Electrical Conductance of the System LiCl–KCl–$CaCrO_4$

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Specific conductance (κ) has been measured as a function of temperature and composition for mixtures of lithium chloride, potassium chloride, and calcium chromate. Expressions were obtained relating κ to concentration of $CaCrO_4$ and to temperature for mixtures of $CaCrO_4$ and the LiCl–KCl binary eutectic. For the LiCl–KCl–$CaCrO_4$ ternary eutectic κ was related to temperature according to the Kohlrausch equation Density of the ternary eutectic was measured as a function of temperature, and equivalent conductance (Λ) was calculated. An Arrhenius-type plot was made and activation energies were calculated.

THE SALT MIXTURE LiCl–KCl–$CaCrO_4$ is an electrolyte-cathodic depolarizer combination used in thermal cells (voltaic cells employing a molten salt electrolyte). Thermal cells of the type Ca/LiCl–KCl, $CaCrO_4$/Ni have been studied (*7*). Temperature-composition studies of the LiCl–KCl–$CaCrO_4$ system have been conducted (*1*, *6*).

An important consideration in the use of this material in thermal cells is electrical conductance. Although the conductance of LiCl–KCl binary mixtures has been established (*9*), similar data for the ternary mixture LiCl–KCl–$CaCrO_4$ have not previously been published.

In this work, specific conductance has been measured as a function of temperature for a variety of LiCl–KCl–$CaCrO_4$ compositions. Data were not obtained above 700° C. because of the thermal decomposition of $CaCrO_4$ (*2*). Data are reported only at temperatures above that of the liquidus. LiCl–KCl–$CaCrO_4$ in the eutectic composition (*6*) has been studied in more detail.

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, Ferguson, and Osteryoung (*8*) to remove H_2O, oxide and hydroxyl ions, and heavy metal impurities; $CaCrO_4$ (Mineral Pigments Corp.) which assayed at 98.0%, and $CaCrO_4$ prepared from reagent grade $CaCl_2$ and K_2CrO_4 (*6*), which assayed at 99.75%.

All work was conducted in a controlled atmosphere "dry room." Moisture content was maintained below 2% RH (<500 p.p.m. at 22° C.) by circulating the room air through beds of hot Al_2O_3.

The conductance cell (Figure 1) is a magnesia dip-type.

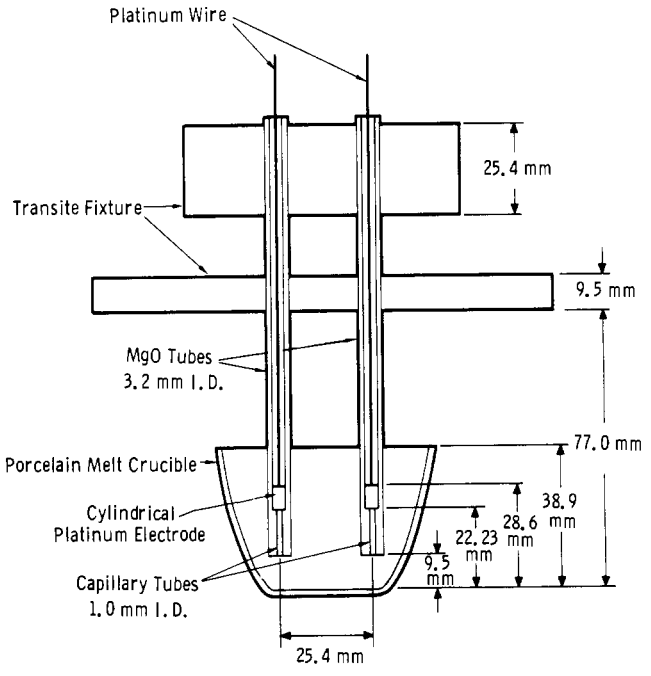

Figure 1. Conductance cell

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Cylindrical platinum electrodes (3-mm. o.d. × 6 mm. high) rest on the shelf at the top of the capillary tubing. A Chromel-Alumel thermocouple sheathed in 6-mm. o.d. 95% silica glass was used for temperature measurements. A 55-gram salt sample was contained in a porcelain crucible in the low-moisture air atmosphere. The complete apparatus was placed in a Hevi-Duty Electric Co. Type 80 furnace assembly capable of temperatures to 1000° C. Conductivity was measured as a function of frequency over the range 500 Hz to 5 kHz for a few compositions using a General Radio Corp. Model 1650A impedance bridge. Data obtained were plotted *vs.* (frequency)$^{-1/2}$ and extrapolated to infinite frequency. Less than 2% change occurred between 1 kHz and ∞. Therefore, for most compositions, measurements were made at 1 kHz only. Consequently, more data could be obtained in a reasonable time period.

