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The self-diffusion coefficient of sodium in sodium chloride and sodium bromide has been measured as a function of temperature. A comparison of the self-diffusion coefficient with the electrolytic conductivity reveals that the Einstein relation is satisfied at high but not at low temperatures. The temperature dependence of the diffusion coefficient may be explained by the Schottky-Wagner vacancy theory if the presence of impurity ions is taken into account. A possible explanation for the failure of the Einstein relation in terms of association between multivalent foreign ions and vacancies is suggested.

I T is generally believed that lattice imperfections of the type known as Schottky defects are responsible for ionic mobility in the alkali halide crystals.[1] Schottky defects, as illustrated in Fig. 1, consist of vacant lattice sites. The migration of these vacancies, as neighboring ions jump into them, provides a mechanism for ionic self-diffusion and, in the presence of an electric field, for electrolytic conduction.

The transference number measurements of Tubandt show that, except at quite high temperatures, the electrical conductivity of sodium chloride is due entirely to migration of the sodium ion.[2] Presumably, the activation energy for the jump of a chloride ion into a chloride ion vacancy is much greater than that associated with the jump of a sodium ion into a sodium ion vacancy.

The vacancy mechanism of migration[1] leads to the following equations for the temperature dependence of the self-diffusion coefficient and of the electric conductivity of an alkali halide, such as sodium chloride, when it is assumed that the crystal is in thermodynamic equilibrium.

$$D = D_0 \exp\left(-\frac{\epsilon + \epsilon'/2}{kT} \right), \qquad (1)$$

$$\sigma = \frac{\sigma_0}{T} \exp\left(-\frac{\epsilon + \epsilon'/2}{kT} \right). \qquad (2)$$

The quantities D and σ are the self-diffusion coefficient and conductivity, respectively. D_0 and σ_0 are constants. The activation energy for the jump of a sodium ion into a vacancy is represented by ϵ, while ϵ' is the work necessary to create a positive and a negative ion vacancy by moving the ions from the interior to the surface of the crystal. The ratio σ/D has the simple form

$$\sigma/D = N e^2/kT, \qquad (3)$$

which is known as the Einstein relation.[1] The number of sodium ions per unit volume of crystal is given by N while the other symbols have their usual significance.

The validity of the Einstein relation rests upon the assumption that both self-diffusion and conductivity are due to the same mechanism—in this case the migration of single vacancies. If a substantial fraction of the single positive and negative ion vacancies is paired as a result of the electrostatic attraction between them, the migration of these pairs affects the magnitude of the self-diffusion coefficient but not that of the conductivity since the pairs are electrically neutral.[1] Pairs are illustrated in Fig. 2. A calculation by Dienes[3] indicates that the pairs have an activation energy, ϵ_p, for diffusion about half as large as that of single, positive ion vacancies.

The present work is an experimental test of the Einstein relation for sodium chloride and sodium bromide. The self-diffusion coefficient and the conductivity have been measured over a range of temperature upon the same crystal samples. The conductivity of these salts has been investigated previously, notably by Lehfeldt.[4]

Single crystals in the form of cubes approximately 1 centimeter on edge were used for the measurement of the diffusion coefficient. A film of radioactive salt about 5×10^{-4} centimeter thick was deposited upon one face of each cube by evaporation in a vacuum from an electrically heated platinum boat. The faces of the crystals were masked during this operation so that the evaporated salt was deposited over a circular area whose

FIG. 1. Schottky defects.

