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PHASE DIAGRAM FOR THE TERNARY SYSTEM CaCl₂-KCl-CaCrO₄*

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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-CaCrO₄ has been shown to be a stable diagonal section of the Ca,K//Cl, CrO₄ reciprocal ternary system. The 3 binary systems are: $CaCl_2-KCl$ which exhibits a congruently melting compound (CaKCl₃) melting at 741 °C with eutectics at 24.0 mole % KCl (m.p. 615 °C) and 74.3 mole % KCl (m.p. 594 °C); CaCl₂-CaCrO₄ which shows a eutectic at 23.4 mole % CaCrO₄ (m.p. 660 °C); and KCl-CaCrO₄ with a eutectic at 24.2 mole % CaCrO₄ (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 CaKCl₃-CaCrO₄ at 12.9 mole % CaCrO₄ (m.p. 672°C). Ternary eutectics exist at 71.8 mole % CaCl₂-17.3% KCl-10.9% CaCrO₄ (m.p. 575°C) and 23.2 mole % CaCl₂-71.2% KCl-5.6% CaCrO₄ (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 mixture⁴ of LiCl– KCl–CaCrO₄. 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–CaCrO₄ exists and a knowledge of the phase relationships in that system is important to thermal cell technology. $CaCl_2$ -KCl–CaCrO₄ is a stable diagonal section of the Ca, K//Cl, CrO₄ reciprocal ternary system.

The three binary systems have been previously studied. The phase diagram for KCl-CaCrO₄ was reported as part of a general investigation of the LiCl-KCl-

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CaCrO₄ ternary system¹. The phase diagrams for the other 2 binary mixtures, CaCl₂-CaCrO₄ and CaCl₂-KCl, have also recently been reported³.

EXPERIMENTAL

The samples used in this investigation were reagent grade KCl, vacuum dried for 16 h at 120°C; high-purity CaCrO₄ (assay 99.85%) prepared from reagent grade CaCO₃ and Na₂CrO₄ using a method previously described¹; and ultra-pure anhydrous CaCl₂ (99.95%) from Research Organic/Inorganic Chemical Corporation, Sun Valley, Calif. The CaCrO₄ was vacuum dried at 400°C for 4 h and the CaCl₂ 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 H₂O 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 H₂O, <1 ppm O₂, and <1 ppm N₂) 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 % CaCrO₄. Further data cannot be obtained because the CaCrO₄ 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

$CaCl_2$ -CaCrO₄ binary system

The phase diagram for this system has been previously reported³ and is shown in Fig. 1. This diagram shows a simple eutectic system with a eutectic composition of 23.4 mole % CaCrO₄ which melts at 660 °C.



Fig. 1. CaCl2~CaCrO4 binary phase diagram.

KCl-CaCrO₄ binary system

KCl and CaCrO₄ also form a simple eutectic of composition 24.2 mole % CaCrO₄, which melts at 651 °C. The phase diagram, as previously reported¹, is shown in Fig. 2.



Fig. 2. KCl-CcCrO₄ binary phase diagram.



Fig. 3. CaCl₂-KCl binary phase diagram.



Fig. 4. CaKCl₃-CaCrO₄ pseudobinary phase diagram.

CaCl₂-KCl binary system

This binary system has been recently studied³ and the resulting phase diagram is shown in Fig. 3. This system exhibits a congruently melting compound (CaKCl₃) 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).

CaKCl₃-CaCrO₄ pseudobinary system

The pseudobinary system consisting of the congruently melting double salt CaKCl₃ and CaCrO₄ 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 % CaCrO₄ with a melting point of 672°C.

CaCl₂-KCl-CaCrO₄ ternary system

The complete set of DTA data obtained for the CaCl₂-KCl-CaCrO₄ 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₋) 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 (y or $CaCrO_4$) is also liquid. Curve (b) is for a composition in which the three phases which exist in the solidus are $\alpha(CaCl_2)$, $\gamma(CaCrO_4)$,

Mole %			Crystallization temperature (°C)				
CaCl₂	KCI	CaCrO₄	α (CaCl ₂)	β (KCl)	γ (CaCrO₄)	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 1

DTA DTA FOR PHASE DIAGRAM FOR CaCI-KCI-CaCrO, SYSTEM

(Table continued on p. 118).

