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Solid Solutions of Ice and NH_4F and Their Dielectric Properties*

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(Received June 27, 1955)

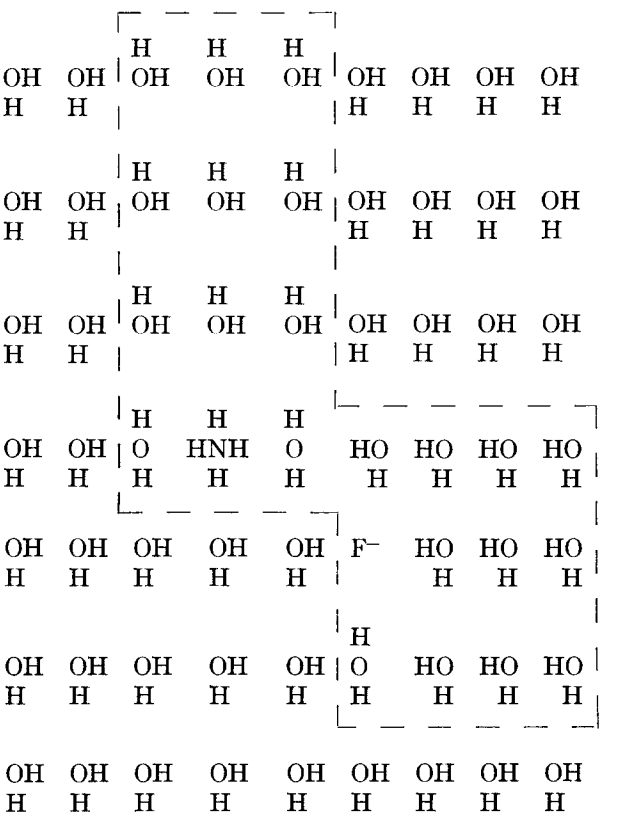
The solidus curve for the system H_2O-NH_4F was partly determined by means of chemical analyses, heating curves and a dilatometric method, and partly estimated from the liquidus curve using a thermodynamic relation. The solubility limit thus estimated is roughly 10%. The dielectric relaxation times, τ, of solid solutions of ice containing 0.002 to 10 weight percent NH_4F were measured at temperatures of about $-60°$ to $-10°$C. The activation energies for dipole rotation were only about 4 kcal/mole as compared with 13 kcal/mole in pure ice. At low concentrations the frequency factor increases with increasing concentration of NH_4F. At high concentrations of NH_4F this trend is reversed.

I. SOLUBILITY OF NH_4F IN ICE

a. Introduction

BECAUSE the shape and dimensions of water molecules and their binding forces differ appreciably from most other compounds, the possibility of forming solid solutions of ice has appeared doubtful until recently.[1] The two molecules resembling water most closely, HF and NH_3, have approximately the same dimensions, but differ in the numbers of hydrogen bonds that could be formed per molecule. Substitution of an HF for an H_2O in the ice lattice would require the disappearance of one hydrogen bond and therefore weaken the structure. Similarly, since both the H−N−H angles in ammonia and the H−O−H angle in water are approximately tetrahedral, substitution of an H_2O by an NH_3 would require the presence of two H atoms along one of the original hydrogen bonds, which would not only destroy the bond but also involve repulsion between the positively charged hydrogens.

However, replacement of two H_2O molecules in ice by one NH_3 and one HF would not affect the total number of hydrogen bonds, but might require a rearrangement of the hydrogens. Although a random configuration of hydrogens was shown by Pauling[2] to agree with the residual entropy of ice, others have argued for a partly ordered configuration.[3,4] If the latter view is correct, then such substitution would produce some disordered regions such as the one surrounded by dotted lines in the following schematic arrangement:



The possibility of forming solid solutions of ice and NH_4F was further suggested by the isomorphism of the two substances,[5] and by the effective radii of H_2O, NH_4^+ and F^-. The distances between adjacent oxygens and between a nitrogen and a fluoride are 2.76 and 2.66 A, respectively.

For the system H_2O-NH_4F, the liquidus lines and the eutectic point have been determined by Iatlov and Poliakova.[6] Table I and the liquidus curve in Fig. 1 are taken from their paper. Although the solid phases found by these authors are listed as ice, ice+$NH_4F\cdot H_2O$,

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† Condensed from the dissertation of S. Zaromb submitted to the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (Present address of S. Zaromb: International Business Machines Corporation, Poughkeepsie, New York.)

[1] K. E. Mironov and A. G. Bergman, Proc. Acad. Sci. (U.S.S.R.) **81**, 1081 (1951).

[2] L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1939).

[3] N. Bjerrum, Kgl. Danske Videnskab Selskab, Mat.-fys. Medd. **27**, No. 1 (1951).

[4] R. E. Rundle, J. Chem. Phys. **21**, 1311 (1953); **22**, 344 (1954).

[5] K. Lonsdale, Nature **158**, 582 (1948).

[6] V. S. Iatlov and E. M. Poliakova, J. Gen. Chem. (U.S.S.R.) **15**, 724 (1945).