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[1] N. Mott and R. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940), Chapter II.
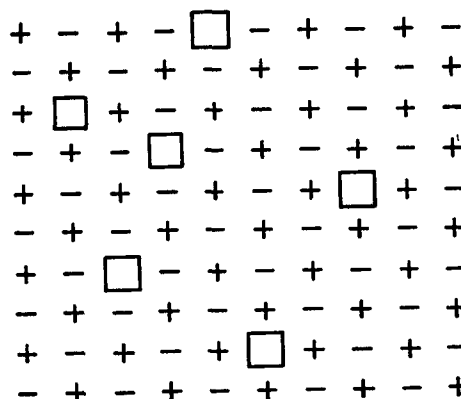[2] C. Tubandt, *Handbuch der Experimental Physik*, Vol. II, Part 1.
[3] G. J. Dienes, J. Chem. Phys. 16, 620 (1948).
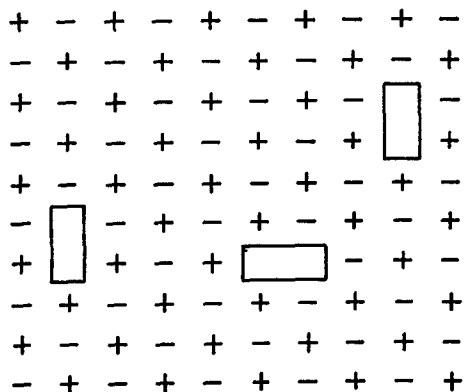[4] W. Lehfeldt, Zeits. f. Physik 85, 717 (1933).
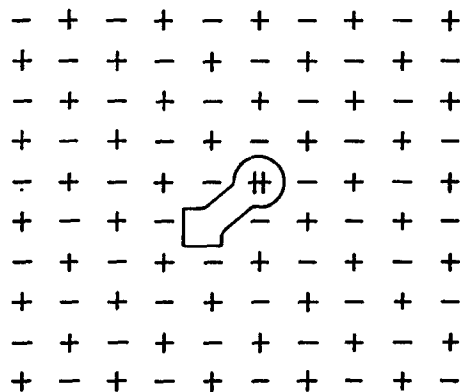
FIG. 2. Paired vacancies

FIG. 3. Divalent ion-vacancy complex

diameter was $\frac{11}{32}$ inches. The salt was activated by neutron irradiation at Oak Ridge, Tennessee. The chlorine activity was negligible in comparison with that of the Na^{24}.

Following the evaporation procedure, the crystals were transferred to constant temperature ovens where diffusion proceeded for a known time. During this process the crystals were sealed in Pyrex capsules at an air pressure of about 0.1 millimeter of mercury. At the higher temperatures, the crystals were placed in stainless steel cartridges, which, when sealed in Pyrex, prevented the Pyrex from collapsing about the crystals. Two crystals were placed in each capsule to provide a check upon the consistency of the data. The oven temperature was regulated to ±0.5°C and the temperature of the crystals was determined with chromel-alumel thermocouples which were placed in contact with the outer surface of the capsule.

At the conclusion of a diffusion run, the crystals were removed from the capsules and sectioned with a microtome, slices being taken parallel to the face upon which the radioactive salt had been deposited. For this purpose, two microtomes were constructed. The first microtome which was used for the measurements upon sodium chloride was similar in principle to the second instrument but less elaborate in construction.

The microtome possessed a knife which was moved in a vertical direction by means of a precision screw which was calibrated by an interferometer. The crystal was attached to a carriage which was moved horizontally on precision ways by a motor-driven screw. In this manner, the knife edge was passed over the face of the crystal in the sectioning process. The crystal was held under the knife by a vise with micrometer adjustments for positioning the crystal face in the plane swept out by the knife edge. The proper placement of the crystal in this position was determined by reflection of a light beam from a mirror resting on the crystal face.

During the operation of sectioning the crystal, the knife and crystal were observed with a binocular microscope. The material removed from the crystal by the knife was in the form of a fine powder which was collected in the following manner. Before each passage of the knife over the crystal a strip of adhesive Cellophane tape was pressed to the crystal face. As the knife passed across the crystal the tape was removed carrying with it the sectioned material in the form of a fine powder which adhered to the tape. The samples were mounted on brass rings and the radioactive intensity of each was determined with conventional Geiger counters and scale of sixty-four circuits. The time of diffusion was limited to seven or eight half-lives of the Na^{24} and the depth of penetration of the radioactive sodium into the crystal was of the order of 10^{-2} cm. The thickness of individual slices taken with the microtome was about 5×10^{-4} cm.

The data obtained in the manner outlined was used to obtain diffusion coefficients by comparison with the equation

$$c(x,\, t) = \frac{c_0}{(\pi D t)^{\frac{1}{2}}} \exp\left(-\frac{x^2}{4Dt}\right), \qquad (4)$$

which is the solution of the diffusion equation appropriate to the geometry and boundary conditions of the present experiment. The concentration of radioactive sodium at time, t, and distance, x, from the face of the crystal is represented by $c(x,\, t)$. The initial surface concentration of radioactive sodium is represented by c_0 and D is the diffusion coefficient. In Fig. 4, which is a plot of typical data obtained from sodium chloride, the logarithm of the counts per minute obtained from a given slice is plotted against the square of the distance of the slice from the surface. In agreement with Eq. 4, the data, when plotted in this manner, yield straight lines, the slope of which is $(4Dt)^{-1}$. The precision of the determinations of the diffusion coefficients is rather difficult to estimate but is believed to be within 10 percent in the middle of the temperature range, rising to not more than 20 percent at the highest temperatures and 15 percent at the lowest temperatures. The self-diffusion coefficient of sodium in the two salts is shown as a function of temperature in Figs. 5 and 6.

