

UNCLASSIFIED

ISC-686

Subject Category: CHEMISTRY

Physical Sciences Reading Room

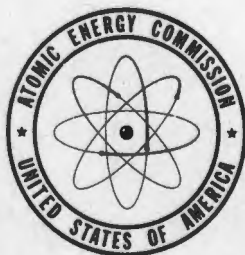
UNITED STATES ATOMIC ENERGY COMMISSION

**TEMPERATURE COEFFICIENT OF ELECTRICAL
CONDUCTIVITY IN THE SYSTEM POTASSIUM
CHLORIDE - ZINC CHLORIDE**

By
R. A. Fleming
F. R. Duke

December 1955

Ames Laboratory
Iowa State College
Ames, Iowa



Technical Information Service Extension, Oak Ridge, Tenn.

UNCLASSIFIED

Work performed under Contract No. W-7405-Eng-82.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

This report has been reproduced directly from the best available copy.

Printed in USA, Price 30 cents. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

TABLE OF CONTENTS

	Page
ABSTRACT	iv
INTRODUCTION	1
EXPERIMENTAL	6
RESULTS	19
DISCUSSION	29
LITERATURE CITED	35

TEMPERATURE COEFFICIENT OF ELECTRICAL CONDUCTIVITY
IN THE SYSTEM POTASSIUM CHLORIDE - ZINC CHLORIDE*

by

R. A. Fleming and F. R. Duke

ABSTRACT

The phase diagram of the system $KCl-ZnCl_2$ has been constructed. Values of specific conductivity and density have been determined at eight temperatures in the range 475-650°C. for a series of compositions covering the concentration range. From these data, equivalent conductivities were calculated. The temperature coefficient of conductivity as expressed by the activation energy of ionic migration was calculated at four temperatures for each mixture.

The phase diagram indicates compound formation in the solid state with the compound $2KCl-ZnCl_2$ melting at about 450°C. Density isotherms are "S" shaped, deviating from additivity in a positive direction at low concentrations of potassium chloride and exhibiting a slight negative deviation at high concentrations of potassium chloride. Isotherms of equivalent conductivity are approximately additive in the range $0.00 < X_{KCl} < 0.30$ but then begin to deviate negatively, reaching a maximum negative deviation near $X_{KCl} = 0.71$. The activation energy at constant temperature falls rapidly from that of zinc(II) chloride as the concentration of potassium chloride increases until X_{KCl} has reached 0.30. The activation energy then slowly falls to the limiting value for pure potassium chloride in an approximately linear manner.

The deviations noted in the isotherms of equivalent conductivity agree with the predictions of Bloom and Heymann (23). A knowledge of the transport numbers of the individual ions is necessary for meaningful interpretation of the isotherms of activation energy.

*This report is based on an M.S. thesis by R. A. Fleming submitted December 1955 to Iowa State College, Ames, Iowa. This work was done under contract with the Atomic Energy Commission.

INTRODUCTION

The early work of Kohlrausch, done prior to the year 1900, on the conductances of electrolytic solutions was followed by a considerable amount of data on this subject published by numerous investigators. In most cases the equipment and techniques were basically the same as those used by Kohlrausch. In the year 1926, Morgan and Lammert (1) reviewed the literature and pointed out that the accuracy of all published data was much in doubt. They noted that although many improvements had been made in individual parts of conductivity equipment and many sources of experimental error had been discovered, a comprehensive analysis of the whole experimental approach to the problem was lacking.

Two years later, in the first of a series of papers entitled "The Measurement of the Conductance of Electrolytes" by Dr. Grinnel Jones and his associates (2,3,4,5,6,7,8,9,10), this analysis was begun. In the first paper Jones and Josephs (2) described an extremely complete investigation of sources of error in measurements of resistance using the alternating current Wheatstone Bridge and described the construction of a bridge in which no component had an inaccuracy greater than 0.001%.

Somewhat later, Shedlovsky (11) discussed in detail the sources of error due to capacitative shunts and the principles behind adequate electrostatic shielding. Cell design and its importance was covered by Jones and G. Bollinger (4) and a discussion of alternating current polarization and attendant problems was presented by Jones and Cristian (7). Jones and D. Bollinger (8) compared different criteria as to the quality and sufficiency of electrode platinization. The specific conductances of standard potassium chloride solutions at different temperatures were reported by Jones and Bradshaw (6) and are currently accepted as standards for determination of cell constants.

The use of the cathode ray oscilloscope as a null point detector for the conductivity bridge was described in papers by Horvoka and Mendenhall (12), Jones, Mysels, and Juda (10), and also by Haszeldine and Woolf (13) who included a discussion of the technique of balancing resistance and capacitance by reference to the elliptical trace produced.

Lorenz and Kalmus (14), Goodwin and Mailey (15), and Sandonnini (16,17,18) were among the earliest investigators of electrical conductivity in fused salts and fused salt mixtures. Their data as well as later data of Kapman and Jaeger (19), Biltz and Klemm (20,21,22) and others are somewhat under suspicion because of the previously mentioned uncertainty in experimental apparatus and techniques.

Bloom and Heymann (23) in 1947 reviewed concepts earlier advanced by Frenkel, Schottky, Jost and others (24, ch. 2) that the expression

$$\kappa = \text{const.} \times \exp - \frac{\frac{1}{2}W + U}{kT}$$

relates the specific conductivity (κ) of a solid salt at high temperatures to the number of lattice defects per cubic centimeter and their mobility when the conductivity is due to one type of ion only. In this expression the energy required to produce a single lattice defect is W and the energy barrier to migration is represented by U . The physical concept of a fused salt as a very disordered solid with large numbers of free ions allows one to take the W term as equal to zero. Assuming the additivity of conductivity we may rewrite the expression for a compound as

$$\kappa = A_1 \times \exp (-C_1/RT) + A_2 \times \exp (-C_2/RT)$$

where C_1 and C_2 represent the activation energies of ionic migration of the two types of ions. The absolute temperature is T and R is the gas constant. This equation is identical in form with the one obtained by substitution of Λ , the equivalent conductivity, for κ , the specific conductivity.

$$\Lambda = A'_1 \times \exp (-C'_1/RT) + A'_2 \times \exp (-C'_2/RT)$$

The constants C and C' in the equations are often denoted as E_{κ}^{\dagger} and E_{Λ}^{\dagger} respectively.

Bloom and Heymann commented that if C'_1 and C'_2 were of almost equal magnitude or if one was considerably larger than the other, the conductivity could be expressed quite well by the expression

$$\Lambda = A \times \exp (-E_{\Lambda}^{\dagger}/RT)$$

and E_{Λ}^{\dagger} could be determined. The slope of the line on a $\log \Lambda$ vs. $1/T$ plot would be equal to $-E_{\Lambda}^{\dagger}/2.303 R$.

After investigating a number of binary systems and reviewing previously published data, Bloom and Heymann (23) advanced these generalizations:

1. Conductivity isotherms of systems showing no evidence of intermediate compound formation in the solid state generally exhibit moderate negative deviations from additivity.

2. In systems whose phase diagrams indicate the presence of congruently melting compounds, complex ions are likely to exist in the

molten mixture. Conductivities will not be additive but rather, strong deviations from additivity are to be expected in the negative direction.

3. For systems in which more than one intermediate compound is indicated by the phase diagram, more than one minimum is sometimes found in conductivity isotherms at temperatures close to the freezing point of the mixture. A minimum corresponding to an incongruently melting compound will disappear as the temperature is increased.

4. Activation energies near compositions corresponding to unstable intermediate compounds will have maximum values, the value of E_A^* containing part of the energy of dissociation of the proposed complex. Such a maximum is not associated with compositions corresponding to stable complexes.

5. The position of the minimum in the conductivity isotherm does not necessarily correspond to the composition of the respective compound in the solid state.

In the analysis of their data on one system for example, Bloom and Heymann suggested the existence of the complexes $[CdCl_3]^-$ and $[CdCl_4]^{2-}$ in the $KCl-CdCl_2$ melt, the latter complex dissociating some 30° to 40° above the melting point of the compound $CdCl_2 \cdot 4KCl$. They deduced the existence of the complexes from the strong minima in the conductivity isotherms (Figure 1) and their formulas from the phase diagram of the system (Figure 2). The instability of the latter complex was indicated by the $d\Lambda/dT$ plot (Figure 3).

In 1953, a contribution by Bloom, Knaggs, Molloy and Welch (25) listed electrical conductivities and densities for eight systems. Isotherms of equivalent conductivity (Λ) and activation energies of ionic migration (E_A^*) were plotted. In three systems showing no intermediate solid phase ($NaNO_2-NaNO_3$, $CdCl_2-CdI_2$ and $KI-NaCl$), isotherms of Λ were found to be approximately linear and values of E_A^* showed no marked deviation from a constant value. Strong negative deviations of Λ from ideality were found in the three systems having congruently melting compounds ($KBr-BaBr_2$, 28% deviation; $LiCl-CdCl_2$, 28% deviation; and $KCl-NaI$, 18% deviation). Incongruently melting compounds were found in the systems CdI_2-KI and KNO_3-KBr . In the former the equivalent conductivity isotherms deviated strongly in a negative direction while the activation energy was approximately constant. On the other hand, in the latter system the conductivity isotherms were almost ideal but the activation energies had a definite maximum at the composition CdI_2-3KI . They concluded that the properties of fused salt mixtures were not unambiguously predictable from a knowledge of the phase diagrams.

