$CaCrO_4$ eutectic with the KCl-rich ternary eutectic. The section in Fig. 10 ($CaCl_2$ to KCl ratio equal to 78/22) intersects 2 three-phase lines; one connecting the $CaCl_2$-rich ternary eutectic with the $CaCl_2$-rich binary eutectic in the $CaCl_2$–KCl system and the other connecting the same ternary eutectic with the $CaKCl_3$–$CaCrO_4$ pseudobinary eutectic.

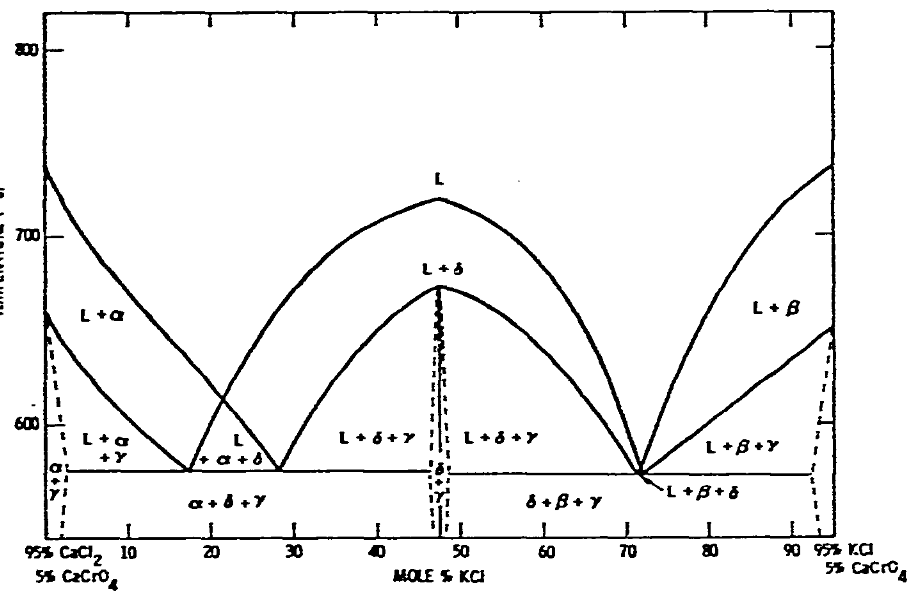


Fig. 11. Constant 5 mole % $CaCrO_4$ vertical section through the $CaCl_2$–KCl–$CaCrO_4$ phase diagram.

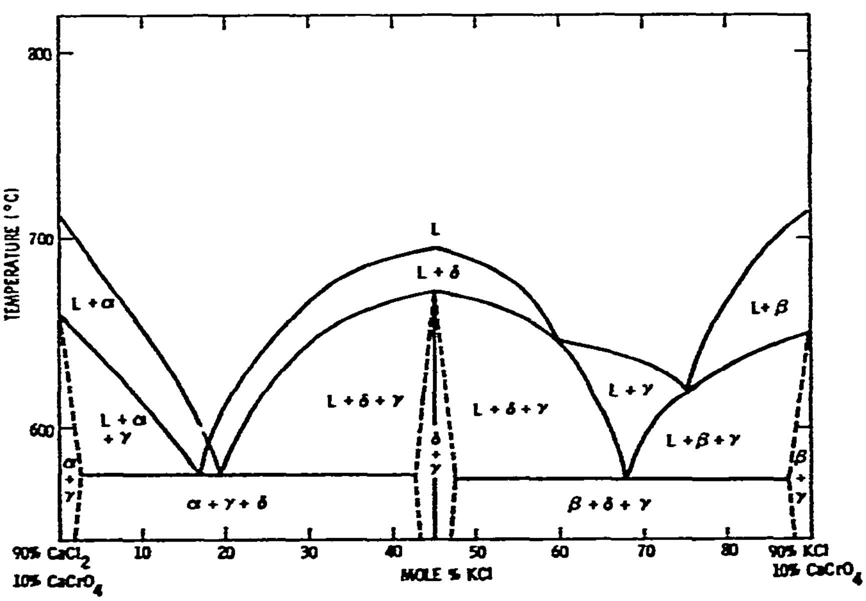


Fig. 12. Constant 10 mole % $CaCrO_4$ vertical section through the $CaCl_2$–KCl–$CaCrO_4$ phase diagram.