The samples used for the diffusion measurements were cleaved into slabs about 2 millimeters on edge and less

than a millimeter thick for the measurement of the electrical conductivity. Electrodes were applied to the faces of the sodium chloride slabs by painting with a suspension of colloidal graphite in methyl alcohol. Sodium bromide is sufficiently hygroscopic to necessitate handling in a dry room. Graphite electrodes were applied by slightly roughing the surfaces and rubbing with a graphite pencil.

The crystal slabs were held in a constant temperature oven between nickel electrodes which were clad with platinum foil. The entire electrode assembly was mounted in a quartz tube through which a slow current of purified helium was passed. The electrically heated oven which surrounded the quartz tube was temperature-regulated to within $\pm 0.5°$C. The temperature of the crystals was determined by a chromel-alumel thermocouple mounted in one of the nickel electrodes.

In order to avoid polarization of the crystals as a result of the passage of charge, the resistance was measured with the circuit illustrated in Fig. 7. The crystal, x, was subjected to single d.c. pulses of constant duration by means of the timing switch, T, and the resulting deflection of the ballistic galvanometer, G, observed. The pulse voltage was determined by the setting of the potentiometer, P, and measured with the voltmeter, V. The direction of the current through the crystal was reversed after each pulse with the switch, S. By means of the switch, C, the known resistance, R, was substituted for the crystal in the circuit and was adjusted to give the same deflection of the galvanometer.

The ballistic galvanometer had an undamped charge sensitivity of 3×10^{-10} coulomb per millimeter and a period of 27 seconds. The charge passed through the crystal during a single pulse varied from 10^{-8} coulomb at the lowest temperatures to 10^{-6} coulomb at the highest temperatures. The standard resistance, R, consisted of two four decade resistance boxes with a maximum series resistance of 22 megohms. At the lowest temperatures, the crystal resistance rose to 100 megohms. The maximum voltage applied to the crystal under these circumstances was 40 volts.

The timing switch, T, was a snap action switch actuated by a rotating cam. Pulse durations of 0.05, 0.091, and 0.20 second were used. A manually operated switch and relay, H, was used to allow the switch, T, which was periodically closed, to deliver isolated pulses to the crystal.

The measured crystal resistance was independent of the pulse duration indicating that polarization was avoided. Ohm's Law was verified by changing the magnitude of the applied voltage pulse. A typical result of such a check is shown in Fig. 8. Surface conduction over the sides of the crystals was shown to be negligible by the following procedure. After the resistance of a sodium chloride crystal had been measured it was split into halves along a plane perpendicular to the electrode faces and replaced between the electrodes. Although splitting the crystal increased the surface area of the sides by

50 percent, the measured resistance was unchanged over the entire temperature range within the experimental error of 5 percent.

The results of the conductivity measurements upon sodium chloride and sodium bromide are presented in Figs. 5 and 6. With the use of the Einstein relation (Eq. (3)) and the measured conductivity, a diffusion coefficient has been calculated and is shown as a function of the temperature. A typical curve obtained from a sodium bromide crystal is shown in Fig. 9. Four such curves, taken from four crystal samples, were averaged to obtain the data from which the calculated diffusion coefficient-temperature curve of Fig. 6 was drawn. The average deviation of the four individual curves from the average curve was less than 5 percent. The maximum deviation from the average curve occurred at the highest temperature where it was 13 percent.