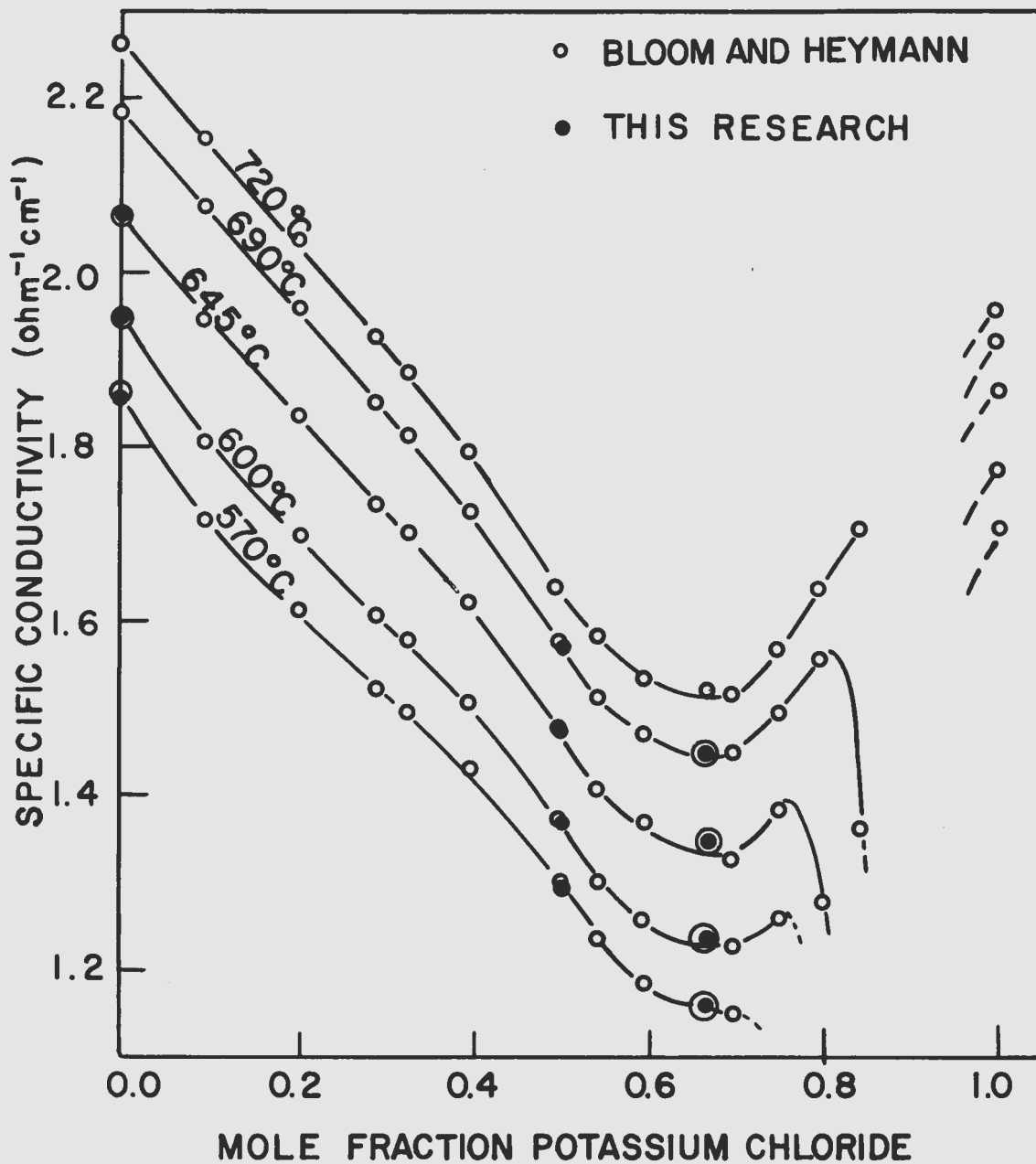


Figure 1. Specific conductivity isotherms in the system KCl-CdCl₂

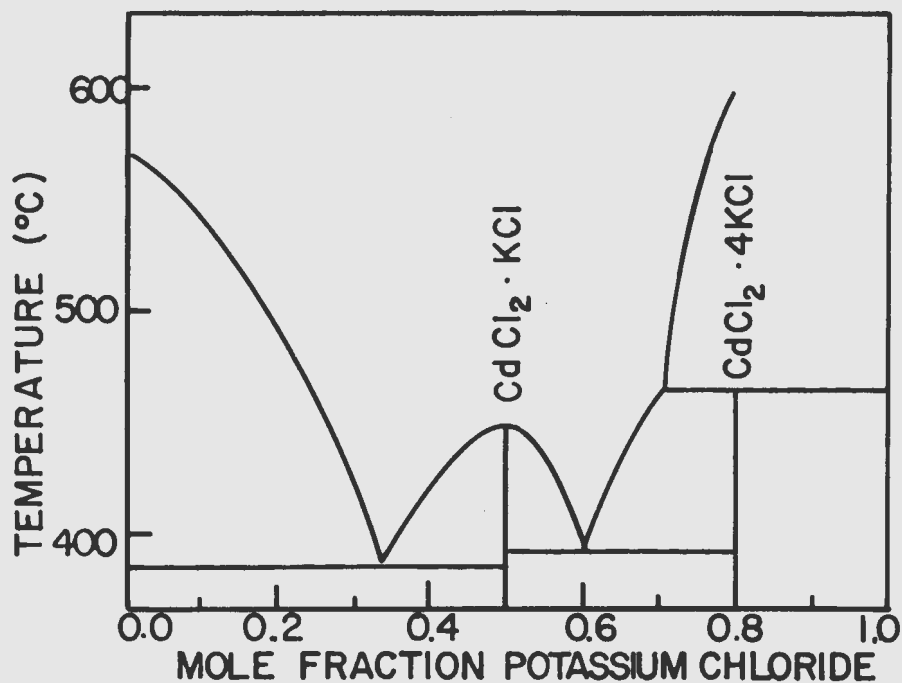


Figure 2. Phase diagram of the system $\text{KCl}-\text{CdCl}_2$

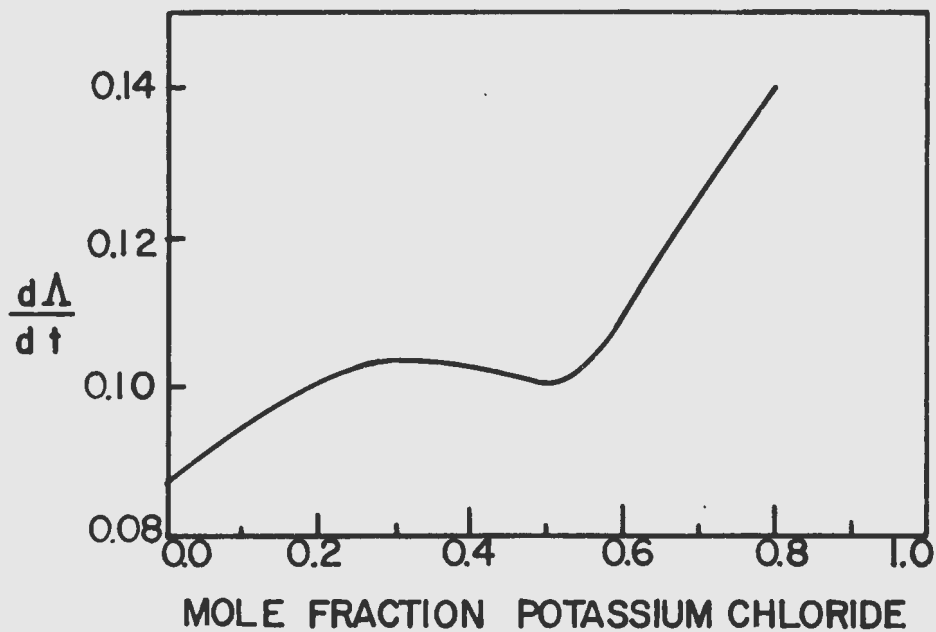


Figure 3. Temperature coefficient of conductivity for the system $\text{KCl}-\text{CdCl}_2$ (23)

Harrup and Heymann (26) in 1955 published conductivity data on the systems AgCl-AgBr , $\text{PbCl}_2\text{-PbBr}_2$, AgCl-PbCl_2 , AgCl-KCl and AgBr-KBr . They pointed out that the equivalent conductivity isotherms of all five showed negative deviations from ideality although none of the phase diagrams indicated the formation of intermediate phases. The first two exhibited solid solution formation over the complete composition range. Simple eutectics were found in the last three.

In the same year, the systems KCl-LiCl , KCl-KI and KI and KCl-NaCl were reexamined by Van Artsdalen and Yaffe (27). The first two systems showed distinct minima in the equivalent conductivity isotherms although no intermediate phases were indicated by the phase diagrams.

The present research was begun in order to secure additional information on the electrical properties of a fused salt system whose phase diagram indicated compound formation in the solid state. Reference was found to the existence of a compound $2\text{KCl}\cdot\text{ZnCl}_2$ (28, Vol. IV, p. 551). Since no previous work had been reported on the conductivity of this mixture in the fused state, research on the system was undertaken.

EXPERIMENTAL

A. Conductivity Determinations

1. Description of apparatus

The equipment and apparatus necessary for the determination of conductivity data may conveniently be considered in three general categories. The conductivity cell is the first of these. The conductivity bridge and associated elements form the second, while temperature controlling and temperature measuring devices compose the last group.

a. The conductivity cell. After a determination of the order of magnitude of electrical conductivity in Pyrex glass at elevated temperatures, the dip-type conductivity cell was rejected and a cell of the closed capillary type was selected for subsequent work. Many variations in the structure of the cell were considered and a number of these were tested. The final form of the cell as used in these determinations is shown in Figure 5. The factors affecting the construction of the cell will be considered.

In order to minimize the effects of thermal gradients within the

furnace it is desirable that the capillary portion of the cell occupy as small a volume as possible. It is also desirable to have the values of measured resistance always above a given value determinable on the basis of error considerations. Furthermore, the diameter of the capillary cannot be made too small, for then a small amount of cell corrosion during a run could produce a large change in cell constant. Taking all of these factors into account, the capillary portion of the cell was constructed of six centimeter lengths of approximately 1.5 millimeter inside diameter Pyrex tubing. This yielded cells whose constants were all in the range $400 \pm 100 \text{ cm}^{-1}$.

In the presence of water, zinc (II) chloride may hydrolyze and form the oxide which is yellow at high temperatures. If the oxide is treated with hydrogen chloride gas it is reconverted to the chloride and water vapor, the latter being expelled from the melt. The long arm of the cell extended out of the furnace so that gas could be passed through it into the cell. The bulb on the short arm served two purposes. It prevented expulsion of the melt from the cell during the passage of hydrogen chloride gas. It also allowed the use of larger samples, thus making chemical analysis of the composition of the melt easier and more accurate. The bubbling of the hydrogen chloride gas prior to a run also insured the homogeneity of the melt. After measurement of the electrical resistance (R) at 25.0°C . when filled with a 1.0000 demal potassium chloride solution, the cell constant (K) for each cell was calculated according to the relationship $K = LR$, where L is the specific conductivity of the solution. The bridge was balanced as later described at a frequency of 1000 cycles per second. The specific conductivity value reported by Jones and Bradshaw (6) for an aqueous potassium chloride solution under these conditions was used and the solution was prepared according to their directions.

The "cell constant" is a function of the geometry of the cell and is therefore subject to change under any conditions which would cause change in the geometry of the cell. It is instructive to calculate the change in cell constant caused by temperature variations.

Given: K^{25} = cell constant at 25°C .

L = length of cell at 25°C .

C = coefficient of linear expansion of cell material

r = radius of cell capillary at 25°C .

$$\overline{\Delta L} = C L \overline{\Delta T}$$

$$\overline{\Delta r} = C r \overline{\Delta T}$$

$$\overline{\Delta A} = \pi \overline{\Delta r^2} = \pi \left[2r \overline{\Delta r} + (\overline{\Delta r})^2 \right] \approx 2\pi r \overline{\Delta r}$$

The $(\overline{\Delta r})^2$ term was dropped as infinitesimal in the simplification. The following derivation is made in a straightforward manner with the subscript "t" referring to a centigrade temperature.

$$K_t = \frac{L_t}{A_t} = \frac{L + \overline{\Delta L}}{A + \overline{\Delta A}} = \frac{L + CL \overline{\Delta T}}{A + 2\pi r \overline{\Delta r}} = \frac{L}{\pi r^2} \frac{1 + C \overline{\Delta T}}{1 + 2C \overline{\Delta T}}$$

$$K_t = K^{25} \left[1 - \frac{C \overline{\Delta T}}{1 + 2C \overline{\Delta T}} \right]$$

Since C is such a small number, it is approximately true that

$$K_t = K^{25} \sqrt{1 - C \overline{\Delta T}}$$

The cell constants were calculated from data determined at 25°C. but the cells were later used at an average temperature of about 560°C. resulting in $\overline{\Delta T} = 535^\circ\text{C}$. The correction factor is thus $(1 - C \overline{\Delta T})$ which amounts to 0.9982, and this is the correction applied to the data. It can be seen that although strictly speaking a different factor can be applied to each temperature on the potassium chloride - zinc (II) chloride determinations, they are all close enough so that no appreciable error will be introduced by the use of this average factor. The value for the coefficient of linear expansion of Pyrex glass used was 33×10^{-7} .

b. The conductivity bridge and associated elements. The circuit diagram of the bridge is shown in Figure 4. It is patterned after the bridges used by Jones and Josephs (2), Shedlovsky (11) and others. Complete descriptions of the theory behind and the operation of the alternating current conductivity bridge are given by Jones and coworkers in the previously mentioned series of papers which is entitled "The Measurement of the Conductance of Electrolytes." A discussion of the use of the cathode ray oscilloscope as a visual, null point indicator is given by Haszeldine and Woolf (13).

