

Conduction and Tritium Diffusion Studies in Single Crystals of Potassium Hydrogen Sulfate

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Direct-current electrical conductivity of single crystals of KHSO_4 doped with 5, 11, 30, and 437 ppm of cobalt-II is studied in the temperature range 25 to 165°C. The point defect parameters are calculated by graphical analysis of the conductivity data. Various parameters are obtained: enthalpy for the migration of proton (referred to as the enthalpy for the rotation of HSO_4 ion), $H_M = 0.55 \pm 0.01$ eV; the enthalpy for the formation of the intrinsic defects (referred to as the enthalpy for the breaking of the HSO_4 dimers), $H_F = 1.30 \pm 0.01$ eV; and the enthalpy for the impurity-vacancy association $H_a = -0.14 \pm 0.01$ eV. The tritium diffusion studies in the pure KHSO_4 single crystals give 0.22 ± 0.01 eV and -1.09×10^{-3} eV K^{-1} as the activation enthalpy and entropy for the process, respectively. The Nernst-Einstein relation is not obeyed. The mechanisms for the conduction and diffusion processes in this crystal are discussed.

Introduction

The considerable interest devoted to the study of electrical conduction in hydrogen-bonded crystals (1-11) in the last few years has led to very important results concerning both the transport number of protons and the conduction mechanism. Similarly, some authors (3, 11) have also compared the results of electrical conduction and tritium self-diffusion studies to elucidate the mechanism of proton conduction in H-bonded crystals. Most of this work is focused on K^+ and NH_4^+ salts of acid phosphates (1, 3-8) and acid arsenates (9). However, no attention has been paid to the study of single crystals of KHSO_4 . The crystal structure, however, has been studied by various authors (20-23). According to Loopstra and MacGillavry (20) the crystal is orthorhombic. There are two types of HSO_4^- tetrahedra in the crystal resulting from the hydrogen bond linkage (S_1 and S_2). S_1 tetrahedra exist in pairs and are linked by a double hydrogen bridge on both sides of the symmetry centre, forming a double molecule (as frequently found with organic molecules

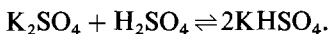
containing carboxyl group). S_2 tetrahedra, however, are linked by a bridge repeating through the glide plane (100) thus forming an infinite chain along the a -axis. This type of infinite H-bond linkage is similar to the one found in KH_2PO_4 (17). The presence of S_1 - and S_2 -type tetrahedra, therefore, makes it interesting to investigate the mechanisms of conduction and diffusion in the KHSO_4 single crystal. Acid phosphate, which has S_2 -tetrahedra, does not show any knee in the conduction plot (3, 6, 17), the Einstein relationship is not obeyed (3, 17), and doped crystals also show no break in the conductivity plot (17). Whether KHSO_4 which has S_1 - and S_2 -type tetrahedra would behave in a manner similar to acid phosphate is worth examining.

In our earlier work (12) we established that KHSO_4 is a pure protonic conductor and possesses an irreversible phase transition around 170°C. The present paper deals with the study of the quantitative effect of a divalent dopant (Co-II) on the electrical conduction of KHSO_4 single crystals and the various point defect parameters. Tritium diffusion is also studied to understand the mechanisms of

conduction and diffusion processes in this crystal.

Experimental Procedure and Results

A pure crystal of KHSO_4 (A.R. grade KHSO_4 was freshly crystallized three times to exclude the presence of any other cations) was grown by the slow evaporation technique. Attempts to grow single crystals were made at different pH values and different temperatures. At pH 1.5, flakes or needle-shaped crystals were obtained. At pH values less than one, good hexagonal thin plates resulted. The acid concentration was essential to force the equilibrium toward KHSO_4 ; otherwise, one gets a crystal of only K_2SO_4 :



Pure crystals and crystals doped with (Co-II) were, therefore, grown at pH values of less than one. $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ was used as a dopant and $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ solution (in H_2SO_4) labeled with ^{60}Co was used as a tracer. The number of

defects depends upon the Co-II concentration only as all other conditions were kept constant.

