$$2[C—(C)(H)_3] + 4[C—(C)_2(H)_2] = 46.6$$

$$2[C—(C)(H)_3] + 5[C—(C)_2(H)_2] = 53.7$$

Solving, $[C—(C)_2(H)_2] = 7.1$ and $[C—(C)(H)_3] = 9.1$.

The C_p of n-octane may then be estimated as $2[C—(C)(H)_3] + 6[C—(C)_2(H)_2] = 60.8$ (cf. 60.7 observed). The other groups were obtained similarly. In practice, when there is a large amount of measured data, the groups are derived by computer, using a least squares regression program (9). This was the case in the alkanes, alkenes, aromatics, and sulfur compounds. In some cases, it is not possible to determine a group independently of other groups. For example, methanol is $[C—(O)(H)_3] + [O—(C)(H)] = 19.5$. Continuing the practice adopted for gases (3), all $[C—(X)(H)_3]$ groups, where X is an atom other than C, were assigned the same value as $[C—(C)(H)_3] = 8.8$. It follows that $[O—(C)(H)] = 10.7$. This practice in no way affects the system; it only makes the computation simpler. In other cases, when pairs of groups are obtained and when one of them is not a $[C—(X)(H)_3]$, one group is arbitrarily assigned. In a number of cases, there were so many unknown groups that no assignments were made.

Group additivity does not take into account next to nearest neighbor interactions, such as gauche effects (3) or cis effects. The fit of the observed minus estimated for the alkenes improved only slightly using gauche corrections, so it was felt that the gain in precision was not worthwhile. The cis effect for olefins is significant and is included.

Table I shows that for all the data, the precision in estimating $C_p(l)$ is ± 1.5 cal. mole^{-1} deg.$^{-1}$, and in most cases is better than ± 1 cal. mole^{-1} deg.$^{-1}$.

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Phase Diagram of the System LiCl–KCl–CaCrO₄

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The phase diagram has been determined for the system LiCl–KCl–CaCrO₄. Binary eutectics have been located at 60 wt. % KCl–40 wt. % CaCrO₄ (m.p. 651° C.) and 62 wt. % LiCl–38 wt. % CaCrO₄ (m.p. 638° C.). A ternary eutectic was found at 41 wt. % LiCl–50 wt. % KCl–9 wt. % CaCrO₄ (m.p. 342° C.). It has been verified by x-ray diffraction that LiCl–KCl–CaCrO₄ is the stable diagonal section in the quaternary reciprocal system K, Li, Ca/ /CrO₄, Cl.

THE SALT mixture LiCl-KCl-CaCrO₄ is an electrolyte-depolarizer combination used in thermal cells (voltaic cells employing a molten salt electrolyte). The cell Ca/LiCl-KCl-CaCrO₄/Ni has been studied by Jennings (4). Recent investigations of this thermal cell system have demonstrated a need for a detailed phase diagram determination of the mixture LiCl-KCl-CaCrO₄. This ternary system is actually a stable diagonal section of the K, Li, Ca/ /CrO₄, Cl quaternary reciprocal system.

The sides of the ternary diagram are the binary system LiCl-KCl and the stable diagonals of the ternary reciprocal systems K, Ca/ /Cl, CrO₄ and Li, Ca/ /Cl, CrO₄. That LiCl-CaCrO₄, KCl-CaCrO₄, and LiCl-KCl-CaCrO₄ are indeed stable systems has been confirmed by x-ray diffraction studies at Sandia Laboratories.

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This system has been recently studied also by Abrabad-zhan and Bergman (1). Discrepancies exist between Bergman's results and those reported in the present work. The data herein have been verified independently at Catalyst Research Corp. and Sandia Laboratories. The eutectic data for the system KCl-CaCrO₄ reported by Bergman are probably in error. In addition, the α/β LiCl phase transition reported by Bergman, but not verified by crystallographic data, was not noted in the present work.

