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Activation Energy for the Diffusion of Coupled Pairs of Vacancies in Alkali Halide Crystals*

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The theoretical activation energy for the diffusion of neutral combined pairs of positive- and negative-ion vacancies in alkali halides has been determined. Changes in Coulombic, repulsive, and polarization energies were taken into account with appropriate corrections for second-order effects. Calculations for the rigid and distorted lattice showed that distortion effects during diffusion are of appreciable magnitude. This energy contribution has been estimated as accurately as possible near

the saddle point. An activation energy of 0.375 ev was obtained for diffusion in the KCl lattice. This activation energy value shows that migration of neutral combined pairs of positive- and negative-ion vacancies, rather than diffusion via single vacancies, may well be the predominant process. The experimental evidence for this type of migration is discussed. It is concluded that diffusion by means of neutral combined pairs of vacancies is supported rather than prohibited by the theoretical results.

INTRODUCTION

IT was first suggested by Frenkel¹ that in a crystal in thermodynamic equilibrium there exist a number of imperfections. The researches of Schottky,² Wagner,³ and Jost⁴ established the two types of imperfections of general interest, namely, interstitial atoms and lattice vacancies. The theoretical work of Schottky and Jost, more recently refined by Mott and Littleton,⁵ showed on energetic grounds that only the formation and migration of lattice vacancies is of importance in alkali halides. The present study will be concerned with the migration of lattice vacancies.

The mobility of vacancies is of great importance in interpreting conductivity and diffusion data and in understanding the nature of *F*-centers.⁶ Mott and Littleton⁶ made a careful study of the energy of formation and migration

of single positive- and negative-ion vacancies in NaCl. In the case of single vacancies long-range polarization and, therefore, the theory of the dielectric constant play very important roles. They obtained an activation energy of 0.51 and 0.56 ev for the migration of the positive- and negative-ion vacancies, respectively. Experimentally it is known^{7,8} that in KCl at room temperature practically all the current is transported by positive ions. The experimental activation energy for diffusion from these conductivity measurements is about 0.82 ev.

It was shown recently by Seitz⁸ that positive- and negative-ion vacancies have a tendency to combine into neutral pairs, or even larger clusters. For a neutral pair of vacancies the energy of combination in KCl is about 0.93 ev. The jump frequency of the negative ions is very low^{7,8} but as a result of the high mobility of the positive ions isolated single vacancies would combine to form neutral pairs in less than a day at room temperature. At this temperature, then, the number of neutral pairs is expected to be considerably higher than the number of single vacancies. It is interesting to know how mobile the neutral pairs of vacancies are. It was pointed out by Huntington⁹ that, because of the absence of ions of the opposite sign, as shown in Fig. 1A, ions of a given kind are less restricted in jumping into the corresponding vacancies than in the case of the single vacancy illustrated in Fig. 1B.

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¹ J. Frenkel, *Zeits. f. Physik* **35**, 652 (1926).

² W. Schottky, *Zeits. f. physik. Chemie* **B29**, 335 (1935).

³ C. Wagner and W. Schottky, *Zeits. f. physik. Chemie* **B11**, 163 (1930).

⁴ W. Jost, *J. Chem. Phys.* **1**, 466 (1933); *Zeits. f. physik. Chemie* **A169**, 129 (1934); *Diffusion und chemische Reaktion in festen Stoffen* (Theodor Steinkopf Verlag, Dresden, 1937).

⁵ N. F. Mott and M. J. Littleton, *Trans. Faraday Soc.* **34**, 485 (1938).

⁶ For recent surveys see: N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1940); F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

⁷ C. Tubandt, *Handbuch d. Exp. Phys.*, Vol. XII.

⁸ F. Seitz, *Rev. Mod. Phys.* **18**, 384 (1946).

⁹ Private communication. See also reference 8, p. 403.

No quantitative study has been made of this process to the present time.

The most important experimental evidence in favor of diffusion mechanisms via neutral pairs comes from the work of Stern, Estermann, and Leivo (as discussed by Seitz⁸) on density changes accompanying heavy darkening of alkali halide crystals by x-rays. These measurements suggest very strongly that the major portion of the vacancies diffuse from the surface of the crystal. The low jump frequency of the halogen ions shows that at room temperature individual halogen vacancies diffuse extremely slowly from the surface into the lattice. Experimental evidence indicates, however, that under x-ray bombardment equilibrium darkening is established within a day, and the observed darkening extends to a depth of about 0.1 mm. The halogen ions would have jumped only a few lattice distances during this time and cannot, therefore, diffuse to the interior within the required time without assistance. Accordingly, Seitz⁸ suggested that the vacancies migrate in the form of neutral pairs of positive- and negative-ion vacancies. To account for the experimentally observed diffusion the activation energy for the migration of neutral pairs should be about 0.5 ev or less.

It is evident that the magnitude of the activation energy for the diffusion of neutral pairs plays a critical role in the foregoing interpretation. It is the purpose of this study to determine theoretically this activation energy.

ACTIVATION ENERGY IN THE RIGID LATTICE

In order that a neutral pair may diffuse it is necessary that ions of both charges jump into their corresponding vacancies. Since the negative vacancy is much less mobile than the positive one, the rate-determining step in such a diffusion mechanism must be the migration of a negative ion as indicated in Fig. 1A. The negative ions immediately adjacent to the positive vacancy will be the more mobile ones since they are less restricted. Thus, the problem of determining the activation energy for the migration of the neutral pair reduces to the calculation of the activation energy for the negative jump shown in Fig. 1A. Since a great deal of experimental information for potassium chloride is available, the numerical

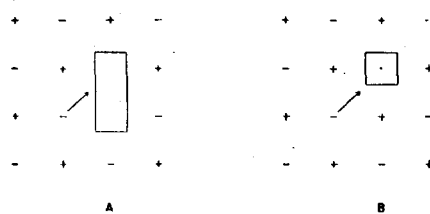


FIG. 1. A. Configuration of ions about a pair of vacancies. B. Configuration of ions about a single vacancy.

calculation will be carried out for this substance. The general techniques are applicable to all the alkali halides having the NaCl structure.

The calculation of the activation energy for the jump of a negative ion toward a neutral pair of vacancies will be carried out first for the rigid lattice. The surrounding ions will not be allowed to move away from their mean positions. They are polarizable, however, with polarizabilities α_- and α_+ . The problem is to calculate the position and energy of the saddle point of the energy barrier as the configuration changes from state A through the activated state B to state C, as illustrated in Fig. 2. Most of the techniques applicable in the rigid lattice can also be used with minor modifications for calculations in the distorted lattice. As the negative ion moves from the (0 0 0) position toward the (1 1 0) position the activation energy is determined by changes occurring in the Coulombic, repulsive, and polarization energies of the system.