TABLE	I	(continued)
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$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Mole %			Crystallization temperature (°C)				
27.469.82.857358461823.074.32.759757557318.878.52.764658057318.878.52.668058457310.986.52.67055905737.290.32.57277985733.594.02.574261957392.7-7.372666055292.7-7.372666157571.811.46.860657562185.47.57.167861557571.821.46.860657562165.527.96.657559266159.534.06.55755326617046496.267271442.951.06.157367077.856.26.057365579.271.25.657357333.661.25.957363569232.961.25.957373.856.26.057365273.271.25.657357373.357363465860373.357363569232.961.25.957373.357363665773.45.465860373.3 <th>CaCl₂</th> <th>KCI</th> <th>CaCrO₄</th> <th>a (CaCl₂)</th> <th>β (KCl)</th> <th>? (CaCrO₄)</th> <th>δ (CaKCl₃)</th>	CaCl ₂	KCI	CaCrO₄	a (CaCl ₂)	β (KCl)	? (CaCrO₄)	δ (CaKCl ₃)	
23.074.32.759757357318.878.52.764658057318.878.52.670559057310.986.52.67055905737.290.32.57275985733.594.02.5742619573 $$ 7.372666053457592.77.372666057593.414.67.063653857571.821.46.860657562165.527.96.657559266159.534.06.557559266157.340.06.357565269253.740.06.357565269232.961.25.957365569232.961.25.957363569232.271.25.657357357315.279.45.465860357311.283.55.368661557373.367.465260057562155.634.59.957365257373.367.465860357311.283.55.366062473.365.562165773.45.465860357375.5661 <td>27.4</td> <td>69.8</td> <td>2.8</td> <td></td> <td>573</td> <td>584</td> <td>618</td>	27.4	69.8	2.8		573	584	618	
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 - 97.6 2.4 749 652 92.7 - 7.3 726 660 85.4 7.5 7.1 678 615 575 7.4 14.6 70 636 598 575 7.8 21.4 6.8 606 575 621 655 53.7 40.0 6.3 575 622 661 704 44.9 6.9 6.2 672 714 429 51.0 61 573 655 692 232 714 429 51.0 61 573 632 687 232 714 429 51.0 61 573 633 656 627 232 714 429 51.0 5.1 727 613 573	23.0	74.3	2.7		597	575	573	
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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 92.7 - 7.3 726 660 575 534 615 575 71.8 21.4 6.8 606 575 621 655 575 632 687 53.7 740.0 6.3 575 632 687 575 632 687 53.7 40.0 6.3 575 632 687 573 632 687 53.7 40.0 6.1 573 672 714 42.9 51.0 6.1 573 655 692 32.9 61.2 5.9 573 633 656 627 733 573 </td <td>10.9</td> <td>86.5</td> <td>2.6</td> <td></td> <td>705</td> <td>590</td> <td>573</td>	1 0.9	86.5	2.6		705	590	573	
3.5 94.0 2.5 742 619 573 - 97.6 2.4 749 652 35.4 7.5 7.1 678 615 575 38.4 14.6 70 636 598 575 71.8 21.4 6.8 606 575 621 65.5 27.9 6.6 575 532 661 704 59.5 34.0 6.5 575 622 672 714 42.9 61.0 6.1 573 670 706 37.8 562 6.0 573 635 692 23.2 61.2 5.9 573 634 670 23.2 71.2 5.6 573 635 692 23.2 71.2 5.6 573 573 573 11.2 5.5 624 587 573 573 12.2 79.4 5.4 658 603	7.2	90.3	2.5		727	598	573	
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92.7-7.372660035.47.57.167861557538.414.67063659857571.821.46.860657562165.527.96.657559266153.740.06.357566170446.96.267271442.951.06.157367078.475.15.565362232.961.25.957363478.456.26057363478.55.262458757378.475.15.562458773.387.55.271062773.387.55.271062773.387.55.271062773.373.55.271062773.373.55.271062773.373.55.271062773.373.55.271062773.373.55.271062773.373.55.271062773.373.55.271062773.373.55.271062773.373.55.271062773.373.55.271062773.373.55.271062773.473.566661574.6		97.6	2.4		749	652		
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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 5.8 573 634 670 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 7.3 87.5 5.2 710 627 573	46.9	46.9	6.2			672	714	
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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 5.0 737 652 660 81.5 7.6 10.9 660 624 573 7.4 14.8 10.6 623 605 575 67.9 21.7 10.4 575 605 621 61.7 28.2 10.1 575 663 683 49.8 40.5 9.7 668 692 45.2 45.3 9.5 672 697 31.0 51.7 9.2 573 663 683 49.8 40.5 9.7 668 689 34.0 56.9 9.1 573 635 641 29.1 62.0 8.9 573 635 641 29.1 62.0 8.9 573 632 598 40.5 9.1 573 632 573 15.7 75.9 8.4 638 621 573 16.6 8	37.8	56.2	6.0		573	655	692	