The procedure used in obtaining diffusion and conductivity data was somewhat different for sodium chloride and sodium bromide. A fresh crystal sample was used for each diffusion experiment with sodium chloride. The conductivity of this sample was measured later at a temperature near that of the diffusion experiment. The sodium chloride samples were obtained at different times from the Harshaw Chemical Company
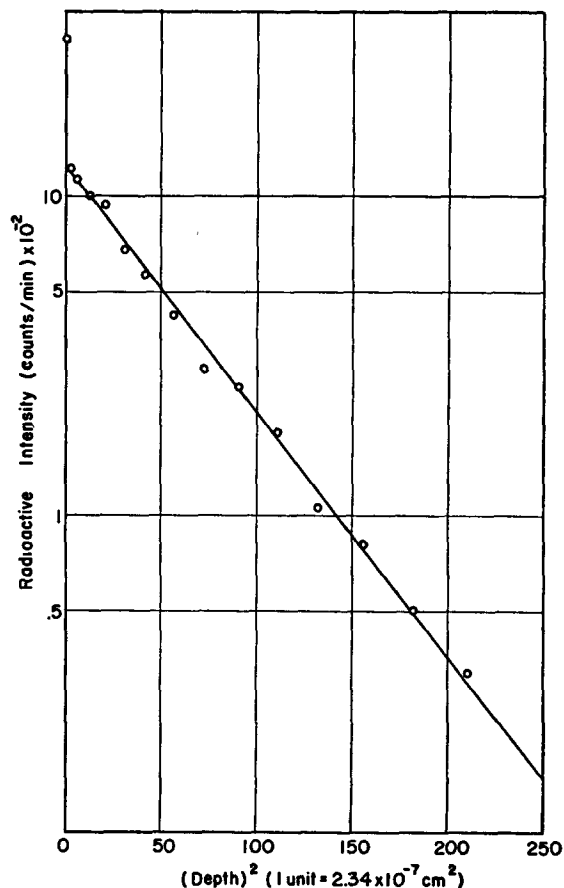

FIG. 4. Distribution of radioactive sodium in sodium chloride. $T = 603°$C. $t = 5.92$ hours. $D = 1.52 \times 10^{-10}$ cm^2/sec.
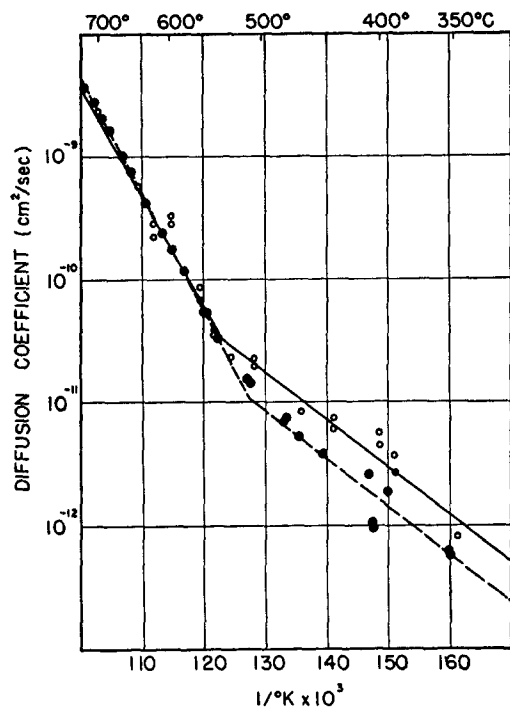
FIG. 5. Temperature dependence of self-diffusion coefficient of sodium in sodium chloride. O Directly measured. ● Calculated from measured conductivity.

and probably possessed different impurity contents. They were used as received without annealing.

The sodium bromide data was obtained from eight crystal samples, which were cleaved from one single crystal that had been grown by the Kyropolous[5] method in a platinum crucible. Eimer and Amend C.P. salt was used. Each sample was used for several diffusion experiments. Before each diffusion experiment, the crystal samples were annealed by raising their temperature to 720°C in a time of one hour. After holding the crystals at this temperature for four hours they were cooled to room temperature at a rate of 0.6°C per minute. This annealing procedure was conducted in an atmosphere of purified helium.

The radioactive Na^{24} used for the diffusion experiments with sodium bromide was evaporated upon a plane face of the crystal in the form of sodium chloride. Because of the small mobility of the chloride and bromide ions this procedure appeared unobjectionable.

In Table I are collected the values of the constants of Eqs. (1) and (5), obtained by fitting these equations to the data of Figs. 5 and 6. It is assumed that Eqs. (1) and (5) represent the behavior of the diffusion coefficient in the high and low temperature regions, respectively.

