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A Note on the Hole Theory of Diffusion

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The activation energy Q_x for diffusion in a dilute metallic solution cannot be less than the activation energy Q_0 for self-diffusion, if the solute atoms can move only through the medium of "holes" which diffuse to them from the solvent lattice, displace them, and leave in another direction. Since the experiments show that generally $Q_x < Q_0$ an alternative mechanism is required. Solute atoms which are not so firmly bound in the lattice as are solvent atoms will tend to trap holes to form solute-hole molecules. These molecules can move as units through the dense solvent lattice by cycles of inversion and re-orientation. This mechanism yields for the diffusion constant the value

$$D = A^* \exp[-(W+S)/RT],$$

where W is the energy required to form a hole adjacent to a solute atom, and S is the activation energy for re-orientation or inversion of a solute-hole molecule. $Q_x (\equiv W+S)$ may be much smaller than either Q_0 or the binding energy of the solvent. A^* should be significantly less than the corresponding A for self-diffusion. Both these predictions are in accord with the data. The same considerations should apply also to diffusion in liquids.

1. The Problem and the Proposed Mechanism

Stiegman, Shockley and Nix[1] (SSN) decide from energy considerations that diffusion in dilute solid metallic solutions probably occurs through the medium of vacant lattice sites ("holes") rather than by simple interchange of position between pairs of atoms or by a process involving interstitial atoms. According to the hole theory the diffusion constant, they say, is

$$D_x = \nu\delta^2 \exp[-(H_0+J_x)/RT] \equiv A \exp[-Q_x/RT], \quad (1)$$

where ν is the frequency of the atomic vibrations and δ is the lattice spacing; H_0, the energy required for forming a hole in the solvent lattice, is of the order of the binding energy and J_x, the activation energy for passage of a solute atom into an adjacent hole, is presumably considerably smaller. The data accumulated in Table II of SSN show that for a given solvent Q_x has its greatest value (Q_0) for self-diffusion and may be as low as $Q_0/2$ for other solute elements. They conclude: "If hole diffusion is the dominant process, the energy H_0 should be the same for a given solvent (the concentration of the solute in all cases is small) and therefore all changes in Q should come from J_x. We are, therefore, forced to assume either that J_x is at least as large as H_0 and is very sensitive to the nature of the solute or that another process of diffusion is involved."

Actually the matter is more desperate than SSN indicate. Eq. (1) gives correctly the diffusion constant for self-diffusion and for the diffusion of solutes for which $J_x > J_0$, J_0 being the activation energy for passage of a solvent atom into an adjacent hole. But to the cases of practical interest, where $Q_x < Q_0$, Eq. (1) does not apply. Briefly, the diffusion of the solute atoms is finally limited by the rate at which holes diffuse to them from the hinterland of the solvent. Even if $J_x = 0$, D_x should exceed D_0 only by a numerical factor of the order of the coordination number, and Q_x should be identical with Q_0. This conclusion seems to be inevitable so long as diffusion of solute atoms is supposed to occur by means of holes which approach from the reaches of the solvent lattice, pass through solute atoms and displace them, and retreat in another direction.

There is another mechanism of diffusion, involving holes, which avoids this impasse. If the binding between a solute atom and its neighboring solvent atoms is less tight than the binding between neighboring solvent atoms, holes will appear preferentially in sites adjacent to solute atoms. Statistically the lattice will contain a certain concentration of solute-hole molecules; the fraction of the solute atoms instantaneously associated with holes to form diatomic molecules will be

$$z \exp[-W/RT],$$

where z is the coordination number and W is the

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[1] J. Stiegman, W. Shockley and F. C. Nix, Phys. Rev. **56**, 13 (1939).

energy required for removing a solvent atom from a site adjacent to a solute atom. A solute-hole molecule can proceed amoeba-like through the lattice by cyclic changes in its orientation—that is, by cyclic rearrangements of the surrounding solvent atoms—without having to wait for an additional hole to diffuse to it from the solvent lattice. It is this random drift of solute-hole molecules which is proposed as the dominant process in the diffusion of solute atoms, in the cases where $Q_x < Q_0$. This mechanism yields for the value of the diffusion constant

$$D_x = A^* \exp\left[-(W+S)/RT\right] \equiv A^* \exp\left[-Q_x/RT\right],$$

where S is the activation energy for passage of a solvent atom into an adjacent hole, when both the solvent atom and the hole are near neighbors of a solute atom. Neither of the two terms now composing Q_x is directly related to H_0, J_0, or J_x defined above. It appears that Q_x need not be restricted to a narrow range of values; it may be considerably smaller than either Q_0 or the binding energy of the solvent. A^* should be smaller than the corresponding A_a for self-diffusion by a factor which decreases exponentially with the number of moves a trapped hole must make to complete a cycle displacing the solute-hole molecule by one lattice-spacing. Some such trend appears in the A values in Table II of SSN: for Cu, $A_a/A^* > 100$; for *Pb*, $A_a/A^* \cong 12$. The serious uncertainty of measured or calculated A values limits, of course, the worth of this apparent agreement.

The arguments basic to these statements are presented in the following sections.

