The Phase Diagram for the Binary System K_2CrO_4–$CaCrO_4$*

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The phase diagram for the binary system K_2CrO_4–$CaCrO_4$ has been determined for $CaCrO_4$ concentrations up to 60 mole %, using the techniques of differential thermal analysis, X-ray diffraction, and drop calorimetry. Essential features of the phase diagram are: the solid–solid phase transition for pure K_2CrO_4 at 670°C, β-$K_2CrO_4 \rightleftarrows \alpha$-$K_2CrO_4$; a eutectoid reaction at 14 mole % $CaCrO_4$ and 548°C, β-$K_2CrO_4 \rightleftarrows \alpha$-$K_2CrO_4 + K_2CrO_4 \cdot CaCrO_4$; a peritectoid event at 50 mole % $CaCrO_4$ and 640°C, β-$K_2CrO_4 + CaCrO_4 \rightleftarrows K_2CrO_4 \cdot CaCrO_4$; and a eutectic reaction at 51 mole % $CaCrO_4$ and 678°C, $L \rightleftarrows \beta$-$K_2CrO_4 + CaCrO_4$. X-ray diffraction studies lead to the determination of the unit cell dimensions for the $K_2CrO_4 \cdot CaCrO_4$ double salt, a C-centered monoclinic form with $a_0 = 7.615(6)$ Å, $b_0 = 22.797(15)$ Å, $c_0 = 9.777(9)$ Å, $\beta = 115.45(5)°$.

Introduction

Metal chromates are often used as cathodic depolarizers in thermal voltaic cells. One common thermal cell employs a calcium anode, an iron cathode, $CaCrO_4$ as the cathodic depolarizer, and a LiCl–KCl eutectic electrolyte (*1*).

In this electrochemical system, an undesirable side reaction can produce a metallic Li–Ca alloy which is molten above 231°C (*2*). Under certain conditions, this molten metal can bridge the anode and cathode, causing shorting and electrical noise. Replacement of the $CaCrO_4$ depolarizer with a mixture of $CaCrO_4$ and K_2CrO_4 has been found to retard the formation of the troublesome Ca–Li alloy (*3*). The knowledge of the phase diagram of this binary system contributes to the understanding of the thermal cell operation.

The chromate system, $CaCrO_4$–Na_2CrO_4, has been investigated by Vil'nyanskii and Pudovkina (*4*), and Khitrov (*5*) studied the reciprocal system K^+, Ca^{2+}/CrO_4^{2-}, NO_3^-, but no data are given for the binary of interest. In the present work, the phase relationships were studied by thermal methods with verification of the interpretations by X-ray diffraction and calorimetry.

Because $CaCrO_4$ is unstable above 1000°C (*6*) at ambient pressure, compositions studied in the present investigation were limited to those with $CaCrO_4$ concentrations no greater than 60 mole %.

Experimental

Materials

High-purity $CaCrO_4$ (assay 99.85 %) was prepared from reagent-grade $CaCO_3$ and Na_2CrO_4, using a method previously described (*7*). The K_2CrO_4 was analytical reagent grade from Fisher Scientific Company and assayed >99.6 %. The $CaCrO_4$ was vacuum-dried at 400°C for 4 hr and K_2CrO_4 at 120°C for 2 hr.

Apparatus and Procedure

A series of K_2CrO_4–$CaCrO_4$ compositions was prepared and analyzed by differential thermal analysis with confirmation of the

interpretation by X-ray diffraction, including elevated temperature diffraction, and by drop calorimetry measurements. Samples weighing approximately 15 g were prepared by thoroughly mixing the desired amounts of powdered $CaCrO_4$ and K_2CrO_4. In some cases, the samples were prefused to assure homogeneity. Each sample was subjected additionally to several heating cycles well into the melt which also promoted homogeneity.

The sample and an equal weight of calcined alumina reference material were placed in similar quartz tubes. The tubes were placed at symmetrical positions in a massive nickel holder and heated in a vertical tube furnace.