DISCUSSION

The curves of Figs. 5 and 6 possess well-defined high and low temperature regions. Above a fairly well-defined temperature which is about 550°C for sodium chloride

[5] S. Kyropolous, Zeits. f. anorg allgem. Chemie 154, 308 (1926).

and 425°C for sodium bromide the Einstein relation is satisfied by the data. Not only do the curves exhibit a change in slope at these temperatures but, below them, the Einstein relation is not valid.

In the high temperature region, the slope of the calculated diffusion coefficient curve appears to be slightly greater than that of the measured diffusion temperature curve. Extrapolation of Tubandt's transference number data indicates that this effect is due to the small contribution of the anions to the measured conductivity.

The low temperature behavior of the crystals appears to be due to the presence of multivalent cation impurities. The replacement of a sodium ion in the lattice by a divalent ion such as lead introduces a positive ion vacancy into the crystal in order that it remain electrically neutral. At low temperatures, the temperature independent concentration of these added positive ion vacancies is much larger than the temperature dependent concentration of "natural" vacancies. Under these circumstances the low temperature diffusion coefficient is given by the equation

$$D = D_0' \exp(-\epsilon/kT). \qquad (5)$$

In support of this interpretation, there exist the experiments of Koch and Wagner[6] and others[4,7,8] which show that the low temperature conductivity is extremely
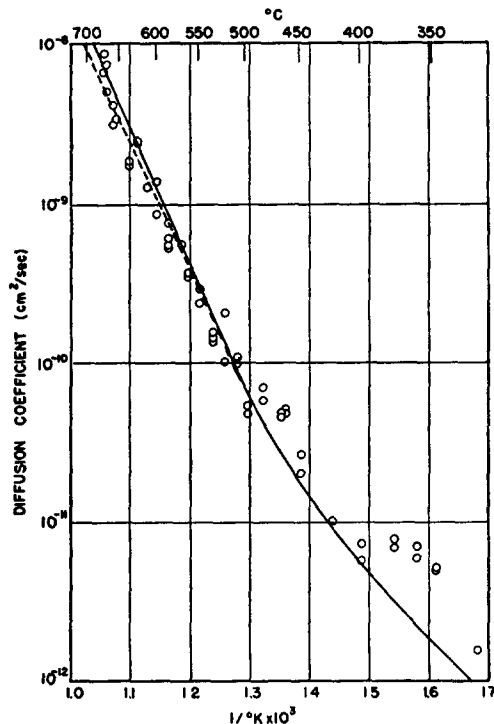

FIG. 6. Temperature dependence of self-diffusion coefficient of sodium in sodium bromide. -- ⊖ -- Directly measured. —— Calculated from measured conductivity.

[6] E. Koch and C. Wagner, Zeits. f. physik. Chemie (B) 38, 295 (1937).
[7] H. Etzel and R. Maurer, J. Chem. Phys. 18, 1003 (1950).
[8] Z. Gyulai, Zeits. f. Physik 67, 812 (1931).

sensitive to the presence of minute traces of divalent impurities, a few parts per million being sufficient to account for our data. We have found that the low temperature conductivity of Harshaw sodium chloride crystals varies from lot to lot even though subjected to identical annealing procedures. The same behavior is exhibited by crystals grown by us. Etzel and Maurer[7] found that the low temperature conductivity of sodium chloride was not affected by rather violent changes in annealing procedure.

These experiments argue against the suggestion by Schottky and Wagner that the low temperature behavior is due to a non-equilibrium state.[9] At low temperatures the mobility of the anion vacancies is assumed by these authors to become too small to permit the maintainance of the equilibrium vacancy concentration by diffusion to and from the crystal surface. If such an effect exists it appears that substantially purer crystals are needed for its observation.

An interpretation of the low temperature behavior in terms of a "frozen equilibrium" is inconsistent with an explanation of the failure of the Einstein relation in terms of pairs. The presence of pairs provides at low temperatures a mechanism for maintaining thermodynamic equilibrium. It appears dubious, however, that the low temperature failure of the Einstein relation is explainable in terms of pairs. An elementary treatment gives for the diffusion coefficient of the pairs the equation

$$D_p = (\text{constant})\ \exp\left(-\frac{\epsilon_p - \epsilon_p' + \epsilon'}{kT}\right), \qquad (6)$$

where ϵ_p' is the binding energy of a pair. Using the theoretical estimates of $\epsilon_p = 0.4$ ev and $\epsilon_p' = 1$ ev for sodium chloride[1,3] and taking $\epsilon' = 2.06$ ev from Table I, the ratio of D_p to the diffusion coefficient of the single vacancies, D, is

$$D_p/D = (\text{constant})\ \exp(0.34/kT). \qquad (7)$$

Assuming $(D_p/D) = 1$ at 500°C in order to account for the low temperature failure of the Einstein relation, the value of the ratio at 700°C is approximately 0.3. This result is in disagreement with the observed validity of the Einstein relation in the high temperature region.