1. Coulombic Energy Contribution

The most general mathematical technique for calculating Coulombic potentials in ionic crystals has been worked out by Ewald.¹⁰ The potential at any point in the lattice is given by a slowly converging series of the type

$$\phi(x, y, z) = \sum_n \sum_k e_k / |\mathbf{r}_k^n - \mathbf{r}|, \quad (1)$$

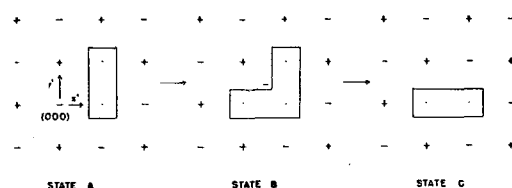


FIG. 2. Diffusion process in the rigid lattice.

¹⁰ P. P. Ewald, *Ann. d. Physik* **64**, 253 (1921); see also M. Born, *Problems in Atomic Dynamics* (Massachusetts Institute of Technology, 1926), pp. 158-164.

TABLE I. Ewald potentials as a function of x' and y' .

	$V_E(r_0/e)$				
y'/x'	0.40	0.45	0.50	0.55	0.60
0.2	-0.4662	-0.2271	0.0000	0.2271	0.4662
0.3	-0.3051	-0.1501	0.0000	0.1501	0.3051
0.4	-0.1509	-0.0729	0.0000	0.0729	0.1509
0.5	0.0000	0.0000	0.0000	0.0000	0.0000
0.6	0.1509	0.0729	0.0000	-0.0729	-0.1509
0.7	0.3051	0.1501	0.0000	-0.1501	-0.3051

where \mathbf{r} =vector from any origin 0 to any point in the cell, \mathbf{r}_k =vector from any origin 0 to any lattice point, k =basis index, n =cell index, e_k =electrostatic charge at point k of the basis, and \sum_n =summation over n . With the help of the theory of theta-functions Ewald succeeded in expressing Eq. (1) in terms of two rapidly convergent series. The following formulas will be needed in the present calculations. The potential, ϕ , at any arbitrary point, \mathbf{r} , is given by

$$\phi(\mathbf{r}) = \sum_k e_k \psi(\mathbf{r} - \mathbf{r}_k), \quad (2)$$

where

$$\psi(\mathbf{r}) = \psi_1(\mathbf{r}) + \psi_2(\mathbf{r}), \quad (3)$$

$$\psi_1(\mathbf{r}) = (4\pi/\Delta) \sum_n' \frac{\exp[-(1/4\epsilon^2)|\mathbf{q}^n|^2 + i\mathbf{q}^n \cdot \mathbf{r}]}{|\mathbf{q}^n|^2}, \quad (4)$$

$$V_E(x, y, z) = \frac{e}{r_0} \left[- \sum_{H_i} \frac{\exp[-(\pi^2/\epsilon^2 a^2) \sum (2H_i - 1)^2] (8 \cos \pi x' (2H_1 - 1) \cos \pi y' (2H_2 - 1) \cos \pi z' (2H_3 - 1))}{(\pi/4) \sum (2H_i - 1)^2} \right. \\ \left. - \sqrt{\pi} \sum_n \frac{G[\epsilon(a/2)[(n_1 - x')^2 + (n_2 - y')^2 + (n_3 - z')^2]^{\frac{1}{2}}}{\sqrt{\pi}[(n_1 - x')^2 + (n_2 - y')^2 + (n_3 - z')^2]^{\frac{1}{2}}} (-1)^{n_1 + n_2 + n_3} \right], \quad (6)$$

where $x' = x/r_0$, $y' = y/r_0$, $z' = z/r_0$, r_0 =anion-cation distance, $a = 2r_0$ =lattice constant, and $V_E(x, y, z)$ =Ewald potential at any point (x, y, z) . It has been found in practice that the series are very rapidly convergent and that three terms of each series are sufficient in the majority of cases if ϵ is taken to have the value $\epsilon a = 2(\pi)^{\frac{1}{2}}$. Numerical values of the Ewald potential for the perfect KCl lattice are shown in Table I as functions of x' and y' .

The potential at any point in a lattice containing a pair of neutral vacancies (Fig. 2) is obtained by subtracting the Coulombic potential contribution of the missing ions.

$$\psi_2(\mathbf{r}) = \sum_n \frac{G(\epsilon|\mathbf{r}^n - \mathbf{r}|)}{|\mathbf{r}^n - \mathbf{r}|} - \frac{\pi}{\Delta \epsilon^2}. \quad (5)$$

The symbols have the following meaning:

$\mathbf{r}^n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$ =translation vector of the basis, n_1, n_2, n_3 are integers ($-\infty$ to ∞ including 0) and \mathbf{a}_i are the vectors defining the unit cell.

$\Delta = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$ =volume of the cell.

$\mathbf{q}^n = 2\pi(n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2 + n_3 \mathbf{b}_3)$ =translation vector in reciprocal lattice.

\mathbf{b}_i =base vectors of the reciprocal lattice defined by $\mathbf{a}_i \cdot \mathbf{b}_k = \delta_{ik}$.

ϵ =arbitrary dividing value for expressing ψ as the sum of ψ_1 and ψ_2 .

$$G(x) = (2/\sqrt{\pi}) \int_x^\infty \exp(-\alpha^2) d\alpha.$$

The apostrophe over the summation sign in Eq. (4) means that the substitution $n_1 = n_2 = n_3 = 0$ is to be omitted.

For the purposes of this study these general expressions can be specialized for the sodium chloride type of lattice. The final equation for numerical computations, with the origin placed at a negative lattice point, as in Fig. 2A, is given by¹¹

As the negative ion is moved from the (0 0 0) position toward the (1 1 0) position the Coulombic potential energy of the whole system is changed. The total change in the Coulombic potential energy of the system, however, is equal to the change in the Coulombic potential energy of the moving ion.

This energy term is given by

$$E_- = -e[V_-(x', y', z') - V_-(0, 0, 0)] \\ = e[V_-(0, 0, 0) - V_-(x', y', z')]. \quad (7)$$

¹¹ For details see G. J. Dienes, thesis, Carnegie Institute of Technology, May 1947.

Here

$$\begin{aligned} V_-(0, 0, 0) &= (e/r_0)[1.7476 - (+\text{vacancy}) \\ &\quad + (-\text{vacancy})] \\ &= (e/r_0)[1.7476 - 1 + (1/\sqrt{2})] \\ &= 1.4547(e/r_0), \end{aligned} \quad (8)$$

in which $1.7476(e/r_0)$ is the Ewald or Madelung potential at a negative lattice site. $V_-(x', y', z')$ is given by

$$\begin{aligned} V_-(x', y', z') &= V_E(x', y', z') \\ &\quad + \frac{e}{r_0} \left[-\frac{1}{[(1-x')^2 + y'^2 + z'^2]^{\frac{1}{2}}} \right. \\ &\quad \left. + \frac{1}{[(1-x')^2 + (1-y')^2 + z'^2]^{\frac{1}{2}}} + \frac{1}{[x'^2 + y'^2 + z'^2]^{\frac{1}{2}}} \right], \end{aligned} \quad (9)$$

where $V_E(x', y', z')$ is the Ewald potential in a perfect lattice given by Eq. (6).