The audio-frequency vacuum tube oscillator used was Hewlett-Packard Model 200-CR. It was connected through an isolation transformer to a Leeds and Northrup Wheatstone Bridge (Type S Test Set No. 5300). The fre-

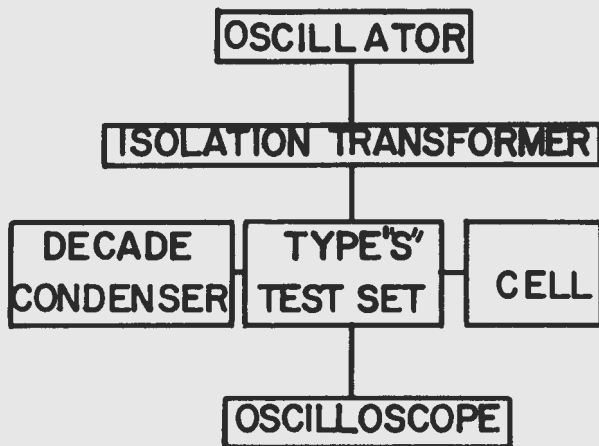
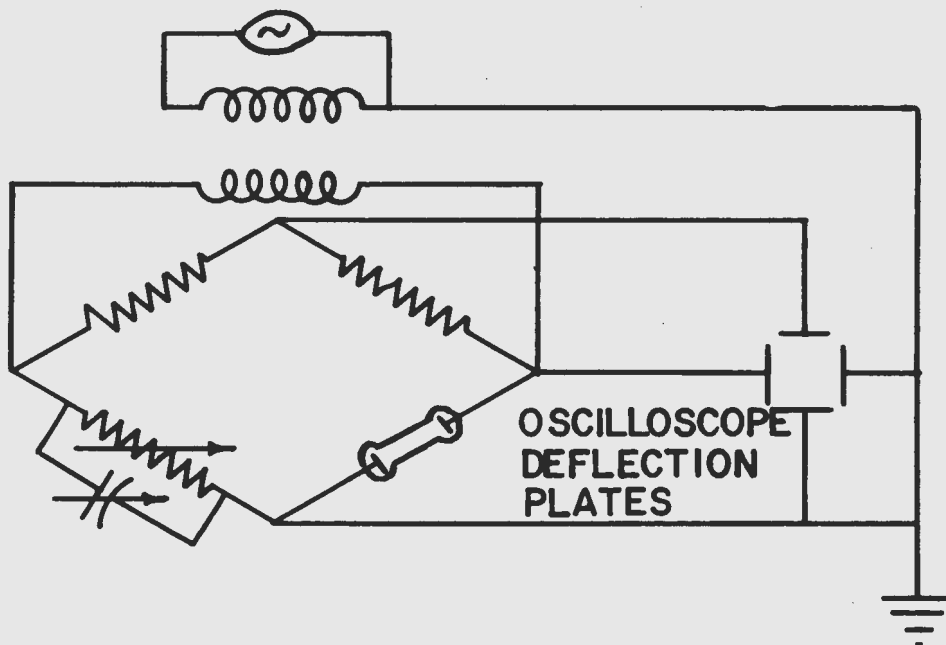


Figure 4. The conductivity bridge: circuit and block diagrams

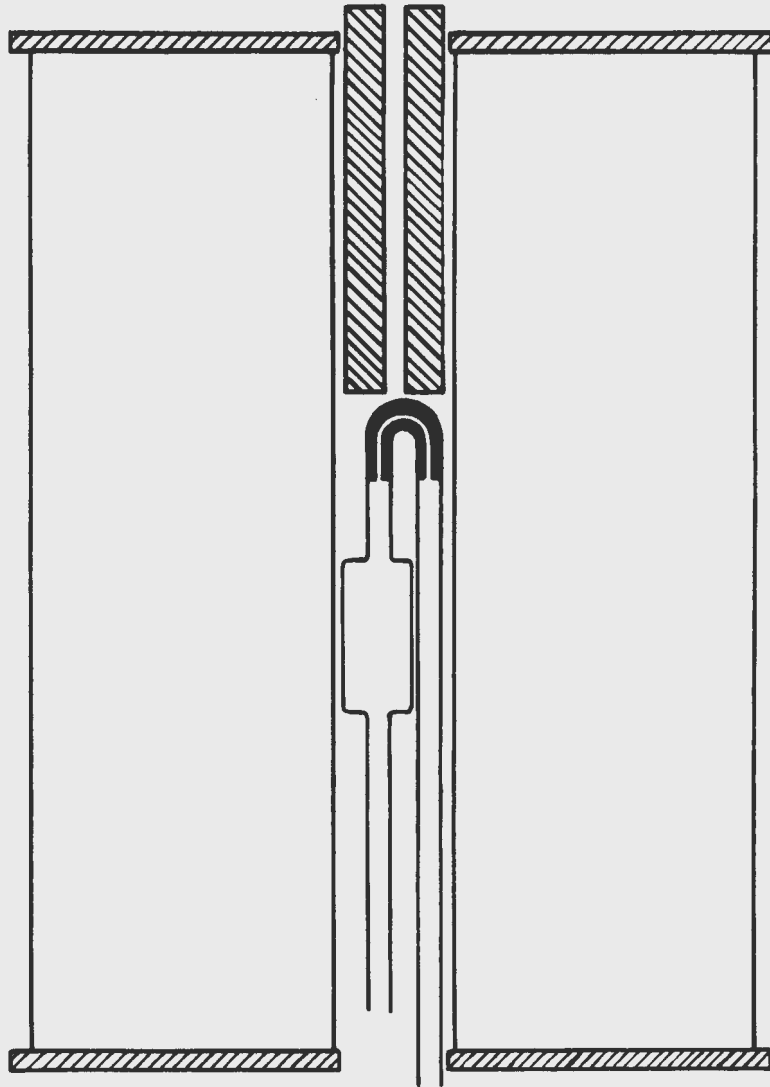


Figure 5. Cutaway view of furnace with conductivity cell in position.

quency used was 1000 cycles per second in all cases since no appreciable variation of resistance with frequency was noted. The waveform delivered by the oscillator was excellent as viewed on an oscilloscope. A Heathkit Decade Condenser Model DC-1 was used to balance capacity in the bridge. The cathode ray oscilloscope used as a visual, null point indicator was a Heathkit Model O-8. All connecting leads were shielded. These shields and all of the instruments were connected to a common ground.

The electrodes were open cylinders of platinum with a length of three-eighths of an inch and a diameter of three-sixteenths of an inch. They were each connected to ten-inch platinum leads. The electrodes were platinized before use and as noted by other investigators, the platinum black was converted to platinum grey at elevated temperatures. One platinum lead was shorter than the other to insure that the same lead was always used in the same arm, during runs as well as during determinations of cell constants.

c. Temperature controlling and measuring devices. The furnace (Figure 5) was of the open tube type. The eighteen-inch long length of two-inch alundum tubing was wound with resistance wire and insulated with dicalite. The diameter of the furnace was about thirteen inches. Temperature was controlled by a chromel-alumel thermocouple mounted through the bottom of the furnace and connected to a Brown Indicating Controller operating through a proportioning motor. The chromel-alumel indicating thermocouple was connected to a Leeds and Northrup No. 8662 Potentiometer with a reference junction compensator. The thermocouple was checked periodically for drift against a mercury thermometer in a constant temperature salt bath maintained at about 275°C.

2. Experimental procedure

a. Preparation of sample. "Bakers Analyzed broken lump" zinc (II) chloride meeting A. C. S. specifications was fused in a weighed Pyrex test tube in the furnace at a temperature of about 400°C. The test tube was then transferred to an oven maintained at 110°C. and the contents were allowed to solidify. The test tube and contents were then removed from the oven, allowed to cool, and quickly weighed before much water could be absorbed from the atmosphere by the hygroscopic salt. A predetermined amount of Baker and Adamson reagent grade crystalline potassium chloride was added and the mixture then returned to the furnace.

At this time hydrogen chloride gas from a compressed gas cylinder (The Matheson Company, Inc., Joliet, Illinois) was passed through the

melt if any yellow zinc oxide was observed to be present. Otherwise the mixture was then poured from the test tube into a preheated cell. Hydrogen chloride gas was then passed through the cell, thus completing the preparation of the sample. It was found that samples prepared with care had compositions within one percent of desired values.

b. Resistance measurements. The Brown Controller was initially set so that the cell would attain a temperature of slightly more than 650°C ., or approximately 652°C . When this temperature was reached, the controller was readjusted for a temperature about 10° less. This resulted in a very gradual temperature decline within the cell. The time rate of change of temperature was on approximately one degree in five minutes. When the desired temperature was reached on the cooling cycle, the resistance of the melt was measured at 1000 cycles per second by the bridge, using an oscilloscope as a visual, null point detector. As soon as this reading was recorded, the controller was readjusted so that the temperature of the cell rose past the desired temperature at about the same slow rate. A resistance reading was recorded on this heating phase of the cycle. This cycling was repeated at every temperature for which resistance readings were required.

To take a reading of resistance, the bridge was energized by a potentiometer located at the oscillator. An elliptical trace appeared on the face of the cathode ray tube and by adjustment of the variable capacitor, a decade condenser, this ellipse was flattened into a line. Next the variable resistance was adjusted so that the line trace was horizontal. Under these conditions the balancing of the bridge was complete, and the cell resistance equalled the resistance of the variable resistor which was then read and recorded. By this method one could at once determine whether or not the melt was in equilibrium with the surroundings. The temperature of the cell must always lag the temperature of the furnace, and to a larger degree than the shielded thermocouple whose heat capacity is considerably less. One would expect the measured resistance on the cooling part to be less than on the heating part of the cycle since the resistance of the melt decreases with increasing temperature. This lag also would be expected to become smaller and approach zero as the rate of the cycling decreased and thermal equilibrium between the cell, thermocouple and surroundings was approached. Consequently if the resistance readings on the heating and on the cooling parts of the cycle differed in the wrong direction or by unacceptably large values, the readings were repeated. The standardization of the potentiometer was checked before every pair of readings.