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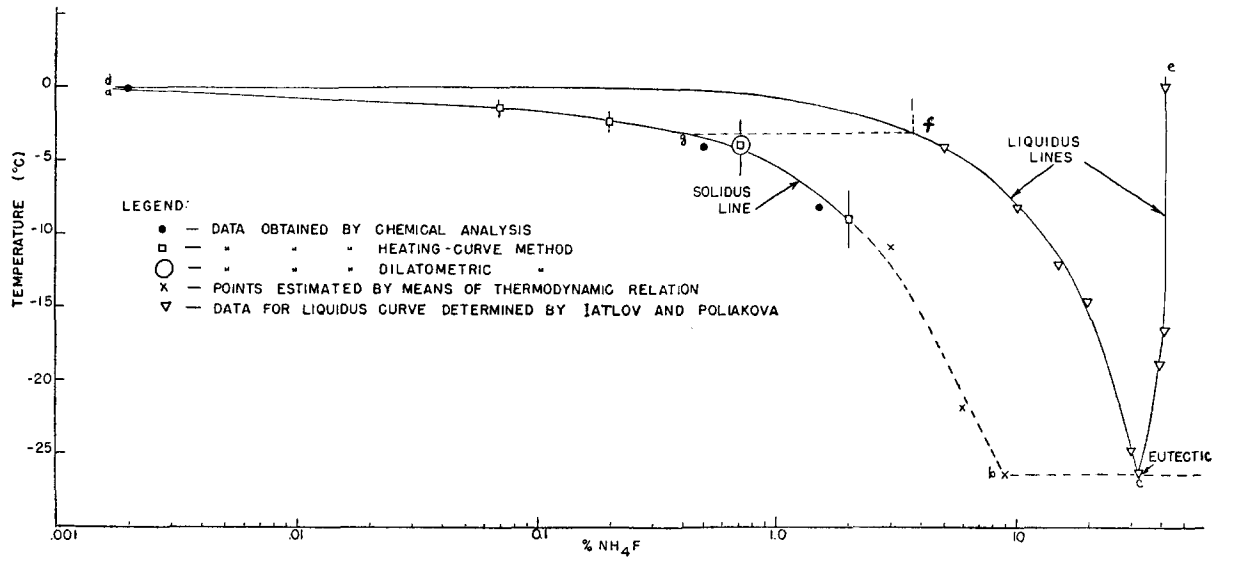

FIG. 1. Phase diagram for the system H_2O-NH_4F.

$NH_4F \cdot H_2O + NH_4F$, and NH_4F, the composition of the ice was obviously not determined by them.

We used the data of the liquidus curve to estimate corresponding points on the solidus line, making use of the equation[7]

$$\ln\frac{N_l}{N_s}=\frac{H}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right) \qquad (1)$$

where H is the heat of melting of ice, T_0 its melting point, and T the melting point of the mixed crystals. N_l and N_s are the concentrations of H_2O in the liquid and the solid phase, respectively.

b. Experimental

Preliminary tests of solubility of NH_4F in ice consisted of slowly freezing a solution of about 0.1% NH_4F, isolating a single crystal from the remaining ice, melting off its outer surface and wiping with filter paper, and testing for the presence of NH_4^+ ions in the crystal. Sizeable single crystals were obtained by surface-cooling *circa* 20 liters of the solution in an insulated aluminum container; the rate of freezing was *circa* 1 liter in 5 hours. The single crystals were readily recognized through crossed polaroids. All these crystals gave positive tests for NH_3 with Nessler's reagent.‡

TABLE I. The liquidus line for the system H_2O-NH_4F.

Temperature °C	% NH_4F in liquid	Solid phase
− 4.1	5.0	Ice
− 8.2	10.0	Ice
−12.1	15.0	Ice
−14.7	20.0	Ice
−24.9	30.0	Ice
−26.5	32.3	Ice+$NH_4F \cdot H_2O$

Preliminary quantitative determinations of the amount of NH_4F absorbed in ice from aqueous solutions of NH_4F gave the approximate results shown in Table II.

The procedure consisted in filling one 1500-cc beaker with a solution of NH_4F and one with a solution of NH_3 of the same nitrogen content, placing the beakers into 4-quart open mouth Dewar flasks, and leaving the flasks, covered with cork, overnight in a dry ice storage box. Fairly large crystals were thus obtained from dilute solutions. The nitrogen content of these crystals was determined colorimetrically using Nessler's reagent and a set of 12 Nessler tubes.[8] However, solutions of several percent NH_4F yielded extremely thin platelets of ice which could not be separated from each other. It was then assumed that the amount of nitrogen trapped in the grain boundaries was approximately the same with NH_4F as with NH_3, and that the NH_3 was present only in the boundaries—e.g., the ice obtained from a solution of about 5% NH_4F contained 0.66% NH_4F, while that from a solution of 2.5% NH_3 contained 0.06% NH_3 or the equivalent of 0.12% NH_4F. The actual amount of NH_4F absorbed by the ice crystals was therefore estimated at 0.66−0.12 or 0.5%. The error due to the presence of solution in the grain boundaries was thus of the order of 20%.

