THE ACTIVATION ENERGY OF dc ELECTRICAL
CONDUCTIVITY OF ICE DOPED WITH HF AND NH_3

by

S. Y. Chai
P. O. Vogelhut

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Abstract. The activation energies of ice doped with varying amounts of impurities were investigated using sintered platinum electrodes. For both types of impurities a minimum in the activation energy was found at a concentration of 10^{-4} M. The experimental arrangement and possible reasons for the existence of a minimum in activation energy are discussed.

The activation energy of the dc electrical conductivity in pure ice has been investigated by many authors.[1,2] There seems to be some disagreement about the values of the activation energy owing to difficulties in the interpretation of the data and possible sources of error, as well as establishment of a good ohmic contact with the sample substance. The error that is hardest to identify stems from the difficulty of growing very pure single crystals of ice. Since many of the hardships in a study of pure ice result from measurements that are very susceptible to errors due to the possible presence of small amounts of impurities, valuable information can be obtained from an investigation of doped ice.

To arrive at a theoretical analysis of the proton transport mechanism in ice (analogous to the basic theory of electronic semiconductors as was proposed by Eigen and De Maeyer[3]) it is necessary to investigate the dc conductivity of ice doped with "hydroxide" and "hydronium" ions at varying concentrations and at several temperatures. A set of such data for doped ice is not available as yet due to the above-mentioned difficulty of obtaining reproducible results;

in the case of doped samples this difficulty consists mainly in the measurement of a time-dependent current (nonohmic contact) caused by electrode polarization and space charge effects.

The first obscuring effect--electrode polarization-- can be somewhat alleviated by the use of "sandwich" electrodes, a method developed in studies of electronic semiconductors and adapted for ice studies by some investigators.[4, 5] In our study we selected as a suitable ohmic contact sintered porous platinum disks with a porosity of 35 percent, manufactured by Engelhard Industries, Inc. The electrodes were soaked in solutions of HF or NH_3 at concentrations one hundred times those of the actual samples. This method proved not to be suitable in the case of pure ice samples.

The second effect--space charge accumulation--leads to considerable changes of the potential distribution in the ice sample and to a time-dependent current. This effect seems to be due mainly to dissolved air and movement of grain boundaries of the crystals. The crystals were allowed to age for one day before measurement, thereby removing most major imperfections in the grain structure. The internal field distribution was measured by placing five equally spaced platinum probes in the sample and monitoring the potential distribution with a Keithley differential voltmeter model 660; the electric field was found to vary linearly with distance between the electrodes.

Solutions of HF and NH_3 were prepared using distilled and demineralized water . The ice samples were grown on a platinum disk fitted into a copper block at an average rate of 0. 5 mm per minute. Experiments were carried out in the temperature range between -5°C and -20°C. After the ice crystal was grown, the porous electrode was attached by pressure, and the sample aged for 30 hours. Currents were measured with a Hewelitt-Packard Model 425 A micro-ammeter and a Varian recorder in order to

observe time-dependence of the current. Most measurements were nearly constant with time; in those cases where a sudden change appeared only the instantaneous value of current at the first application of the electric field was used, since the discontinuity in the reading seemed to stem from the appearance of cracks due to thermal shock of the sample by ohmic heating. A change of sample temperature due to resistive heating was precluded by applying the electric field for 30 seconds only after an intermittent period of 90 seconds. Currents were recorded at electric fields of 10, 50, 100, and 200 volts and at two polarities; the average value was used for further computations. In almost all the experiments the currents varied linearly with the applied electric field.

Analysis of the data showed that the conductivity of the sample follows the relation of a typical semiconductor:

$$\sigma = \sigma_0 \exp(-E/kT).$$

The activation energy E was calculated using this expression. Figs. 1 and 2 show the change in conductivity of the samples as a function of the amount of doping with HF and NH_3, respectively; Fig. 3 shows the variation of the activation energy as a function of concentration of HF and NH_3. The minimum of the activation energy at 10^{-4} M concentration of impurities corresponds to the critical concentration at which the polarization mechanism responsible for the dielectric constant changes abruptly. [5]

The results indicate that the dc conductivity of doped ice at constant temperature is not directly proportional to the concentration of impurities. Since the conductivity is a function of both impurity content and charge-carrier mobility, it is believed that the mobility causes the nonlinear change in conductivity with the concentration of impurities. Unfortunately, conductivity in the region of impurity content of less than 10^{-5} M concentration cannot be measured accurately

as yet. However, there should exist an inversion point to decrease the conductivity such that it can be extrapolated to the pure ice conductivity of 10^{-8} to 10^{-9} ohm^{-1} cm^{-1}.