Cell constants were determined over the temperature range 350° to 700° C. using LiCl–KCl binary eutectic obtained from the Anderson Physical Laboratories as a standard. Values between 15 and 20 cm.$^{-1}$ were obtained based on previously published data (*9*). Conductivity measurements agreed to within ±1% for LiCl–KCl mixtures prepared by the two different methods. Measurements were reproducible to ±2% and are believed to be accurate within ±2%, based primarily on temperature variations and frequency dependence. This type of accuracy is adequate for the applications anticipated.

The density of the LiCl–KCl–$CaCrO_4$ eutectic was measured using the standard dilatometer method similar to that described by Boardman, Dorman, and Heymann (*5*). The fused salt was placed in a 6-mm. o.d. quartz tube which was sealed at one end and on which two reference lines were placed. These lines were calibrated by determining the volume of mercury between them. The tube was then placed in a brass insert which was, in turn, lowered into a Marshall furnace provided with a means of observing the molten salt in the tube while in the furnace. A Welch cathetometer was used to measure the volume as a function

Table I. Specific Conductance (κ) of LiCl–KCl–$CaCrO_4$ Mixtures as a Function of Temperature

Composition, Wt. %							
	LiCl	48	40	63	90	42.8	41
	KCl	49	57	34	5	52.2	50
	$CaCrO_4$	3	3	3	5	5	9
Liquidus Temp., ° C.		388	380	470	569	347	342
Temp., ° C.		Specific Conductance, Ohm^{-1} Cm.$^{-1}$					
700		1.69	1.78	2.44	2.55	1.98	1.56
690		1.68	1.77	2.42	2.53	1.94	1.54
660		1.65	1.73	2.36	2.50	1.83	1.45
650		1.64	1.71	2.34	2.49	1.79	1.41
640		1.62	1.69	2.31	2.46	1.76	1.39
610		1.54	1.60	2.23	2.34	1.67	1.32
600		1.52	1.57	2.18	2.26	1.65	1.29
590		1.48	1.53	2.14	2.19	1.62	1.26
560		1.38	1.42	2.04		1.52	1.18
550		1.34	1.38	1.98		1.48	1.15
540		1.31	1.33	1.94		1.45	1.13
510		1.18	1.19	1.77		1.35	1.05
500		1.14	1.15	1.72		1.31	1.03
490		1.09	1.10	1.64		1.27	0.991
460		0.961	0.956			1.15	0.882
450		0.909	0.907			1.11	0.846
440		0.863	0.858			1.06	0.808
410		0.716	0.705			0.908	0.677
400		0.673	0.667			0.862	0.642
390		0.620	0.615			0.794	0.596
360						0.669	0.492
350						0.593	0.447

Composition, Wt. %							
	LiCl	45	36	40.5	18	70	38
	KCl	45	54	49.5	72	20	47
	$CaCrO_4$	10	10	10	10	10	15
Liquidus Temp., ° C.		375	376	346	578	528	435
Temp., ° C.		Specific Conductance, Ohm^{-1} Cm.$^{-1}$					
700		1.14	1.32	1.23	1.30	2.27	0.924
690		1.12	1.29	1.20	1.27	2.21	0.908
660		1.05	1.19	1.12	1.20	2.07	0.851
650		1.02	1.17	1.09	1.18	2.03	0.833
640		1.01	1.13	1.06	1.14	1.99	0.812
610		0.946	1.06	0.992	1.07	1.85	0.755
600		0.924	1.04	0.969	1.02	1.82	0.738
590		0.905	1.01	0.945	0.953	1.77	0.718
560		0.836	0.930	0.870		1.64	0.670
550		0.814	0.917	0.846		1.61	0.654
540		0.794	0.886	0.827		1.55	0.637
510		0.712	0.808	0.750			0.574
500		0.678	0.778	0.721			0.554
490		0.650	0.750	0.698			0.534
460		0.562	0.666	0.609			0.469