Pt–Pt, 10% Rh thermocouples were placed in quartz wells surrounded by the reference and sample materials. Absolute temperature, measured in the sample, and the differential temperature were recorded. The details of the sample holder–thermocouple arrangement have been described elsewhere (8).

Only cooling curves were used for equilibrium data. Cooling rates ranging from 6 to 9°C/min were employed. The sample temperature was monitored on a dual-channel recorder (9) which had a 2-mV display and automatic ranging to 20 mV which was indicated by a second pen. The differential temperature was displayed on the same chart by a third pen.
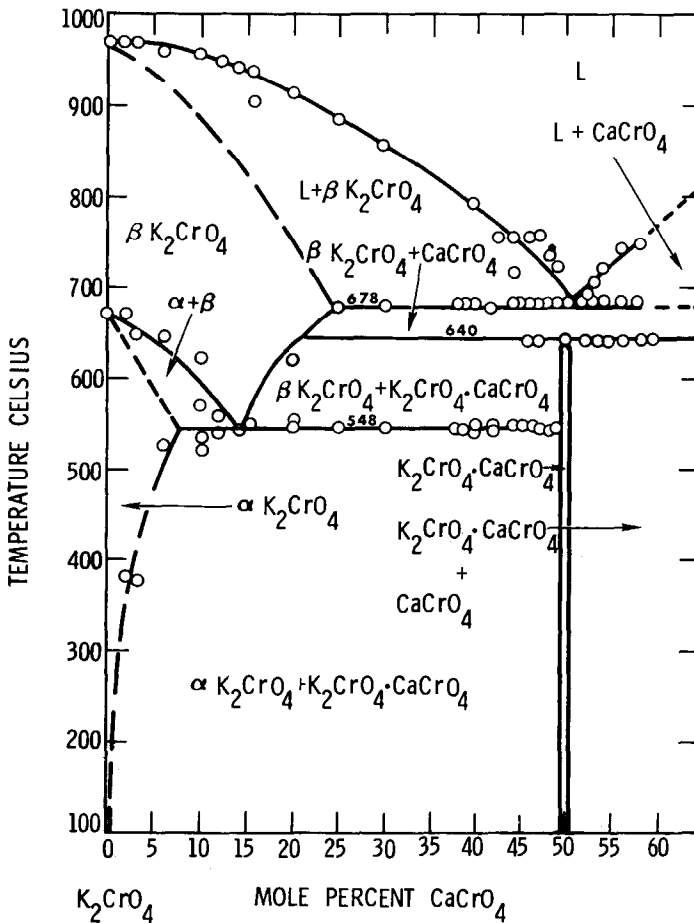

FIG. 1. The K_2CrO_4–$CaCrO_4$ phase diagram.

Room temperature, X-ray powder diffraction patterns were obtained with a 114.6-mm-diameter Philips camera using CuKα (λ = 1.54178 Å) Ni-filtered radiation. Elevated temperature X-ray data (CuKα radiation) were obtained on a Materials Research Corporation high-temperature diffractometer attachment in conjunction with a Norelco powder diffractometer equipped with a graphite monochromator and a scintillation detector. Standard precession and Weissenberg instruments were used for photography of the single crystal patterns.

Enthalpy versus temperature curves were obtained for two mixtures of particular interest. Drop calorimetry techniques previously described were used for these determinations (*10*).

Results

The phase diagram derived from the DTA data is shown in Fig. 1 with thermal discontinuities shown by the open circles. The outstanding thermal events are:

(A) The solid-state phase transition for pure K$_2$CrO$_4$ at 670°C, αK$_2$CrO$_4$ $\rightleftarrows$ βK$_2$CrO$_4$. The α phase is the low-temperature orthorhombic structure as found in the JCPDS (formerly ASTM) card file, Card 15-365, derived from Pistorious (*11*). The β form is hexagonal.