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 15.2 79.4 5.4 658 603 573 15.2 79.4 5.4 658 603 573 15.2 79.4 5.4 658 603 573 7.3 87.5 5.2 710 627 573 7.3 87.5 5.2 710 627 573 3.6 91.3 5.1 727 641 753 68.6 615 575 660 624 573 74.6 14.8 10.6 623 605 575 67.9 21.7 10.4 575 663 683 49.8 40.5 9.7 668 692 697 39.1 573 663 663 683 49.8	32.9	61.2	5.9		573	634	670	
23.271.25.6573573 19.4 75.15.5624387573 15.2 79.45.4658603573 11.2 83.55.3686615573 7.3 87.55.2710627573 3.6 91.35.1727641753 $-$ 95.05.0737652 88.9 $-$ 11.1709660 81.5 7.610.9660624 573 661623605575 67.9 21.710.45756041 659 9.7663683 49.8 40.59.7668 45.2 45.39.5672 672 697 39.1 573635 54.0 56.99.1573 573 668672 573 668689 34.0 56.99.1573 573 6688.7 20.0 71.58.5 603 623573 15.7 75.98.4 638 621 573 632 573 535 667 631 573 573 7.6 8.4 8.9 712 646 573 7.6 8.4 7.7 712 7.6 8.4 7.7 632 7.7 643 7.7 652 7.7 <	28.2	66.0	5.8		573	605	627	
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 7.3 87.5 5.2 710 627 573 $ 95.0$ 5.0 737 652 88.9 $ 11.1$ 709 660 81.5 7.6 10.9 660 624 573 $7.4.6$ 14.8 10.6 623 605 575 67.9 21.7 10.4 575 605 621 61.7 28.2 10.1 575 663 683 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 9.1 573 635 641 24.5 66.8 8.7 573 632 598 20.0 71.5 8.5 603 623 573 11.6 80.2 8.2 667 631 573 11.6 80.2 8.2 667 631 573 3.7 8.4 7.9 712 646 573 7.6 84.4 8.1 692 660 773 7.6 84.4 7.9 712 646 573 7	23.2	71.2	5.6		573	573	573	
15.115.16.15.05.011.283.55.36866155737.387.55.27106275733.691.35.1727641753-95.05.073765288.9-11.170966081.57.610.966062457374.614.810.662360562161.728.210.157564165955.634.59.957566368349.840.59.766869245.245.39.567269739.151.79.257366167429.166.887734.056.99.157366167467429.162.08.957363564129.162.08.957363564129.162.08.957363564129.162.08.957363564124.566.88.757363259820.071.58.560362357315.775.98.46386215737.684.48.16936385737.67.714.764363257570.615.014.4 <td>19.4</td> <td>75.1</td> <td>5.5</td> <td></td> <td>674</td> <td>587</td> <td>573</td>	19.4	75.1	5.5		674	587	573	
13.213.413.413.513.411.283.55.36866155737.387.55.27106275733.691.35.1727641753-95.05.07376525388.9-11.170966062457374.614.810.662360557567.921.710.457560562161.728.210.157566366355.634.59.957566366349.840.59.766869245.245.39.567269739.151.79.257366167429.162.08.957363564124.566.88.757363259820.071.58.560362357311.680.28.266763157315.775.98.463862157315.775.98.46936385737.684.48.16936385733.788.47.9712646573-92.27.87276525733.784.9-15.169266077.615.014.461064357564.022.014.0575650634 <td>15.2</td> <td>79.4</td> <td>54</td> <td></td> <td>658</td> <td>603</td> <td>573</td>	15.2	79.4	54		658	603	573	
11.2 37.5 5.5 710 627 573 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 8.4 638 621 573 11.6 80.2 8.2 667 631 573 11.6 80.2 8.2 667 631 573 7.6 84.4 8.1 693 638 573 7.6 84.4 8.1 693 638 573 7.6 7.7 14.7 643 632 575 70.6 15.0 14.4 610 643 575 64.0 </td <td>11.2</td> <td>83.5</td> <td>53</td> <td></td> <td>686</td> <td>615</td> <td>572</td>	11.2	83.5	53		686	615	572	
1.51.65.21.70 6.71 5.73 -95.05.0737 652 88.9 11.1709 660 81.5 7.610.9 660 624 573 74.6 14.810.6 623 605 575 67.9 21.710.4 575 605 621 61.7 28.210.1 575 641 659 55.6 34.59.9 575 663 683 49.8 40.59.7 668 692 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 8.7 573 635 641 24.5 66.8 8.7 573 635 641 24.5 66.8 8.7 573 635 641 24.5 66.8 8.7 573 635 641 24.5 66.8 8.7 573 635 641 24.5 66.8 8.7 573 635 641 24.5 66.8 8.7 573 635 641 24.5 66.8 8.7 573 655 573 11.6 80.2 8.2 667 631 573 7.6 84.4 8.1 693	73	87.5	5.2		710	677	573	
J.5J.1.5J.1.1J.1.7J.1.7J.1.7J.1.7J.1.7 $-$ 95.05.0737652 88.9 -11.1709660 81.5 7.610.9660624573 74.6 14.810.6623605575 67.9 21.710.4575605621 61.7 28.210.1575641659 55.6 34.59.9575663683 49.8 40.59.7668692 45.2 45.39.5672697 39.1 51.79.2573668689 34.0 56.99.1573661674 29.1 62.08.9573635641 24.5 66.88.7573632598 20.0 71.58.5603623573 11.6 80.28.2667631573 11.6 80.28.2667631573 7.6 84.48.1693638573 3.7 88.47.9712646573 7.6 7.714.7643632575 70.6 15.014.4610643575 64.0 22.014.0575650634	3.6	913	51		710	641	752	
-11.1709660 88.9 -11.1709660 81.5 7.610.9660624573 74.6 14.810.6623605575 67.9 21.710.4575605621 61.7 28.210.1575641659 55.6 34.59.9575663683 49.8 40.59.7668689 45.2 45.39.5672697 39.1 51.79.2573666674 29.1 62.08.9573635641 24.5 66.88.7573632598 20.0 71.58.5603623573 11.6 80.28.2667631573 11.6 80.28.2667631573 7.6 84.48.1693638573 $-$ 92.27.8727652573 84.9 -15.169266077.6 77.6 7.714.7643632575 64.0 22.014.0575650634		95.0	50		737	652	155	