The Coulombic potential energy changes, calculated according to Eqs. (7), (8), and (9) as functions of x' and y' are shown in Table II. It will be shown later that because of the high degree of symmetry in the z direction the moving negative ion has no tendency to move out of the $x'y'$ plane. From symmetry it is clear that the energy terms have to be symmetrical about the diagonal line running from the positive ion at (0 1 0) to the positive vacancy at (1 0 0). This is related to the fact that the process of moving the negative ion at (0 0 0) into the negative vacancy at (1 1 0) is symmetrically equivalent to the process of moving the negative ion from (1 1 0) into a negative vacancy at (0 0 0). Symmetrically equivalent positions are given by $(x', y', 0)$ and $(1-y', 1-x', 0)$ for the coordinates employed. Thus, the energy barrier is symmetrical with respect to the diagonal, and the saddle point must occur somewhere along this line. The energy barrier is not symmetrical with respect to the diagonal from (0 0 0) to (1 1 0)

TABLE II. Coulombic potential energy changes in the rigid lattice.

Energies in electron volts.					
y'/x'	0.40	0.45	0.50	0.55	0.60
0.2	1.2069	1.4949	1.7902	2.0868	
0.3	0.7529	1.0373	1.3253	1.6133	1.8986
0.4	0.2075	0.4921	0.7905	1.0840	1.3616
0.5	-0.4853	-0.1447	0.1837	0.4957	0.7905
0.6			-0.4853	-0.1220	0.2075
0.7					-0.3837

because of the presence of a pair of vacancies rather than a single vacancy. Thus, the position of the saddle point on the (0 1 0) to (1 0 0) diagonal cannot be completely fixed by symmetry considerations. The calculated values of the Coulombic energy changes reflect, of course, the symmetry mentioned (compare, for example, positions (0.4 0.4 0) to (0.6 0.6 0) in Table II).

2. Repulsive Energy Contribution

It is generally agreed that the exponential repulsive law is the best available at the present time. Following Born,¹² Born and Mayer,¹³ and Pauling¹⁴ the repulsive potential function

$$\phi = c_{12} b e^{(r_1 + r_2 - r)/\rho} \quad (10)$$

has been used in the present study. For potassium chloride the following values of the constants were employed¹³

$$\begin{aligned} c_{++} &= 1.25, & r_0 &= 3.137 \times 10^{-8} \text{ cm}, \\ c_{--} &= 0.75, & r_+ &= r_1 = 1.33 \times 10^{-8} \text{ cm}, \\ c_{+-} &= 1.00, & r_- &= r_2 = 1.81 \times 10^{-8} \text{ cm}, \\ \rho &= 0.345 \times 10^{-8} \text{ cm}, & b &= 0.229 \times 10^{-12} \text{ ergs}. \end{aligned}$$

In calculating the repulsive energies, nearest (+-interaction) and next nearest neighbors (--interaction) surrounding the negative ion at the (0 0 0) position were taken into account. The expressions for the repulsive energies are (in ergs):

Nearest neighbors:

$$\begin{aligned} \phi_r(x', y', z') &= b e^{(r_1 + r_2)/\rho} \left[\sum'_{n_1^2 + n_2^2 + n_3^2 = 1} \exp[-(r/\rho)((n_1 - x')^2 + (n_2 - y')^2 + (n_3 - z')^2)^{\frac{1}{2}}] \right] \\ &= 0.229 \times 10^{-12} e^{9.1015} \left[\sum'_{n_1^2 + n_2^2 + n_3^2 = 1} \exp[-9.0925((n_1 - x')^2 + (n_2 - y')^2 + (n_3 - z')^2)^{\frac{1}{2}}] \right]. \end{aligned} \quad (11)$$

¹² M. Born and M. Goppert-Mayer, *Handbuch der Physik* 24/2, 623 (1933).

¹³ M. Born and J. E. Mayer, *Zeits. f. Physik* 75, 1 (1932).

¹⁴ L. Pauling, *Zeits. f. Krist.* 67, 377 (1928).

In this expression the substitution (1 0 0) corresponding to the positive-ion vacancy is to be omitted.

Next nearest neighbors:

$$\begin{aligned}\phi_r(x', y', z') &= 0.75be^{(2\pi a/\rho)} \left[\sum'_{n_1^2+n_2^2+n_3^2=2} \exp[-(r/\rho)((n_1-x')^2+(n_2-y')^2+(n_3-z')^2)^{\frac{1}{2}}] \right] \\ &= 0.17175 \times 10^{-12} e^{10.4930} \left[\sum'_{n_1^2+n_2^2+n_3^2=2} \exp[-9.0925((n_1-x')^2+(n_2-y')^2+(n_3-z')^2)^{\frac{1}{2}}] \right]. \quad (12)\end{aligned}$$

In Eq. (12) the substitution (1 1 0) corresponding to the negative-ion vacancy is to be omitted.

The equilibrium repulsive energies are obtained, of course, by letting $x'=y'=z'=0$, and the change in repulsive energy is given by

$$\Delta E_R = \phi_r(x', y', z') - \phi_r(0, 0, 0). \quad (13)$$

The contribution of ions further away is negligibly small.

The total energy changes caused by Coulombic and repulsive interactions are given in Table III. It will be noted that the energies are not completely symmetrical (compare (0.4 0.4 0) to (0.6 0.6 0)). The reason for this is that the calculations were made for the nearest and next nearest neighbors surrounding the (0 0 0) position which for simplicity were taken to be the same as those around the equivalent (1 1 0) position. The discrepancy is about 5 percent at the (0.6 0.6 0) position and is less than that near the saddle point. Such a small difference caused by asymmetry did not warrant any further calculations at this point. Asymmetry and distortion effects will be discussed later and have been included in the final energy values.

Interpolation along the diagonal gives a saddle point at $x'=0.55$, $y'=0.45$ with an energy of 1.324 ev. The position of the saddle point shows that the moving negative ion is attracted toward

the vacancies. This is to be expected physically since the positive vacancy provides additional room for the passage of the negative ion (Fig. 2B).

Calculations were made in the $x'=0.5$ and $x'=0.6$ plane for $z'=\pm 0.10$. The results showed that the energy is a minimum in the $x'y'$ plane and, therefore, the moving negative ion has no tendency to move out of this plane. This result is as expected from the symmetry in the z' direction.