Data at compositions greater than 60 to 70 wt. % CaCrO₄ could not be obtained, owing to the thermal decomposition of CaCrO₄ (2). Decomposition of CaCrO₄ begins to occur slightly above 800° C.

EXPERIMENTAL

The samples used in the experiments consisted of reagent grade LiCl and KCl, vacuum dried for 16 hours at 120° C.; LiCl-KCl mixtures (Anderson Physical Laboratories, Inc.), prepared according to the method of Laitinen et al. (5) to remove H_2O, oxide and hydroxyl ions, and heavy metal impurities; CaCrO₄ (Mineral Pigments Corp.) assayed at 98.0%; and CaCrO₄ prepared from reagent grade CaCl₂ and K₂CrO₄, which assayed at 99.85%. All CaCrO₄ samples were vacuum dried at 400° C. for 4 hours.

The high purity CaCrO₄ was prepared in the following manner. Equimolar quantities of CaCO₃ and concentrated HCl were mixed by slowly adding the CaCO₃ to the HCl. This mixture was heated to boiling, and a stoichiometric quantity of Na₂CrO₄ ($\sim 3M$ solution) was slowly added with vigorous stirring. The boiling mixture was agitated for 30 minutes and the CaCrO₄ precipitate was washed by decantation with boiling water. The washing was continued until the wash solution was free of chloride ion. The latter was detected by the addition of AgNO₃ to a small sample of wash solution, which had been previously freed from the interfering chromate ion by precipitation with Ba(NO₃)₂. The CaCrO₄ was filtered, vacuum-dried at 110° C. for 2 hours, and heated to 400° C. for 4 hours. All chemicals used were of analytical reagent grade. Agreement within ±1° C. was found for thermal analyses between samples using the two types of CaCrO₄.

The majority of the freezing points were obtained by analyzing the temperature vs. time curves as the sample was cooled slowly from 800° C. to room temperature. Phase transition points were determined by observing the tem-

peratures at which changes in slope occurred. Since the transitions were accompanied by a rounding of the temperature vs. time curve rather than an abrupt slope change, the transition temperature selected was determined by the intersection of extrapolations of the slopes before and after the transition.

Five-gram salt samples were placed in a 96% silica-glass test tube (18 mm. o.d. × 150 mm. long). A Chromel-Alumel thermocouple was sheathed in a closed-end 96% silica-glass tube (6 mm. o.d.),which was in turn positioned in the sample. The salt mixture was heated to 800° C., using a crucible furnace (Hevi Duty Electric Co., Type 80) and rheostat (Superior Electric Co., Type 1126 Powerstat). The molten sample was stirred to assure homogeneity and cooled at a rate of approximately 5° C. per minute. Sample temperature was measured using a 2-mv. input strip chart recorder (Brown Instrument Co.). A potentiometer in series with the recorder was used to buck out all but 2 mv. of the initial thermocouple output. As the temperature and thermocouple voltage decreased, the potentiometer was reset manually in 2-mv. intervals. Cooling curves for each sample were run in triplicate and two samples of each composition were tested.

For better definition of thermal data near the eutectic compositions and as spot checks on data for a variety of compositions, differential thermal analyses were run. Five-gram samples were heated in a platinum crucible with an Al₂O₃ reference of equal weight in a similar crucible. The crucibles were placed in a massive nickel holder at symmetrical positions, and the holder was heated in a vertical tube furnace (Marshall Equipment Division, National Research Corp., Model 1044). Platinum-platinum (10% rhodium) thermocouples were placed directly in the sample and in the alumina reference. Only the cooling curves were used for equilibrium data. Cooling rates, ranging from 0.5° to 2.0° C. per minute, were employed. The absolute temperature was recorded on a 1-mv. display strip chart recorder (Leeds and Northrup) with 99-mv. automatic ranging, and the differential thermocouple signal was amplified (L & M Model 9864 amplifier) and recorded (L & N Speedomax G). The chart speeds were synchronized so that a thermal event was detected on the differential record, and the temperature at that time was read on the absolute recorder.