36.7 7.6 10.9 660 624 573 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 9.2 573 661 674 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 11.6 80.2 8.2 667 631 573 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$ 7.8 727 652 575 70.6 15.0 14.4 610 643 575 64.0 22.0 14.0 575 650 634	88.0		111	709		660		
31.5 1.6 10.5 600 624 515 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 11.6 80.2 8.2 667 631 573 7.6 84.4 8.1 693 633 573 3.7 88.4 7.9 712 646 573 $ 92.2$ 7.8 727 652 573 84.9 $ 15.1$ 692 660 775 70.6 15.0 14.4 610 643 575 64.0 22.0 14.0 575 650 634	81.5	76	10.9	660		674	572	
14.314.314.310.0 62.3 60.3 51.3 67.921.710.457560562161.728.210.157564165955.634.59.957566368349.840.59.766869245.245.39.567269739.151.79.257366167429.162.08.957363564124.566.88.757363259820.071.58.560362357315.775.98.463862157316.680.28.266763157316.680.28.26676315733.788.47.9712646573-92.27.872765257384.915.169266077.617.714.764363257564.022.014.0575650634	74.6	14.9	10.5	617		024	575	
61.7 28.2 10.4 575 603 621 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 $ 92.2$ 7.8 727 652 573 $ 92.2$ 7.8 727 652 573 $ 92.2$ 7.8 727 652 573 $ 92.2$ 7.8 727 652 573 $ 92.2$ 7.8 643 632 575 70.6 15.0 14.4 610 643 575 64.0 22.0 14.0 575 650 634	67.0	217	10.0	575		605	575	
61.7 26.2 10.1 57.5 641 0.39 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$ 692 660 775 70.6 15.0 14.4 610 643 575 64.0 22.0 14.0 575 650 634	61.7	21.7	10.4	575		603	650	
33.0 34.3 3.3 37.3 57.3 663 633 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$ 7.8 727 652 575 84.9 $ 15.1$ 692 660 77.6 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	55.6	34.5	0.0	575		667	697	
49.840.39.7 008 092 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$ 7.8 727 652 575 84.9 $ 15.1$ 692 660 77.6 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	10.9	J4.J 40.5	<i>3.3</i>	575		005	603	
43.2 43.3 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 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	47.0	40.3	9.7			608	692	
33.1 51.7 51.2 31.3 6088 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 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	43.2	517	9.5		577	012	697	
34.0 50.3 9.1 573 601 674 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 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	37.1	56.0	9.2		515	608	089	
25.1 02.0 0.5 0.5 573 033 041 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$ 7.8 727 652 575 84.9 $ 15.1$ 692 660 77.6 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	34.0 20 1	62.0	9.1 9.0		573	001 625	674	
24.5 60.6 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 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	27.1	66.8	0.7		573	635	609	
20.0 71.3 8.3 603 623 573 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 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	24.3	71.5	0./		573	632	598	
13.7 73.9 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 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	20.0	71.5	8.5		003	623	573	
11.6 30.2 8.2 607 631 573 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 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	13.7	13.9	8-4		560 667	621	573	
7.5 64.4 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	11.0	0U Q.A. 4	ō-2 0 1		00/	031 678	515	
3.7 66.4 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 15.014.4 610 643 575 64.0 22.014.0 575 650 634	7.0	04.4 80 1	5-1 7 0		5 C C C C C C C C C C C C C C C C C C C	540	515	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	3.1	00.4	1.9		/12	040	5/5	
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		944	1.8	(02	121	652	573	
71.0 1.1 14.1 643 632 575 70.6 15.0 14.4 610 643 575 64.0 22.0 14.0 575 650 634	04.Y		15.1	092		660	676	
10.6 15.0 14.4 610 643 575 64.0 22.0 14.0 575 650 634	11.0	1.7	14./	643		632	575	
04.0 22.0 14.0 575 650 634	/0.6	15.0	14.4	610		643	575	
	04.V	22.0	14.0	575		650	634	

