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Diffusion of Hydroxide Ion in Potassium Chloride Single Crystals†

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The diffusion coefficient of OH^- in KCl was measured by desorption of OH^- from single crystals grown from melts of purified KCl doped with KOH. These desorption experiments were conducted in vacuum and under 1/3 atm Cl_2. The change in OH^- concentration as a function of time was measured optically. It was found that a reactive atmosphere was required to obtain reliable results. Under Cl_2 at 1/3 atm the diffusion coefficient of OH^- in KCl is given by the relation, $D_{OH^-} = 3.0 \times 10^5 \exp(-1.95\ \mathrm{eV/kT})$, in the temperature range between 397 and 515°C.

Introduction

The most common impurity in alkali halide crystals is the hydroxide ion. Many commercial crystals contain OH^- in concentrations comparable to impurity doping levels used in optical and transport experiments. Unfortunately, OH^- is not a passive impurity. Fritz, Lüty, and Anger (*1*) have shown Ca^{2+} reacts with OH^- in KCl. This reaction strongly suppresses the extrinsic conductivity expected from the Ca^{2+} and the 204 nm OH^- band is not present. However, the 2.8 μ infrared O–H band remains observable. Recent work (*2*) in our laboratory has shown similar behavior for Hg^{2+} and OH^- in KCl. Beaumont and Jacobs (*3*) observed that the purity of inert gas atmospheres used in conductivity cells affected the knee temperature of pure KCl. Such an effect can occur if H_2O is present in the inert gas or can be desorbed from surfaces in the conductivity cell which were not baked out in the preliminary gas flushing of the cell. Both cases have been observed in conductivity measurements in this laboratory (*2*).

This problem has become more complicated recently because anions have been shown to be much more mobile (*4*) in the alkali halides than earlier work (*5*) suggested. Lidiard (*6*) explained this by migration through electrically neutral vacancy pairs. Fuller and Reily's (*7*) study of the ionic conductivity of RbCl showed that Cl^- contributes importantly to charge transfer processes in this substance. Fuller (*8*) has found that the host anion in KCl diffuses with a jump activation energy of 0.95 eV and the vacancy pair contribution to the Cl^- diffusion varies from 50% near the melting point to 8% at 525°C.

The hydroxide ion can lead to serious errors in optical and transport measurements in alkali halides. Yet few measurements have been made on its transport properties. Because of the importance of OH^- to transport studies of divalent ions in KCl, we undertook to measure its diffusion coefficient under conditions similar to those used in transport experiments.

In pure KCl the diffusion coefficient D of OH^- should be independent of the OH^- concentration. Then Fick's second law can be applied in the simple form

$$\partial C/\partial t = \mathrm{D}(\partial^2 C/\partial x^2). \tag{1}$$

When solved for plane sheet boundary conditions

$$\text{at } t = 0 \quad C = \text{const} \quad 0 < x < d,$$

$$\text{and at } t > 0 \quad C = 0 \qquad 0 = x = d.$$

Crank (*9*) obtains a solution for short times of the form

$$\frac{M_t}{M_\infty} = 2\frac{(Dt)^{1/2}}{(d^2)}\left\{\pi^{1/2} + 2\sum_{n=1}^{\infty}(-1)^n \operatorname{erfc}\frac{nd}{(Dt)^{1/2}}\right\}. \tag{2}$$