Figures 11–14 are vertical sections with constant $CaCrO_4$ concentration. Values for the four figures range from 5 to 25 mole % $CaCrO_4$. The changes in the secondary crystallization surface, as well as the liquidus, are easily observed from these figures.

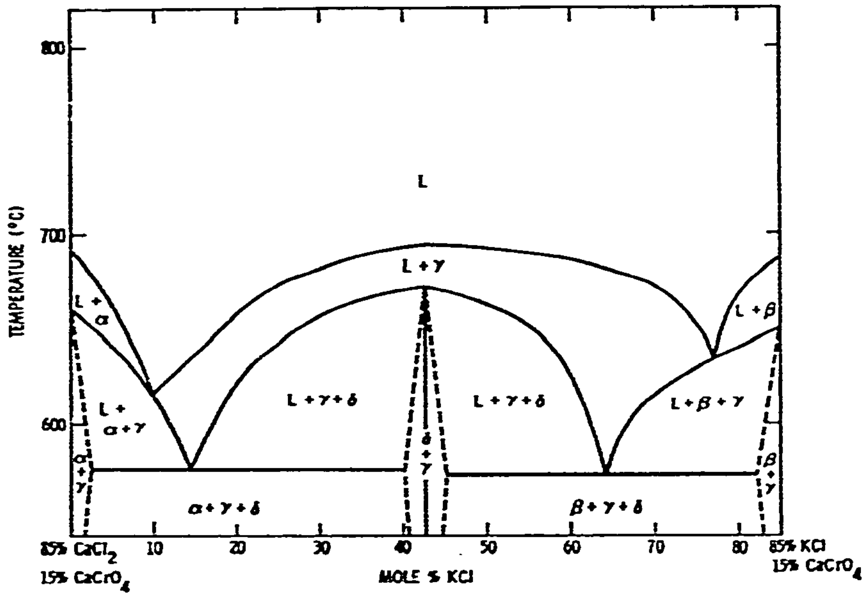


Fig. 13. Constant 15 mole % $CaCrO_4$ vertical section through the $CaCl_2$–KCl–$CaCrO_4$ phase diagram.

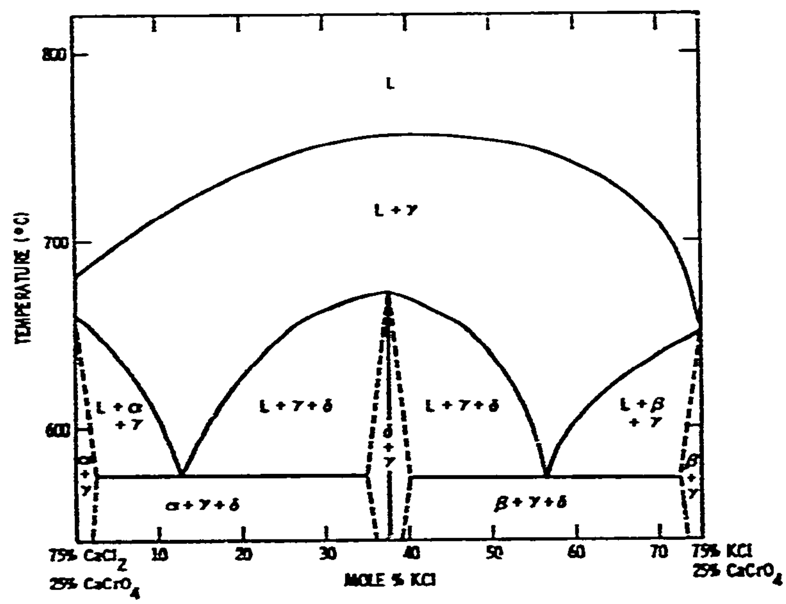


Fig. 14. Constant 25 mole % $CaCrO_4$ vertical section through the $CaCl_2$–KCl–$CaCrO_4$ phase diagram.