Some authors[6] have found a similar change in activation energy with concentration of impurities in the doped ice. The evidence now supports the conclusion that lower activation energies are associated with higher impurity content within the region of less than 10^{-4} M impurity concentration. The activation energy of dc conductivity in pure ice is reported to lie between 0.5 ev. and 1.2 ev.[1,2] Our data also justify this point of view.

It is believed that the dc conductivity in doped ice requires proton transfer through the hydrogen bond by tunneling and the orientational motion of water molecules to maintain the favorable path for further transfer of protons.[5] Hence the activation energy includes the proton tunneling energy and the water molecule's rotational energy (with the aid of double (D) and vacant (L) defects) as well as the dissociation energy of the impurity molecules. Because of the many processes involved it is not yet possible to determine which portion of the energy contributes to the change in activation energy with impurity concentration. The change in potential curves for protons in the hydrogen bond of O-F and O-N from that in O-O bonds[7] together with an analysis of the rotational mechanism of D and L defects may lead to the explanation of the curves represented in Fig. 3.

It is possible to consider that at concentrations higher than 10^{-4} M the rate of the proton transport mechanism is controlled by the rate of water molecule rotation. As the impurity concentration increases, the number of D or L defects also increases and higher activation energy results. This trend may exist because the required number of water-molecule rotations to produce a favorable proton path increases with concentration of impurities. As the concentration

is lowered below 10^{-4} M, the rate determining factor will be the proton tunneling process because the number of defects that undergo rotation is reduced eventually to a negligible amount. The proton tunneling seems more difficult as the numbers of impurities decrease. The proton tunneling becomes harder as the structure becomes more nearly perfect, which seems to be due to the higher proton tunneling energy through O-O hydrogen bonds as compared to that of O-N or O-F bonds.

Qualitatively, the lowest activation energy at 10^{-4} M impurity concentration may be interpreted in terms of a change in rate-determining step from orientational motion to proton tunneling through the hydrogen bonds.

S. Y. CHAI
P. O. VOGELHUT

Department of Electrical Engineering
Electronics Research Laboratory
University of California, Berkeley