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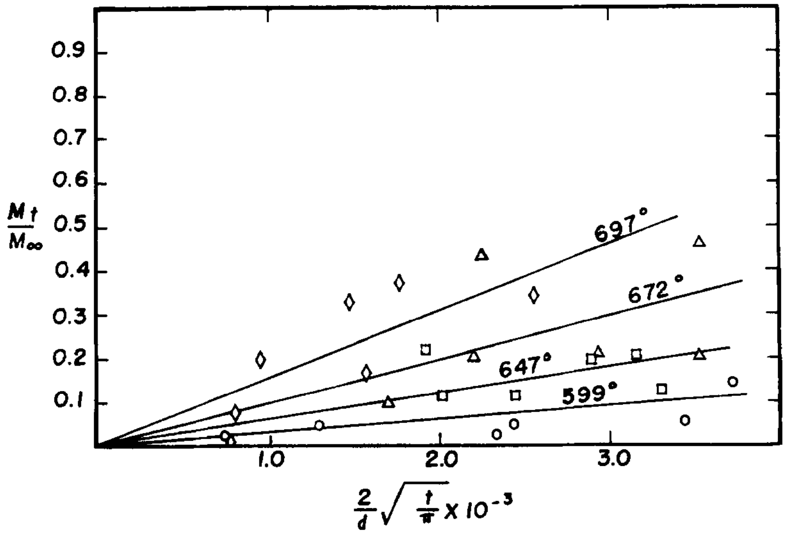

FIG. 1. Desorption of OH^- from $KCl:OH^-$ crystals at an initial external pressure of 10^{-6} Torr.

For a desorption experiment M_t/M_∞ is the fraction of OH^- lost, d is the thickness of the crystal, and t the desorption time. In the region where d is much larger than $(Dt)^{1/2}$, i.e. $d \gg (Dt)^{1/2}$, the erfc $nd/(Dt)^{1/2} \to 0$ and the solution in this region becomes

$$M_t/M_\infty = (4Dt)^{1/2}/\pi d^2. \tag{3}$$

Thus, the measurement of M_t/M_∞ at a specific t and d will provide an estimate of D if $d \gg Dt$.

Experimental

The desorption of OH^- from $KCl:OH^-$ single crystals satisfies the necessary requirements of Eq. (3) if the doping is uniform, the sample approximates a plane sheet and the OH^- concentration remains vanishingly small outside the crystal. The change in concentration can be followed by the change in absorbance at 204 nm. Gie and Klein (*10*) have shown that the OH^- concentration is given by

$$\frac{\alpha(204\text{ nm})}{C} = \frac{0.4d}{(\text{cm})(10^{-6}\text{ mole fraction})}, \tag{4}$$

where α is the absorption coefficient, C is the concentration of OH^-, and d is the sample thickness.

The samples used in these measurements were cut from single crystals of KCl doped with KOH and grown under vacuum in quartz tubes by the Stockbarger method. Merk Reagent grade KCl was purified by the ion exchange technique followed by chlorination (*11*). The hydroxide ion was introduced by adding KOH to the KCl in the growth tube after the chlorination. All crystals were annealed in the growth tube at 600°C for 2 days. Samples $1 \times 1 \times 0.1$–0.2 cm were cut from these crystals.

Eight samples for each desorption temperature were sealed in quartz diffusion tubes after their initial OH^- concentration had been measured. Each sample contained about 2×10^{-5} mole fraction of

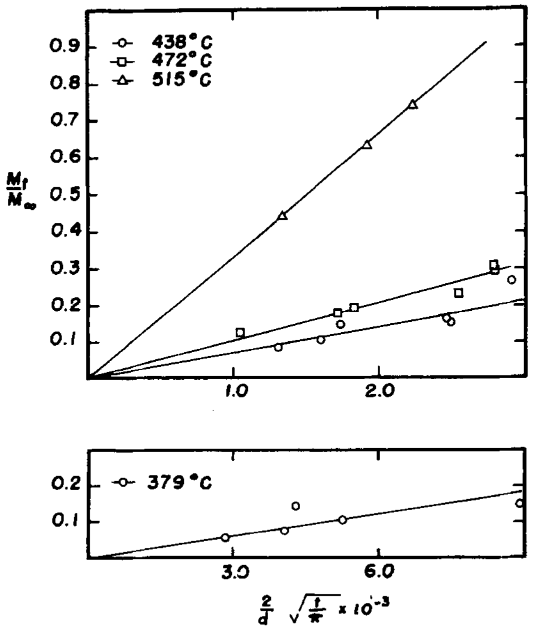

FIG. 2. Desorption of OH^- from $KCl:OH$ crystals at an initial external pressure of 1/3 atm Cl_2.