The tracer technique was developed to find out the amount of dopant present in the grown crystal and also to calculate the distribution coefficient of dopant between the saturate solution from which the crystal was grown and the grown crystals (17). The amount of activity, and hence, the number of Co-II atoms present in each crystal, and the distribution coefficient of Co-II in each grown crystal with respect to its mother liquid were calculated as discussed elsewhere (17). The distribution coefficient was found to be 3.49×10^{-2} . The conductivity of Co-II-doped single crystals was measured along the *c*-axis (temperature range, 25–165°C). No measurements were made above this temperature because the crystal undergoes a phase transition around 170°C (12). The crystal plate was sandwiched between two platinum electrodes in such a manner that surface conduction was minimized by using the guard ring technique (12). The conductivity plots ($\log \sigma T$

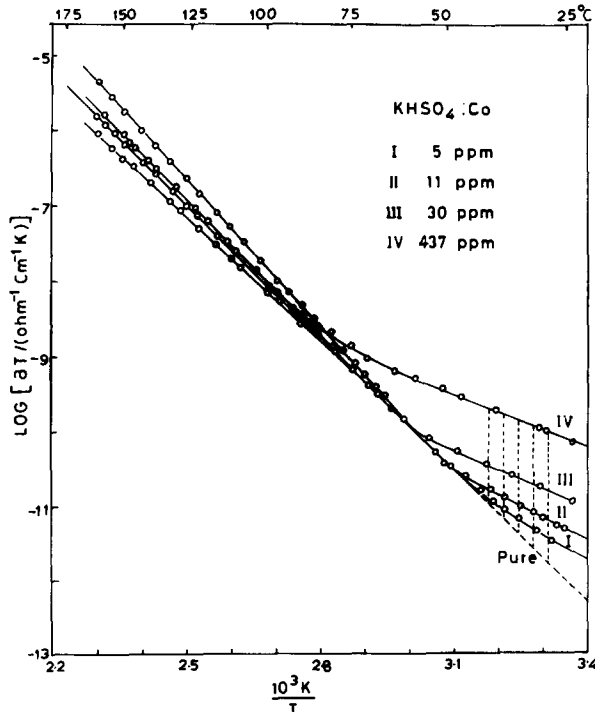


FIG. 1. Conductivity curves of KHSO_4 single crystals doped with divalent cation (cobalt-II).

TABLE I

ENTHALPY H , INTERCEPT A , AND ENTROPY CHANGE ΔS FOR CONDUCTIVITY (ALONG c -AXIS) IN KHSO_4 SINGLE CRYSTAL^a

Single KHSO_4 doped with Co-II containing				
	5 ppm	11 ppm	30 ppm	437 ppm
$H_{\text{obs(H)}} \text{ (eV)}$	1.29 ± 0.01	1.08 ± 0.01	1.21 ± 0.01	1.15 ± 0.01
$A_{\text{H}} \text{ (ohm}^{-1} \text{ cm}^{-1}\text{)}$	4.508×10^9	3.369×10^6	2.031×10^8	3.195×10^7
$\Delta S_{\text{H}} \text{ (eV K}^{-1}\text{)}$	8.56×10^{-4}	2.67×10^{-4}	6.03×10^{-4}	4.52×10^{-4}
$H_{\text{obs(L)}} \text{ (eV)}$	0.89 ± 0.01	0.49 ± 0.02	0.48 ± 0.01	0.48 ± 0.01
$A_{\text{L}} \text{ (ohm}^{-1} \text{ cm}^{-1}\text{)}$	3.024×10^{-3}	7.998×10^{-3}	2.040×10^{-3}	8.453×10^{-3}
$\Delta S_{\text{L}} \text{ (eV K}^{-1}\text{)}$	-3.048×10^{-4}	-1.54×10^{-3}	-1.46×10^{-3}	-1.35×10^{-3}

^a $\sigma T = A^* \exp(-H/kT) \text{ ohm}^{-1} \text{ cm}^{-1} \text{ K}$; L, lower temperature region; H, higher temperature region.

versus $1/T$) for crystals containing 5, 11, 30, and 437 ppm of Co-II are shown in Fig. 1.