The Coulombic and repulsive energy changes were also calculated for the perfect lattice containing a single vacancy. The ion-jump under consideration is shown in Fig. 1B. The activation energy obtained was 1.75 ev. Thus, a lowering of about 0.45 ev can be expected in the Coulombic and repulsive energies as a result of the fact that two vacancies are present instead of one. It is known, of course, that polarization plays a very important part in this process. The problem of determining the polarization energy contribution (including distortion of the lattice) was solved by Mott and Littleton who found an activation energy of 0.56 and 0.51 ev for the motion of the negative- and positive-ion vacancies in NaCl, respectively. Since a pair of vacancies creates essentially a dipole field, it would be expected that the lowering caused by polarization would be smaller than in the case of a single vacancy where long-range polarization plays an important role. If the difference in polarization for the single and double vacancies is greater than the differences in the Coulombic and repulsive terms for the two cases, the single vacancy type of diffusion would be favored. It is clear, then, that polarization contributions are of crucial importance in this problem.

3. Polarization Energy Contribution

The polarization energy contribution is conveniently separated into two parts; namely,

TABLE III.* Coulombic and repulsive energy changes in the rigid lattice.

Energies in electron volts					
y'/x'	0.40	0.45	0.50	0.55	0.60
0.2	1.0469	1.3501	1.6086		
0.3	1.0830	1.1983	1.3520	1.5400	
0.4	1.4939	1.3644	1.3115	1.3407	1.4208
0.5	2.7754	2.1318	1.6892	1.4159	1.2785
0.6					1.4259
0.7					1.8760

* The repulsive energy terms (ΔE_R) are not listed separately to conserve space. They are obtainable as the differences in the entries of Tables II and III.

a part arising from the negative ions and a part arising from the rest of the lattice. The ions surrounding the vacancies become polarized since the field arising from the vacancies is finite at the positions these ions occupy. This polarization has associated with it a dipole field and a certain polarization energy. The polarization of the moving negative ion changes as it moves because the Coulombic and dipole fields vary from point to point. The problem is to calculate the difference in polarization energy between a configuration in which the negative ion is at $(x' y' 0)$ (Fig. 2B) and the equilibrium configuration in which it is at $(0 0 0)$.

Klemm's¹⁵ technique of calculating polarization energies in a lattice containing a pair of vacancies can be applied directly to the equilibrium configuration. Consider the configuration of Fig. 3 in which the origin of the coordinate system is for the purposes of this section chosen at the missing positive ion site, the negative ion vacancy being taken at $(1 0 0)$. The dipole field, due to the pair of vacancies, is equivalent to that produced by a negative charge at $(0 0 0)$ and a positive charge at $(1 0 0)$. At any lattice point $(k m n)$ the electric field as the result of these charges is given by

$$\mathbf{E}_{kmn} = (e/r_0^2) \left[\frac{-(k, m, n)}{L_-^3} + \frac{(k-1, m, n)}{L_+^3} \right],$$

where

$$L_- = k^2 + m^2 + n^2, \quad L_+ = (k-1)^2 + m^2 + n^2.$$

Using parenthetical notation for vectors the foregoing expression may be written

$$\mathbf{E}_{kmn} = \frac{e}{r_0^2} \left[\frac{k-1}{L_+^3} - \frac{k}{L_-^3}, \frac{m}{L_+^3} - \frac{m}{L_-^3}, \frac{n}{L_+^3} - \frac{n}{L_-^3} \right].$$

The energy of the dipole induced on the ion at $(k m n)$ is given by

$$\epsilon_P = -\frac{1}{2} \alpha \mathbf{E} \cdot \mathbf{E}, \quad (14)$$

where α is the polarizability. Summing over the lattice points, Eq. (14) is easily transformed into

$$E_P = -\frac{1}{2} (e^2/r_0^4) [\alpha_- + \alpha_+] \left[\sum_{k+m+n=\text{even}} \mathbf{E}_{kmn}^2 \right]. \quad (15)$$

This expression is applicable to the calculation of

¹⁵ W. Klemm, Zeits. f. Physik 82, 529 (1933).

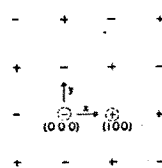


FIG. 3. Equivalent charges responsible for polarization. Rigid lattice, equilibrium configuration.

the polarization energy of a rigid lattice containing a neutral pair of vacancies. In numerical computations it is usually more convenient to carry out explicitly the dot product multiplications of Eq. (14) instead of using the summation formula of Eq. (15). This expression (Eq. (15)) includes the polarization energy of the negative ion which is eventually moved.

Klemm¹⁵ found that the polarization of the nearest neighbors surrounding the vacancies gave a good approximation to the polarization energy. The contribution of more remote ions will be estimated and discussed later. Long-range polarization, which is very important in the case of a single vacancy,⁵ is comparatively small in this case.

As the negative ion, which we shall assume is initially at $(0 1 0)$, moves to a point $(x y 0)$ the polarization energy of the configuration illustrated in Fig. 4 is to be calculated. A method analogous to Klemm's technique can also be used in this case. The field responsible for polarization arises from four point charges which produce the following electric fields at any lattice point $(k m n)$:

Negative charge at $(0 0 0)$:

$$\mathbf{E}_1 = -[e/r_0^2][(k, m, n)/L_-^3], \quad L_- = k^2 + m^2 + n^2,$$

Positive charge at $(1 0 0)$:

$$\mathbf{E}_2 = [e/r_0^2][(k-1, m, n)/L_+^3], \quad L_+ = (k-1)^2 + m^2 + n^2.$$

Positive charge at $(0 1 0)$:

$$\mathbf{E}_3 = [e/r_0^2][(k, m-1, n)/L'^3], \quad L' = k^2 + (m-1)^2 + n^2.$$

Negative charge at $(x y 0)$:

$$\mathbf{E}_4 = -[e/r_0^2][(k-x, m-y, n)/R^3], \quad R = (k-x)^2 + (m-y)^2 + n^2.$$

The polarization energy of the stationary ion at

TABLE IV.

