*Thermochimica Acta*, 12 (1975) 309–314


# PHASE DIAGRAMS FOR THE BINARY SYSTEMS $CaCl_2$–KCl AND $CaCl_2$–$CaCrO_4$

ROBERT P. CLARK AND FREDERICK W. REINHARDT
*Sandia Laboratories, Albuquerque, N.M. 87115 (U.S.A.)*
(Received 24 February 1975)

ABSTRACT

Phase diagrams have been determined using differential thermal analysis for the binary systems $CaCl_2$–KCl and $CaCl_2$–$CaCrO_4$. $CaCl_2$–KCl phase diagrams have been previously reported but results were not consistent. No prior studies have been reported for the $CaCl_2$–$CaCrO_4$ system. In the $CaCl_2$–KCl binary system two eutectics have been located at 24.0 mole % KCl (m.p. 615°C) and 74.3 mole % KCl (m.p. 594°C). A double salt of composition $CaKCl_3$ melting congruently at 741°C has been found. The $CaCl_2$–$CaCrO_4$ system is a simple eutectic system with the eutectic occurring at 23.4 mole % $CaCrO_4$ and melting at 660°C.

## INTRODUCTION

Thermal cells (voltaic cells employing a molten salt electrolyte) frequently employ a calcium anode and an electrolyte–cathodic depolarizer mixture of LiCl–KCl–$CaCrO_4$[11]. At the elevated internal temperatures (500 to 600°C) attained in thermal cells the Ca anode will react with the LiCl to form $CaCl_2$[3]. 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. The phase diagram for the binary system KCl–$CaCrO_4$ has been previously reported[2] as part of a general investigation of the ternary system LiCl–KCl–$CaCrO_4$. The phase diagrams for the other binary systems, $CaCl_2$–$CaCrO_4$ and $CaCl_2$–KCl are reported in this work and the investigation of the ternary system will be concluded at a later date.

Phase diagrams for the $CaCl_2$–KCl system have been published many times in the past[1,4–10] but agreement between the various workers is very poor. In all the published results, the $CaCl_2$–KCl phase diagram is shown with two binary eutectics, one on either side of a $CaCl_2$–KCl double salt melting congruently. However, there is considerable variance in the reported compositions and liquidus temperatures of the eutectics and of the double salts. For example, both $CaCl_2$:KCl and $3CaCl_2$:2KCl have been reported for the double salt composition, and published congruent melting points for the double salt have ranged from 725 to 760°C. Eutectic compositions and melting points on the $CaCl_2$ rich side of the diagram varied from 24.0 to 28.0 mole % KCl and from 608 to 655°C. On the KCl rich side the reported eutectic compositions

ranged from 69.1 to 75.0 mole % KCl with melting points between 583 and 630°C. Even the melting point of $CaCl_2$ appears to be in question with values reported ranging from 710 to 806.4°C, although most of the values are between 750 and 782°C. Because of these wide discrepancies, it was considered necessary to redetermine the diagram.

The phase diagram for the $CaCl_2$–$CaCrO_4$ system has not been previously reported. Data were obtained up to ~52 mole % $CaCrO_4$. Further data cannot be obtained because $CaCrO_4$ decomposes above this composition at temperatures of interest.

## 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[2]; and ultra pure anhydrous $CaCl_2$ (99.95%) from Research Organic/Inorganic Chemical Corporation, Sun Valley, Calif. $CaCrO_4$ was vacuum dried at 400°C for 4 h and $CaCl_2$ 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 to 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.

Phase change data were determined using DTA. All thermograms 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.