The main technique employed in this work—i.e., temperature vs. time phenomena—was initially checked out by making determinations on LiCl, KCl, and mixtures of the two chlorides. The results were compared with those
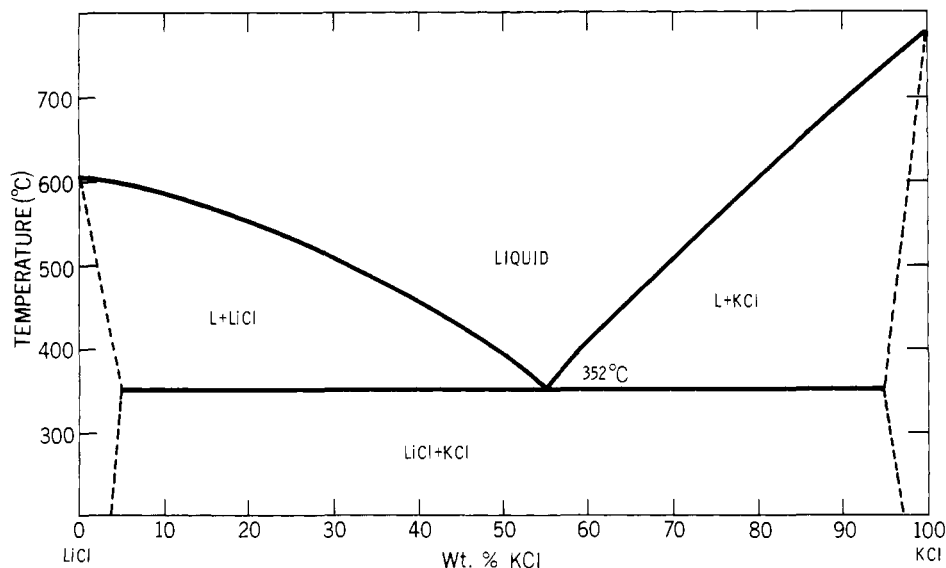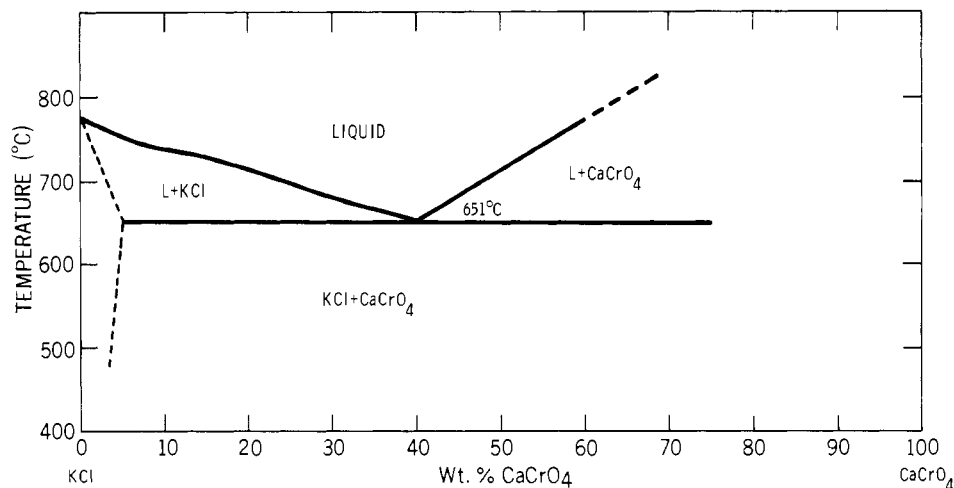