However, the above procedure did not give conclusive

[7] H. Seltz, J. Am. Chem. Soc. **56**, 307 (1934); A. Eucken, *Lehrbuch der chemischen Physik* (Akad. Verlagsgesellschaft, Leipzig 1950), II, 84.

‡ The following substances were also similarly tested, in the order listed, with negative results: LiOH, NH_3, KF, NH_3+LiOH, NH_3+NaOH, NH_3+KOH, NH_4Cl+KCN, Na_2S+HCl, formaldehyde, formic acid, and glycerol.

[8] I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis* (MacMillan Company, New York, 1949).

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proof that mixed ice-NH_4F crystals were actually formed. The possibility of microcrystalline inclusions of NH_4F had to be considered, even though such inclusions were not seen in a single crystal of ice containing NH_4F, when examined through a microscope at magnifications of 100 and 300 times. For further proof we determined melting points of ice-NH_4F mixtures.

Finely powdered ice samples containing known amounts of NH_4F were allowed to recrystallize at temperatures just below their estimated melting points, to ensure uniformity of composition. They were cooled, before testing, to $-80°C$, and reground. Heating curves from $-40°C$ to above $0°C$ were obtained with equipment consisting of two parallel screw conveyers interconnected with channels at both extremities, for the purpose of mixing the samples, and placed in a silvered Dewar flask externally warmed by running water, as shown in Fig. 2. The running water was maintained at a constant temperature, while readings were taken of the temperatures of the sample at given times.

One thawing point was determined more accurately by measuring the effective coefficient of expansion of a solid solution at different temperatures.

The apparatus consisted of a 50-ml-U-tube closed by a stopcock at one end and terminating with the outer part of a ground glass joint at the other end. A 0.2-ml pipette graduated in 0.001-ml divisions was connected to the inner part of the ground glass joint, as shown in Fig. 3. The U-tube was filled with powdered solid solution of ice-NH_4F, and the space between the grains of solid was filled with *n*-hexane. Then the inner ground joint was connected, the U-tube was placed in a thermostat bath, and the level of the hexane in the graduated capillary was raised to the lowest mark by opening the stopcock. Readings of the capillary were then taken for different bath temperatures, as these temperatures were slowly increased. Incipient melting was indicated by a sharp reversal in the sign of the effective coefficient of expansion. Figure 4 shows a plot of the readings of the capillary at different temperatures for a solid solution of 0.7% NH_4F. It can be seen from this figure that thawing starts between -3.5 and $-4°C$, which is in agreement with the results obtained by means of heating curves. Since the eutectic temperature of the system ice-NH_4F is at $-26.5°C$,[6] these results clearly confirm the existence of mixed crystals.

TABLE II. Solubility of NH_4F in ice.

% NH_4F	
In liquid	In ice
0.1	0.002
5	0.5
10	1.5

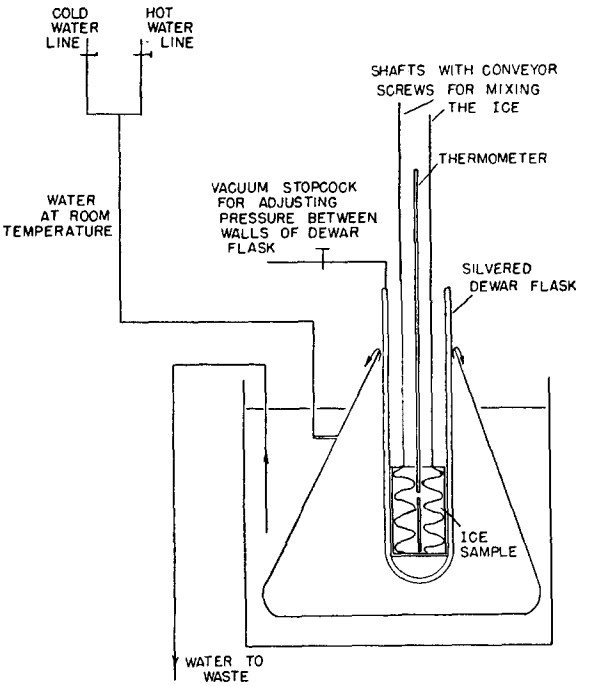

FIG. 2. Schematic diagram of apparatus for heating-curve measurements.

c. Conclusions

Figure 5 shows that our values agree well with Eq. (1). From the straight line one obtains:

$$\log\frac{N_l}{N_s} = -\frac{320}{T} + 1.17. \qquad (2)$$

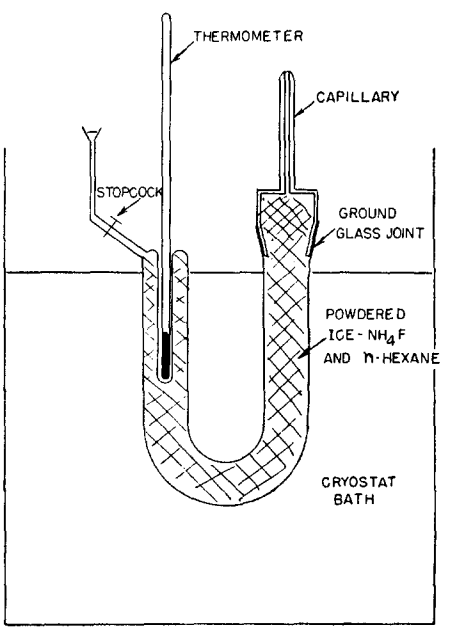

FIG. 3. Schematic diagram of apparatus for dilatometric measurements.