Change of polarization energy of stationary ions (units of electron volts)				Dipole potential at $x', y', 0$ generated by polarized stationary ions		
ΔE_P^s				$V_P(r_0/e)$		
y'/z'	0.4	0.5	0.6	0.4	0.5	0.6
0.3	-0.0590	-0.1646		0.2003	0.2274	
0.4	-0.0227	-0.0875	-0.1778	0.1998	0.2109	0.2325
0.5	-0.0308	-0.0376	-0.0875	0.2233	0.2075	0.2109
0.6		-0.0308	-0.0227		0.2233	0.1998

($k m n$) is, then, given by

$$\epsilon_P' = -\frac{1}{2}\alpha\mathbf{E}' \cdot \mathbf{E}', \quad (16)$$

where $\alpha = \alpha_-$ for $k+m+n = \text{odd}$, $\alpha = \alpha_+$ for $k+m+n = \text{even}$, $\mathbf{E}' = \mathbf{E}_1 + \mathbf{E}_2 + \mathbf{E}_3 + \mathbf{E}_4$. We shall designate the sum of ϵ_P' over all stationary ions by E_P' . The change in the polarization energy of the stationary ions surrounding the vacancies is then from Eq. (16) and (14),

$$\Delta E_P^s = E_P' - E_P. \quad (17)$$

The energy ΔE_P^s is negative in the sense that the ions become more polarized during the jump of the negative ion, thereby lowering the activation energy. The numerical values of the energy are summarized in Table IV. The coordinates in this table are given in terms of the original system, $x'y'z'$, with the moving negative ion originally at (0 0 0).

The potential at ($x y 0$) due to the dipole at ($k m n$) is given by

$$v_P(x, y, 0) = (\alpha/r_0^2)\mathbf{E} \cdot [[-(k-x), -(m-y), -n]/R^3], \quad (18)$$

where

$$(1/r_0^2)[[-(k-x), -(m-y), -n]/R^3] = \text{radius vector from } (k m n) \text{ to } (x y 0).$$

Values of the total dipole potential at the position of the moving ion are given in Table IV. V_P is the sum of v_P over all k, m, n .

The most important change in the polarization energy of the system is caused by the polariza-

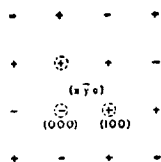


FIG. 4. Equivalent charges responsible for polarization. Rigid lattice, activated state.

TABLE V.* Sum of Coulombic, repulsive, and polarization energy changes in the rigid lattice.

Energies in electron volts			
y'/x'	0.4	0.5	0.6
0.3	0.4294	0.6921	
0.4	0.4453	0.4834	0.7269
0.5	0.7077	0.4089	0.4504
0.6		0.7077	0.3776

* The total polarization energy changes are not tabulated but are obtainable as the differences in the entries of Tables V and III.

bility of the moving negative ion. Since the Coulombic potentials and the dipole potentials at any point ($x' y' 0$) (in terms of the original coordinate system) are known, the field effective in polarizing the negative ion is easily obtained by graphical methods as the negative gradient of the total potential. Denoting this field by $\mathbf{F}(x', y')$ the polarization energy, E_P'' , of the negative ion when at position ($x' y' 0$) will be

$$E_P'' = -\frac{1}{2}\alpha_- \mathbf{F}(x', y')^2, \quad (19)$$

and the total change in polarization energy is given by

$$\Delta E_P = E_P' + E_P'' - E_P. \quad (20)$$

E_P'' was computed using the dipole field given in Table IV as well as the field \mathbf{E}' , arising from the four Coulomb charges. The total change in energy is finally given by

$$\Delta E_{\text{Total}} = \Delta E_C + \Delta E_R + \Delta E_P. \quad (21)$$

The values of ΔE_{Total} are shown in Table V.

The values of the ionic polarizabilities used in these calculations are those given by Pauling,¹⁶ i.e., $\alpha_- = 3.66 \times 10^{-24} \text{ cm}^3$, $\alpha_+ = 0.83 \times 10^{-24} \text{ cm}^3$. In magnitude the total polarization energy changes are comparable to the Coulombic and repulsive energy contributions.

Interpolation of the data of Table V along the diagonal from (0 1 0) to (1 0 0) determines the position and magnitude of the activation energy. The total energy curve is constructed from ΔE_C , ΔE_R , and ΔE_P versus distance along diagonal plots and the minimum determined graphically. A value of 0.400 ev was obtained at $x' = 0.514$, $y' = 0.486$.

4. Second-Order Energy Terms

The most important second-order effects in the rigid lattice result from the approximations

¹⁶ L. Pauling, Proc. Roy. Soc. A114, 181 (1927).

made in calculating the polarization energy changes. Energy contributions of the van der Waals type were neglected in this study. This will be estimated and discussed later.

We shall assume once again that the moving negative ion is at (0 0 0) and that the positive and negative ion vacancies are at (1 0 0) and (1 1 0), as in Fig. 2. The contribution of the next nearest neighbors to the polarization part of the activation energy was calculated near the saddle point, namely at $x'=0.5$, $y'=0.5$. This calculation included both the polarization energy of the next nearest neighbors and the change in the polarization energy of the negative ion at (0.5 0.5 0) arising from the change produced in the dipole field when the influence of next nearest neighbors is included. These two effects combine to decrease the activation energy by about 0.12 ev, which is about 10 percent of the total change in polarization energy.

There is also a dipole-dipole interaction term, which is rather difficult to calculate, arising from the strong dipole on the moving negative ion. An estimate can be made, however, of this energy contribution. Dipole-dipole interactions correspond to short-range forces, the energy of interaction falling off as $1/r^3$. Thus, it is reasonable to suppose that the most important contribution will come from the positive ion nearest the moving negative ion, i.e., the (0 1 0) position. This interaction was estimated for the case in which the negative ion is near the saddle point, namely, at $x'=0.5$, $y'=0.5$. The magnitude and orientation of the dipole on the negative ion is known. The field at (0 1 0), in the direction of decreasing r and θ (in this case θ is 180°), arising from a dipole of strength p on the negative ion at (0.5 0.5 0), is given by

$$\begin{aligned} E_r &= 2p \cos\theta/r^3 = -2p/r^3, \\ E_\theta &= p \sin\theta/r^3 = 0, \end{aligned} \quad (22)$$

where

$$p = 1.49\alpha_-(e/r_0^2).$$

This field is found to decrease the polarization energy of the positive ion at (0 1 0) by 0.21 ev. Since this ion is subject to a higher moment the dipole field polarizing the negative ion is changed by about 3 percent, giving approximately a 6 percent change in the polarization energy of the negative ion, or $\Delta E \sim \pm 0.07$ ev.

The contribution of ions further away is very small. Calculation for the negative ion at (1 -1 0) showed that its polarization energy was only changed by about one percent. If the other ions surrounding the vacancies contribute about the same amount, then the change in ΔE_p , from all stationary ions except that at (0 1 0), would be about 0.004 ev. With this is associated a change in dipole potential of about 1.5 percent, which in turn changes the polarization energy of the moving negative ion by about 3 percent or 0.04 ev. Thus, the dipole-dipole energy contribution of ions other than the positive ion at (0 1 0) is estimated to be about ± 0.05 ev.