Figure 1. Phase diagram of binary system LiCl-KCl
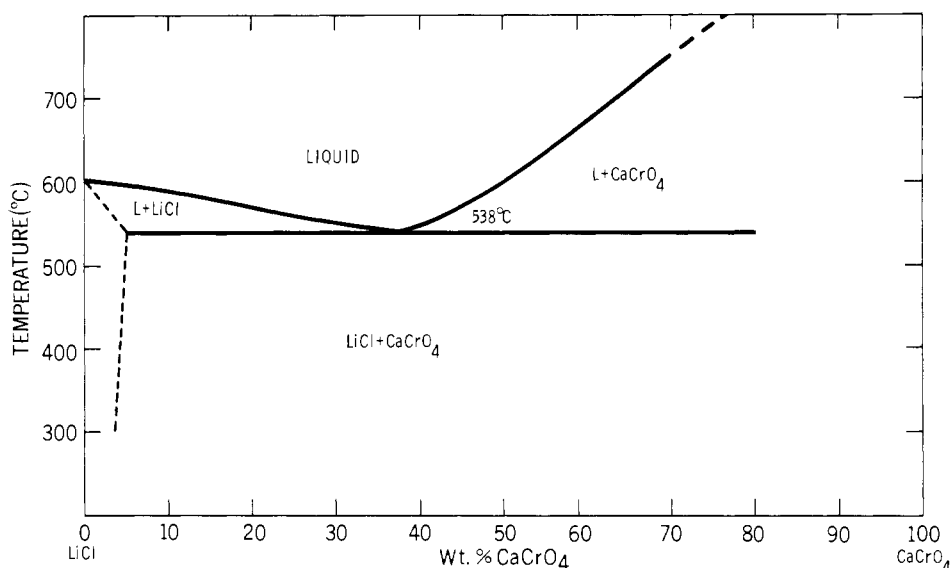
Figure 2. Phase diagram of binary system KCl–CaCrO₄

Figure 3. Phase diagram of binary system LiCl–CaCrO₄

of Elchardus and Laffitte (3), and agreed within ±2° C. The LiCl-KCl eutectic freezing point was 351.5° ± 0.5° C., which agrees well with 352° C. found by Laitinen et al. (5). Results were independent of the source of LiCl and KCl used.

Heating, as well as cooling curves, were run on several samples. Agreement between the two was within 2° C. if the sample had been fused and homogenized prior to heating, and once a technique for interpreting the curves had been established based on curves for samples with known phase changes.

The validity of the data was further verified by comparing them with data obtained for a few selected samples using Stone DTA equipment with Platinel thermocouples and 5-mg. sample weight. Agreement with data obtained by the other techniques was ±2° C.

RESULTS

LiCl–KCl Binary System. This system, studied by many investigators (3), exhibits a eutectic of composition, 55 wt. % KCl–45 wt. % LiCl, which has a freezing point of 352° C. (Figure 1). This binary mixture was not rein-

vestigated in the present work, other than as a check on experimental techniques, as previously described.

KCl–CaCrO₄ Binary System. KCl and CaCrO₄ form a simple eutectic system with a eutectic composition of 60 wt. % KCl–40 wt. % CaCrO₄, which freezes at 651° C. (Figure 2). This is in disagreement with the work of Bergman (1), who reported 50.5 mole % K₂Cl₂ and 49.5 mole % CaCrO₄ freezing at 668° C. Converted to weight percentages, this would be 49.4 wt. % KCl–50.6 wt. % CaCrO₄. Results, verified independently at Sandia Laboratories and at Catalyst Research Corp., show the results reported by Bergman to be incorrect.

LiCl–CaCrO₄ Binary System. The binary system LiCl–CaCrO₄ exhibited a eutectic at 62 wt. % LiCl–38 wt. % CaCrO₄, with a freezing point of 538° C. (Figure 3). These are contrasted to the values of Abrabadzhan and Bergman, which were 64 wt. % LiCl and a freezing point of 565° C.