(B) A eutectoid at 14 mole% CaCrO$_4$ and 548°C, β-K$_2$CrO$_4$ $\rightleftarrows$ α-K$_2$CrO$_4$ + K$_2$ CrO$_4$·CaCrO$_4$.

(C) A peritectoid event at 50 mole% CaCrO$_4$ and 640°C with the formation of the double salt, K$_2$CrO$_4$·CaCrO$_4$, β-K$_2$CrO$_4$ + CaCrO$_4$ $\rightleftarrows$ K$_2$CrO$_4$·CaCrO$_4$.

(D) A eutectic event at 51 mole% CaCrO$_4$ and 678°C, Liquid $\rightleftarrows$ β-K$_2$CrO$_4$ + CaCrO$_4$.

High-temperature X-ray diffraction studies on samples consisting of 6, 20, 50, and 56 mole% CaCrO$_4$ were made for verification of the interpretation of these events.

It should be stated that the exact temperatures could not be determined in conjunction with the use of the high-temperature diffractometer attachment; however, data can be reported in 50°C ranges. The results of the X-ray studies are:

TABLE I

COMPARISON OF OBSERVED AND CALCULATED d-SPACINGS FOR K$_2$CrO$_4$·CaCrO$_4$

d observed (Å)	d calculated (Å)	$h\ k\ l$	I/I_o
6.61	6.586	1 1 0	30
4.78	4.788	0 4 1	30
3.88	3.837	$\bar{1}$ 5 1	10
3.54	3.553	$\bar{2}$ 0 2	20
3.44	3.440	2 0 0	20
3.17	3.165	$\bar{2}$ 4 1	100
3.12	3.121	1 1 2	30
2.99	2.995	$\bar{1}$ 3 3	80
2.84	2.849	0 8 0	80
2.65	2.651	$\bar{1}$ 5 3	60
2.39	2.394	0 8 2	60
2.265	2.264	1 7 2	40
2.099	2.097	$\bar{3}$ 1 4	60
1.998	2.000	$\bar{1}$ 9 3	10
1.974	1.974	1 9 2	20
1.946	1.951	3 3 1	10
1.903	1.903	$\bar{4}$ 0 2	60
1.847	1.846	3 5 1	40
1.773	1.770	$\bar{1}$ 5 5	10
1.745	1.745	0 8 4	10
1.699	1.700	$\bar{2}$ 12 1	30
1.685	1.687	0 4 5	30
1.626	1.628	1 7 4	20
1.581	1.583	$\bar{4}$ 8 2	20
1.543	1.544	$\bar{1}$ 13 3	10
1.447	1.446	3 11 1	10
1.424	1.425	0 16 0	30
1.415	1.415	$\bar{2}$ 8 6	30
1.396	1.397	$\bar{5}$ 3 5	10
1.378	1.377	3 7 3	30
1.358	1.357	$\bar{5}$ 5 5	10
1.325	1.324	3 13 1	10
1.291	1.291	$\bar{1}$ 17 2	30
1.267	1.267	5 7 0	10
1.240	1.240	$\bar{1}$ 17 3	40

(A) 6 *mole*% CaCrO$_4$. From RT to 600°C, only α-K$_2$CrO$_4$ was detected. The amount of double salt is probably too small to detect. From 600 to 700°C, the pattern changes to that for β-K$_2$CrO$_4$. The pattern at 700°C is slightly different from that for β-K$_2$CrO$_4$, presumably due to the solution of CaCrO$_4$ in the β-K$_2$CrO$_4$ lattice.

(B) 20 *mole %* CaCrO$_4$. From RT to 600°C, two phases exist, α-K$_2$CrO$_4$ and the double salt, K$_2$CrO$_4$·CaCrO$_4$ (the β-phase was not observed in the pattern). Above 600°C, only the β-K$_2$CrO$_4$ phase was found.

(C) 50 *mole %* CaCrO$_4$. From *RT* to 600°C only the K$_2$CrO$_4$·CaCrO$_4$ double salt was found. From 600 to 700°C, β-K$_2$CrO$_4$ and CaCrO$_4$ were the phases detected.