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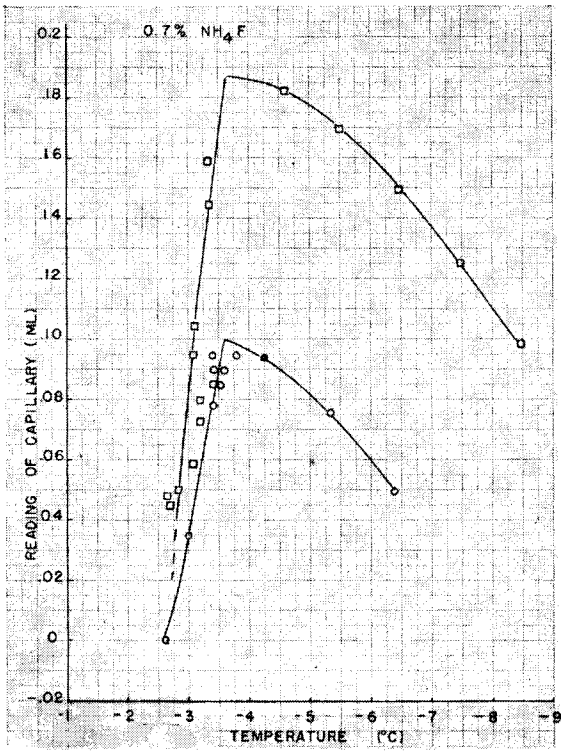

FIG. 4. Typical changes in the volume of ice-NH_4F near the melting point.

This yields $H=1465$ cal-mole, which is in fair agreement with the accepted value of 1437 cal-mole for the heat of fusion of ice, and the small deviation is probably due to the nonideality of the solutions. If we assume that Eq. (2) remains valid for the higher concentrations of NH_4F, then the limit of solubility of NH_4F in ice is roughly 10%. It might perhaps be possible to determine the solubility limit with greater accuracy by measuring the lattice constants of different concentrations of ice-NH_4F at the eutectic temperature (−26.5°C). Efforts to do this have not yet been made.

II. ELECTRICAL PROPERTIES OF ICE-NH_4F SOLUTIONS

a. Introduction

The response of pure ice to alternating currents of various frequencies has been studied by several investigators.[9–14] The most recent and most reliable experimental data are those of Auty and Cole[9] and of Humbel, Jona, and Scherrer.[11] The results of both groups are in good agreement with each other except in the range below −40°C. Their measurements were taken for ice temperatures of −0.1 to −65°C with frequencies of 20 to 50 000 cps. Experiments by Lamb and Turney[12] show that results of the low-frequency measurements can be safely extrapolated up to 2.4×10^{10} cps (1.25-cm wavelength).

For pure ice, the dielectric constant, ϵ, was shown[9] to vary with the frequency f of an applied alternating field according to the relation:

$$\epsilon=\epsilon_\infty+(\epsilon_0-\epsilon_\infty)/(1+i(2\pi f\tau)) \tag{3}$$

where ϵ_0 and ϵ_∞ are the values of ϵ at frequencies of 0 and $>10^{10}$ cps, respectively, and τ is the dielectric relaxation time. If we set

$$\epsilon=\epsilon'-i\epsilon'' \tag{4}$$

where ϵ' and ϵ'' are the real and imaginary parts of the dielectric constant, then, since both ϵ_0 and ϵ_∞ are real numbers, it follows from relations (3) and (4) that

$$\epsilon'=\epsilon_\infty+(\epsilon_0-\epsilon_\infty)/(1+(2\pi f\tau)^2)$$

and

$$\epsilon''=(\epsilon_0-\epsilon_\infty)\frac{2\pi f\tau}{1+(2\pi f\tau)^2}.$$

Elimination of $(2\pi f\tau)$ from these equations yields:

$$\left(\epsilon'-\frac{\epsilon_0+\epsilon_\infty}{2}\right)^2+\epsilon''^2=\left(\frac{\epsilon_0-\epsilon_\infty}{2}\right)^2. \tag{5}$$

Equation (5) shows that when ϵ'' is plotted against ϵ', a semicircle should be obtained with radius $(\epsilon_0-\epsilon_\infty)/2$ and center on the abscissa at $(\epsilon_0+\epsilon_\infty)/2$ from the origin. Such plots are called "Cole plots" after their authors.[15] Since circles can be drawn as easily as straight lines,§ the Cole plots offer a useful method of estimating and compensating for random errors in a series of measurements.