LiCl–KCl–CaCrO₄ Ternary System. A ternary eutectic existed at 41 wt. % LiCl–50 wt. % KCl–9 wt. % CaCrO₄, with a freezing point of 342° C. Bergman reported 42.0 wt. % LiCl–52.6 wt. % KCl–5.4 wt. % CaCrO₄, freezing at 336° C. The reasons for these discrepancies cannot be pinpointed, although it seems that in Bergman's work an insufficient
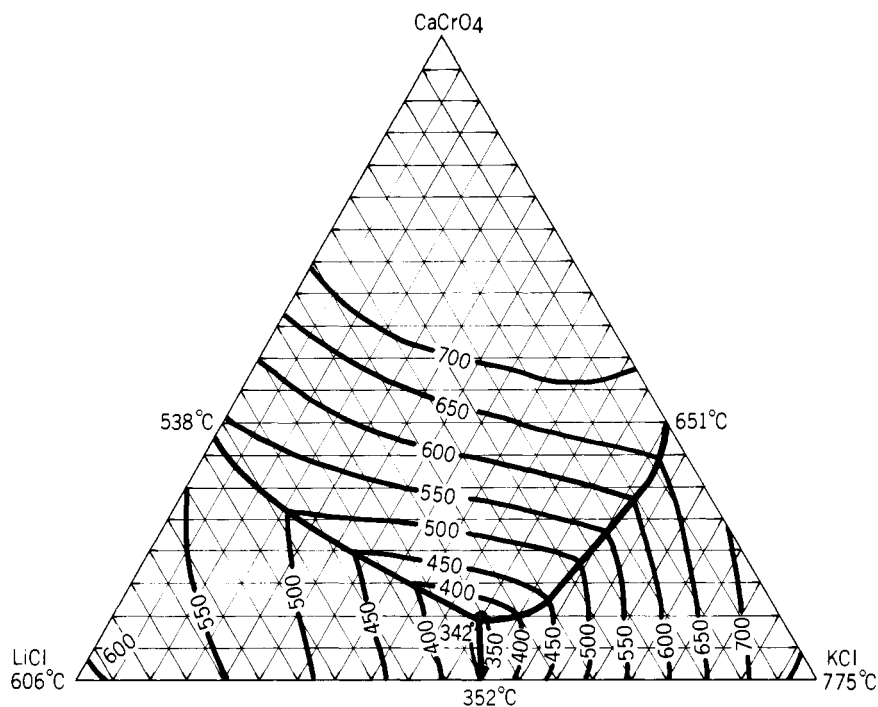
Figure 4. Phase diagram of ternary system LiCl–KCl–CaCrO₄
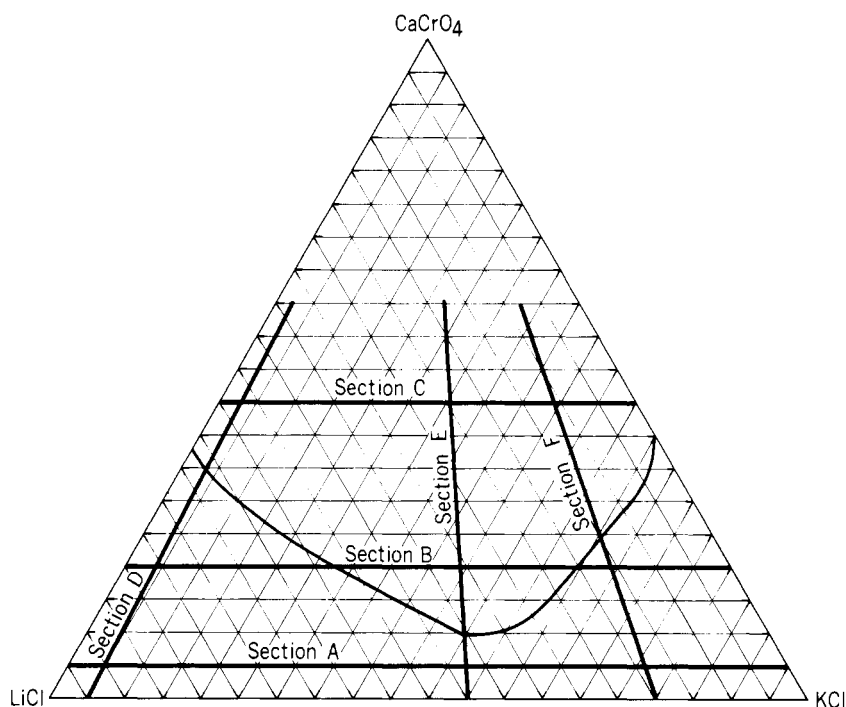