The slopes and the intercepts of linear plots for the high and the low temperature regions for each doped crystal were calculated by the method of least squares (using a computer)

and the values of enthalpy and entropy obtained from these values were calculated (Table I).

The sectioning technique was used to study the self-diffusion of tritium along the c -axis (temperature range, 90–160°C) of a KHSO_4

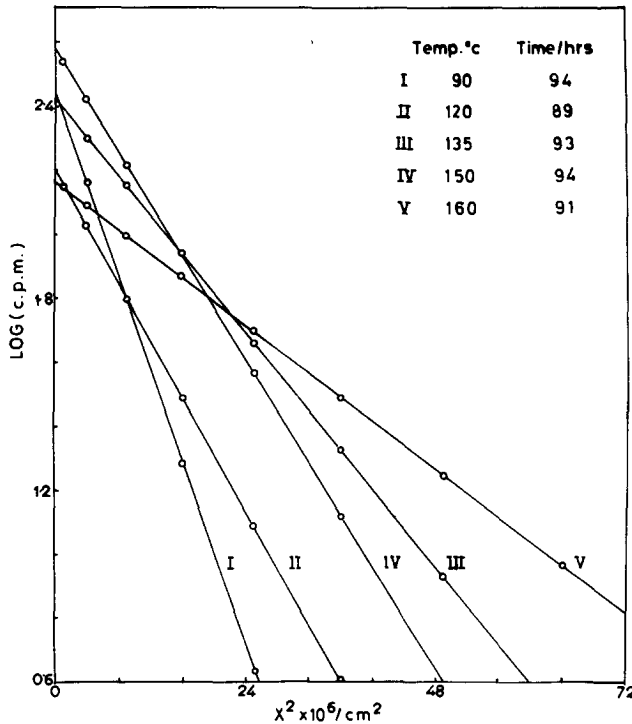


FIG. 2. Distribution of tritium in the KHSO_4 single crystal at various temperatures.

TABLE II
VARIATION OF DIFFUSION COEFFICIENT WITH
TEMPERATURE

T (°C)	D ($\text{cm}^2 \text{sec}^{-1} \times 10^{-11}$)	D_0 ($\text{cm}^2 \text{sec}^{-1}$)
90	0.974	
120	1.701	
133	2.084	9.620×10^{-9}
150	1.815	
160	4.057	

single crystal. The technique for this study was similar to that reported elsewhere (3). Annealing of the crystal for diffusion was carried out in a dry nitrogen atmosphere to avoid the exchange of tritium with atmospheric moisture. To measure the diffused activity, 10- μm cuttings of the crystal were collected in 20-ml counting vials and each vial was counted by the liquid scintillation coincidence counter (ECIL) after adding 15.0 ml of dioxane (AR grade), 2.0 ml of liquid scintillator (NE 210), and 1.0 g of silica gel. This method gave an efficiency of 35% for tritium counting.

The log of activity (C), in counts per minute of each vial was plotted versus (thickness) (2) and from the slope of the linear plot (Fig. 2), the diffusion coefficient D at temperature T was calculated by using the equation (3):

$$C(X, t) = \frac{C_0}{(\pi Dt)^{1/2}} \exp\left(-\frac{X^2}{4Dt}\right), \quad (1)$$

where, C , C_0 , and t are the activity at distance X , activity at $X = 0$, and the time for annealing respectively. The values of the diffusion coefficient obtained at different temperatures are given in Table II.