References and Notes

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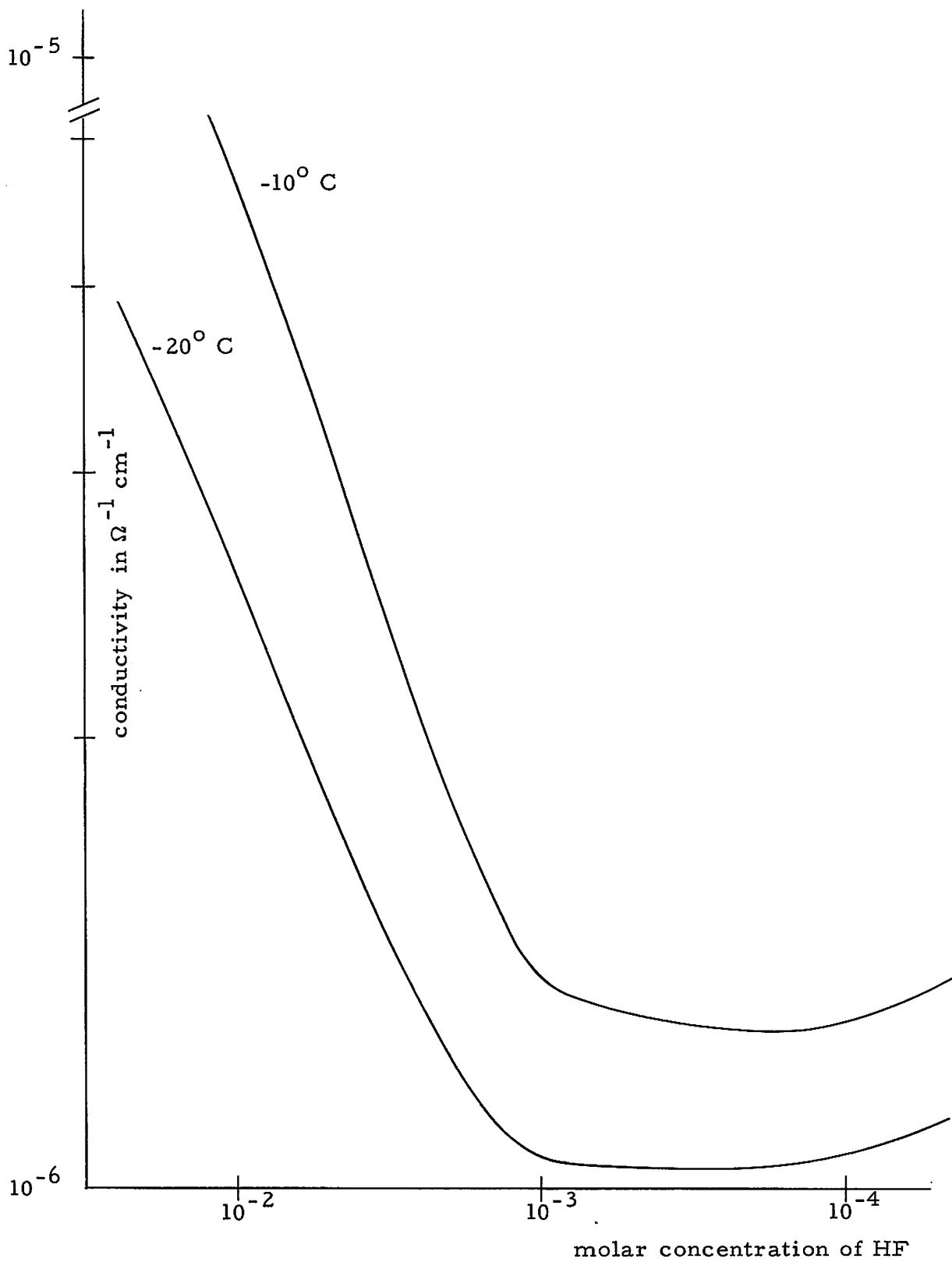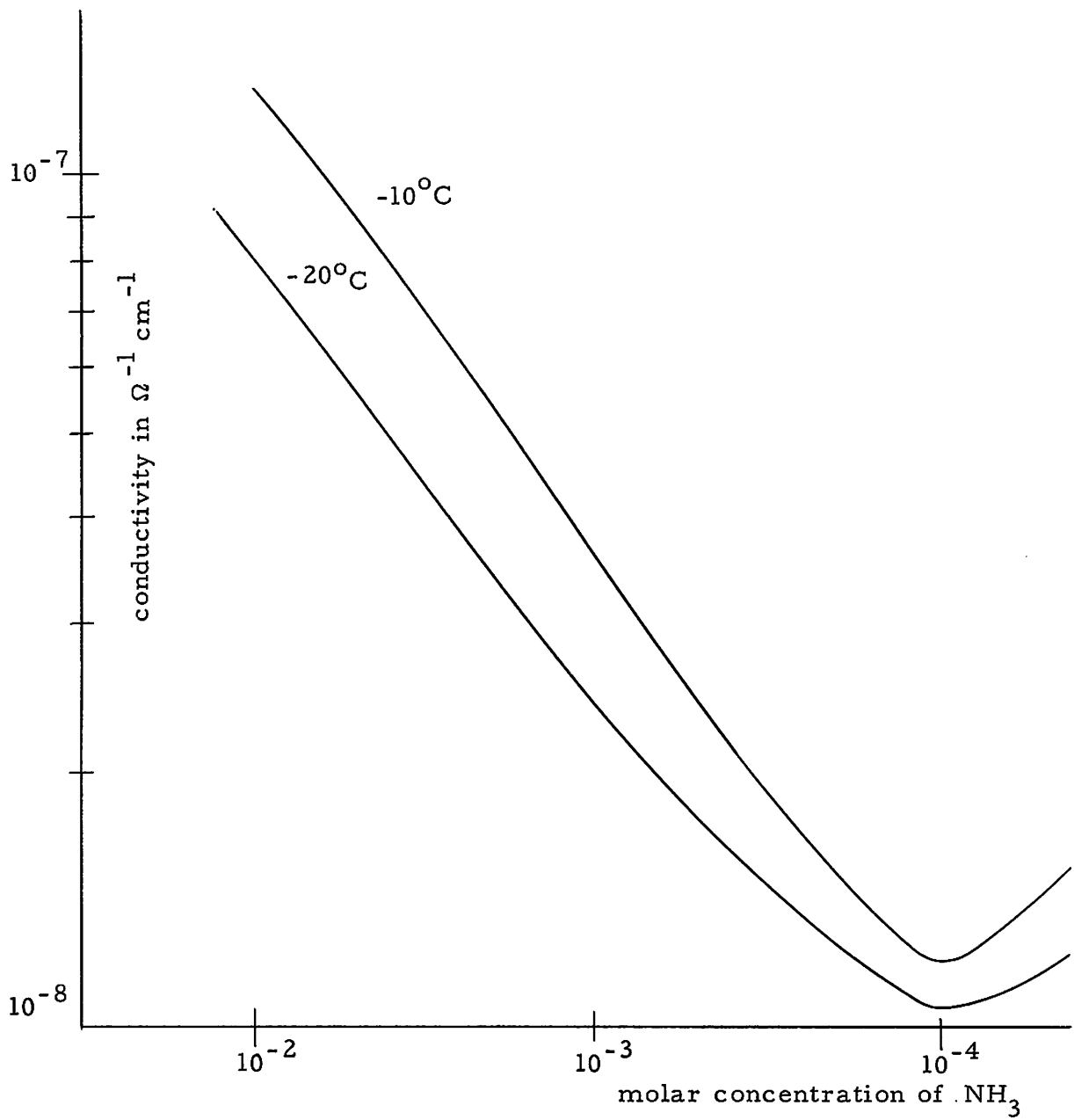Fig. 1. Conductivity