Figure 5. Locations of sections through the LiCl–KCl–CaCrO₄ phase diagram

number of data points were obtained to locate the eutectic compositions accurately. Also, Bergman failed to mention the purity or source of the chemicals used in his work.

The over-all phase diagram for the LiCl–KCl–CaCrO₄ system is shown with the isothermal representation in Figure 4. Figures 6 to 11 are six sections whose locations in the ternary diagram are shown in Figure 5. This eutectic system is a classic example of a Class I four-phase equilibrium (6).

To verify that LiCl–KCl–CaCrO₄ is the stable ternary diagonal section in the quaternary reciprocal system Li, K, Ca/ /CrO₄, Cl, three mixtures were prepared, as shown in Table I. The mixtures were equivalent with respect to weight percentages of Li^-, K^-, Ca^{-2}, CrO_4^{-2}, and Cl^-. However, the three mixtures differed in the initial compounds used to obtain these ionic percentages. Sample 1 is the ternary eutectic composition.

The differential thermal analyses for the three fused samples were identical. Each exhibited the ternary eutectic behavior. X-ray diffraction analyses after fusion also were identical, and only three compounds (LiCl, KCl, and CaCrO₄) were present in each sample.
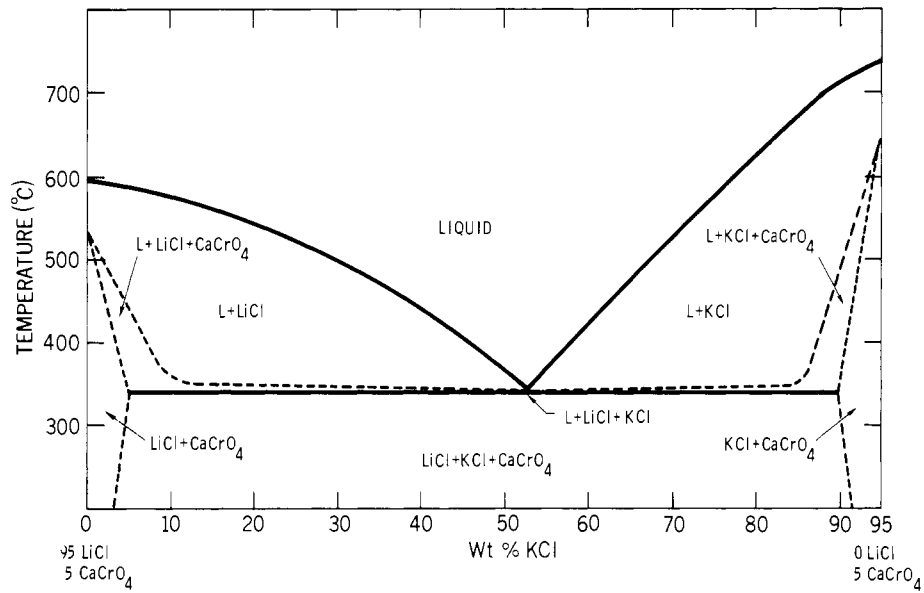
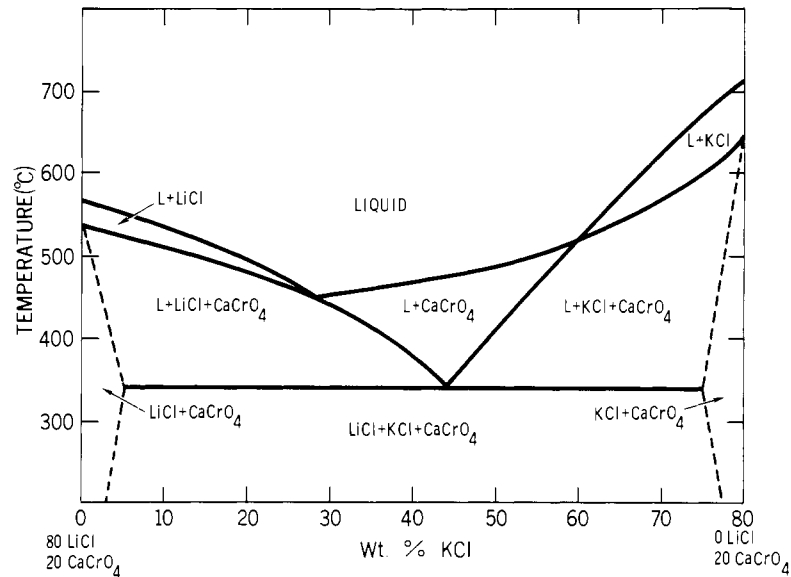Figure 6. Section A (Figure 5) through the LiCl–KCl–CaCrO₄ phase diagram