The assumption that the low temperature behavior of the crystal is determined by the presence of excess positive ion vacancies resulting from the presence of impurities leads rather naturally to an explanation of the failure of Einstein's relation at low temperatures. It is to be expected that, as illustrated in Fig. 3, a fraction of the divalent impurity ions will be associated with vacancies to form a "complex" in which a positive ion vacancy is a nearest neighbor of the impurity ion.[10] Not only does there exist an electrostatic attraction between

[9] W. Jost, *Diffusion und Chemische Reaktion in Festen Stoffen* (Steinkopf, 1937), p. 77.
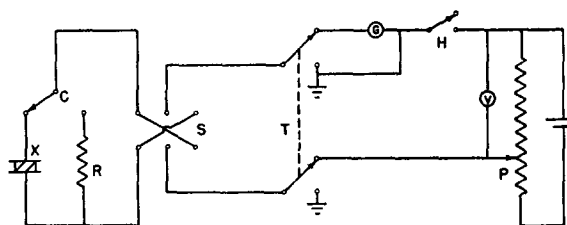[10] O. Stasiw and J. Teltow, Ann. d. Physik (6) **1**, 261 (1947).

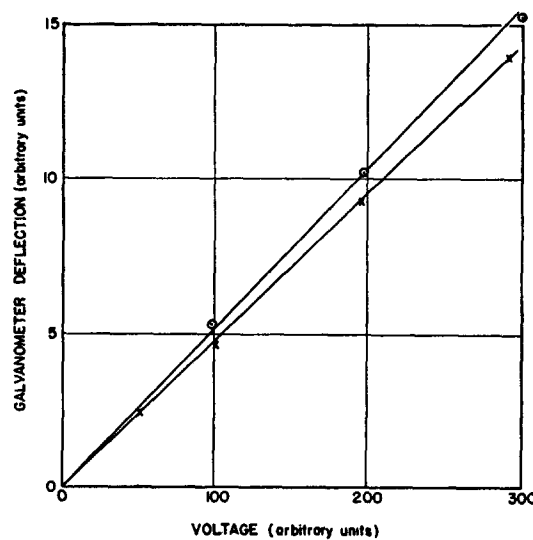FIG. 7. Circuit for measurement of crystal resistance.

FIG. 8. Test of Ohm's Law for sodium chloride.
O 721°C X 504°C.

a multivalent positive ion and a positive ion vacancy but also the stress in the lattice surrounding the foreign ion may be partially relieved by the vacancy.

Such complexes will contribute nothing to the measured conductivity. Assuming the presence of complexes, an elementary treatment following that of Seitz[11] gives for the self-diffusion coefficient of the sodium ion

$$D_m = d^2/3(\bar{\nu}n_v'/n + \bar{\nu}_c n_v^c/3n), \qquad (8)$$

where d is the spacing of the lattice planes. The jump frequencies of the sodium ion into free and associated vacancies are $\bar{\nu}$ and $\bar{\nu}_c$ respectively. The concentration of free positive ion vacancies is n_v' and of associated vacancies is n_v^c. The ratio of the measured diffusion coefficient to that calculated from the conductivity is now

$$D_m/D_c = 1 + \frac{1}{3}(\bar{\nu}_c/\bar{\nu})(n_v^c/n_v'). \qquad (9)$$

Since, experimentally, D_m/D_c is approximately two at low temperatures the concentrations of associated and free vacancies are of the same order of magnitude. This conclusion assumes that the jump frequencies $\bar{\nu}_c$ and $\bar{\nu}$ are approximately the same.

It is clear that above the knee of the diffusion curve where the concentration of positive ion vacancies is

[11] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 548.

TABLE I.