Composition, Wt. %							
	LiCl	45	36	40.5	18	70	38
	KCl	45	54	49.5	72	20	47
	$CaCrO_4$	10	10	10	10	10	15
Liquidus Temp., ° C.		375	376	346	578	528	435
Temp., ° C.		Specific Conductance, Ohm^{-1} Cm.$^{-1}$					
450		0.534	0.635	0.585			0.438
440		0.506	0.605	0.555			0.412
410		0.415	0.512	0.471			
400		0.389	0.483	0.448			
390		0.357	0.452	0.417			
360				0.329			
350				0.273			

Composition, Wt. %							
	LiCl	28	80	55	20	33.8	60
	KCl	53	0	25	60	41.2	10
	$CaCrO_4$	19	20	20	20	25	30
Liquidus Temp., ° C.		488	570	467	539	530	515
Temp., ° C.		Specific Conductance, Ohm^{-1} Cm.$^{-1}$					
700		1.001	2.42	0.864	0.602	0.626	1.27
690		0.979	2.38	0.836	0.581	0.594	1.25
660		0.912	2.28	0.770	0.516	0.573	1.17
650		0.893	2.26	0.750	0.496	0.557	1.15
640		0.871	2.25	0.723	0.476	0.521	1.12
610		0.792	2.16	0.658	0.416	0.497	1.06
600		0.767	2.14	0.642	0.398	0.475	1.04
590		0.748	2.11	0.622	0.378	0.459	1.01
560		0.665		0.558	0.329	0.414	0.947
550		0.638		0.541	0.313	0.410	0.928
540		0.613		0.525	0.298	0.407	0.905
510		0.541		0.467			
500		0.518		0.451			
490		0.444		0.426			

Composition, Wt. %						
	LiCl	10	40	15	27	54
	KCl	60	20	45	33	3
	$CaCrO_4$	30	40	40	40	43
Liquidus Temp., ° C.		605	610	652	640	574
Temp., ° C.		Specific Conductance Ohm^{-1} Cm.$^{-1}$				
700		0.774	0.687	0.689	0.578	0.847
690		0.759	0.665	0.674	0.566	0.820
660		0.694	0.626	0.615	0.507	0.731
650		0.674	0.615		0.411	0.711
640		0.660	0.586		0.408	0.688
610		0.591	0.534			0.612
600						0.593
590						0.575

of temperature. The technique was first tested with LiCl-KCl eutectic. Data obtained agreed with those of Van Artsdalen and Yaffe (9) to within ±1%.

RESULTS

Conductance measurements were made between 350° and 700° C. Data are listed in Table I, for temperatures above that of the liquidus.

An expression was determined by regression analysis relating the specific conductance of mixtures of calcium chromate with the lithium chloride–potassium chloride binary eutectic to temperature and to $CaCrO_4$ concentration. The analysis was limited to mixtures which were liquid and covered the temperature range 500° to 700° C.

Two models were fitted. The first,

$$\kappa = \frac{1}{A_0 + \frac{A_1}{t + A_2} + A_3 W + A_4 t W} \quad (1)$$

was derived through separate studies of the effects of t on κ, W on κ, and t on the relationship of W and κ. The resulting equation was

$$\kappa = \frac{1}{0.102 + \frac{111}{t - 240} + 0.1240W - 1.193 \times 10^{-4} tW} \quad (2)$$

The standard deviation was 0.12 ohm^{-1} cm.$^{-1}$ and the squared correlation coefficient was 0.97. The second model,

$$\kappa = B_0 + B_1 t + B_2 W + B_3 Wt + B_4 W^2 + B_5 W^2 t + B_6 W^3 + B_7 W^3 t \quad (3)$$

was derived from a visual inspection of a graph of the data. The resulting equation was

$$\kappa = 0.5026 + 0.1709t' - 0.4058W' + 0.8822W'^2 + 0.1170W'^2 t' - 0.6068W' - 0.2194W'^3 t' \quad (4)$$

where

$$t' = (t - 600)/100 \quad (5)$$

and

$$W' = (W - 22)/22 \quad (6)$$

The standard deviation was 0.076 ohm^{-1} cm.$^{-1}$ and the squared correlation coefficient was 0.99. These equations are of particular significance to practical thermal cell work where the general practice is to add varying amounts of $CaCrO_4$ to an LiCl-KCl binary eutectic electrolyte. The conductance of the resulting mixture is a major consideration in the design of such cells. While Equation 4 is more accurate, Equation 2 appears simpler to use.