Mole %			Crystallization temperature (°C)				
CaCl ₂	KCl	CaCrO₄	α (CaCl₂)	β (KCl)	7 (CaCrO₄)	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		793	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	645	573	
	86.3	13.7		694	652	515	
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	67:	
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	
60.0	15 7	26.2	575		774	500	

TABLE 1 (continued)

(Table continued on p. 120).

Mole %			Crystallization temperature (°C)				
CaCl ₂	KCl	CaCrO₄	а (CaCl ₂)	β (KCl)	γ (CaCrO₄)	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	22.3	29.7	575 .		770	642	
40.7	30.3	29.0	575		774	661	
35.8	35.8	29.0	575		775	672	
29.1	43 3	27.6		573	772	657	
73.7	45.5 AQ A	26.9		573	765	678	
185	557	26.3		573	765	573	
13.6	60.7	20.5		606	744	573	
90	65.0	23.7		678	731	573	
0.7 4 7	710	23.2		643	707	573	
4.5	75.8	24.1 74.7		657	652	515	
<u> </u>	75.0	24.2	660	0.2	759		
55.0	9 7	35.8	616		773	575	
JJ. J	16.2	34.8	575		794	614	
47.0	10.2	22.0	575		707	650	
94.4	20.7	221	575		760	670	
30.2	30-1	22.0			801	677	
33.0	33.0	32.0		561	702	670	
30.2	43.9	32.5		573	796	647	
24.0 10.7	43. 3 50 î	31.5		573	794	603	
17.2	55.0	30.7		500	700	573	
14.1	55.5	30.0		625	752	573	
9.2 A 5	61.5	29.3		643	731	573	
4.3	71.0	20.7		652	681	- 575	
59.4	71.9	28.1	660	052	799		
51 1	<u> </u>	41-0	607		802	575	
31.1 41 7	14.5	40.4	575		8002	637	
377	74.0	39.3	575		912	650	
31.1	24.0	28.2	575		815	677	
31.J 35.6	21.2 20 A	31.3		577	01J 917	653	
20.0	33.U	30.4 35.6		515	01J 911	624	
<u>_0.0</u>	577-2 50 0	33.3		313 506	804	573	
14.0	50.8 62 7	24.0 22 0		610	00 1 707	573	
9.J	20.7	33.8 77 I		640	192 761	573	
4.0	02.3 67 7	33.1 33.2		657	701	212	
	01.1	32.3		032	/14		