The total dipole-dipole contribution is, therefore,

$$\Delta E = -(0.21 \pm 0.12) \text{ ev.}$$

Thus, a lowering in the activation energy of 0.09 ev or more is expected from this effect.

In other words, the combined contribution of the next nearest neighbors and of the dipole-dipole interactions will produce a lowering in the activation energy of about 0.21 ev or more. This lowers the activation energy for diffusion in the rigid lattice to about 0.20 electron volt.

Although the discussion of this and the previous sections is restricted to the rigid lattice, it is interesting to consider at this point the lowering of the activation energy which would result if the positive ion at (0 1 0) is allowed to move slightly outward along the line from (0 1 0) to (0.5 0.5 0). This would give more room for the passage of the negative ion. In order to calculate the energies involved in such a process the Coulombic, repulsive, and polarization energy changes for the negative ion at (0.5 0.5 0) and for the moving positive ion have to be taken into account. These calculations were carried out by procedures exactly analogous to those used previously. It was found that the positive ion would tend to move outward a distance of $0.014r_0$ and that the activation energy would be lowered by 0.027 ev as a result. The dipole-dipole interaction was neglected in this calculation and its inclusion might nullify the small displacement and energy change calculated above. It is concluded that only a very small displacement and lowering in activation energy can be expected from this effect.

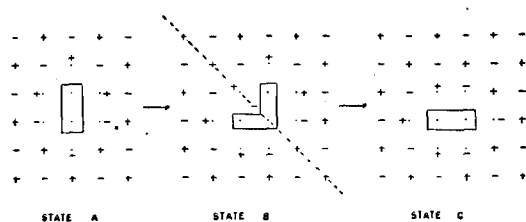


FIG. 5. Diffusion process in the distorted lattice.
— — — Line of symmetry.

ACTIVATED ENERGY IN THE DISTORTED LATTICE

The diffusion process in the rigid lattice investigated in the previous sections represents an idealized case. In the actual crystal the ions around the vacancies are displaced, that is, the lattice is distorted before the diffusion process starts. Thus, the starting configuration resembles state *A* of Fig. 5. During the jump of the negative ion the distortion changes continuously (state *B* of Fig. 5) and must end in a symmetrically equivalent arrangement, as illustrated in state *C* of Fig. 5. The ions adjacent to the vacancies in the *z* direction are also understood to be displaced. The detailed investigation of this process is very difficult because of the continuous change in distortion. The activation energy can be calculated, however, in a simply distorted lattice and the effect of continuous distortion on the saddle-point energy estimated. The first step in this calculation is the determination of the equilibrium distortion around the vacancies.

1. Equilibrium Distortion Around a Pair of Vacancies

In order to make such a calculation feasible in practice it is convenient to assume that all the ions immediately adjacent to the vacancies are displaced by the same amount. The ions will be displaced directly outward as shown in state *A* of Fig. 5, as a result of the missing electrostatic attractive forces. The configuration actually will be more complex because of the missing electrostatic repulsive forces. The investigation of configuration *A*, however, will provide a fair picture of the magnitude of the displacements. The Coulombic, repulsive, and polarization energy changes have to be calculated for the distortion process. The calculations will be described for a displacement of $0.1r_0$.

The change in Coulombic energy is calculated as follows: The potential of any ion in a displaced position is given by

$$V_d = V_{\text{Ewald}} - (\text{ion at lattice site}) - (+\text{vacancy}) \\ - (-\text{vacancy}) + (\text{ions in displaced positions}) - (\text{ions at ideal lattice sites}).$$

The equilibrium potential is given by

$$V = V_E - (+\text{vacancy}) - (-\text{vacancy}) + (\text{ions in displaced positions}) - (\text{ions at ideal lattice sites}).$$

The change in Coulombic energy is given by

$$\Delta E_C = ze(V_d - V), \quad (23)$$

where *z* is the valency. The ΔE_C terms were separately calculated for each displacement and summed up to give the total change in Coulombic energy.

The repulsive energy change was calculated directly as the difference between the total repulsive energy of state *A* (Fig. 5) and of the undistorted lattice, considering only the nearest neighbors of the displaced ions. The ion at $(-0.1 \ 0 \ 0)$, for example, has one neighbor at a distance of $1.0r_0$, one at $0.9r_0$, and three at $(1.01)\frac{1}{2}r_0$, whereas in the undistorted lattice it has five neighbors at a distance of $1.0r_0$.

The polarization energy of displacement was calculated from Eq. (14) as the difference between the polarization energy of ions in the displaced position and the polarization energy of the ions at the lattice sites.

The results of these calculations are represented by the curves of Fig. 6. Construction of the total energy curve from the data of Fig. 6 shows that the maximum decrease in total energy occurs at a displacement of $0.1r_0$. Thus, a distortion of the order of magnitude of 10 percent is to be expected around a pair of neutral vacancies.

2. Energy Changes in the Distorted Lattice

Once the equilibrium distortion around the pair of vacancies is known one can proceed with the calculation of the activation energy for diffusion in the distorted lattice. Since no simplified technique is available for taking into account the continuous change in distortion, the most convenient procedure at this point is to calculate the

various energy contributions assuming that the equilibrium distortion around the vacancies remains unchanged during diffusion. The change in the saddle-point energy due to change in distortion will be estimated later.

The Coulombic energy change can be calculated by a technique analogous to the one used in the case of the rigid lattice. The potential at any point $(x' y' 0)$ is given by

$$\begin{aligned} V(x', y', 0) &= V_E - (\text{ion at } 0\ 0\ 0) \\ &\quad - (+\text{vacancy}) - (-\text{vacancy}) \\ &\quad + (\text{ions in displaced positions}) \\ &\quad - (\text{ions at ideal lattice sites}) \\ &= V(\text{rigid lattice}) \\ &\quad + (\text{ions in displaced positions}) \\ &\quad - (\text{ions at ideal lattice sites}). \quad (24) \end{aligned}$$

The reference state will be $V(-0.1, 0, 0)$ and the Coulombic energy change is given by

$$\Delta E_C = e[V(-0.1, 0, 0) - V(x', y', 0)]. \quad (25)$$

The Coulombic energy changes calculated by Eq. (25) are considerably larger than the corresponding contributions in the rigid lattice. They are also obviously asymmetrical, the discrepancy becoming quite large (in such a direction as to raise ΔE_C) as x' and y' increase past the diagonal in the transition from $(0\ 1\ 0)$ to $(1\ 0\ 0)$. Thus, considerable error is introduced by neglecting the continuous change in ion displacement, and this error will tend to raise the activation energy. This effect will be discussed in detail later.