The Cole plots are most useful, however, in the study of substances having more than one relaxation time. This occurs in anisotropic solids which exhibit a different behavior along different crystal axes, and also in mixtures or solutions. The latter, even though macroscopically homogeneous, must still contain microscopic regions in the vicinity of the solute particles which are different from the bulk of the substance. Yet, in most of these cases it is found that the plots of ϵ'' against ϵ' are still circular arcs, though of less than 180°. This can be shown[16] to mean that Eq. (3) must be modified to (6):

$$\epsilon=\epsilon_\infty+(\epsilon_0-\epsilon_\infty)/(1+(i2\pi f\tau_0)^{1-h}) \tag{6}$$

where $(1-h)\pi$ is the circular arc subtended by the ϵ' axis, and τ_0 is some average value around which the

[9] R. Auty and R. H. Cole, J. Chem. Phys. **20**, 1309 (1952).
[10] M. Errera, J. Phys. (U.S.S.R.) **5**, 304 (1924).
[11] Humbel, Jona, and Scherrer, Helv. Phys. Acta **26**, 17 (1953).
[12] J. Lamb and A. Turney, Proc. Phys. Soc. (London) **62B**, 272 (1949).
[13] E. J. Murphy, Trans. Am. Electrochem. Soc. **65**, 309 (1934).
[14] C. P. Smyth and C. S. Hitchcock, J. Am. Chem. Soc. **54**, 4631 (1932).
[15] K. S. Cole and R. H. Cole, J. Chem. Phys. **9**, 341 (1941).
§ To draw the best circle readily through a set of plotted points, use can be made of semitransparent polar coordinate graph paper.
[16] C. J. F. Böttcher, *Theory of Electric Polarization* (Elsevier, Amsterdam, 1952).

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relaxation times are spread. Furthermore, as a corollary of Eq. (6), the values of τ_0 can be obtained from any point P_1 in the Cole plot corresponding to a frequency f_1 by means of the relation[16]:

$$v_1/u_1=(2\pi f_1\tau_0)^{1-h} \tag{7}$$

where u_1 and v_1 are the distances from P_1 to the intersection points ϵ_∞ and ϵ_0 of the curve with the abscissa, respectively.

This offers a simple method of determining τ_0.

Besides its value in defining the frequency-dependence of the dielectric constant, as given by Eqs. (1) or (6), the dielectric relaxation time is important in the study of the behavior of the dipoles composing a given substance. By regarding dielectric relaxation as a chemical rate process it can be shown[16–19] that dipoles shift from one position of maximum stability to another with an average frequency, $1/\tau^*$, where

$$\tau^*=\tau(\epsilon_\infty+2)/(\epsilon_0+2). \tag{8}$$

τ^* is called the intrinsic (or "the Debye") relaxation time. Like any other chemical reaction rate, $1/\tau$ is describable by means of the Arrhenius relation:

$$1/\tau=Ae^{-E/RT} \tag{9}$$

where A is a frequency factor, E an activation energy, R the gas constant, and T the absolute temperatures.

The present work is concerned with the variation of τ with temperature and concentration in solid solutions of ice-NH_4F, as deduced from measurements of real and imaginary dielectric constants for frequencies of 20 cps to 600 kc.

b. Experimental

1. Preparation of Aqueous Solutions

Distilled water, having a specific conductivity of 10^{-6} (ohm-cm)$^{-1}$ and a *p*H of 6.6, was redistilled under vacuum in a Pyrex glass apparatus. The vacuum was used to remove absorbed gases from the water. The conductivity of the redistilled water was about 5×10^{-7} (ohm-cm)$^{-1}$. The water was then kept in air-tight polyethylene containers, and was not exposed to air except for brief periods of time. A weighed quantity of NH_4F (analyzed sample of the Fisher Scientific Company containing as major impurity only 0.09% Cl) was dissolved in one of the containers so as to make up a 10% solution. Of this solution, 20 cc was added from a polystyrene burette to 180 cc of water in another polyethylene bottle. This procedure was continued until solutions of all the desired concentrations were obtained. All containers used in preparing these solutions had been previously soaked in distilled water for 24 hours and then rinsed until the water from the last rinsing had a conductivity of not more than 10^{-6} (ohm-cm)$^{-1}$.

[17] H. Eyring, J. Chem. Phys. 4, 283 (1936).
[18] F. C. Frank, Trans. Faraday Soc. 32, 1634 (1936).
[19] W. Kauzman, Revs. Modern Phys. 14, 12 (1942).