OH^-. All absorption measurements were made with a prepurified N_2 flushed Perkin-Elmer 450 spectrophotometer.† The samples were repositioned in the spectrophotometer beam several times to assess the homogeneity of the OH^- concentration within the sample. If the absorbance varied more than 2% over the sample, that sample was rejected. Two groups of these sample tubes were prepared. One group in which the crystals were sealed in vacuum at 1×10^{-6} Torr. Similar to conditions sometimes used for diffusion and conductivity measurements. The other group sealed under 1/3 atm of Cl_2 as sometimes used in cation diffusion studies. Seven of the sample tubes were placed in a preheated Marshall metallurgical testing furnace. The temperature was controlled within ±1°C by a Wheelco model 407 controller and a Wheelco SCR power controller model 620A. The eighth tube was kept to assess whether the sealing process and exposure to the various atmospheres affected the OH^- concentration. No effects were found.

Desorption anneals at four different temperatures were conducted on each group of tubes. At the lower temperatures the tubes were removed from the furnace at about 24 h intervals. At the higher temperatures the samples were removed at about 6 h intervals. The sample tubes cooled in air and were opened just prior to the second spectrophotometric measurement of OH^- concentration.

An opaque mask covered the edges of the crystal during the second absorption measurements. This eliminates the transverse concentration gradients due to diffusion from the edges of the crystal plate.

TABLE I

DIFFUSION COEFFICIENTS OF OH^- IN KCl

Temp. (°C)	D(cm²/sec)	Standard deviation
Vacuum		
599	9.31×10^{-10}	1.53×10^{-10}
647	3.53×10^{-9}	0.59×10^{-9}
672	9.50×10^{-9}	0.23×10^{-9}
697	2.28×10^{-8}	0.46×10^{-8}
Chlorine atmosphere		
379	3.96×10^{-10}	0.41×10^{-10}
438	4.97×10^{-9}	0.15×10^{-9}
472	1.04×10^{-8}	0.01×10^{-8}
515	1.09×10^{-8}	0.00

This is necessary if the experiment is to approximate a one-dimensional diffusion as given in Eq. (3).

Figures 1 and 2 show M_t/M_∞ vs $(4t)^{1/2}/\pi d^2)$. Those samples diffused under 1/3 atm of Cl_2 show good agreement with the solution of Ficks second law for the boundary conditions of these experiments. The vacuum experiments show much more scatter. This will be discussed later.

Table I gives the values of the diffusion coefficient calculated by least-squares analysis of the data at each temperature.

The computed standard error in the absorption measurements is 2.1%. This includes error due to transverse concentration gradients. At high temperatures a small systematic error arises from evaporation of some KCl. The change in crystal thickness due to this effect could not be detected on remeasurement of crystal thickness and no correction was made for it.

Discussion

When the data in Table I are plotted as $\log D$ vs $1/T$ (Fig. 3) the diffusion coefficient can be described by the equations

$$D_{OH^-} = 3.0 \times 10^5 \exp(-1.95\,\mathrm{eV}/kT) \qquad (4)$$

in 1/3 atm Cl_2, and by

$$D_{OH^-} = 1.2 \times 10^3 \exp(-2.09\,\mathrm{eV}/kT) \qquad (5)$$

in vacuum.

Figures 1 and 2 clearly show diffusion in a Cl_2 atmosphere provides more reliable data than diffusion in a vacuum.

The problem that exists in the desorption of OH^- into a vacuum is due to poorly controlled boundary conditions. Unless a sink is provided for the KOH formed as the OH^- reaches the surface the boundary conditions imposed by Eq. (3) cannot be met. If not removed the KOH on the surface can either diffuse back into the crystal or it can vaporize and settle on a colder portion of the sample tube or back on the crystal. Vaporization would not be very effective in removing KOH because of the low vapor pressure of KOH at these temperatures. The above processes would all cause the diffusion coefficient to appear smaller than when the boundary conditions of Eq. (3) are met. Because the factors governing the desorption cannot be well controlled, considerable scatter will occur in the data.