When the last readings had been taken at the lowest temperature, the temperature of the cell was raised so that the melt would be well

above its freezing point. The cell was then removed from the furnace and its contents emptied into a weighed preheated crucible. The sample was then ready for analysis.

c. Analysis of sample. 1,2-diaminocyclohexane-tetraacetic acid (Alrose Chemical Co., Providence, Rhode Island), hereafter referred to as CDTA, was standardized against zinc (II) chloride prepared by reaction of Bunker Hill brand electrolytic zinc with a minimum purity of 99.99% and Baker and Adamson hydrochloric acid in which the maximum heavy metal impurity was 0.0008%. The CDTA was used to titrate the zinc (II) ions in an aliquot of the sample which had been removed from the crucible, dissolved in water and diluted to the mark in a volumetric flask. The titration was done in the presence of an ammonium hydroxide - ammonium chloride buffer, using as the indicator Eriochromeblack T from the Hach Chemical Company, Ames, Iowa, according to the method of Loomis (29).

Knowing the weight of the sample and the calculated weight of the zinc (II) chloride, the weight of the potassium chloride was found by difference and the composition then calculated in terms of mole fractions.

3. Preliminary investigations.

a. Effectiveness of sample analysis. For this examination, pure zinc (II) chloride was fused and purified as previously described. Three samples were removed on a weighed glass rod thrust into the melt. The rods and the salt solidified on them were then quickly weighed so that the true sample weight could be determined by difference. Aliquots of the three samples were analyzed as outlined above and the weights of zinc (II) chloride in the original samples were calculated. The average relative error in the calculated weights was $\pm 1.3 \times 10^{-3}$ which was less than the value of $+ 3.5 \times 10^{-3}$ which had been determined to be the maximum relative error. Using this latter value, the maximum relative error in the mole fraction of potassium chloride can be shown to be $\pm 6 \times 10^{-3}$.

b. Electrical conductivity in glass at elevated temperatures.

A section of Pyrex capillary tubing was sealed on one end, then joined at the other end to a piece of seven millimeter tubing. To this closed tube was added a KCl-CdCl₂ mixture whose composition was about thirty-five mole percent CdCl₂. The tube was then immersed in a salt bath of the same composition and resistance readings were taken at different temperatures.

Calculation of the corresponding conductances through the walls of the Pyrex tube at the different temperatures showed that the conductivity became relatively large at high temperatures and was in fact disturbingly large even at 550°C. When the magnitude of this conductivity was compared with the magnitude of conductivity to be expected in fused salts, it was decided to abandon the dip-type cell in favor of the U-shaped cell of the closed capillary type.

For example, a simple calculation will show what minimum resistance (R_g) the cell walls must have to insure that the introduced error is less than 0.1%:

$$R_o^{-1} = R_m^{-1} + R_g^{-1}$$

where R_m , the resistance due to the melt alone, is approximately 400 ohms. Let the observed resistance, R_o , equal 400 - 1% or 399.6 ohms.

$$399.6^{-1} = 400^{-1} + R_g^{-1}$$

The introduced error is negative since by providing an alternate path for current flow the measured resistance will be decreased. The value of R_g in the above example is on the order of 4×10^5 ohms.

c. Stability of measurements of resistance with respect to time.

The conductivity at a given temperature of a mixture of given composition would not be expected to vary with time. However, the calculated conductivity is a function of many factors, some of which conceivably may not remain constant over the duration of a run. Of these factors, the one which is the most important is the cell constant. The second very important factor which should be considered is composition. Changes with time in either of these variables would be reflected in changes in the measured resistance of the cell and melt. Accordingly the furnace was allowed to come to thermal equilibrium and a new cell containing a KCl-ZnCl₂ mixture was placed inside. Hydrogen chloride gas was passed through the cell and a series of resistance measurements was taken. It was found that over a period of five hours, the maximum length of time required for one complete series of determinations on a mixture, the average measured resistance at a given temperature changed by only $\pm 0.05\%$. This value is a measure of the reproducibility of results under nearly ideal conditions and is considered to indicate acceptable stability of the measurements. It is concluded that the

calculated conductances and the chemical analyses were thus not significantly affected by elapsed time in runs which were completed in five hours.

d. Reinvestigation of some compounds and one binary system. When the final form of the conductivity cell had been decided upon and all of the components of the apparatus assembled, data were taken on some compounds and one system which had been previously reported in the literature. Lead (II) chloride was examined initially and the data in Table 1 obtained.

Table 1. Resistance - temperature* data on PbCl_2

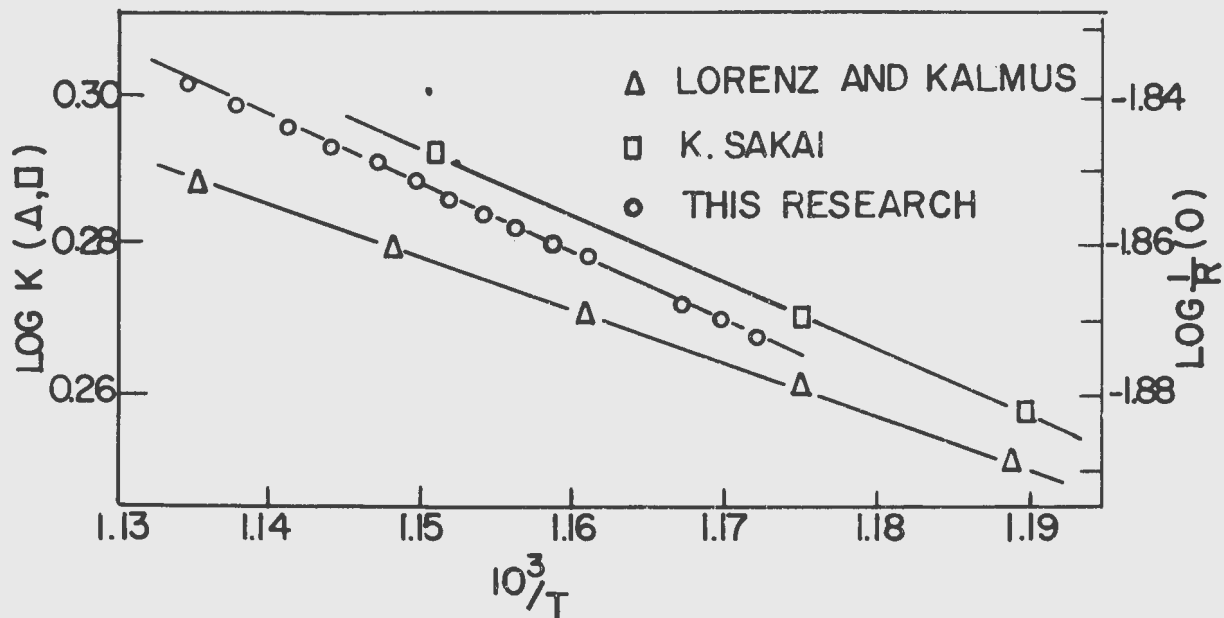
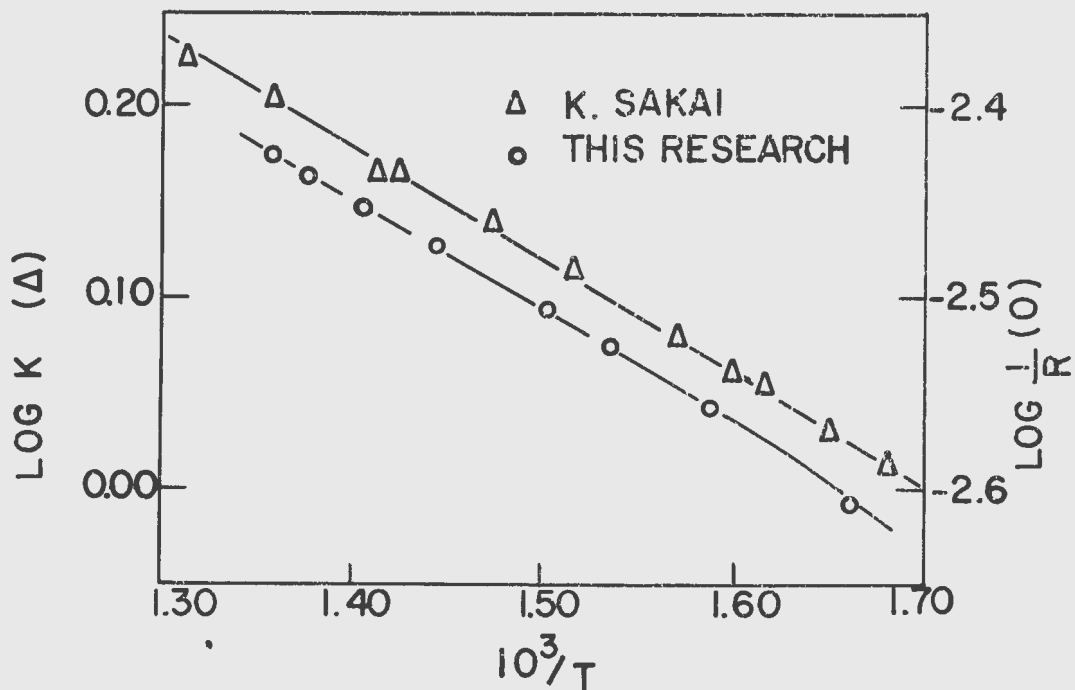
$10^3/T$	$R(\Omega)$	Log R	$10^3/T$	$R(\Omega)$	Log R	$10^3/T$	$R(\Omega)$	Log R
1.134 ⁵	69.05	1.839	1.149 ⁵	71.05	1.852	1.161	72.75	1.862
1.1375	69.43	1.842	1.151 ⁵	71.43	1.854	1.167	73.80	1.868
1.141	69.90	1.844	1.154	71.75	1.856	1.169 ⁵	74.20	1.870
1.144	70.25	1.847	1.156	72.10	1.858	1.172	74.50	1.872
1.147	70.53	1.849	1.158	72.40	1.860			

*Values of $10^3/T$ are based on an average of two readings.

Since the cell constant was not determined, only a comparison of activation energies may be made with literature values. As was discussed on page three, agreement in activation energies is reflected in agreement in the slopes of the lines when two sets of data are plotted on a log R vs. $1/T$ graph. The above values are reproduced in Figure 6 where the slope may be compared with those obtained by Lorenz and Kalmus (14) and K. Sakai (30) on the same compound. A similar study on NaNO_3 yielded the data in Table 2.

These values are reproduced in Figure 7 for comparison of the activation energy (slope) with that obtained by K. Sakai (30).

Bloom and Heymann(23) recently investigated the system potassium chloride - cadmium (II) chloride. As a final check on the reliability

Figure 6. Activation energy of PbCl_2 Figure 7. Activation energy of NaNO_3

of the apparatus and method, a conductivity study was made on this system. The data obtained are reproduced in Table 3 and the very close agreement between these values and those of Bloom and Heymann is shown in Figure 1.