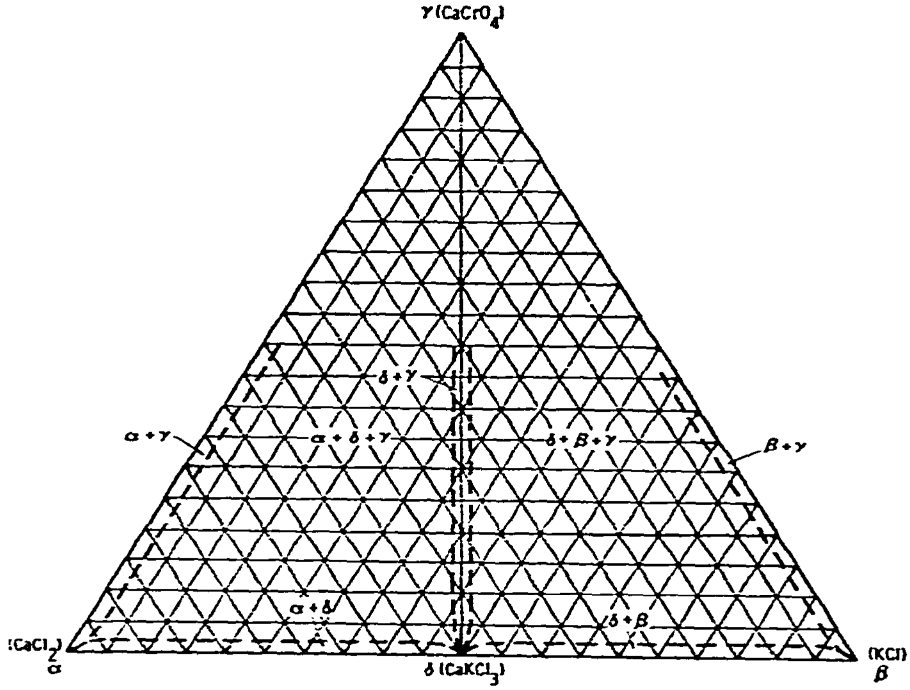


Fig. 15. The 550°C isothermal section through the $CaCl_2$–KCl–$CaCrO_4$ phase diagram.