Figure 7. Section B (Figure 5) through the LiCl–KCl–CaCrO₄ phase diagram
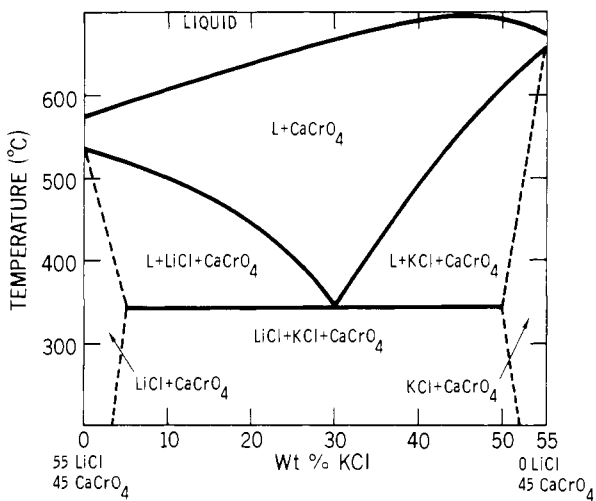

Figure 8. Section C (Figure 5) through
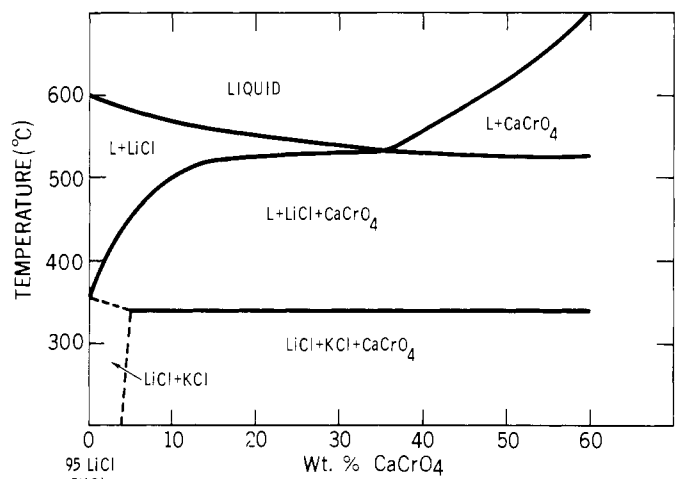the LiCl–KCl–CaCrO₄ phase diagram