Discussion

Figure 1 shows a break in each conductivity curve, and the temperature at which it occurs depends upon the concentration of dopant present in the crystal. Because KHSO_4 has no phase transition in the temperature range 25–165°C and because the conductivity in the

low temperature region increases with increase of temperature, the break in the conductivity plot is attributed to a point of separation of intrinsic and extrinsic regions. It is usual practice to assume that the observed enthalpy of conductance in the high temperature region is a combination of enthalpy for formation (H_F) of defects and their migration H_m (i.e., $H_{\text{obs}} = 0.5 H_F + H_m$), whereas in the low temperature region, it is due to the enthalpy for migration of defect. The latter is true only if in the low temperature region, i.e., in the extrinsic region the defects have not formed impurity–vacancy complexes. If there is such formation, Drefus (13) has shown that the enthalpy in the extrinsic region should be expressed as $H_{\text{obs}(1)} = H_m + 0.5 H_a$ where H_a is the enthalpy for the formation of the impurity–vacancy complex. In order to calculate H_F , the value of H_m , and therefore the value of H_a , must be calculated by the isotherm equation developed for divalent impurity by Lidiard (14). The isotherm equation is given as

$$C = (\theta + 1)x_0 \frac{\sigma_c}{\sigma_0} + (\theta + 1)^2 x_0^2 K_2(T) \left(\frac{\sigma_c}{\sigma_0}\right)^2 \quad (2)$$

or

$$C/(\sigma_c/\sigma_0) = (\theta + 1)x_0 + (\theta + 1)^2 x_0^2 K_2(T) \left(\frac{\sigma_c}{\sigma_0}\right), \quad (3)$$

where C is the concentration of dopant, θ is μ_2/μ_1 (μ_2 and μ_1 are the mobilities of two complementary types of defects), x_0 is the product of x_1 and x_2 (x_1 and x_2 are the mole fractions of two complementary defects), $K_2(T)$ is the association constant of the impurity–vacancy complex, and σ_0 and σ_c are the conductivities for the ideally pure and the doped crystal, which are given by the general relations:

$$\sigma_0 = qN x_0 (\mu_1 + \mu_2) \quad (4)$$

and

$$\sigma_c = qN (x_1 \mu_1 + \mu_2 x_2). \quad (5)$$

If μ_2 is zero, i.e., if only the cation is responsible for the conduction, then Eq. (4) reduces to

$$\sigma_0 = qN x_0 \mu_1, \quad (6)$$

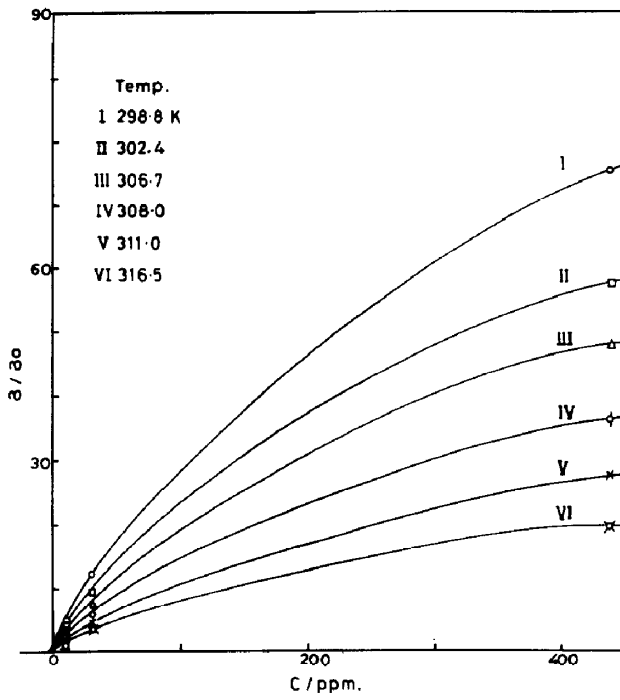


FIG. 3. Conductivity isotherms for KHSO_4 : cobalt-II.