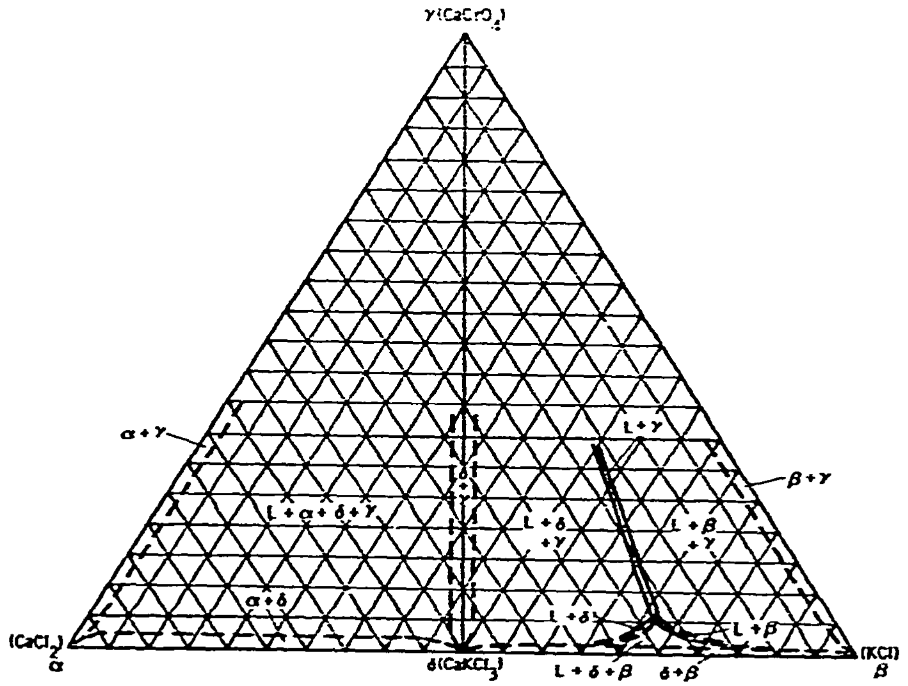


Fig. 16. The 575°C isothermal section through the $CaCl_2$–KCl–$CaCrO_4$ phase diagram.

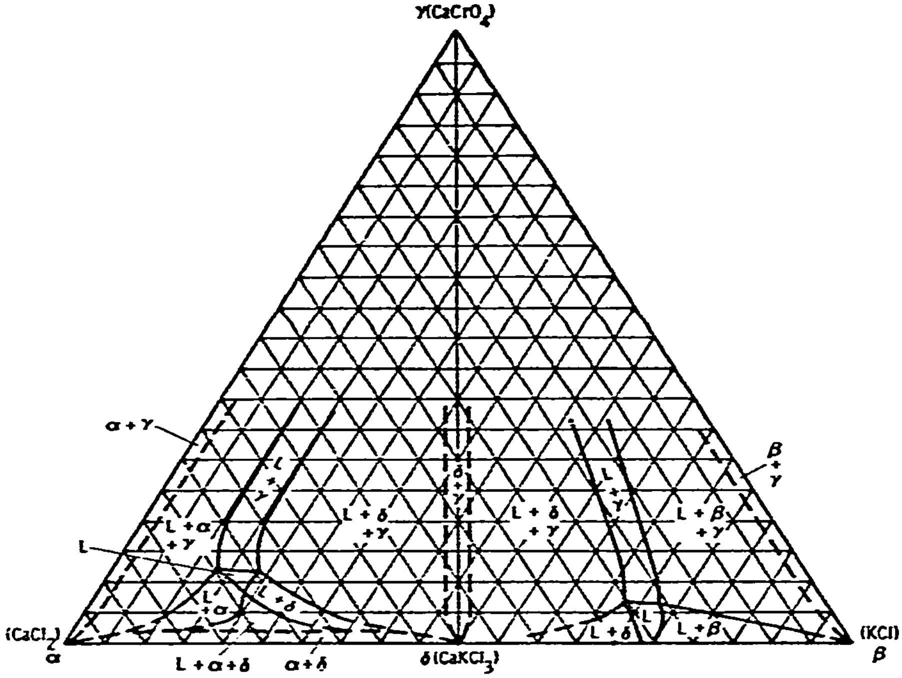


Fig. 17. The 600 °C isothermal section through the $CaCl_2$–KCl–$CaCrO_4$ phase diagram.