Table 2. Resistance - temperature data on NaNO_3

$10^3/T$	$R(\Omega)$	Log R	$10^3/T$	$R(\Omega)$	Log R	$10^3/T$	$R(\Omega)$	Log R
1.359	267.6	2.427	1.443	297.8	2.474	1.587	363.1	2.560
1.376	273.9	2.438	1.501	322.4	2.508	1.661	405.8	2.608
1.406	284.3	2.454	1.534	336.2	2.527			

Table 3. Specific conductivity in the system $\text{KCl}-\text{CdCl}_2$

X KCl	Values of specific conductivity at different temperatures ($^{\circ}\text{C}.$)			
	690	645	600	570
0.000	---	---	1.950	1.859
0.500	1.569	1.474	1.366	1.291
0.667	1.445	1.343	1.233	1.155

B. Density Determinations

1. Description of apparatus

The apparatus used for density determinations was essentially the same as that used by most other investigators. The melt was contained in a tubular Pyrex container held on a platform. This platform was placed in the tube of a Marshall vertical tube furnace (Marshall Products Co., Columbus, Ohio) and was mounted on an elevating screw so that its

position could be adjusted. The furnace had two one-half inch observation windows on opposite sides situated at the midpoint. Temperature control and measurement were as described in the previous section. An analytical balance was mounted above the furnace. A platinum wire attached to the left arm of the balance beam went through a small hole in the base of the balance case and descended into the furnace. A platinum sinker attached to the lower end of the support wire swung freely.

The condensation of vapors of volatile salts on the suspension wire can cause serious errors in density determinations. The method of Peake and Bothwell (35) was used with success in combating this problem. A vertical Pyrex anticondensation tube about 50 cm. long and 12 mm. in diameter surrounded the suspension wire and extended into the furnace to within about one inch of the melt. Near the top of the tube, which extended out of the furnace, a side arm allowed the introduction of air. Just above the sidearm the 12 mm. tubing was joined to a two inch piece of 8 mm. tubing through a ground glass joint. The slow moving air current prevented the entry of vapors into the anti-condensation tube and their subsequent condensation upon the wire supporting the sinker. The modification consisting of the ground glass seal and the short length of 8 mm. tubing served two purposes. The resulting constriction at the top insured an air flow down the tube and the ground glass seal permitted easy removal of the platinum sinker.

2. Experimental procedure

The Pyrex container holding the sample was placed on the platform under the furnace and raised to the desired height by the elevating screw. The temperature of the sample was raised to 450°C. and hydrogen chloride gas was passed through the melt until it was transparent by visual observation.

The weight of the sinker and wire was measured in air and when temperature equilibrium had been attained, the sinker was lowered through the anti-condensation tube, held for a minute inside and near the end of the tube for temperature equilibration, then lowered into the melt to a predetermined and constant depth. A three-eighths of an inch clearance was maintained between the sinker and the surface of the melt for all runs. After the weighing of the submerged sinker had been accomplished, it was removed from the furnace and examined for traces of salt on the suspension wire. It was then cleaned in dilute hydrochloric acid and reweighed in air while the furnace was approaching equilibrium at the next temperature, 650°C. Weighings were then made at centigrade temperatures of about 650°, 600°, 550°, 500°, and 450°.

A glass tube inserted through the anti-condensation tube after the weighing at 650° was used to remove a three or four gram sample for analysis. A second sample was removed after the last weighing and the whole run was discarded if the difference in mole fraction of potassium chloride amounted to more than 0.5%. The run was also discarded if the initial measurement of density at 450°C . differed from the second 450°C . measurement by more than $\pm 0.5\%$.

C. Phase Diagram Construction

The standard method of thermal analysis was used. A container of the sample was introduced into a small furnace and the temperature raised considerably above the melting point of the salt or salt mixture. The current to the furnace was then shut off. The homogeneity of the melt was maintained and uniform cooling aided by mechanical stirring of the melt provided by a motor with a Pyrex stirring rod which projected through the furnace lid into the melt. A chromel-alumel thermocouple in a Pyrex sheath was immersed in the melt also. A thermocouple reading was taken every sixty seconds until the salt had completely solidified. A sample removed from the melt before cooling had begun was analyzed as previously described.

RESULTS

A. The Phase Diagram

A compound corresponding to the composition $2\text{KCl}\cdot\text{ZnCl}_2$ was reported by various investigators (28, Vol. IV, p. 551). Its existence has been confirmed by the method of thermal analysis. Cooling curves recorded at a number of different compositions yielded the data in Table 4 which has been reproduced graphically in Figure 8.

The compound has a melting point of about 450°C . Eutectic points are found at $X_{\text{KCl}} = 0.69$ ($t = 433^{\circ}\text{C}$.) and $X_{\text{KCl}} = 0.51$ ($t = 230^{\circ}\text{C}$.). It was desirable to locate the position of the liquidus closely since in the region on the phase diagram below this line the composition of the melt is not the same as the overall composition of the system. Thus conductivity isotherms would be expected to show considerable deviation when entering the area on the graph below the liquidus.

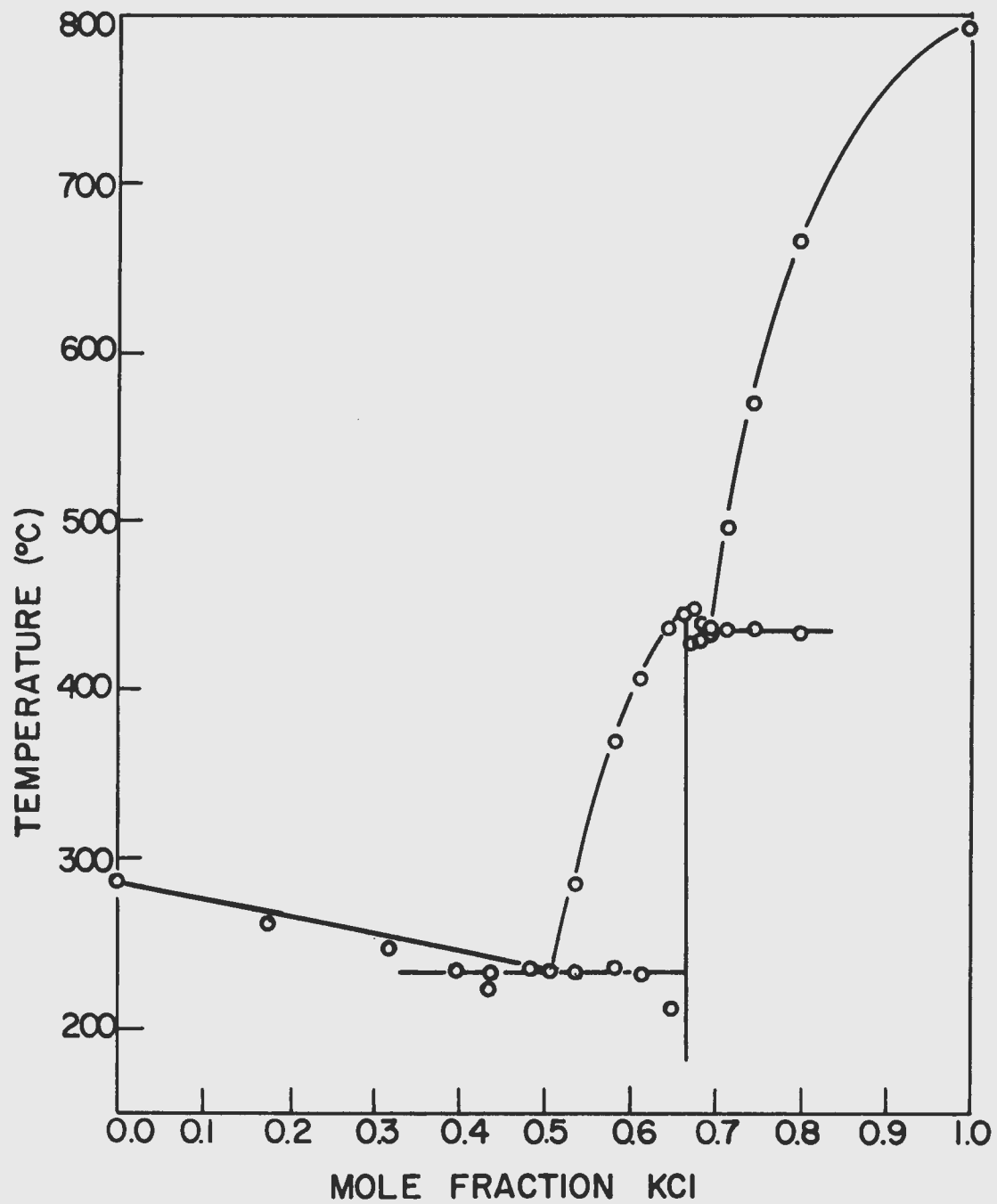


Figure 8. Phase diagram of the system KCl-ZnCl₂

Table 4. Cooling curve data for the system KCl-ZnCl₂

X _{KCl}	Temperature in °C.		X _{KCl}	Temperature in °C.	
	Liquidus	Eutectic		Liquidus	Eutectic
0.000	*	285	0.612	406	230
0.176	261	**	0.646	436	209
0.316	247	**	0.665	*	443
0.395	233	**	0.673	448	427
0.434	223	230	0.683	439	426
0.481	*	234	0.695	436	430
0.506	*	231	0.714	494	434
0.535	284	232	0.746	568	434
0.582	369	234	0.798	665	432

* Cooling was not carried to the eutectic temperature.

** No liquidus break was noted.

B. Specific Conductivity Values

Each cell constant was determined at 25.0°C. and then the value of the cell constant at the elevated temperature was calculated according to the method on page 8. Specific conductivities (κ) were determined by the relationship

$$\kappa = \frac{K}{R}$$

and are reproduced in Table 5. The maximum relative error in the reported values has been calculated to be ± 0.0042 . The errors associated with the temperature and composition for which the value of conductivity is reported are $\pm 2^\circ\text{C}$. and $\pm 0.6\%$ respectively.

C. Density Values

The value for the density of platinum at 20°C. was given as

Table 5. Specific conductivity in the system KCl-ZnCl₂

Mixture	X _{KCl}	Values of specific conductivity at different temperatures (°C.)							
		650	625	600	575	550	525	500	475
16	0.000	0.365	0.306	0.253	0.203	0.159	0.122	0.090	0.063
15	0.080	0.598	0.529	0.462	0.401	0.344	0.290	0.240	0.196
4	0.176	0.750	0.686	0.623	0.561	0.500	0.442	0.392	0.339
9	0.284	1.001	0.939	0.882	0.822	0.754	0.689	0.623	0.560
7	0.395	1.040	0.982	0.925	0.864	0.803	0.741	0.686	0.621
11	0.506	1.109	1.052	0.991	0.931	0.869	0.803	0.739	0.671
5	0.582	1.118	1.054	0.998	0.937	0.874	0.811	0.748	0.684
3	0.670	1.161	1.092	1.026	0.964	0.896	0.830	0.765	0.701
10	0.722	1.202	1.133	1.067	0.997	0.924	0.850	0.776	0.690
19	0.790	1.270	1.195	1.028	0.884	0.772	0.675	0.587	0.512
12	0.834	1.259	1.173	1.055	0.885	0.761	0.657	0.571	0.494

21.45 gm/cm³ by Kieffer and Hotop (31) and confirmed by the value of 21.447 ± 0.02 gm/cm³ found by Austin (32). Holborn and Day's (33) data on the average coefficient of linear thermal expansion of platinum (\bar{C}_1) were reproduced almost exactly by Austin (32) as is indicated in Table 6. For the following calculations a density of 21.45 gm/cm³ and the expansion data of Austin were used. To a good approximation $\bar{C} = 3\bar{C}_1$ where \bar{C} is the average coefficient of cubical thermal expansion.

Table 6. Average coefficient of expansion of platinum.