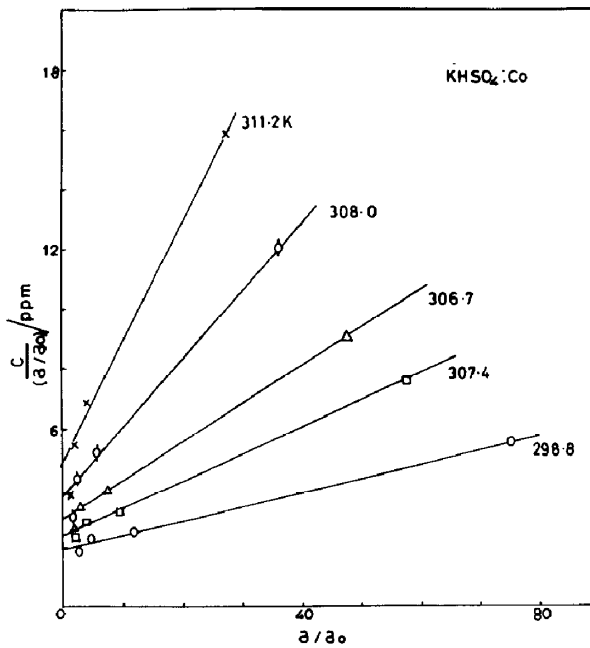


FIG. 4. Variation of $C/(\sigma_c/\sigma_0)$ with σ_c/σ_0 .

TABLE III

VARIATION OF INTRINSIC DEFECT CONCENTRATION x_0 AND ASSOCIATION CONSTANT K_2 WITH TEMPERATURE^a

T (°K)	x_0 (ppm)	K_2 ($\times 10^{-2}$)
299.0	1.9	1.30
302.0	2.4	1.58
306.0	3.0	1.39
308.0	3.0	1.56
311.2	4.9	1.72

^a Log x_0 versus $1/T$ and log K_2 versus $1/T$ were plotted (Figs. 5 and 6) to calculate the values of H_F and $H_a(16)$ from their respective slopes. These values came out to be 1.18 ± 0.01 and -0.14 ± 0.01 eV, respectively.

where q is the charge on the ion and N is the number of conducting defects.

For the present work the values of σ_0 were calculated graphically by extrapolating the intrinsic region to the lower temperature

region (Fig. 1), and the values of σ_c/σ_0 versus C were plotted (Fig. 3) at different temperatures. The method of extrapolating to lower temperature eliminates any error due to the presence of any inherent impurities or defects which might be present in the crystal.

These parabolic isotherms meet at $\sigma_c/\sigma_0 = 1$ and show a minimum at its zero value (for negative C). By applying the condition (16) of minima to isotherm Eq. (2), i.e., $\sigma_c/\sigma_0 = 2\theta^{1/2}/(\theta - 1)$, θ came out to be 0. Substitution of $\theta = 0$ in the transport number relationship:

$$t_1 = \frac{\mu_1}{\mu_2 + \mu_1} = \frac{1}{1 + \theta} \quad (7)$$

gives the transport number of the cation (proton) as 1, which is in agreement with the value of t_{H^+} obtained (12) from coulometric studies.

The isotherms $C/(\sigma_c/\sigma_0)$ versus (σ_c/σ_0) plotted at different temperatures are shown in Fig. 4. The values of x_0 and $K_2(T)$ at these temperatures were calculated from the inter-

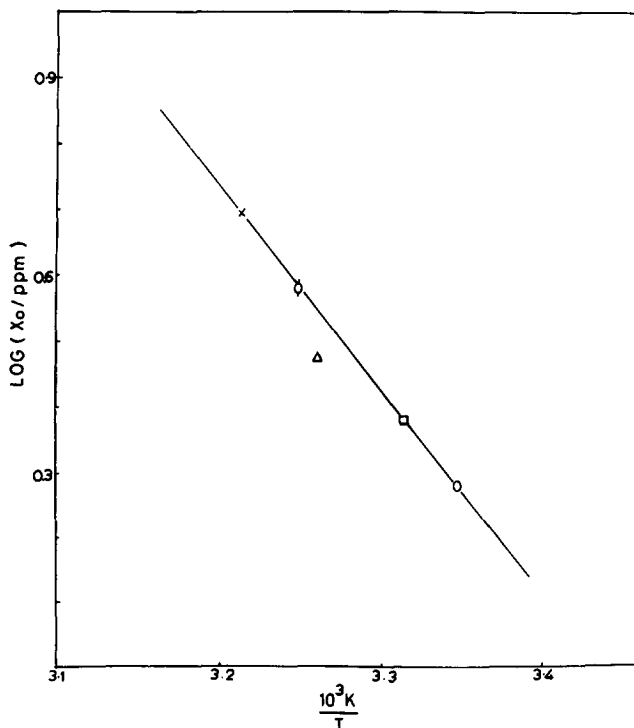


FIG. 5. Variation of log x_0 with $1/T$ for the cobalt-II-doped KHSO_4 single crystal.