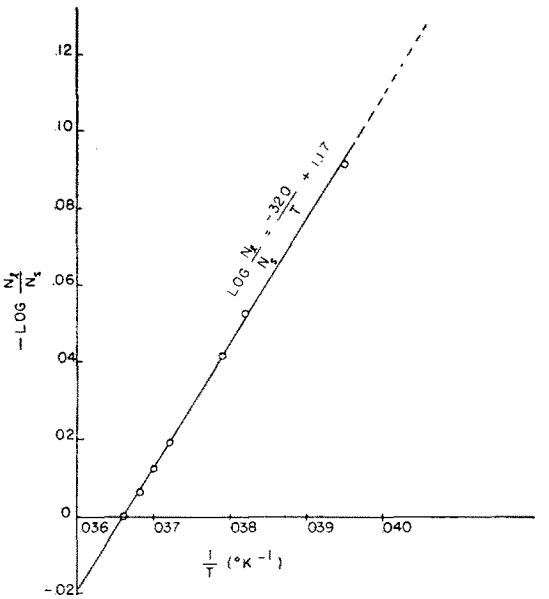

FIG. 5. Relation between liquidus and solidus curves for the system H_2O-NH_4F.

The absence of bubbles in samples frozen from these solutions subsequently indicated that absorbed gases had been effectively removed by the redistillation. It is also believed that the above procedure ensured a satisfactory purity in the samples studied.

2. Freezing of the Solutions

Aqueous solutions of 0.006 to 10 weight-% NH_4F were introduced into the annular space between two concentric cylindrical rhodium-plated brass tubes which fitted tightly into a Teflon base. A loose Teflon plug formed the cover of the condenser and also ensured concentricity of the tubes. The outside diameter of the inner tube, the inner diameter of the outer one, and the length between the Teflon plugs were 0.566 in., 0.870 in., and 2.75 in., respectively.

The condenser was placed in a cylindrical brass container, 1.5 in. in diameter and 9 in. deep, connected electrically to the ground. This assembly was immersed in a 4-quart Dewar flask containing acetone at about −70°C.

A second procedure was used to prepare a condenser filled with ice containing 0.002% NH_4F. A rectangular aluminum plate, 1 in.×3 in. in area, cooled at the center by a tube filled with dry ice was suspended over 1 liter of a solution of 0.12% NH_4F so as to just wet its surface. The initial temperature of the solution was circa 3°C. Within a half hour, a slab of ice-NH_4F, about $\frac{1}{4}$ in. thick adhered to the plate. The slab was then partly melted between parallel brass plates, until it formed a rectangular plate with smooth, parallel surfaces. This was then inserted between one fixed and one movable rhodium-plated brass electrode. A spring caused the movable electrode to press towards

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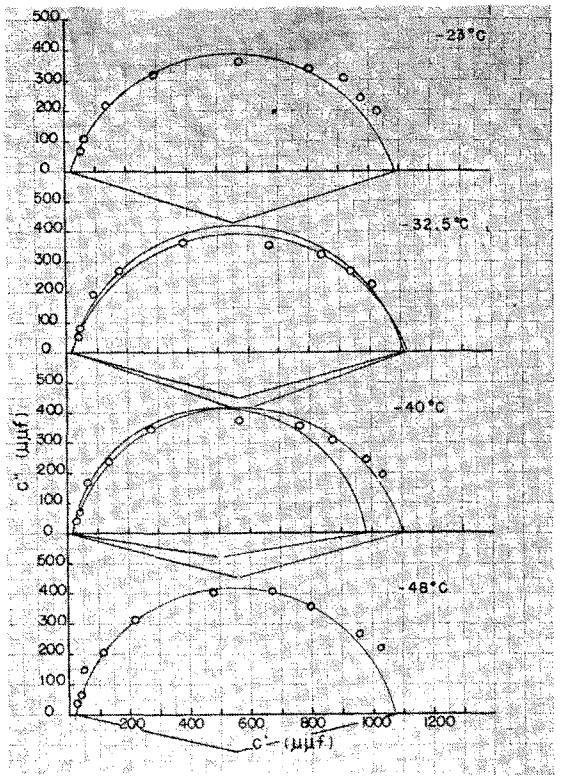

FIG. 6. Cole plots for ice containing 0.005% NH_4F.

the fixed one, thereby eliminating air gaps between electrodes and sample. The parallel plate condenser thus formed was then tested in the same way as the cylindrical condensers.

3. *Electrical Measurements*

As the temperature of the acetone bath in the Dewar container was slowly rising from $-70°C$ to $-10°C$ over a period of 4–5 hours, measurements were taken of the parallel capacitance, C_p, and resistance, R_p, of the condenser for frequencies of 20 cps to 600 kc. In order to test the reproducibility of these measurements, two identical condensers were immersed in the bath in each experiment, and each was measured alternately over the entire frequency range. It was usually possible to cover the frequency range about 5 or 6 times in a single experiment.

For frequencies up to 40 kc a type 650-A impedance bridge, manufactured by the General Radio Company, Cambridge, Massachusetts, was used. A Hewlett-Packard Model 200-AB Audio Oscillator was used as a variable source of frequencies of 20 cps to 40 kc in conjunction with a Shielded Transformer Type 578-B made by the General Radio Company. The detector used for balancing the bridge was a cathode ray oscilloscope, manufactured by the DuMont Laboratories Inc., Passaic, New Jersey. For frequencies above 40 kc, a radio-frequency bridge Type B-601, manufactured by the Wayne Kerr Laboratories, Great Britain, was used in conjunction with a radio-frequency oscillator Type WR-67A, manufactured by the Radio Corporation of America, and the following detectors: (a) Amplifier Model 102-B, manufactured by the Kalbfell Laboratories, Inc., San Diego, California, in conjunction with the above-mentioned oscilloscope for frequencies up to 300 kc; and (b) A Hallicrafter Radio receiver which detected an audio-modulated voltage at 600 kc. Bridge Type B-601 should, according to the Manufacturer's specifications, be accurate to within 1%. However, a subsequent calibration showed deviations much larger than 1% from the correct values.