## RESULTS

Typical DTA curves are shown in Fig. 1 for the $CaCl_2$–KCl system. The DTA results for all the $CaCl_2$–KCl mixtures are listed in Table 1 and the resulting phase

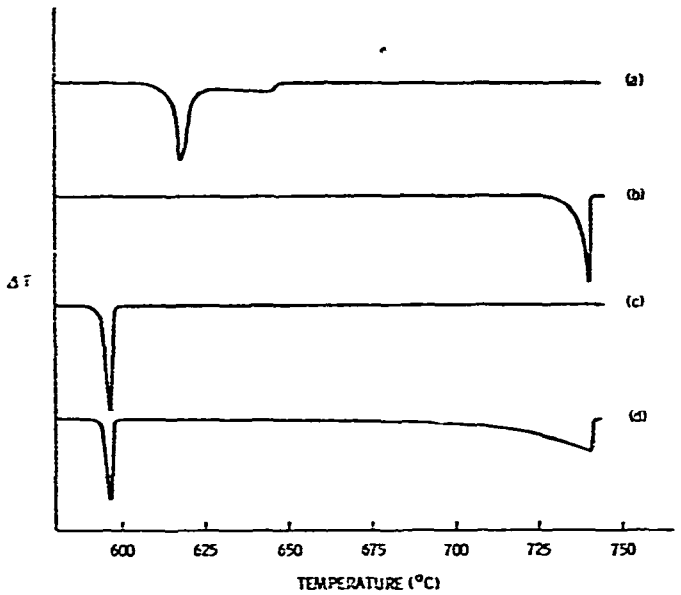


Fig. 1. Typical DTA curves for the system $CaCl_2$–KCl. (a) 25.9 mole % KCl; (b) 50 mole % KCl; (c) 74.3 mole % KCl; (d) 93.1 mole % KCl.

TABLE 1

DTA RESULTS FOR $CaCl_2$–KCl MIXTURES

| *Mole % KCl* | *Liquidus* (°C) | *Solidus* (°C) |
|---|---|---|
| 0 | 761 | — |
| 7.3 | 724 | 612 |
| 14.2 | 687 | 614 |
| 20.8 | 647 | 616 |
| 24.0 | 616 | 616 |
| 25.9 | 648 | 616 |
| 33.2 | 695 | 616 |
| 38.9 | 718 | 614 |
| 44.5 | 731 | 614 |
| 50.0 | 741 | — |
| 54.9 | 728 | 592 |
| 59.8 | 713 | 594 |
| 69.1 | 648 | 593 |
| 74.3 | 594 | 594 |
| 77.6 | 635 | 596 |
| 81.7 | 670 | 596 |
| 85.6 | 696 | 594 |
| 93.1 | 741 | 594 |
| 100 | 773 | — |

diagram is shown in Fig. 2. Features of this $CaCl_2$–KCl phase diagram include a double salt of composition $CaKCl_3$ melting congruently at 741 °C, melting points of 761 °C for $CaCl_2$ and 773 °C for KCl, a eutectic at 24.0 mole % KCl melting at 615 °C and a second eutectic at 74.3 mole % KCl with a melting point of 594 °C. These results do not duplicate any of those previously reported, but they fall within the range of all prior results. Agreement is best with the recently published data of Burlakova and Bukhalova[1]. Comparison of their data with the present results is shown in Table 2.