Reference	$\bar{C}_1 \times 10^6$ (cm ⁻¹ deg ⁻¹) between 0°C. and t°C.				
	t = 450°C.	500°C.	550°C.	600°C.	650°C.
33	9.46	9.53	9.60	9.66	9.73
32	9.47	9.54	9.60	9.66	9.72

According to the buoyancy method of density determination it can be shown that at any temperature "t"

$$1) \quad V_s^t = V_m^t = \frac{M_m}{d_m^t} = \frac{M_s - M_{sm}^t}{d_m^t}$$

$$2) \quad V_s^t = V_s^{20} (1 + \bar{C} \Delta t)$$

$$3) \quad V_s^{20} = \frac{M_s}{d_s^{20}}$$

where V_s^t is the volume of the sinker

V_m^t is the volume of melt displaced by the sinker

M_m is the mass of the melt displaced

d_m^t is the density of the melt

M_s is the mass of the sinker

M_{sm}^t is the apparent mass of the sinker when suspended in the melt

\bar{C} is the average volume coefficient of expansion of the sinker material over the temperature range 20 - t°C.

$\Delta t = t - 20$ when t is in centigrade degrees

d_s^{20} is the density of the sinker at 20.0°C.

V_s^{20} is the volume of the sinker at 20.0°C.

Combination of these three equations yields

$$d_m^t = \left(\frac{M_s - M_{sm}^t}{M_s} \right) \left(\frac{d_s^{20}}{1 + \bar{C} \Delta t} \right)$$

by means of which the densities in Table 7 were calculated. The maximum relative error in the reported values of density is $\pm 6 \times 10^{-4}$. The errors associated with the temperature and composition for which the

Table 7. Density in the system KCl-ZnCl₂

X_{KCl}	t (°C.)	$M_s - M_{sm}^t$ (gms)*	d_m^t (gms/cm ³)
0.000	450	1.9503	2.457
	503	1.9345	2.434
	555	1.9145	2.405
	593	1.9047	2.390
	637	1.8833	2.360
0.094	462	1.9042	2.399
	506	1.8893	2.377
	548	1.8710	2.351
	602	1.8517	2.323
	674	1.8238	2.283
0.158	454	1.8803	2.369
	462	1.8789	2.367
	486	1.8661	2.349
	504	1.8554	2.334
	554	1.8342	2.304
	598	1.8137	2.276
	646	1.7952	2.249
	660	1.7900	2.242
0.313	451	1.7942	2.261
	500	1.7706	2.228
	548	1.7517	2.201
	603	1.7299	2.170
	661	1.7009	2.131
0.452	453	1.7058	2.150
	494	1.6841	2.120
	540	1.6662	2.094
	591	1.6398	2.058
	645	1.6143	2.022
0.639	442	1.5918	2.007
	498	1.5687	1.974
	554	1.5438	1.939
	612	1.5196	1.906
	658	1.4978	1.876

Table 7. (Continued)

X_{KCl}	t (°C.)	$M_s - M_{sm}^t$ (gms)*	d_m^t (gms/cm ³)
0.698	447	1.5468	1.950
	500	1.5232	1.917
	547	1.5023	1.888
	596	1.4801	1.857
	649	1.4607	1.830
0.811	688	1.3483	1.687
	715	1.3373	1.672

*Mass of sinker in air = 16.8147 gms.

densities are reported are $\pm 2^\circ\text{C}$. and $\pm 0.6\%$.

These density data were plotted on graph paper large enough so that no additional error would be introduced. Densities at intermediate temperatures for each composition were determined graphically from the linear density-temperature graph. Densities at intermediate compositions were determined by interpolation on the graph of density vs. composition at constant temperature. These values are found in Table 8.

Table 8. Calculated densities in the system KCl-ZnCl₂

X_{KCl}	Values of density at different temperatures (°C.)							
	650	625	600	575	550	525	500	475
0.000	2.358	2.370	2.383	2.394	2.405	2.420	2.434	2.447
0.080	2.305	2.319	2.333	2.345	2.358	2.371	2.385	2.399
0.176	2.234	2.250	2.265	2.280	2.295	2.310	2.325	2.343
0.284	2.153	2.169	2.185	2.200	2.215	2.232	2.249	2.267
0.395	2.066	2.082	2.099	2.115	2.132	2.148	2.165	2.183
0.506	1.981	1.997	2.013	2.030	2.046	2.061	2.076	2.094
0.582	1.924	1.939	1.954	1.970	1.985	2.000	2.015	2.032
0.670	1.848	1.864	1.880	1.896	1.912	1.926	1.940	1.956
0.722	1.799	1.815	1.831	1.845	1.860	1.875	1.890	1.905
0.790	1.735	*	*	*	*	*	*	*

*This temperature is below the liquidus on a temperature-composition diagram.

D. Calculation of Λ and E_{Λ}^{\dagger} 1. Calculation of Λ , the equivalent conductivity

Conductance in electrolytes is a function of the number of ions per unit volume. Consequently the quantity Λ was introduced to make possible direct comparisons of the relative conductivities of different systems. The equivalent conductivity is defined such that

$$\Lambda = K V_e = K \times \frac{W_e}{d} = K \times \frac{1000}{C}$$

where V_e is the volume in cubic centimeters containing one equivalent weight of electrolyte, W_e is the equivalent weight (or average equivalent weight) of the system and C is the concentration of the electrolyte in equivalents per liter.

For the system $KCl-ZnCl_2$

$$\begin{aligned} W_e &= W_{ZnCl_2} + (W_{KCl} - W_{ZnCl_2}) X_{KCl} \\ &= 68.15 + (74.56 - 68.15) X_{KCl} \\ &= 68.15 + 6.41 X_{KCl} \end{aligned}$$

This relationship resulted in the calculated values for W_e recorded in Table 9.

Table 9. Average equivalent weight (W_e) in the system $KCl-ZnCl_2$

X_{KCl}	W_e	X_{KCl}	W_e	X_{KCl}	W_e
0.000	68.15	0.395	70.68	0.772	72.78
0.080	68.66	0.506	71.39	0.790	73.21
0.176	69.28	0.582	71.88	0.834	73.50
0.284	69.97	0.670	72.45		

The maximum relative error in W_e is determined to be $\pm 5.6 \times 10^{-4}$ if the maximum relative error in composition is ± 0.006 .

Using the relationship $\Lambda = K \times W_e/d$ and the data in Tables 5, 8 and 9, the values of Λ found in Table 10 were calculated. The maximum relative error is given by

$$\frac{\Delta \Lambda}{\Lambda} = \frac{\Delta K}{K} + \frac{\Delta W_e}{W_e} + \frac{\Delta d}{d}$$

Table 10. Equivalent conductivity in the system KCl-ZnCl₂

X_{KCl}	Equivalent conductivity at different temperatures (°C.)							
	650	625	600	575	550	525	500	475
0.000	10.55	8.80	7.23	5.78	4.51	3.43	2.50	1.76
0.080	17.81	15.66	13.58	11.73	10.00	8.41	6.90	5.60
0.176	23.26	21.08	19.06	17.06	15.08	13.25	11.67	10.01
0.284	32.52	30.29	28.24	26.13	23.81	21.61	19.39	17.28
0.395	35.58	33.33	31.13	28.87	26.61	24.38	22.39	20.11
0.506	39.97	37.61	35.13	32.75	30.33	27.83	25.41	22.83
0.582	41.77	39.08	36.71	34.18	31.64	29.15	26.69	24.19
0.670	45.51	42.43	39.52	36.82	33.95	31.22	28.57	25.97
0.722	48.64	45.45	42.40	39.33	36.16	33.00	29.87	26.36
0.790	53.60	*	*	*	*	*	*	*

* This temperature is below the liquidus on a temperature-composition diagram.

Inserting the previously given values in the right side of the above expression it is seen that the maximum relative error in Λ is ± 0.0054 .

2. Calculation of E_A^* , the activation energy of ionic migration

As developed in the introduction

$$\Lambda = A \times \exp \left(-E_A^*/RT \right)$$

$$\text{from which } \log \Lambda = \log A - \left(\frac{1}{T} \times \frac{E_{\Lambda}^{\dagger}}{2.303 R} \right)$$

so that $E_{\Lambda}^{\dagger} = 2.303 \times (\text{slope})$ on a $\log \Lambda$ vs. $1/T$ plot. In Table 11 are activation energies determined at the midpoints of successive pairs of conductivity readings. The equation

$$E_{\Lambda}^{\dagger} = \frac{-(2.303) (1.987) \times \Delta (\log \Lambda)}{\Delta (1/T)}$$

was used with the assumption that the slope at the midpoint of a pair of points was the same as the slope of the straight line through the points. This assumption is justified by noting that the deviation of the data thus plotted from linearity is in all cases less than the experimental error when a temperature range of only 25°C. is considered.

Table 11. Activation energy of ionic migration in the system KCl-ZnCl₂

X _{KCl}	Values of E_{Λ}^{\dagger} at different temperatures (°C.)			
	637.5	587.5	537.5	487.5
0.000	12.00	13.21	14.39	16.23
0.080	8.48	8.61	9.04	9.61
0.176	6.47	6.51	6.68	7.03
0.284	4.68	4.58	5.06	5.29
0.395	4.30	4.44	4.58	4.93
0.506	4.01	4.12	4.50	4.81
0.582	4.39	4.21	4.28	4.53
0.670	4.62	4.16	4.37	4.38
0.722	4.47	4.42	4.77	5.73

The error in E_{Λ}^{\dagger} is expressed by

$$\frac{\Delta E_{\Lambda}^{\dagger}}{E_{\Lambda}^{\dagger}} = \frac{\Delta \overline{\Delta 1/T}}{\overline{\Delta 1/T}} + \frac{\Delta \overline{\Delta \log \Lambda}}{\overline{\Delta \log \Lambda}}$$

The maximum error in $\overline{\Delta T}$ is estimated as $\pm 0.5^{\circ}$ on the basis of an inaccuracy of two millivolts as measured on the potentiometer. This

leads to a relationship

$$\frac{\Delta \frac{\Delta \Lambda}{T}}{\Delta \Lambda} \leq \pm 0.02$$

Using the value for $\Delta \Lambda / \Lambda$ arrived at on page 28 we see that $\Delta E_{\Lambda}^* / E_{\Lambda}^* = \pm 0.025$.

DISCUSSION

It is instructive to add to the data, values of K , d , Λ and E_{Λ}^* for pure potassium chloride. Although the pure compound freezes above the temperature range examined, it is still of value to take data obtained from the melt at higher temperatures and extrapolate to the temperatures in question. In this way it is possible to examine data on the mixtures for deviations from strictly additive relationships. Table 12 lists the extrapolation data as calculated from the indicated sources.

The literature also contains data on the density and specific conductivity of pure zinc (II) chloride. Comparison between the results of this research and interpolated literature values is made in Table 13.

The data reported in Tables 5 and 8 together with the extrapolated values for potassium chloride are graphically presented in Figures 9 and 10.

In the system $KCl-ZnCl_2$, the density isotherms are somewhat "S" shaped. They deviate from additivity in a positive direction at low potassium chloride concentrations and have the suggestion of a negative deviation at low zinc (II) chloride concentrations. Any qualitative discussion of the shape of the isotherms which is based solely on the effect of mixing a salt of ionic form MX with another of the type MX_2 must apply in general to all such binary systems. Density isotherms in the system $KCl-MgCl_2$ (37) have a similar "S" shape while the systems $KCl-BaCl_2$ (36) and $NaCl-MgCl_2$ (36) exhibit only the positive deviations from additivity in the vicinity of pure MX_2 . In the system $KI-CdI_2$ (25), densities have negative deviations near MX_2 while the systems $KBr-BaBr_2$ (25) and $LiCl-CdCl_2$ (25) are approximately additive. It can be seen that no general trend is apparent.