Electrical connections were made with shielded cable and were kept mostly unchanged throughout the entire series of measurements, including the calibration. The latter was performed in order to check the accuracy of the apparatus and to correct for deviations from direct readings. A standard variable condenser in parallel with different carbon resistors was used for the calibration. The correction includes also the effect of the capacitance of the leads.

The temperature of the acetone bath was measured with a Pt-resistance thermometer, and the difference between the temperature of the ice-NH_4F samples and

TABLE III. The temperature- and concentration-dependence of the dielectric relaxation time in ice-NH_4F solutions.

		10% NH_4F		1%		0.4%		0.15%		0.05%		0.015%		0.006%		0.002%	
Temp. °C	$\frac{1000}{T}$	τ_0 milli-sec	(1-h) 180°	τ_0 milli-sec	(1-h) 180°	τ_0 milli-sec	(1-h) 180°	τ_0 milli-sec	(1-h) 180°	τ_0 milli-sec	(1-h) 180°	τ_0 milli-sec	(1-h) 180°	τ_0 milli-sec	(1-h) 180°	τ_0 milli-sec	(1-h) 180°
−65	4.79															0.613	160°
−62	4.74			0.0159	130°					0.0661	150°	0.134	160°				
−60	4.69	0.051	128°														
−55	4.58															0.514	156°
−54	4.56	0.039	132°	0.0109–0.0123	132–139°	0.0095	144°	0.0197	152°	0.0483	154°	0.106	164°				
−48	4.44			0.00996	126°	0.0057	137°	0.0156	149°	0.0378	154°	0.0948	166°	0.156	169°		
−45	4.38	0.029	129°											0.152	168°	0.408	158°
−40	4.29			0.0062	127°	0.0034	158°	0.011	149°	0.0266–0.0332	150–163°	0.0838	166°	0.117	168°		
−36	4.21	0.0166	128°														
−35	4.19															0.29	161°
−32.5	4.15					0.0025	164°	0.0061	138°	0.026	141–150°	0.0690	169°	0.087	171°		
−23	3.995							0.0039	180°	0.0164	144°	0.0462	168°	0.070	173°		
−15	3.87											0.0266–0.0312	169–180°	0.060	168°		

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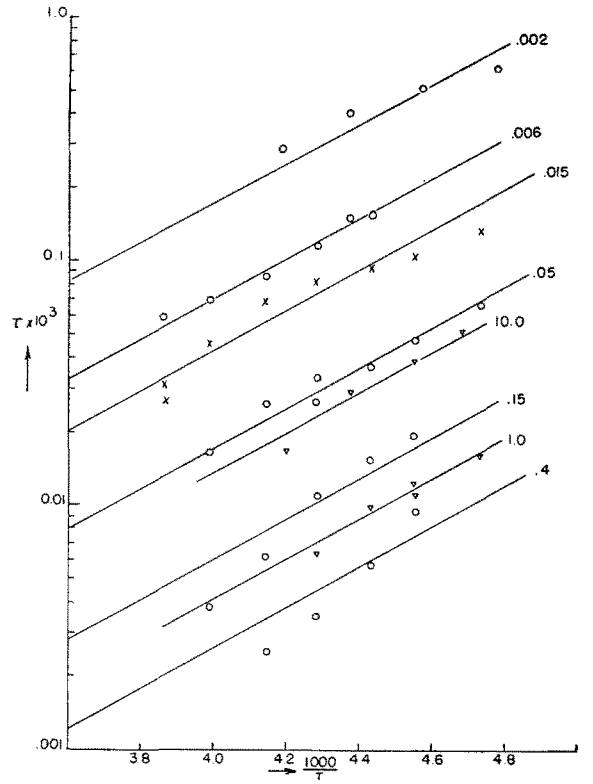

FIG. 7. Effect of temperature and concentration on the dielectric relaxation time of ice-NH_4F.