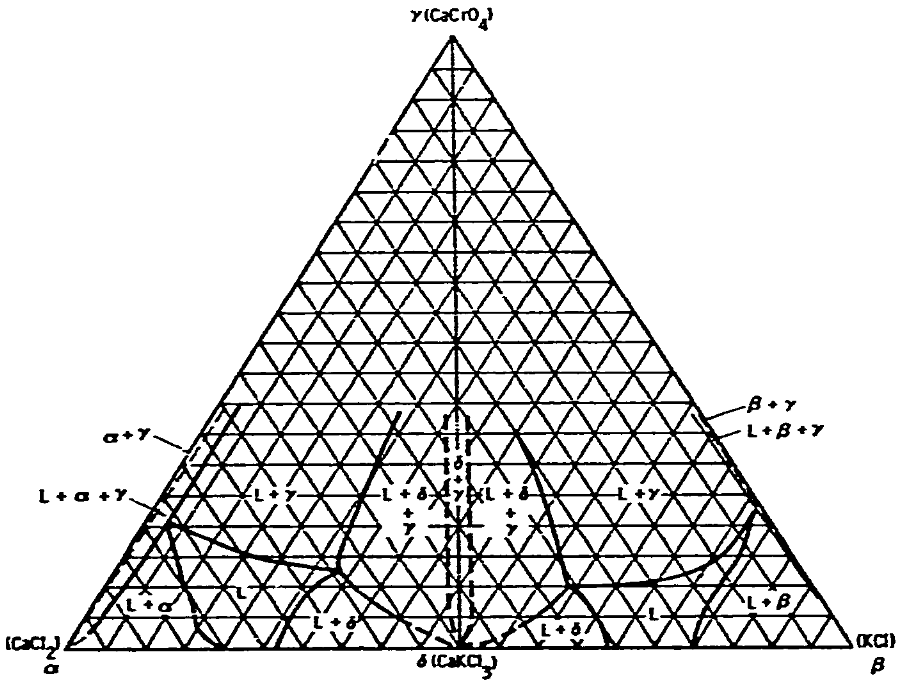


Fig. 18. The 650 °C isothermal section through the $CaCl_2$–KCl–$CaCrO_4$ phase diagram.

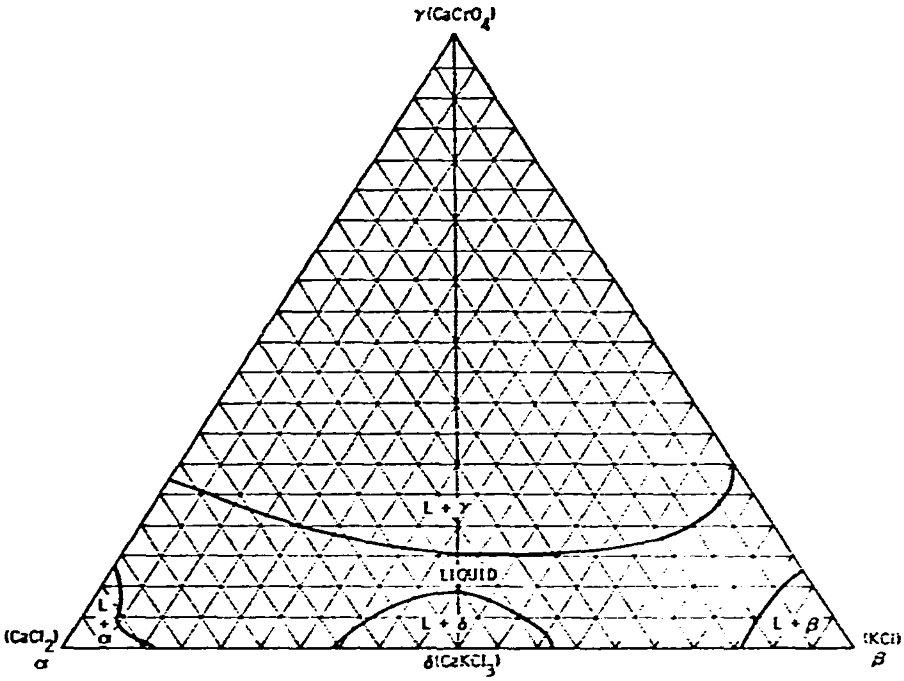


Fig. 19. The 700°C isothermal section through the $CaCl_2$–KCl–$CaCrO_4$ phase diagram.

Five isothermal sections are shown in Fig. 15–19. Each shows the phases present as a function of composition for one constant temperature. At 550°C (Fig. 15) only solid phases exist. At 575°C (Fig. 16) four phases exist over a large range of compositions because this is the melting point of the $CaCl_2$-rich ternary eutectic. Figures 17–19 clearly show the diagram changes which occur as higher temperatures are attained.

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