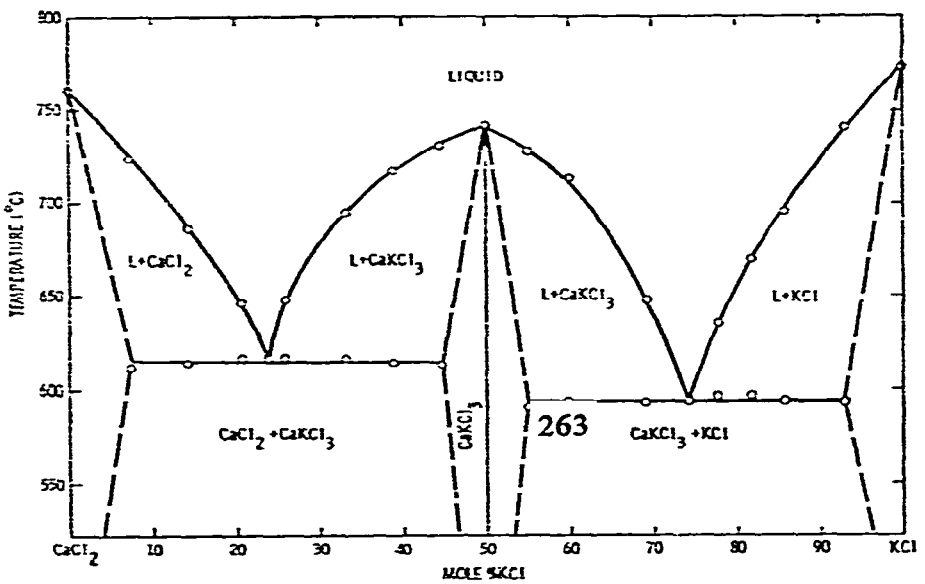


Fig. 2. $CaCl_2$–KCl phase diagram.

TABLE 2

COMPARISON OF $CaCl_2$–KCl RESULTS WITH DATA BY BURLAKOVA AND BUKHALOVA[1]

| | *Double salt* | | *$CaCl_2$-rich eutectic* | | *KCl-rich eutectic* | |
|---|---|---|---|---|---|---|
| | *Composition* | *m.p.* (°C) | *Composition* (*mole % KCl*) | *m.p.* (°C) | *Composition* (*mole % KCl*) | *m.p.* (°C) |
| Burlakova–Bukhalova | $CaKCl_3$ | 740 | 26.1 | 630 | 75.0 | 590 |
| Present work | $CaKCl_3$ | 741 | 24.0 | 615 | 74.3 | 594 |

Typical DTA curves for the $CaCl_2$–$CaCrO_4$ system are shown in Fig. 3, and the DTA results are listed in Table 3. The phase diagram for $CaCl_2$–$CaCrO_4$ up to 52 mole % $CaCrO_4$ is seen in Fig. 4. It is a simple eutectic system with the eutectic occurring at 23.4 mole % $CaCrO_4$ and melting at 660 °C.

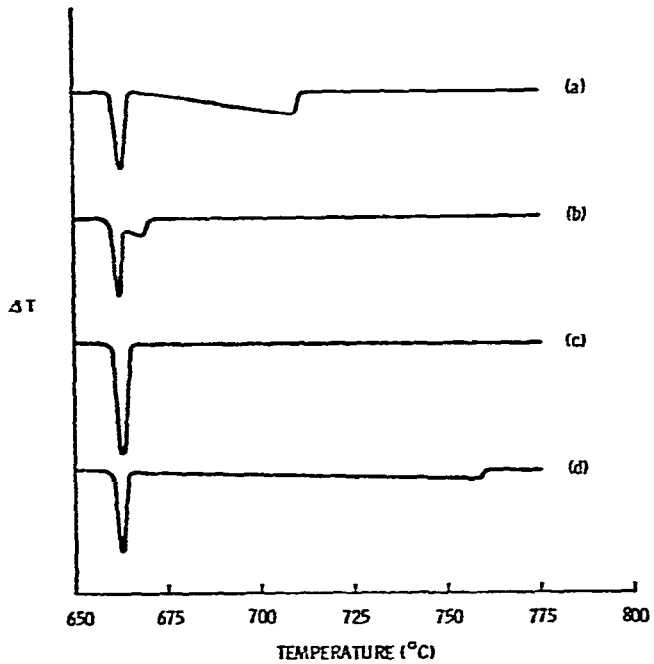


Fig. 3. Typical DTA curves for the system $CaCl_2$–$CaCrO_4$. (a) 11.1 mole % $CaCrO_4$; (b) 21.2 mole % $CaCrO_4$; (c) 23.4 mole % $CaCrO_4$; (d) 36.8 mole % $CaCrO_4$.