		$(\epsilon+\epsilon^i)$ (ev)	D_0 (cm²/sec)	ϵ (ev)	D_0' (cm²/sec)	ϵ' (ev)
NaCl	A	1.80	3.1	0 77	1 6×10⁻⁶	2.06
	B	1 89	14.	0 83	2.5×10⁻⁶	2 12
	C	1 98	63.	0.78	63. ×10⁻⁶	2 40
NaBr	A	1 53	0 67			
	B	1 68	5.98	0 84	10. ×10⁻⁶	1 68
	C	1.85	63	1 02	4 2×10⁻⁶	1 66

(A) Self-diffusion data. (B) From conductivity data.
(C) From Lehfeldt

large compared with that of impurities, the effect of the complexes is negligible and the Einstein relation is satisfied.

The complexes will contribute to the diffusion coefficient in the manner discussed only if they migrate through the crystal as freely as the unassociated vacancies. This condition is met if the jump frequencies of the impurity ion and the neighboring sodium ions into the associated vacancy are of the same magnitude. This implies that the associated impurity ions migrate enormously faster than the sodium ions since the chance that a given sodium ion is a nearest neighbor of a vacancy is only (n_v/n), the ratio of the concentrations of vacancies and of ions in the lattice. According to Etzel and Maurer[7] this ratio is about 5×10^{-6} for "pure" sodium chloride in the low temperature region.

A simple experiment was performed to obtain an order of magnitude estimate of the diffusion coefficient of a divalent ion, cadmium, in sodium chloride. A one-centimeter cube of sodium chloride was packed in a finely ground powder of a solid solution of cadmium chloride in sodium chloride. The concentration of cadmium chloride in the powder was one part in six hundred. The assembly was held at 490°C for 24 hours. The crystal was then removed and the surfaces lightly scraped to remove traces of the powdered salt. Analysis of the crystal by the polarographic method showed a cadmium concentration of one part in five thousand.

The interpretation of this experiment is a bit difficult because the diffusion coefficient of the cadmium ion is expected to depend upon the cadmium concentration. The average cadmium diffusion coefficient is, however, several hundred times larger than the self-diffusion coefficient of the sodium ion in sodium chloride at this temperature.

The degree of association of cadmium ions and vacancies is probably smaller than in the case of other divalent ions whose ionic radii do not agree as well with that of the sodium ion. The data of Etzel and Maurer[7] indicate that less than 1 percent of the cadmium ions form complexes in sodium chloride at a temperature of 450°C and a cadmium concentration of a few parts per million.

Breckenridge[12,13] has discovered and investigated an anomalous low frequency dielectric loss in the alkali halides. This loss is interpreted by Breckenridge as a dipole relaxation phenomenon due to the presence of paired vacancies and complexes of foreign ions and vacancies. The concentrations of complexes and pairs deduced by Breckenridge are much too small to account for the low temperature failure of the Einstein relation as observed in our experiments.

It appears highly desirable to investigate further the problem of association between foreign ions and vacan-
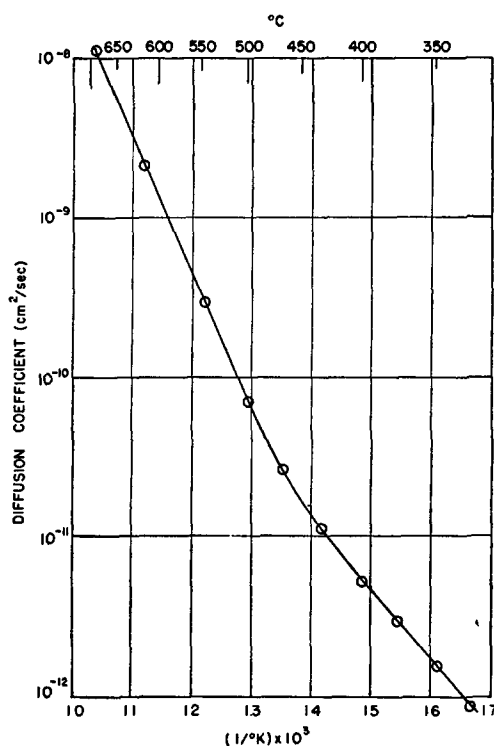

FIG. 9. Typical diffusion coefficient. Temperature curve for sodium bromide calculated from measured conductivity

cies in the alkali halides. A promising method of attack appears to be the study of the concentration dependence of the diffusion coefficients of foreign ions in the alkali halides.

[12] R G. Breckenridge, J. Chem. Phys. 16, 959 (1948).
[13] R G. Breckenridge, Technical Report 26, Laboratory for Insulation Research, MIT, 1949.