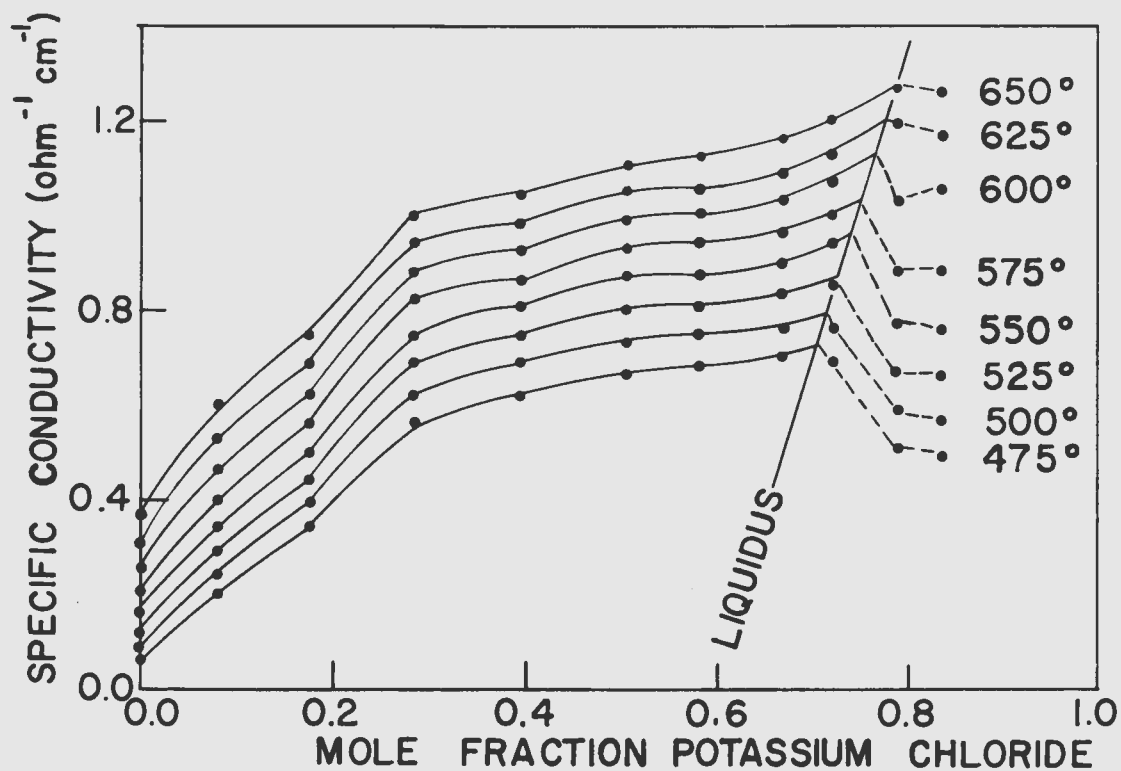


Figure 9. Specific conductivity isotherms in KCl-ZnCl₂ system

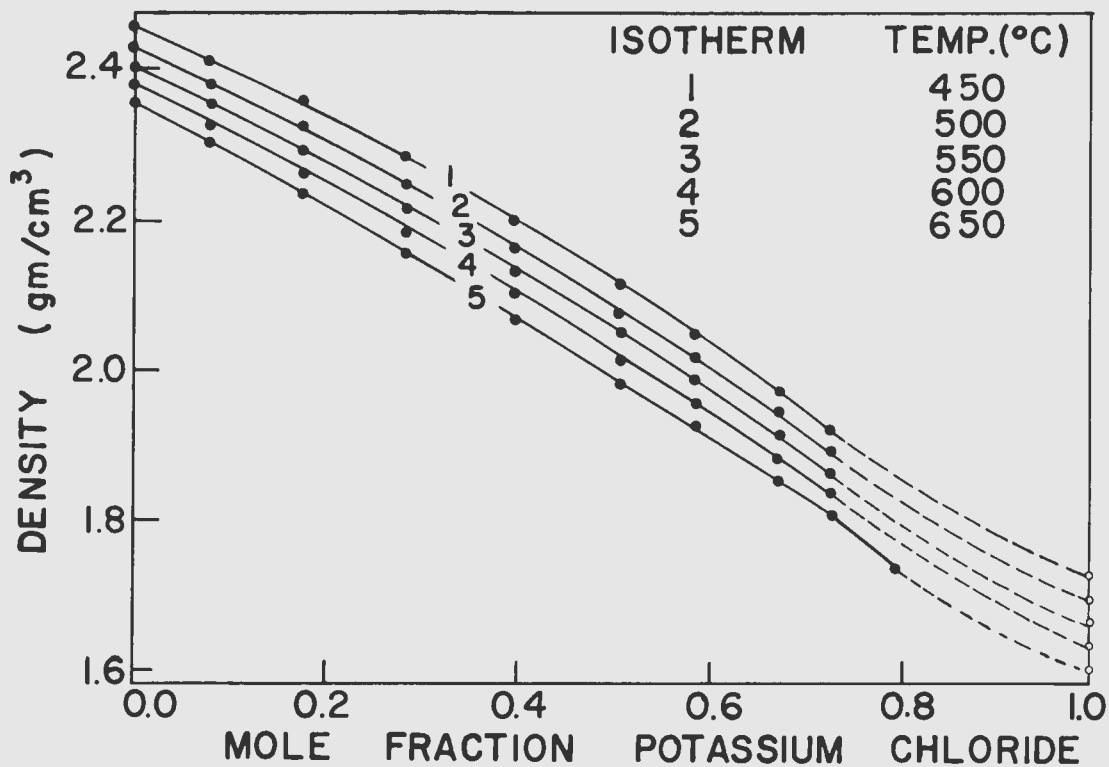


Figure 10. Density isotherms in the system KCl-ZnCl₂

Table 12. Data for KCl extrapolated from data at higher temperatures

Reference	Quantity extrapolated	Temperature to which extrapolated (°C.)							
		650	625	600	575	550	525	500	475
34, 20*	κ ($\Omega^{-1}\text{cm}^{-1}$)	1.844	1.778	1.711	1.643	1.573	1.502	1.431	1.358
35	d (gm/cm^3)	1.595	1.610	1.626	1.642	1.657	1.672	1.688	1.704

* Data from these sources were averaged.

Table 13. Comparison of data on zinc (II) chloride

Reference	Measured quantity	Value of measured quantity at different temperatures (°C.)							
		650	625	600	575	550	525	500	475
20	κ ($\Omega^{-1}\text{cm}^{-1}$)	0.312	0.274	0.236	0.198	0.156	0.120	0.084	0.056
This research	κ ($\Omega^{-1}\text{cm}^{-1}$)	0.365	0.306	0.253	0.203	0.159	0.122	0.090	0.063
36	d (gm/cm^3)	---	---	---	---	2.410	2.422	2.434	2.447
This research	d (gm/cm^3)	2.358	2.370	2.383	2.394	2.405	2.420	2.434	2.447

The behavior of isotherms of equivalent conductivity (see Figure 11) in the range $0.00 < X_{\text{KCl}} < 0.30$ is not far from ideal. Negative deviations from additivity begin at $X_{\text{KCl}} \approx 0.30$ and reach a maximum in the neighborhood of $X_{\text{KCl}} = 0.71$. Isotherms of Λ then begin to rise toward the extrapolated values for pure potassium chloride. The large negative deviations from additivity exhibited by Λ isotherms and the minimum occurring in the neighborhood of the composition corresponding to $2\text{KCl}-\text{ZnCl}_2$ are both in agreement with the proposals of Bloom and Heymann as outlined in the introduction. It is puzzling that the negative deviations begin quite abruptly at $X_{\text{KCl}} \approx 0.30$ following the additive relationship in the range $0.00 < X_{\text{KCl}} < 0.30$.