TABLE 3

DTA RESULTS FOR $CaCl_2$–$CaCrO_4$ MIXTURES

| *Mole % $CaCrO_4$* | *Liquidus (°C)* | *Solidus (°C)* |
|---|---|---|
| 0 | 761 | — |
| 2.9 | 747 | 636 |
| 4.3 | 740 | 656 |
| 7.3 | 725 | 658 |
| 11.1 | 709 | 660 |
| 15.1 | 692 | 658 |
| 17.1 | 686 | 662 |
| 19.2 | 676 | 660 |
| 21.2 | 668 | 660 |
| 23.4 | 660 | 660 |
| 25.5 | 688 | 661 |
| 27.7 | 704 | 661 |
| 32.2 | 730 | 661 |
| 36.8 | 758 | 661 |
| 41.6 | 788 | 658 |
| 51.6 | 851 | 663 |

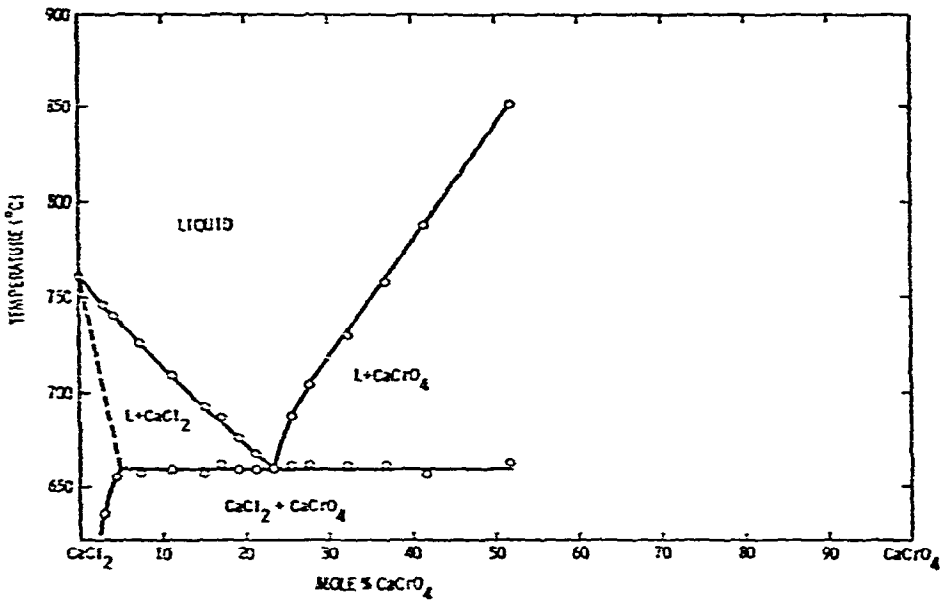


Fig. 4. $CaCl_2$–$CaCrO_4$ phase diagram.

ACKNOWLEDGEMENTS

The authors wish to express appreciation to G. T. Gay of Sandia Laboratories for his X-ray diffraction analyses and to S. L. Erickson, also of Sandia Laboratories, for the analysis of impurities in the $CaCl_2$.

This work was supported by the United States Atomic Energy Commission.

REFERENCES

1 V. M. Burlakova and G. A. Bukhalova, *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.*, 10 (1967) 487.
2 R. P. Clark, R. L. Blucher and H. J. Goldsmith, *J. Chem. Eng. Data*, 14 (1969) 465.
3 R. P. Clark and K. R. Grothaus, *J. Electrochem. Soc.*, 118 (1971) 1680.
4 E. P. Dergunov and A. G. Bergman, *Dokl. Akad. Nauk SSSR*, 74 (1950) 815.
5 M. S. Golubeva and A. G. Bergman, *Zh. Obshch. Khim.* 26 (1956) 328.
6 M. Ishaque, *Bull. Soc. Chim. Fr.*, (1952) 127.
7 A. I. Ivanov, *Dokl. Akad. Nauk SSSR*, 86 (1952) 539.
8 C. A. Lantsberry and R. A. Page, *J. Soc. Chem. Ind.*, 39 (1920) 37T.
9 O. Menge, *Z. Anorg. Chem.*, 72 (1911) 162.
10 V. E. Plyushchev, L. N. Komissarova, L. V. Meshchaninova and L. M. Akukina, *Zh. Neorg. Khim.*, 1 (1956) 820.
11 B. H. Van Domelen and R. D. Wehrle, *A Review of Thermal Battery Technology, Proc. 9th Intersoc. Energy Conversion Eng. Conf.*, The American Society of Mechanical Engineers, 1974.