These X-ray data were essential in establishing the peritectoid reaction. The DTA cooling curves were not definitive in this case, due to the sluggish attainment of equilibrium during cooling as the two solid phases, β-K$_2$CrO$_4$ and CaCrO$_4$, reacted to form the double salt, K$_2$CrO$_4$·CaCrO$_4$. It is postulated that the product of the surface reaction (K$_2$CrO$_4$·CaCrO$_4$) presented a barrier to the completion of the slow solid-state diffusion reaction. To overcome this sluggishness, the X-ray diffraction patterns were recorded after the samples had been heated at temperature for about 1 hr.

(D) 56 *mole %* CaCrO$_4$. From RT to 650°C, the double salt, K$_2$CrO$_4$·CaCrO$_4$, and CaCrO$_4$ were both detected. Above 650°C, the double salt lines disappeared and were replaced by the patterns for β-K$_2$CrO$_4$ and CaCrO$_4$.

Additional confirmation of the diagram in the vicinity of 45 to 55 mole% CaCrO$_4$ was made using drop calorimetry. Enthalpy versus temperature curves for a 45.3 mole% CaCrO$_4$ sample showed a change in slope around 525 to 550°C, a large discontinuity due to melting around 680°C, and a change in slope in the vicinity of 725 to 750°C. Enthalpy versus temperature curves for a 55.4 mole% CaCrO$_4$ sample show no change in slope below the melting discontinuity at ~680°C. There is a probable slope change observed around 725 to 750°C corresponding to the liquidus line.

All of these measurements confirm the phase diagram as shown in Fig. 1.

The observed and calculated *d*-spacings for the K$_2$CrO$_4$·CaCrO$_4$ double salt at room temperature are given in Table I. No corrections for film shrinkage were made to the measured arc lengths due to the absence of observable back reflection lines. Relative intensities were visually estimated.

Precession and Weissenberg photographs of a single crystal of K$_2$CrO$_4$·CaCrO$_4$ indicated that the unit cell is monoclinic. From the extinction conditions observed in these photographs (*hkl*, $h + k = 2n$; *h0l*; $l = 2n$) the space group was established as either *Cc* (No. 9) or *C2/c* (No. 15) (*12*). The lattice parameters obtained by a least-squares fit of 35 measured reflections using the Nelson and Riley extrapolation function are

$$a_0 = 7.615(6) \text{ Å},$$
$$b_0 = 22.797(15) \text{ Å},$$
$$c_0 = 9.777(9) \text{ Å},$$
$$\beta = 115.45(5)°.$$

The density of K$_2$CrO$_4$·CaCrO$_4$ determined experimentally using an air pycnometer

TABLE II

CRYSTALLOGRAPHIC PARAMETERS

	ρ (g/cm^3)	a_0 (Å)	b_0 (Å)	c_0 (Å)	Form
α-K$_2$CrO$_4$	2.732(*13*)	7.663	10.391	5.919	Orthorhombic *Pnam*
β-K$_2$CrO$_4$	24.08(*11*)	6.125	6.125	8.245	Hexagonal (space group not known)
(High-temperature modification)					
K$_2$CrO$_4$·CaCrO$_4$	3.034^a	7.615	22.797	9.777	Monoclinic β = 115.45°
	3.012^b				*Cc* or *C2/c*
CaCrO$_4$	3.142^c	7.242	7.242	6.290	Tetragonal *I4$_1$/amd*

^{a} Theoretical.
^{b} Measured.
^{c} JCPDS card 8-458.

method is 3.012 ± 0.021 g/cm³. The theoretical density based on lattice parameters is 3.034 ± 0.006 g/cm³ with a unit cell containing eight formula units of the double salt.

The resulting unit cell dimensions, density, and crystal form are shown in Table II. Similar data for K_2CrO_4, both α and β, and $CaCrO_4$, card 8-458, from the JCPDS tabulations are shown for comparison.

Acknowledgments

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