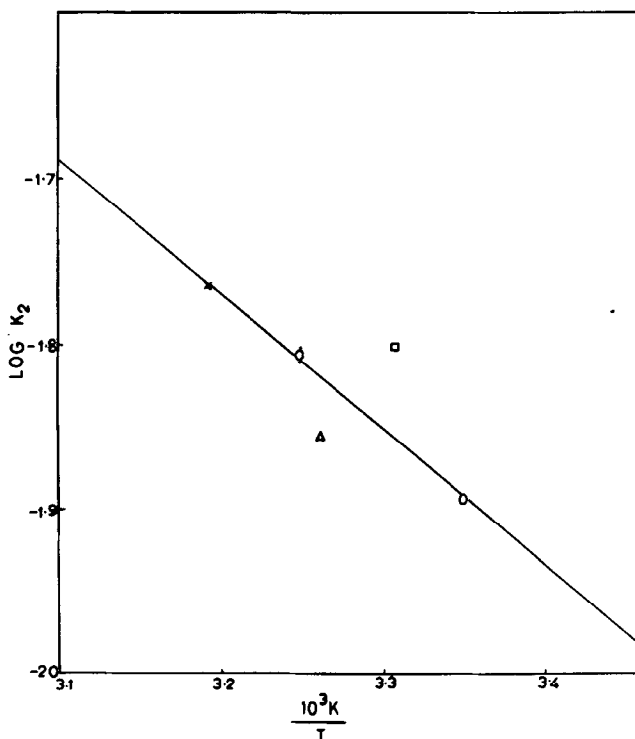


FIG. 6. Variation of $\log K_2$ with $1/T$ for the cobalt-II-doped KHSO_4 single crystal.

cept $[(\theta + 1)x_0]$ and the slope $[(\theta + 1)^2 x_0 K_2(T)]$ of these isotherms (Table III).

The slight positive values of $K_2(T)$ suggest the existence of an impurity-vacancy association. However, the slight negative value of H_a (-0.14 ± 0.01 eV) suggests that dissociation is an overall energy-releasing process. Substitution of H_1 and H_a in relation $H_{\text{obs}(1)} = H_m + 0.5 H_a$ as suggested by Drefus (13) gave 0.55 ± 0.01 eV as the enthalpy for the migration (H_m) of point defects (i.e., proton). Similarly, the substitution of enthalpies $H_{\text{obs}(H)}$ and H_m in the relation (13), $H_{\text{obs}(H)} = H_m + 0.5 H_F$ gave 1.30 ± 0.01 eV as the enthalpy for the formation (H_F) of the intrinsic defects, which is comparable to the value 1.18 ± 0.01 eV obtained from the isotherm calculation.

Comparison of Conduction and Diffusion Data

From the plot of $\log D$ versus $1/T$ (Fig. 7, I) the enthalpy for the tritium diffusion

process was found to be 0.22 ± 0.01 eV, giving a general diffusion equation

$$D = 9.62 \times 10^{-2} \exp \left(- \frac{0.22 \pm 0.01}{kT} \right) \text{cm}^2 \text{sec}^{-1}.$$

The entropy change for the process was found to be -1.09×10^{-3} eV K^{-1} .