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 CaCl2-KCl-CaCrO4 system.

and δ (CaKCl₃). 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 CaCl₂ 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 CaCl₂-KCl-CaCrO₄ 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 CaCl₂-KCl-CaCrO₄ 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–CaCrO₄	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 CaCl₂-KCl-CaCrO₄ 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 CaCl₂ to KCl mole ratio is held constant. The section in Fig. 9 (CaCl₂ to KCl ratio equal to 15/85) intersects the three-phase line connecting the

TABLE	3							
X-RAY	DIFFRACTION	RESULTS	FOR	SEVERAL	CaCl	-KCI-CaCrO4	MIXTURE	ES

Sample composition (mole %)			Phases identified by			
CaCl ₂	KCI CaCrO ₄		- X-ray diffraction			
50.0	50.0	_	CaKCl3			
46.9	46.9	6.2	CaKCl₃ CaCrO₄ (very weak)			
53.6	29.0	17.4	CaKCl₃ CaCl₂ CaCrO₄			
21.3	63.5	15.2	CaKCl₃ KCl CaCrO₄			
37.9	37.9	24.2	CaKCl3 CaCrO4			



Fig. 9. A vertical section through the CaCl₂-KCl-CaCrO₄ phase diagram (CaCl₂ to KCl mole ratio constant at 15/85).

Fig. 10. A vertical section through the $CaCl_2-KCl-CaCrO_4$ phase diagram (CaCl₂ to KCl mole ratio constant at 78/22).

KCl-CaCrO₄ eutectic with the KCl-rich ternary eutectic. The section in Fig. 10 (CaCl₂ to KCl ratio equal to 78/22) intersects 2 three-phase lines; one connecting the CaCl₂-rich ternary eutectic with the CaCl₂-rich binary eutectic in the CaCl₂-KCl system and the other connecting the same ternary eutectic with the CaKCl₃-CaCrO₄ pseudobinary eutectic.



Fig. 11. Constant 5 mole % CaCrO₄ vertical section through the CaCl₂-KCl-CaCrO₄ phase diagram.



Fig. 12. Constant 10 mole % CaCrO₄ vertical section through the CaCl₂-KCl-CaCrO₄ 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-CaCrO₄ phase diagram.



Fig. i4. Constant 25 mole % CaCrO₄ vertical section through the CaCl₂-KCl-CaCrO₄ phase diagram.



Fig. 15. The 550°C isothermal section through the CaCl₂-KCl-CaCrO₄ phase diagram.



Fig. 16. The 575 °C isothermal section through the CaCl₂-KCl-CaCrO₄ phase diagram.



Fig. 17. The 600°C isothermal section through the CaCl₂-KCl-CaCrO₄ phase diagram.



Fig. 18. The 650°C isothermal section through the CaCl₂-KCl-CaCrO₄ phase diagram.



Fig. 19. The 700°C isothermal section through the CaCl₂-KCl-CaCrO₄ 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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REFERENCES

- 1 R. P. Clark, R. L. Blucher and H. J. Goldsmith, J. Chem. Eng. Data, 14 (1969) 465.
- 2 R. P. Clark and K. R. Grothaus, J. Electrochem. Soc., 118 (1971) 1680.
- 3 R. P. Clark and F. W. Reinhardt, Thermochim. Acta, 12 (1975) 309.
- 4 B. H. Van Domelen and R. D. Wehrle, A Review of Thermal Battery Technology, Proc. 9th Intersoc. Energy Conversion Engineering Conf., The American Society of Mechanical Engineers, 1974.