When Cl_2 is present the KOH formed on the surface can react to produce KCl. Thus the back diffusion is eliminated and the OH^- concentration in the atmosphere surrounding the crystal remains

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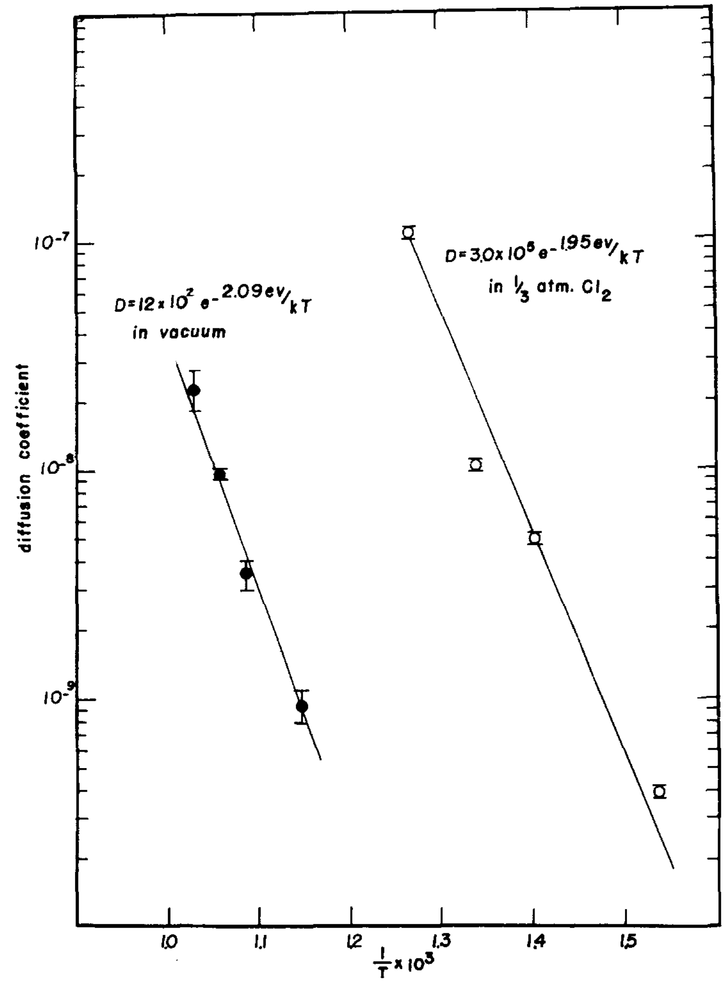

FIG. 3. Diffusion coefficients of OH^- in KCl as a function of $1/T$.

negligible. According to Fuller's data (*8*) the Cl^- diffusion coefficient in this temperature range will be approximately 10^{-12} at the highest diffusion temperature and 10^{-15} at the lowest temperature. [Assuming the $D(T)$ equation is still valid at 380°C.] This experiment more nearly meets the necessary boundary conditions, and we consider Eq. (4) to represent the correct diffusion coefficient.

These boundary condition problems should affect the preexponential term more markedly than the migration energy as was found in Eqs. (4) and (5). The preexponential term is surprisingly large in both equations. However, the migration energy is reasonable. Since ionic species diffuse in the alkali halides by a vacancy mechanism it is usually assumed that the migration energy of a monovalent ion is composed of a jump energy E_a and one-half the energy of formation of a Schottky defect, h_s. Taking Fuller's (*8*) value of 2.31 eV as h_s we obtain $E_a = 0.79$ eV. This compares with $E_a = 0.95$ for Cl^- in KCl (*8*). The hydroxide ion is somewhat smaller than the chloride ion; so, it's reasonable to Expect $E_a(OH^-) < E_a(Cl^-)$.

These experiments show OH^- to be very mobile in KCl compared to other monovalent ions. It moves even more easily than Li^+ (*12*). This mobility and its tendency to form relatively stable complexes with aliovalent cations explains the ease with which it can compensate cationic impurities. Unfortunately when it does it loses its most easily detectable characteristic, the 204 nm absorption band.

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