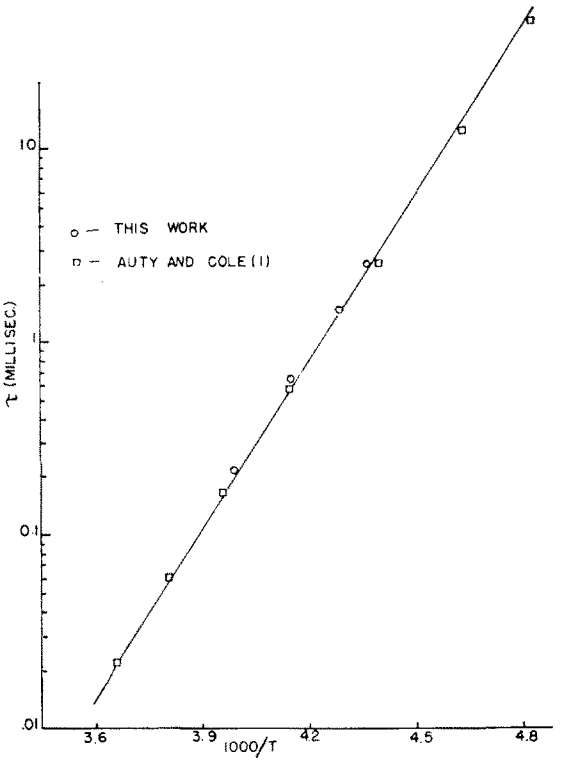

FIG. 8. Dielectric relaxation time for pure ice.

that of the acetone bath was determined by means of copper-constantan thermocouples in conjunction with a microammeter. Temperature gradients in the acetone bath itself were reduced by an air-driven glass stirrer.

Temperatures were read at intervals of 10 to 20 minutes, the time of the readings was noted, and a plot was drawn of sample temperatures against time. The time at which balance was obtained in each bridge measurement was also recorded. The temperature corresponding to each bridge reading was then obtained from the time-temperature plots. Measurements of dc resistance were made at intervals of $\frac{1}{2}$–1 hr with the aid of an ohmmeter, for resistances up to 100 megohms. For resistances higher than 100 megohms no corrections were necessary for the observed values of the imaginary part of the dielectric constant.

4. *Evaluation of Data*

Bridge readings were corrected with the aid of the calibration curves mentioned in the preceding section and also for dc conductivity, and the corrected values of the real and imaginary components of capacitance, C' and C'', were plotted against temperature for different frequencies. It was found convenient to use $C'=\epsilon' C_0$ and $C''=\epsilon'' C_0$, instead of ϵ' and ϵ'', where C_0 is the capacitance of the empty condenser.

From the temperature-capacitance curves, values of C' and C'' at a fixed temperature were read off for different frequencies and plotted on Cole plots. These were then used to determine τ_0 by means of Eq. (7).

c. Discussion of Results

1. *Errors and Reliability of the Measurements*

The values of τ_0 were obtained with a precision estimated at about 20%. This figure was deduced from measurements on pure ice and from the reproducibility of the values for ice-NH_4F solutions. The main sources of error were inhomogeneities in sample composition, polarization due to dc conductivity, and thermal stresses.

However, the measured values of τ_0 are probably valid only for solutions prepared and heat treated in the manner described in Sec. IIb. I.e., although the values of τ_0 can be reproduced with a precision of 20%, the effective concentration of NH_4F to which they correspond is not as certain, because of our ignorance of the diffusion coefficient of NH_4F in ice and of the concentration gradients in our samples during and after freezing. It is therefore not known to what extent the effective concentration of a given sample approached the average value.

Figure 6 gives an example of Cole plots for a sample of 0.05% NH_4F. Two circles were drawn in cases where all the points could not be fitted on a single one, and both values of τ thus obtained were used when the difference was larger than a few percent. The results of all measurements are given in Table III and Fig. 7.

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2. Method of Evaluation

The variation of τ with T yields an activation energy, E, for dipole rotation, in accordance with Eq. (9). Figure 8 shows that this equation is very well obeyed by pure ice. However, in ice-NH_4F solutions, the Cole plots indicate a certain distribution of relaxation times, each of which may have different values of A and E in Eq. (9).

Nevertheless, it seemed reasonable that all the values of E should be the same, because the effect of NH_4F on the dielectric relaxation process must be of essentially the same character, at least within certain temperature and concentration ranges. The possibility of different E values in different ranges had been suggested at first; however, measurements on better defined samples performed by Dr. H. Ender in our laboratory indicated no change in activation energy in the concentration range of 0.002 to 0.5% NH_4F. We therefore drew, in Fig. 7, the set of parallel lines fitting our observed values best. This gives an activation energy for dielectric relaxation of about 4 kcal/mole. The corresponding value for pure ice is about 13 kcal/mole.

Figure 7 also shows that the frequency factor of Eq. (9) first increases with concentration, but then decreases for concentrations above 0.4% NH_4F. These results will be discussed in subsequent communications.

d. Conclusions

1. It is found experimentally that NH_4F greatly facilitates the dielectric relaxation process in ice. This is shown both by first markedly decreasing relaxation times with increasing concentration and by relatively low activation energies observed for the relaxation process as compared with that in pure ice. According to Smyth, Bjerrum, and others, the mechanism of dipole rotation in pure ice would be connected with the presence of lattice faults. If this is right, then NH_4F seems to create fault sites by a process requiring less activation energy.

2. The effect of increasing concentration, c, of NH_4F on the relaxation process appears peculiar. For low concentrations, the frequency factor increases with c; this trend is reversed for the highest concentrations of NH_4F.

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