vs. HF concentration.
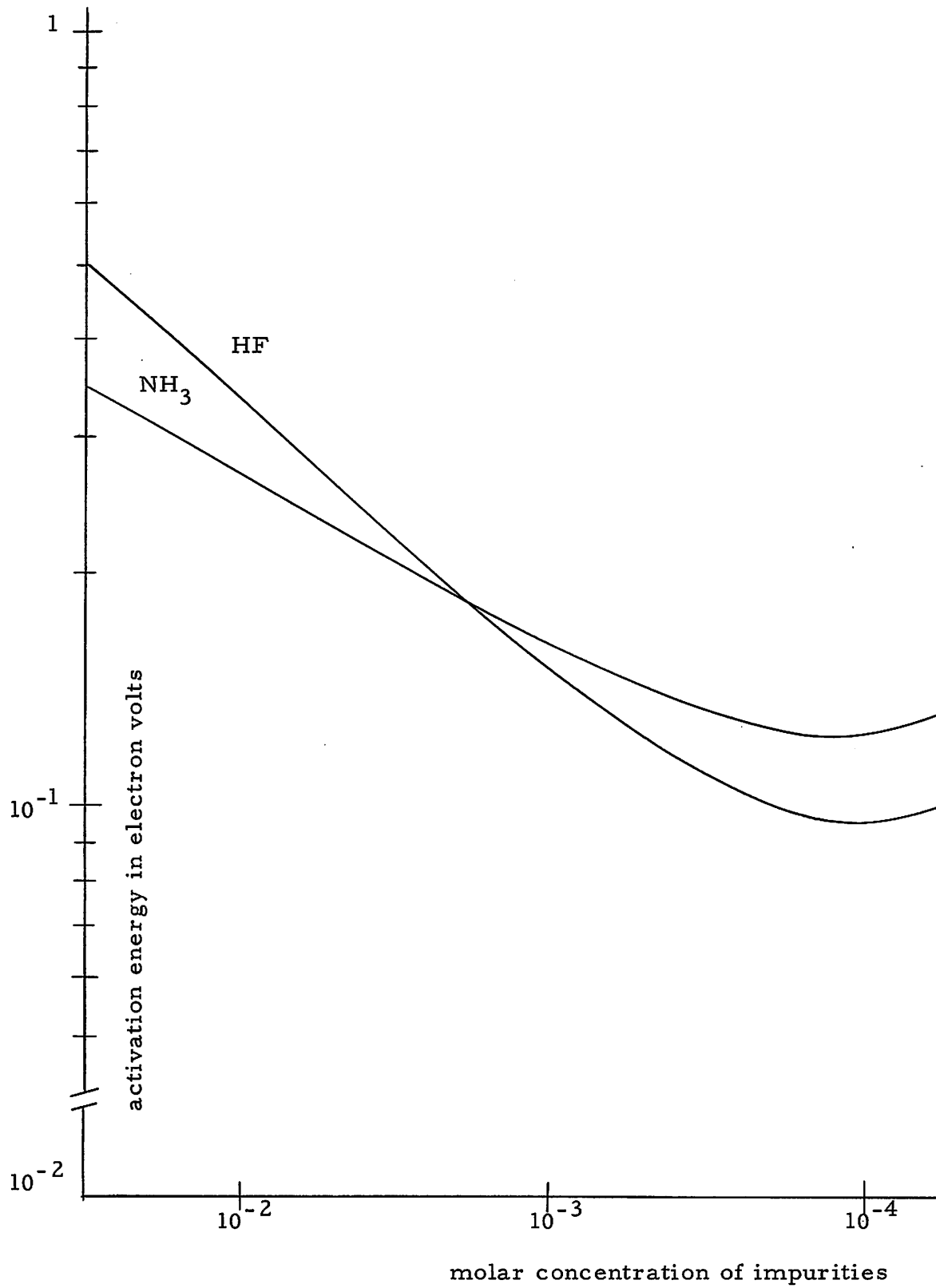
Fig. 2. Conductivity vs. NH_3 concentration.

Fig. 3. Impurity concentration vs. activation energy.