The repulsive energy contribution is calculated with the use of the principles described in the previous paragraph, that is, by adding the contribution of ions in the displaced position and subtracting it in the lattice site position. Both nearest and next nearest neighbors were taken into account. The repulsive energy contributions in the distorted lattice are considerably less than in the rigid lattice. The discrepancy due to asymmetry is in the direction of decreasing ΔE_R , that is, opposite to the one found for ΔE_C ; however, the two discrepancies do not cancel since the repulsive terms contribute considerably less to the activation energy than the Coulombic terms.

The calculation of the polarization energy change represents a straightforward application

TABLE VI. Total energy change in the distorted lattice.

Energies in electron volts					
y'/x'	0.40	0.45	0.50	0.55	0.60
0.25	0.577*				
0.30	0.5455	0.690*	0.8407		
0.35	0.570*	0.672*	0.792*		
0.40	0.6595	0.690*	0.7560	0.890*	1.0811
0.45		0.695*	0.725*	0.832*	
0.50	0.8630	0.719*	0.7264	0.805*	0.9856
0.55		0.820*	0.790*	0.815*	
0.60				0.850*	0.9033

* Interpolations from x' and y' plots of $\Delta E_{\text{electrostatic}}$ and $\Delta E_{\text{repulsive}}$.

of the method described for the rigid lattice. The position vector components k, m, n for the displaced ions, however, are no longer integers. The main difference between the two cases appears in the polarization energy of the moving negative ion. The change in this energy is derived principally from a decrease in the Coulombic field effective in polarizing the negative ion, since the dipole field is not appreciably altered. The net effect is an increase in the polarization energy and a corresponding increase in the activation energy. The asymmetry of the configuration under consideration tends to enhance this effect. As in the case of the rigid lattice, only nearest neighbors were taken into account in calculating

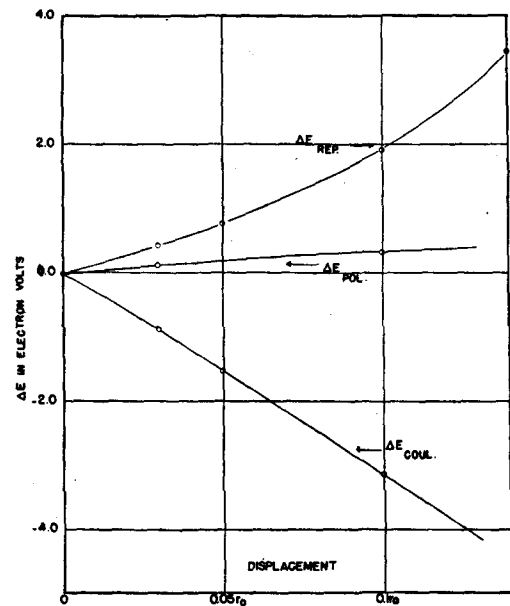


FIG. 6. Energy changes as a function of ion displacement around a pair of vacancies.

the change in polarization energy of the negative ion.

The total energy changes are summarized in Table VI. The starred values are interpolated quantities determined from plots of the electrostatic and repulsive energies *versus* x' and y' . Interpolation along the (0 1 0) to (1 0 0) diagonal from (0.45 0.55 0) to (0.55 0.45 0) fixes the position and energy of the saddle point. A value of 0.710 ev was obtained for the activation energy at $x'=0.507$, $y'=0.493$. The asymmetry of the configuration is clearly shown by the total energy values (compare, for example, (0.4 0.4 0) with (0.6 0.6 0)). The energy change near the saddle point may be too high by 0.1 ev or more because of this effect.

The second-order energy terms can be estimated by procedures analogous to the ones used in the case of the rigid lattice. The polarization energy contribution of the next nearest neighbors will be about the same since these ions are not displaced. This amounts to a lowering of the activation energy by about 0.12 ev.

Since the positive ion at (0 1 0) is now further away than in the rigid lattice, the dipole-dipole interaction will be somewhat less. The lowering of the dipole-dipole contribution is estimated to be

$$\Delta E = 0.12 \pm 0.06 \text{ ev.}$$

Hence, the activation energy is decreased by 0.18 ev or more as a result of these second-order polarization effects. This leads to an activation energy of 0.53 ev or less.

A brief calculation showed the van der Waals energy contributions to be negligible. Nearest neighbors only were considered and the following equation and constants were used:⁶

$$E_{\text{v.d.w.}} = -C/r^6,$$

$$C = 6.5952C_{+-} + 1.8067((C_{++} + C_{--})/2);$$

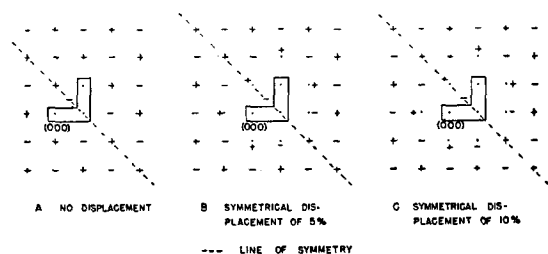


FIG. 7. Ion displacements around saddle-point configuration.

for KCl:

$$C_{++} = 24.3 \times 10^{-60} \text{ erg cm}^{-6},$$

$$C_{+-} = 48.0 \times 10^{-60} \text{ erg cm}^{-6},$$

$$C_{--} = 124.5 \times 10^{-60} \text{ erg cm}^{-6},$$

$$r_0 = 3.137 \times 10^{-8} \text{ cm.}$$

The change in van der Waals energy was computed for the distorted lattice with the moving negative ion at the (0.5 0.5 0) position. A value of 0.014 ev was obtained, which is negligible in comparison with the other energy terms.

2. Effect of Change in Distortion at the Saddle Point

It was pointed out in the last section that considerable errors are introduced by disregarding the change that occurs in distortion during the diffusion process. The magnitude of this effect can be estimated near the saddle point. As the negative ion approaches the saddle point the ions redistribute themselves in a symmetrical manner, as was shown in Fig. 5B. The problem is to calculate the energy changes arising from the changing configuration.

To render the calculation feasible in practice it was assumed again that all the ions are displaced the same distance from their lattice sites. The calculations were carried out for three relatively simple configurations from which the distortion of minimum energy could be obtained by interpolation. The diffusing negative ion was assumed to be at (0.5 0.5 0) which is very close to the saddle point. The configurations are shown in Fig. 7. It should be emphasized that ions immediately adjacent to the vacancies in the z direction, as well as those shown, are displaced. States A and C represent the two extremes. In Case A the distortion is zero, whereas in Case C the distortional displacement is 10 percent and the configuration is symmetrical. In the first case all the ions originally displaced around the pair of vacancies (Fig. 5A) are moved in to their lattice positions. In the second case the ions around (0 0 0) are moved outward 10 percent to create a symmetrical configuration. The actual ionic displacement lies between these two extremes (subject to the assumption that all ions are displaced the same distance). The energies of these three configurations were calculated relative to the energy of the simply distorted

lattice considered previously. The configuration of minimum energy was then determined by interpolation.