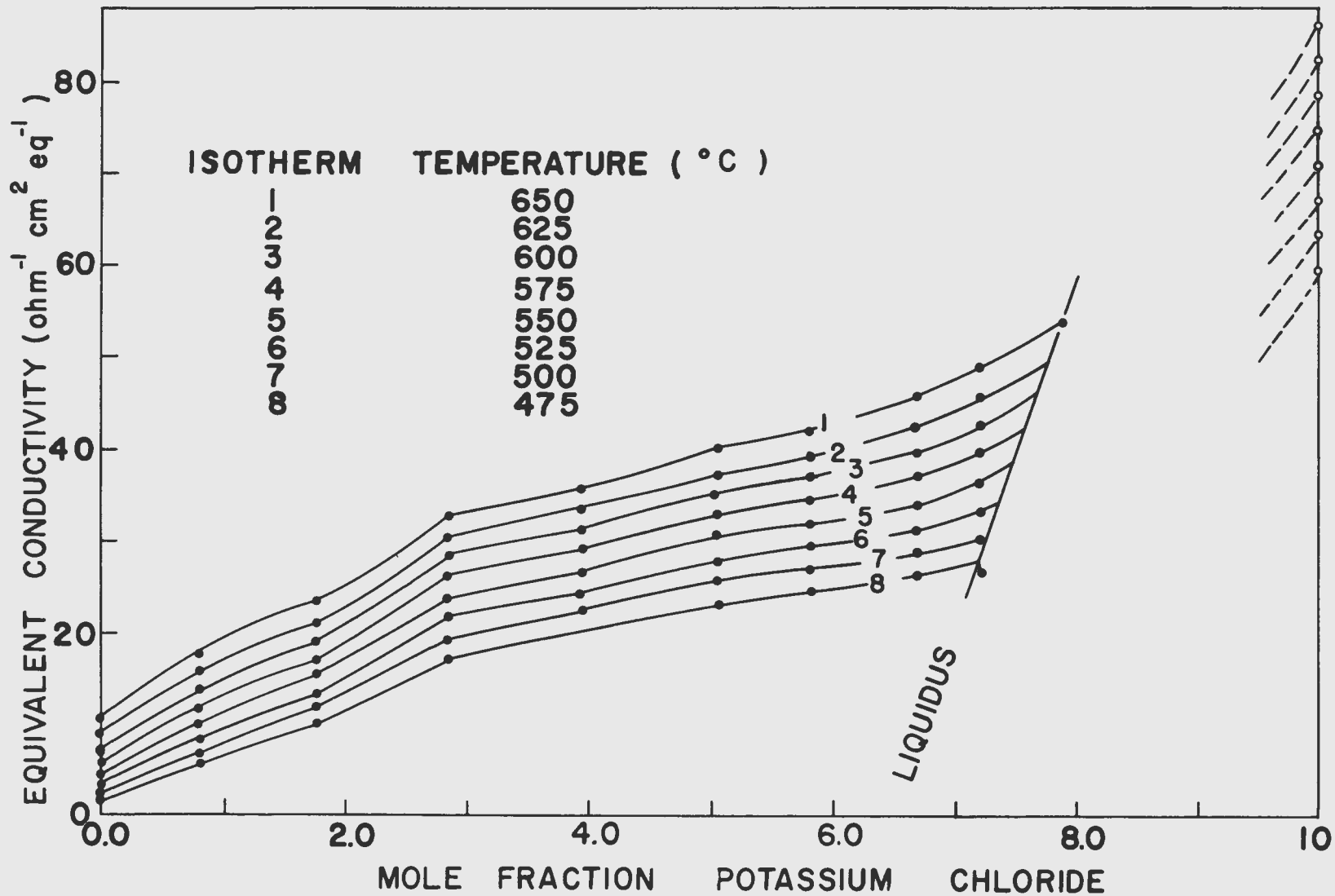


Figure 11. Equivalent conductivity isotherms in the system $KCl-ZnCl_2$

As seen in Figure 12, only a slight change in E_{Λ}^{\dagger} is observed between X_{KCl} values of 1.00 and 0.30. This small change is linear in nature with the exception of values at $X_{KCl} = 0.722$. At this concentration the points to varying degrees lie above a linear plot. A slow increase in E_{Λ}^{\dagger} accompanies decreasing values of X_{KCl} until X_{KCl} has lowered to about 0.300 at which time E_{Λ}^{\dagger} begins a rapid rise to the value for pure zinc (II) chloride. A gross experimental error is the likely cause of the value of E_{Λ}^{\dagger} at $X_{KCl} = 0.672$ (487.5°C.). At $X_{KCl} = 0.722$, the high value for E_{Λ}^{\dagger} at 487.5°C. is explained by the fact that this value was derived from K values taken at temperatures below the initial freezing point of the mixture. The other three points at this mole fraction also lie somewhat above these otherwise linear portions of the isotherms. These data nevertheless conform to linearity within experimental error although high values could be a reflection of incipient crystallization in the melt. The initial freezing point of this composition is near 515°C.

Recent work by Duke and Laity (38) assigns ionic transport numbers t_{+} and t_{-} of 0.25 and 0.75 respectively in lead (II) chloride at 565°C. These results lend experimental support to earlier predictions of a number of authors that alkali halides are predominantly cationic conductors while in the alkaline earth halides the anions carry a larger share of the current. In the system $KCl-ZnCl_2$ presumably K^{+} dominates Λ and E_{Λ}^{\dagger} for pure KCl while Cl^{-} dominates Λ and E_{Λ}^{\dagger} for pure $ZnCl_2$. An interesting proposal is that K^{+} dominates both Λ and E_{Λ}^{\dagger} for the mixture in the range $0.30 < X_{KCl} < 1.00$ and that Cl^{-} begins to become important at $X_{KCl} \approx 0.30$, increasingly dominating Λ and E_{Λ}^{\dagger} from $X_{KCl} \approx 0.30$ to 0.00. This must be regarded as pure speculation however. A prime requisite for attempting any kind of a significant qualitative or quantitative discussion of these E_{Λ}^{\dagger} isotherms is the availability of data on the transport numbers of the ions at different compositions. The literature contains little data on transport numbers in mixtures. Duke, Owens and Ida (39) are currently working on methods of their determination which show promise of yielding significant results.

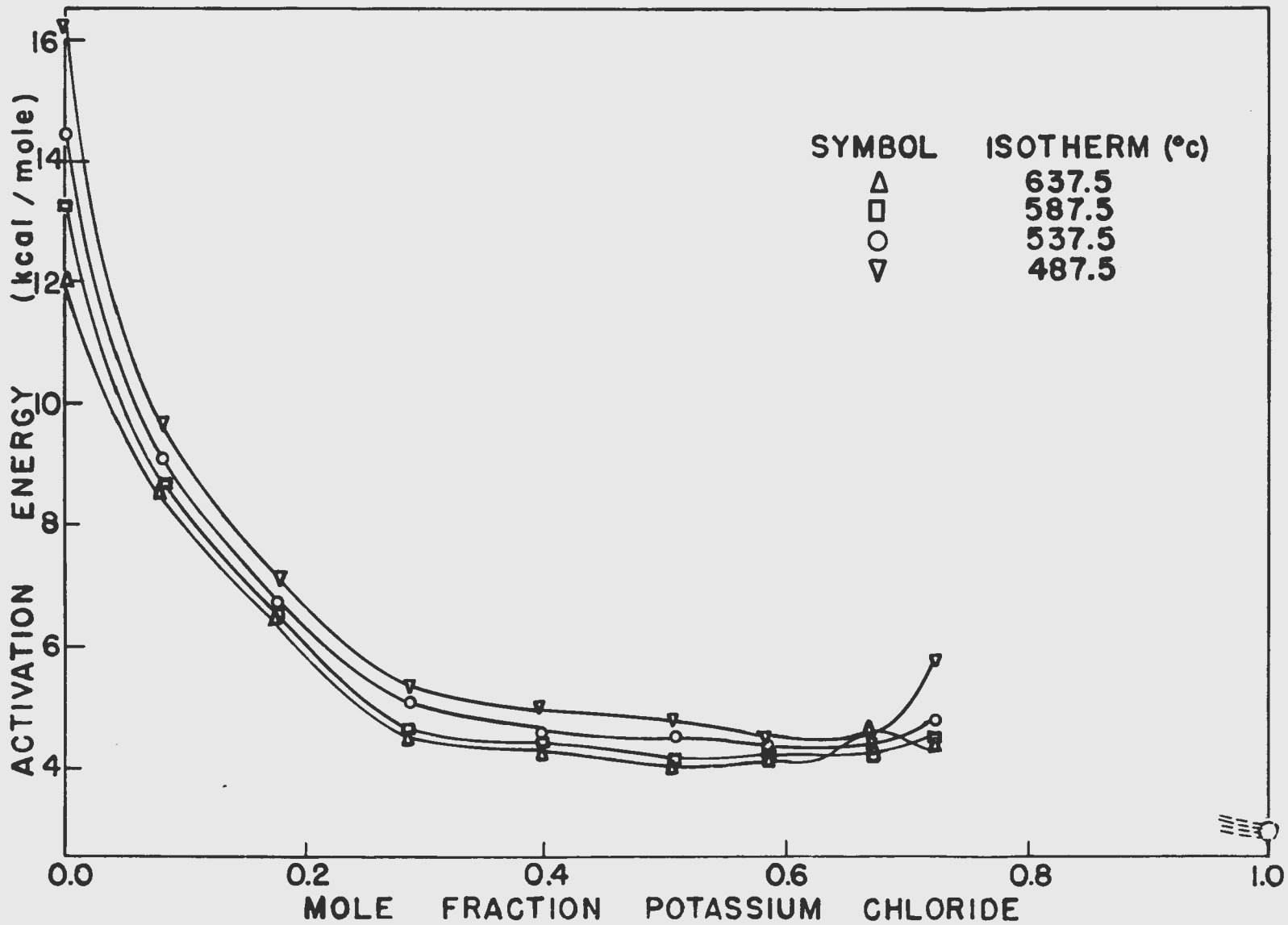


Figure 12. Activation energy of ionic migration in the system $KCl-ZnCl_2$

LITERATURE CITED

1. J. L. R. Morgan and O. M. Lammert, J. Am. Chem. Soc., 48, 1220 (1926).
2. G. Jones and R. C. Josephs, ibid., 50, 1049 (1928).
3. _____ and G. M. Bollinger, ibid., 51, 2407 (1928).
4. _____ and _____, ibid., 53, 411 (1931).
5. _____ and _____, ibid., 53, 1207 (1931).
6. _____ and B. C. Bradshaw, ibid., 55, 1780 (1933).
7. _____ and S. M. Cristian, ibid., 57, 272 (1935).
8. _____ and D. M. Bollinger, ibid., 57, 280 (1935).
9. _____ and M. J. Prendergast, ibid., 59, 731 (1937).
10. _____, K. J. Mysels and W. Juda, ibid., 62, 2919 (1940).
11. T. Shedlovsky, ibid., 52, 1793 (1930).
12. F. Horvoka and E. E. Mendenhall, J. Chem. Ed., 16, 239 (1939).
13. R. N. Haszeldine and A. A. Woolf, Chem. and Inds., 544 (1950).
14. R. Lorenz and H. T. Kalmus, Z. Phys. Chem., 59, 17 (1907).
15. H. M. Goodwin and R. D. Mailey, Phys. Rev., 26, 28 (1908).
16. C. Sandomini, Atti. acad. Lincei, 24, I, 616 (1915).
17. _____, Atti. r. ist. Veneto, 74, 519 (1915).
18. _____, Cazz. Chim. Ital., 50, I, 289 (1920).
19. F. M. Jaeger and B. Kapma, Z. anorg. allgem. Chem., 113, 27 (1920).
20. W. Biltz and W. Klemm, Z. Phys. Chem., 110, 318 (1924).
21. _____ and _____, Z. anorg. allgem. Chem., 152, 225 (1926).

22. W. Biltz and W. Klemm, ibid., 152, 267 (1926).
23. H. Bloom and E. Heymann, Proc. Roy. Soc. (London), A188, 392 (1946).
24. N. F. Mott and R. W. Gurney, "Electronic Processes in Ionic Crystals," 2nd ed., Oxford University Press, London, 1953.
25. H. Bloom, I. W. Knaggs, J. J. Molloy and D. Welch, Trans. Far. Soc., 49, 1458 (1953).
26. B. S. Harrup and E. Heymann, ibid., 51, 259 (1953).
27. E. R. Van Artsdalen and I. S. Yaffe, J. Phys. Chem., 59, 118 (1955).
28. J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1947.
29. T. C. Loomis, "Metal Chelates of Cyclohexenediaminetetraacetic Acid," unpublished Ph. D. Thesis, Iowa State College Library, Ames, Iowa, 1953.
30. K. Sakai, J. Chem. Soc. Japan, Pure Chem. Section, 75, 182 (1954).
31. R. Kieffer and W. Hotop, Kolloid Z., 104, 208 (1943).
32. J. Austin, Physics, 3, 240 (1932).
33. L. Holborn and A. L. Day, Ann. Physik, 4, 104 (1901). (Original not seen.) Referred to by R. F. Vines, "The Platinum Metals and their Alloys," The International Nickel Co., Inc., New York, (1941).
34. E. K. Lee and E. P. Pearson, Trans. Electrochem. Soc., 88, 12 (1945).
35. J. S. Peake and M. R. Bothwell, J. Am. Chem. Soc., 76, 2653 (1954).
36. W. Klemm, Z. anorg. allgem. Chem., 152, 235 (1926).
37. R. W. Huber, E. V. Potter and H. W. St. Clair, U. S. Bureau of Mines Report of Investigations No. 4858 (1952).

38. F. R. Duke and R. W. Laity, J. Phys. Chem., 59, 549 (1955).
39. _____, N. Ida and B. B. Owens, unpublished research, Ames Laboratory of the Atomic Energy Commission, Ames, Iowa, (1955).
40. Leeds and Northrup, Philadelphia, Pennsylvania, Catalog E, Section EF, (1946).
41. _____ and _____, Catalog EN - S2, (1954).
42. H. F. Stimson, J. Res. Natl. Bur. Stds., 42, 209 (1949).
43. International Critical Tables, Vol. 1, McGraw - Hill Book Company, Inc., New York, 1926.