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Physics of the Solid State

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Self Diffusion of Potassium in Potassium Chloride*

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Introduction:

H. Witt of the University of Gottingen has recently published data on the temperature dependence of the self diffusion coefficient of the potassium ion in potassium chloride. In the neighborhood of $600^\circ$ C, where the vacancy content of the crystals should be uninfluenced by impurities, Witt found a deviation from the Einstein relation between diffusion coefficient and electrical conductivity. The Einstein relation may be written

$$\frac{\sigma^+}{D^+} = \frac{N e^2}{kT}$$

where $\sigma^+$ and $D^+$ are the conductivity and self diffusion coefficient of the potassium ion in KCl. The number of potassium ions per unit volume in the crystal is denoted by $N$. The self diffusion coefficient of the potassium ion was approximately twice as large as calculated from the measured electrical conductivity and the transference number of the potassium ion. This behavior of potassium chloride is unlike that of sodium chloride and sodium bromide as determined by the work of Mapother, Crooks and Maurer. In sodium chloride and bromide,

(1) H. Witt, Z. Physik 124, 186 (1953)
(2) F. Kerkhoff, Z. Physik 130, 449 (1951)


at temperatures sufficiently high that the accidental impurities had no effect upon the vacancy concentration, these investigators found the Einstein Relation to be satisfied.

The present work was undertaken to check the data of Witt since his results had most interesting implications. In particular, Witt's data furnish evidence for the existence of pairs of positive and negative ion vacancies in KCl\(^{(4)}\). Such pairs are illustrated in Figure 1.

![Diagram of ion vacancies](image)

**Figure 1**

Being neutral entities, pairs contribute nothing to the d.c. conductivity. They may well have large mobility, however, and contribute significantly to the self diffusion coefficients of the ions. Under these circumstances, the Einstein Relation is not satisfied.

**Experimental:**

The diffusion measurements were performed in essentially the same manner as described by Mapother, Crooks and Maurer\(^{(3)}\).

\(^{(4)}\) G. J. Dienes, J. Chem. Phys. 16, 620 (1948)
A large Harschaw single crystal of KCl was annealed and then cleaved into specimens about 1 cm x 1 cm x 1/2 cm. A piece weighing about 0.1 gm, cleaved from the same crystal, was bombarded by neutrons in the pile at the Argonne National Laboratory for about 24 hours. During this time the $^{41}$K in the sample was activated to give $^{42}$K (half-life 12.44 hours) to a sufficient extent to permit diffusion experiments above 500$^\circ$ C. Upon arrival at Urbana, the activity of the unshielded sample was generally found to be of the order of 10 mr/hr at 4 ft. By evaporation, a thin layer $(5-8 \times 10^{-4}$ cm) of radioactive KCl was made to form on one surface of each specimen. The specimens were then enclosed, 2 at a time, in platinum capsules. The surfaces bearing the evaporated layers of activated KCl were set facing each other, kept separate by a platinum spacer. The platinum capsules were subsequently sealed off in vycor tubes filled with helium gas. The pressure of the helium was such that at the diffusion temperature it would be approximately atmospheric. The helium gas used for this purpose was passed through a liquid nitrogen trap before use. This served to freeze out most extraneous gases, the presence of which might contaminate the specimens. It was also found necessary to coat the inside of the vycor tubes with a thin layer of KCl. Such a layer was prepared by filling the tubes with chunks of KCl and heating them to about 600$^\circ$ C under high vacuum then cooling to room temperature. Without such a coating the specimens became colored during the diffusion. The effect was in the form of a
pink layer extending some distance into the crystal from all sides. It was especially pronounced in preliminary experiments where stainless steel capsules were used, but could also be observed when the specimens were sealed in vycor without the stainless steel capsules. On the basis of these facts it is believed that a metal diffuses into the KCl crystals at high temperatures. The KCl coating, the helium, and the platinum capsules inhibit the reaction between the specimens used and the vycor. It has also been noted that the pink crystals exhibit a considerably higher self diffusion coefficient than the clear ones. This could be expected if di- or tri-valent metallic impurity ions have diffused into the lattice leading further strength to the belief that the pink color is due to such ions.