The calculations are entirely analogous to those made in determining the equilibrium distortion around a pair of vacancies except that more ions are moved. In determining the repulsive energies only nearest neighbors of the displaced ions were taken into account. In calculating the polarization energies the change in the polarization of the moving negative ion was calculated in each case. The change in the polarization energy of the surrounding ions, which is small compared to the polarization of the moving negative ion, was estimated from existing data for states *A* and *C* and was interpolated for state *B*. The following energy changes were obtained:

	No displacement Fig. 7A	5% displacement Fig. 7B	10% displacement Fig. 7C
ΔE_C	1.9630 ev	0.4681 ev	-0.6019 ev
ΔE_R	-0.7260	-0.4470	0.4050
ΔE_P	-0.8717	-0.1747	0.2674
ΔE_{Total}	0.3653 ev	-0.1536 ev	0.0705 ev

If the various energy changes are plotted against the displacement and the total energy *vs.* displacement curve is constructed, a minimum is obtained at a displacement of 4.8 percent. The lowering of activation energy arising from this redistribution of the ions is 0.155 ev. Dipole-dipole interactions were neglected in these calculations. This effect would be very small; moreover, it would tend to lower the activation energy.

On the basis of these calculations the best estimate of the activation energy for the jump of the negative ion in the distorted lattice is 0.375 ev. The activation energy is made up as found in Table VII.

DISCUSSION

It was shown in the previous sections that the activation energy for diffusion in the rigid lattice is 0.20 ev and in the distorted lattice it is 0.375 ev. In evaluating the contribution of second-order effects the estimates for both of these cases were made on the high side. It is recognized that the

TABLE VII. Final composition of terms determining the activation energy for diffusion. (Energies in electron volts.)

Coulombic energy changes, ΔE_C	= +1.330 ev
Change in polarization energy (of moving negative ion + nearest neighbors around vacancies), ΔE_P	= -0.730
Repulsive energy changes, ΔE_R	= +0.110
Second-order polarization terms	= -0.120
Energy change arising from change in distortion around vacancies	= -0.155
Dipole-dipole interaction energy	= -0.060
Total energy change, ΔE_{Total}	+0.375 ev

distorted lattice configurations treated here are somewhat idealized. The lattice distortion around a pair of vacancies and around the saddle-point configuration is undoubtedly more complex than assumed in this work. Any change in activation energy arising from a different distribution of ionic displacements would, however, be small. Moreover, since such a state would be of lower energy, the change would occur in the direction of lower activation energy. Thus, any second-order or distortion effect not sufficiently taken into account would lower the activation energy of 0.375 ev given above.

Our inaccurate knowledge of repulsive potentials is probably the most important source of error in this calculation. The agreement between the calculated and measured total energies for alkali halides is within about 2 percent. If all of this error is due to the repulsive terms, an inaccuracy of six percent in the activation energy can be expected from this source. Van der Waals type of interaction is unlikely to introduce an error larger than two to three percent. Thus, the activation energy may be higher by about ten percent (0.04 ev). On the other hand, all the second-order effects were estimated in such a way as to yield an activation energy on the high side, and the true energy may easily be lower by 0.1 ev or about 25 percent. Our estimate of the error in activation energy is, therefore, +10 percent and -25 percent. It must be admitted, however, that the value of ρ assumed in $\phi_{\text{repulsive}}$ may well vary with distance for such large displacement of ions. At our present state of knowledge there is no way of estimating this effect.

Although these results cannot be compared closely with the work of Mott and Littleton on

the diffusion of single vacancies in sodium chloride, the lower activation energy we have obtained for pairs of vacancies in contrast to their value for single vacancies (0.38 compared to 0.56 ev) shows that the migration of neutral pairs of vacancies may well be the preferred diffusion process when pairs are available. Mott and Littleton's value of 0.51 ev for the diffusion of the positive vacancies is to be compared with experimental activation energies of 0.8 to 0.9 ev. All details of Mott and Littleton's work have not been published and, therefore, the relative magnitude of the various energy terms is not available, but the investigators state that in their opinion the discrepancy is probably caused by the repulsive terms. It is unlikely that an error of such magnitude would be involved in the case of the combined vacancies considered here since the repulsive energy contributions amount only to 0.110 ev.

It will be recalled that the activation energy for the diffusion of the effective agent was estimated to be 0.5 ev or less from experimental studies of the darkening of alkali halide crystals by x-rays. Thus, as far as the experimental evidence is concerned, diffusion by means of neutral combined pairs of vacancies is supported rather than prohibited by these calculations.

SUMMARY

1. The activation energy for the diffusion of neutral combined pairs of positive- and negative-ion vacancies in potassium chloride has been calculated. The main energy contributions are due to Coulombic, repulsive, and polarization energy changes. The main contribution to the polarization part of the activation energy comes from the polarization of the diffusing negative ion. Second-order energy terms, such as polarization of next nearest neighbors, dipole-dipole interactions, and contributions caused by changes in the distortion of the lattice during diffusion have been estimated.

2. Calculations for the rigid KCl lattice show that in this case, when the ions are not allowed

to move away from their mean lattice positions, the theoretical activation energy for diffusion is 0.20 ev.

3. In an actual crystal there is a ten percent lattice distortion around a neutral pair of vacancies. The distortion changes continuously during diffusion. The activation energy was calculated in two steps. The position and energy of the saddle point were determined in a lattice with fixed distortion (10 percent), then the lowering in activation energy at the saddle point, resulting from the redistribution of ionic displacements was calculated. An activation energy of 0.375 ev was obtained for diffusion in the distorted KCl lattice. The estimated error in this energy value is +10 percent and -25 percent. The activation energy is made up as follows:

$$\begin{array}{ll}
 \Delta E_{\text{Coul.}} & = +1.330 \text{ ev,} \\
 \Delta E_{\text{Pol.}} & = -0.730 \text{ ev,} \\
 \Delta E_{\text{Rep.}} & = +0.110 \text{ ev,} \\
 \Delta E_{\text{Second-order terms}} & = -0.335 \text{ ev,} \\
 \hline
 \Delta E_{\text{Total}} & = +0.375 \text{ ev.}
 \end{array}$$

4. Comparison of these results with the work of Mott and Littleton on the diffusion of single vacancies in NaCl shows that the migration of neutral combined pairs of positive- and negative-ion vacancies may be the predominant process when pairs of vacancies are present in appreciable numbers.

5. Experimental evidence from heavy darkening of alkali halide crystals with x-rays indicates that the activation energy for diffusion should be 0.5 ev or less. As far as the experimental evidence is concerned, diffusion by means of neutral combined pairs of vacancies is supported rather than prohibited by the theoretical results.

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