More detailed investigations were conducted with the ternary eutectic (41% LiCl–50% KCl–9% $CaCrO_4$). Specific conductance of the eutectic was related to temperature according to the Kohlrausch equation,

$$\kappa = a + bt + ct^2 \quad (7)$$

Using the method of least squares, the following equation was fitted over the temperature range 350° to 700° C.

$$\kappa = -1.369 + 6.23 \times 10^{-3} t - 2.956 \times 10^{-6} t^2 \quad (8)$$

The standard deviation for this expression was 0.014 ohm^{-1} cm.$^{-1}$ and the squared correlation coefficient was 0.999.

Results of density determinations for the LiCl-KCl-$CaCrO_4$ eutectic between 405° and 607° C. may be expressed mathematically as

$$\rho = -5.64 \times 10^{-4} t + 1.931 \quad (9)$$

The standard deviation for the least squares fit was 0.0035 gram per cm.^{3} with a squared correlation coefficient of 0.992. Equivalent conductance was also calculated for the ternary eutectic according to the relationship

$$\Lambda = \kappa \bar{e} / \rho \quad (10)$$

The mean equivalent weight for the LiCl-KCl-$CaCrO_4$ eutectic is 57.04. Equivalent conductance and temperature are related according to the expression

$$\log_{10} \Lambda = 4.11130 - 2.33931 \left(\frac{10^3}{T}\right) + 4.05882 \log_{10} \left(\frac{10^3}{T}\right) \quad (11)$$

The curve predicted by this expression and the experimental data are shown in Figure 2.

The standard deviation of Λ from this equation is 0.69 ohm^{-1} cm.^{2} equiv.$^{-1}$. The equivalent conductance of the ternary eutectic at 1.1 times its fusion temperature ($1.1T_{fus}$) is compared with that of other fused salts in Table II.

Equivalent conductance (Λ) is shown on semilog paper as a function of $1/T$ for the ternary eutectic (Figure 3).

For the fused salts under consideration, it is assumed

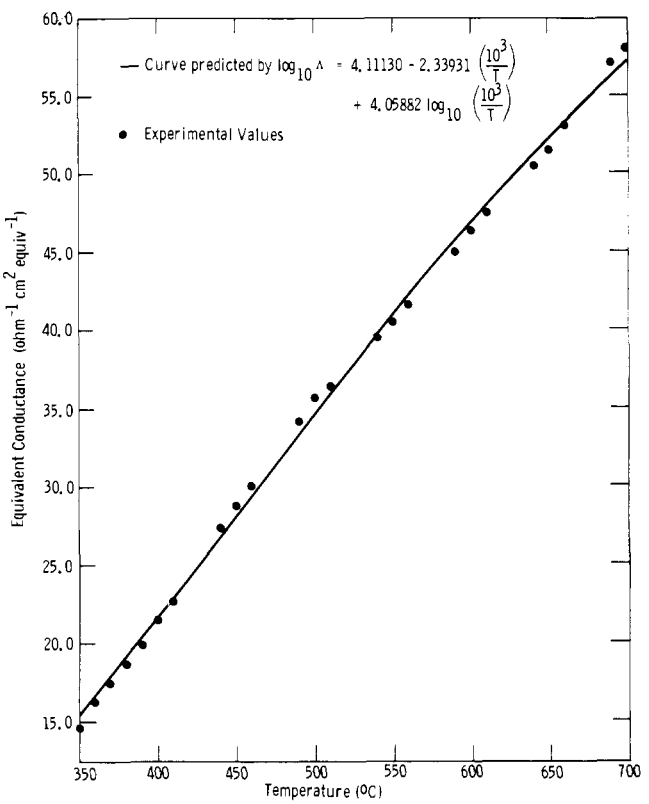

Figure 2. Equivalent conductance vs. temperature for LiCl-KCl-$CaCrO_4$ ternary eutectic