The enthalpy, 0.22 eV, for the diffusion process is lower than the enthalpy, 1.20 eV, obtained from the conduction process and the plot of $\log D$ versus $1/T$ (Fig. 7, II) for values of D calculated from the Nernst-Einstein relation ($\sigma/D = Nq^2/kT$) is not parallel to the experimentally observed plot (Fig. 7, I). This is what one would expect when the enthalpy values for the conduction and the diffusion processes are different. The two factors suggest that the conduction and the diffusion processes are controlled by two different mechanisms. This is in accordance with the results obtained from other H-bonded crystals:

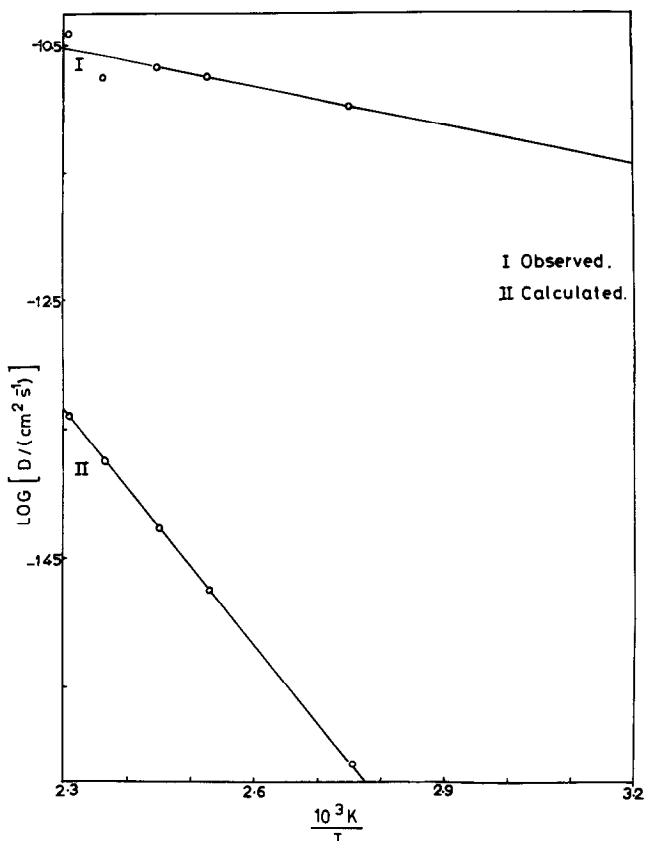


Fig. 7. Comparison of observed and calculated (using the Nernst-Einstein relationship) diffusion coefficients.

ADP (3), ice (11), and KDP (17). The mechanisms for these processes can, however, be explained by considering the structure of KHSO_4 crystal.

KHSO_4 crystal has a dimer and a long chain type structure (20-23). If the conduction process is due to proton migration through the long chain tetrahedron, then one should not have obtained any knee in the conductivity plot (as is the case with KDP, ADP (3, 17). On the other hand, if the dimer takes part in the conduction process, then there should be a two-stage mechanism for proton migration: First, the dimer should break and then be followed by orientation of the chain to align properly with the long chain H-bonds. The breakage of the dimer should require a high activation enthalpy, whereas the migration of protons through the H-bond chain would require lower enthalpy and would be equivalent to the enthalpy for rotation of HSO_4

tetrahedron about its axis of rotation (17, 19). The enthalpy for breakage of the dimer, therefore, can be considered as 1.30 eV (i.e., H_F) and the enthalpy for the rotation of HSO_4 ions can be considered as 0.55 eV (i.e., H_m). On the other hand, like KDP and ADP (17), the enthalpy for the tritium diffusion should be equivalent to the activation energy required for the exchange of tritium with hydrogen atom in an $\text{O}\dots\text{H T}\dots\text{O}$ situation. Therefore, the mechanism for the tritium diffusion is expected to be different from that for the conductance process. This is supported by the fact that the Einstein relationship is not obeyed in the KHSO_4 crystal.

The next pertinent question is to understand the role of Co-II dopant in the conduction process. Considering the ionic size of this dopant, one is tempted to expect it to occupy the K^+ ion lattice and create a proton vacancy

in the HSO_4^- monomer or dimer. The creation of proton vacancies is supported by the fact that the conductivity value in the extrinsic region increases with increasing dopant concentration. Because the transport number for the proton in KHSO_4 is one (12), dopant Co-II is not expected to take part in the conduction process.

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