Still another consequence of the KCl coating of the vycor is the fact that the samples retained the fresh, clear appearance of newly cleaved surfaces. Samples diffused without this coating had greyish, dingy looking surfaces, and in particular the evaporated layer of KCl became greyish yellow in color. Possibly this is due to some organic matter adhering to the vycor. The liquid nitrogen trap also helps in this respect, perhaps freezing out organic vapors present in the system.

The slicing of the KCl specimens was carried out in the same manner as NaCl. However, it was found that the softer KCl was not removed as uniformly by the microtome knife as the NaCl, leading to considerable scattering of data on the log activity vs. (distance)$^2$ curves. If the knife orientation across the crystal surface was
along the 110 direction the KCl came off in long needles rather than in powder form, and effective slicing was almost impossible. But even with the knife oriented in a different direction the slices had to be taken 50 percent thicker than for NaCl. Otherwise there was danger of the scotch tape contacting the knife.

However, neither the errors introduced by the sectioning process nor the errors in temperature control or measurement appear sufficient to account for the scatter of the data shown in Figure 3. It is not known at the present time why KCl data are inferior in precision to NaCl data which are taken by the same personnel using the same equipment.

The conductivity was measured by a method similar to that used by Bean (5). A Hewlett-Packard audio-oscillator, a general Radio 716-C capacitance bridge, and a wave analyser were employed in the circuit. The frequency was varied from 100 cps for the low temperatures to 10,000 cps for the highest ones. The conductivity obtained from a number of different specimens is shown in Figure 2. The specimens are not distinguished in this graph because of the uniformity of behavior. Slight deviation for the various specimens are observable below 400° C. The "knee" of the curve is located near 450° C. This indicates that the purity of the crystals is somewhat better than that of the recrystallized KCl used by Kerkhoff (2). The concentration of vacancies due to impurity ions is of the order of 2 x 10^{15}/cc.

This number has been obtained by taking the data of Kelting and Witt (6) (who have plotted the concentration of thermal vacancies vs. temperature) and by assuming that at the "knee" the concentration of thermal vacancies is equal to the concentration introduced by impurity ions. Harshaw NaCl crystals used in previous work have been found to contain an impurity vacancy content of $10^{17}$/cc, so that the crystals used in the present work are appreciably purer.

Results:

Figure 3 shows the results of 18 diffusion experiments covering the temperature range from 520°C to 660°C. The solid curve represents the diffusion coefficient calculated from the conductivity by means of the Einstein Relation. Since the contribution of the chloride ion to the conductivity is appreciable in KCl at high temperatures, the transference number data of Kerkhoff (2) were used to obtain the contribution due to the potassium ion above. The relation is

$$t_+ = \frac{\sigma_+}{\sigma}$$

where $t_+$ is the transference number of the $K^+$ ion, and $\sigma$ the conductivity shown in Figure 2. For temperatures in excess of 620°C the calculated diffusion coefficient is represented by a dashed line since it was necessary to extrapolate Kerkhoff's data above this temperature.

From the slope of the line in Figure 3 one can get the sum of the activation energy, $U$, and the energy of formation, $\frac{W}{2}$, of a single positive ion vacancy. Unfortunately, neither $U$ nor $\frac{W}{2}$ are known separately with great accuracy. Using the value of 1.20 eV for $\frac{W}{2}$ from Kelting and Witt (6) and 1.88 eV for $U + \frac{W}{2}$ from the present work, we find $U$ to be 0.68 eV.

The data of Witt is also shown in Figure 3. The present data do not agree well with that of Witt and indicate that the Einstein Relation is valid in the temperature range covered by these experiments. We believe Witt's data to be affected by an unknown constant error.

Our conclusion is that the present data lend no support to the theory that vacancy pairs exist in potassium chloride in the temperature range between $520^\circ$ C and $660^\circ$ C. Either the vacancy pairs occur in too small a concentration or possess too small a mobility to influence the self diffusion coefficient of the potassium ion.
ELECTRICAL CONDUCTIVITY OF POTASSIUM CHLORIDE (HARSHAW)
Self diffusion coefficient of $K^+$ in KCl

Measured (Aschner)
Measured (Witt)
Calculated