Table II. Equivalent Conductance at $1.1T_{fus}$ for Pure Fused Salts and Mixtures

Salt	T_{fus}, °K.	$1.1T_{fus}$, °K.	Λ, Ohm^{-1} Cm.^{2} Equiv.$^{-1}$
LiCl (3)	883	971	178.5
KCl (3)	1043	1147	122.4
$PbCl_2$ (3)	773	850	52.3
LiCl-KCl eut. (9)	625	688	45.0
LiCl-KCl-$CaCrO_4$ eut.	615	677	22.0
$BeCl_2$ (3)	678	746	0.22

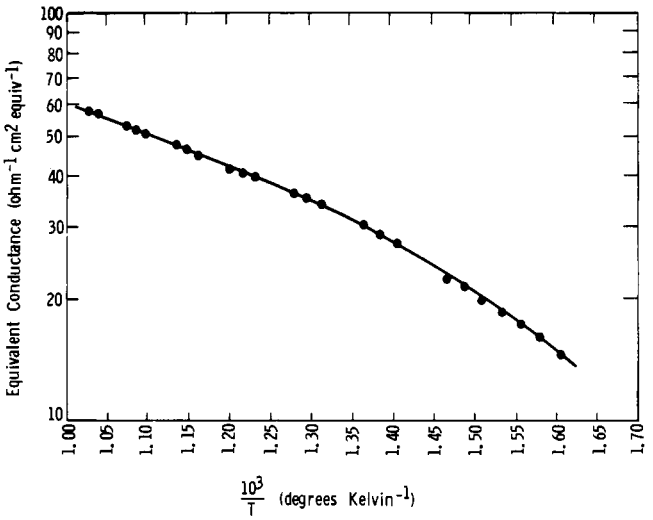

Figure 3. $\text{Log}_{10}\Lambda$ *vs.* $1/T$ for LiCl–KCl–$CaCrO_4$ ternary eutectic

Table III. Values of E_Λ for Fused Salts

Salt	Temp., °C.	E_Λ, Kcal./Mole
LiCl	850	2.1
KCl	850	3.4
	370	6.8
LiCl–KCl–$CaCrO_4$ eut.	480	4.0
	600	3.4

that an anion "semilattice" exists and that the small cations do essentially all the conducting (*9*). Thus, the simple Arrhenius-type equation can be applied to the change of conductance with absolute temperature,

$$\Lambda = A_\Lambda e^{-E_\Lambda/RT} \tag{12}$$

Although it would be expected that, for mixtures of fused salts, terms for each component in the mixture would have to be present, Bloom and Heymann (*4*) have shown that the simple 1-term expression still holds. This indicates that either the activation energies for the individual components are nearly the same or they differ by very large amounts.

Examination of Figure 3, however, reveals that large deviations from linearity occur for $\ln \Lambda$ *vs.* $1/T$. Activation energy (E_Λ) was evaluated at three points along the curve. E_Λ varies from 6.77 to 4.77 to 3.44 kcal. per mole at 370°, 480°, and 600° C., respectively. For comparison other typical E_Λ's are shown in Table III.

NOMENCLATURE

A_0, A_1, A_2, A_3, A_4 = constants for Equation 1
A_Λ = constant for Equation 12
a, b, c = constants for Equation 7
$B_0, B_1, B_2, B_3, B_4, B_5, B_6, B_7$ = constants for Equation 3
E_Λ = activation energy for equivalent conductance, kcal. per mole
$\bar{e}$ = mean equivalent weight of a mixture, grams
κ = specific conductance, ohm^{-1} cm.$^{-1}$
Λ = equivalent conductance, ohm^{-1} cm.^{2} equiv.$^{-1}$
R = gas constant, kcal. per mole °C.
ρ = density, grams per cm.^{3}
T = temperature, °K.
T_{fus} = fusion temperature, °K.
t = temperature, °C.
t' = transformed variable equal to $(t - 600)/100$, °C.
W = weight % $CaCrO_4$
W' = transformed variable equal to $(W - 22)/22$

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