Figure 9. Section D (Figure 5) through
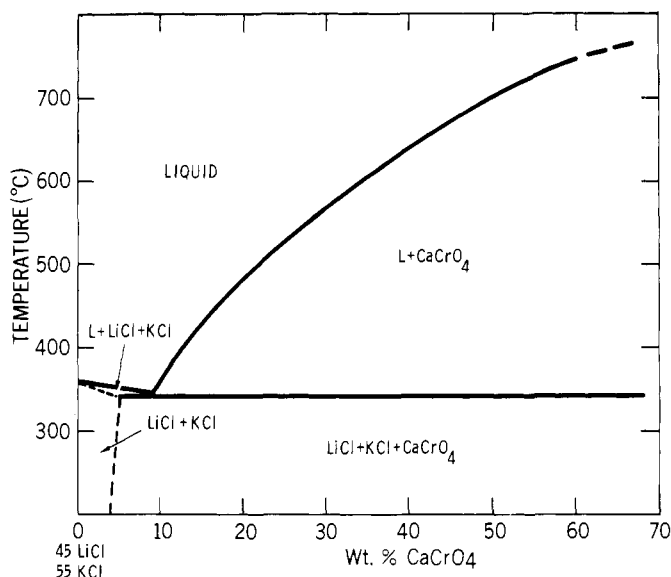the LiCl–KCl–CaCrO₄ phase diagram

Figure 10. Section E (Figure 5) through
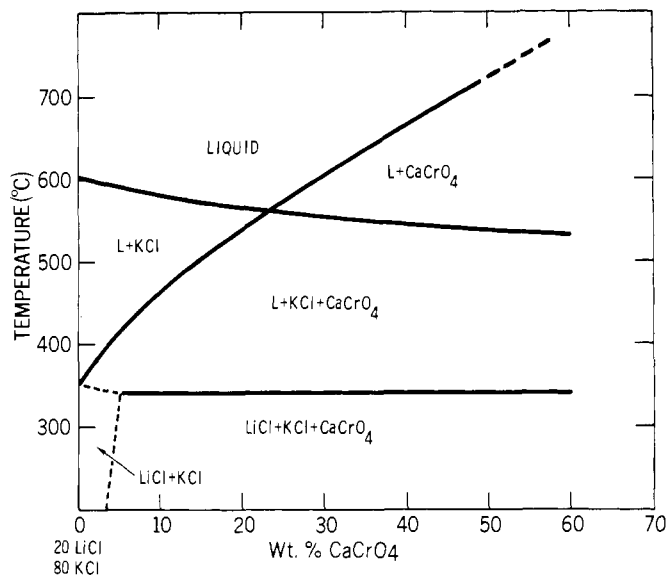the LiCl–KCl–CaCrO₄ phase diagram

Figure 11. Section F (Figure 5) through
the LiCl–KCl–CaCrO₄ phase diagram

Table I. Samples Prepared to Verify
LiCl–KCl–CaCrO₄ Stability

Sample No.	Wt. %					
	$CaCrO_4$	LiCl	KCl	K_2CrO_4	Li_2CrO_4	$CaCl_2$
1	9.00	41.00	50.00	...	...	...
2	...	41.00	41.40	11.20	...	6.40
3	...	36.11	50.00	...	7.49	6.40

ACKNOWLEDGMENT

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Density and Viscosity of Mixtures of 1,1,2,2-Tetrabromoethane and 1-Bromododecane

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Measurements of the density and viscosity of mixtures of 1,1,2,2-tetrabromoethane and 1-bromododecane have been carried out at atmospheric pressure over the entire composition range and in the temperature range between 25° and 40° C. The molal volume of a mixture calculated as the mole fraction weighted average of the pure component molal volumes is within 0.14% of the correct value. Several predictive techniques for the visocosity of a liquid binary mixture were unsatisfactory.

In STUDYING the rheology of suspensions of solid particles, it is often desirable to use a liquid phase which has the same density as the solid particles, a relatively low

viscosity, a very low vapor pressure, especially if a multicomponent fluid, a very low mutual solubility with water, and which does not react with the particles. For many solid particles, mixtures of 1,1,2,2-tetrabromoethane and 1-bromododecane meet these criteria. The density and viscosity of such mixtures were determined at atmospheric pressure and in a temperature range near room temperature.

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