2. Diffusion Constant for Holes

Consider a crystal containing N_a normal atoms a and N_0 holes 0. In equilibrium, when the free energy is a minimum,

$$N_0/N_a = f = \exp\left[-H_0/RT\right].$$

Each hole occasionally moves a distance of one lattice-spacing p. Each such move is assumed independent of all preceding moves—this is true if the frequency n of moves by a particular hole is small in comparison with the frequency ν of the atomic vibrations. If J_0 is the activation energy for passage of a hole to an adjacent lattice site,

$$n = \nu \exp\left[-J_0/RT\right].$$

After n moves of a particular hole (which will on the average require unit time) the vector displacement[2] of the hole from its original position will be

$$\mathbf{S}_0 = \sum_n \mathbf{p}_i,$$

each vector $\mathbf{p}_i$ having one of the several possible directions. Forming the scalar product of each side by itself, and averaging over many holes each of which has made n moves:

$$\langle S_0{}^2\rangle_{\text{Av}} = \langle \sum_n \mathbf{p}_i \cdot \mathbf{p}_i \rangle_{\text{Av}} + \langle \sum_{i\neq j}\sum \mathbf{p}_i \cdot \mathbf{p}_j \rangle_{\text{Av}} = np^2,$$

the products $\mathbf{p}_i \cdot \mathbf{p}_j$ being as often positive as negative. The expression np^2 is clearly identical, except for a numerical factor determined by the geometry, with the diffusion constant D_0 for holes in the diffusion equation

$$\dot{N}_0 = D_0 \nabla^2 N_0;$$

that is,

$$D_0 = np^2 = \nu p^2 \exp\left[-J_0/RT\right].$$

This same device will be generally used hereafter: an $\langle S^2\rangle_{\text{Av}}$ will be calculated and set identical with the corresponding diffusion constant D.

3. Constant of Self-Diffusion

A move by a hole is obviously identical with a move (in the opposite sense) by an atom. Let a few of the a atoms be marked (for example, be made radioactive). The probability that a single move by a particular hole will also be a move of a particular marked atom is $1/N_a$. The total displacement S_a of a particular marked atom from its original position, after the N_0 holes in the crystal have made an average of n moves each, will be given by

$$\langle S_a{}^2\rangle_{\text{Av}} = n\frac{N_0}{N_a}p^2.$$

It follows that

$$D_a = fD_0 = D_0 \exp\left[-H_0/RT\right] = \nu p^2 \exp\left[-(H_0+J_0)/RT\right].$$

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[2] This method was suggested by M. J. Polissar, J. Chem. Phys. 6, 833 (1938).

That is, the diffusion constant for self-diffusion is smaller than the constant for hole-diffusion by a factor which is just the fractional concentration of holes. The division of Q_0 into two terms, one the energy H_0 required to form a hole and the other the energy of activation J_0 for an atom to move into an adjacent hole, is patently justified.

4. CONSTANT FOR DIFFUSION OF IMPURITY ATOMS

Let the few marked a atoms be replaced by chemically-different atoms x. If an x atom requires an energy of activation $J_x > J_0$ for moving into an adjacent hole, the probability that it will so move is only $\exp[-(J_x - J_0)/RT]$ times the probability that a marked a atom in the same position would move into the hole. It follows that

$$\begin{aligned} D_x &= D_a \exp[-(J_x - J_0)/RT] \\ &= \nu p^2 \exp[-(H_0 + J_x)/RT] \qquad (2) \\ &\equiv A_0 \exp[-Q_x/RT]. \end{aligned}$$

This case of $J_x > J_0$ appears, however, to be without practical interest, for Table II of SSN shows that $Q_x < Q_0$ for all the dilute metallic solutions listed there. It is clear on reflection that Eq. (2) is not applicable when $J_x < J_0$—that is, when an x atom is more likely than an a atom to move into an adjacent hole. The successive moves of an x atom are then not generally independent, for the x atom will interchange positions with an adjacent hole a number of times before the hole can escape by capturing one of the a atoms; it is certainly not legitimate to count these to-and-fro moves as contributing to the mean square displacement of the x atom from its original position. An *upper bound* for D_x, if only this mechanism of hole-capture-hole-release is operative, can be calculated as follows: Consider the case most favorable for x atom diffusion, in which J_x has the extreme value zero. Imagine each x atom surrounded by a "sphere of influence" containing several a atoms, and assume that whenever a hole reaches the boundary of this sphere it inevitably and immediately gravitates in to the x atom and displaces it by one lattice-spacing, passing out of the sphere in another direction. The probability that a single move of a particular hole will place it on the boundary of a particular sphere of influence is b/N_a, where b is the number of a atoms on this boundary and is of the order of magnitude of the coordination number. This by assumption is also the probability that a single move by a particular hole will result in a move of the particular x atom in this sphere. The total displacement S_x of the particular x atom after each of the N_0 holes present has made an average of n moves will be given by

$$\langle S_x^2 \rangle_{\text{Av}} = bnp^2 N_0/N_a,$$

and it follows that

$$D_x = bD_a.$$

The diffusion constant, even for $J_x = 0$, is seen to exceed the constant for self-diffusion only by a factor of the order of 10, and the Q values for the two are the same except for a possible temperature dependence (presumably negligible) of the size of the sphere of influence.

This mechanism, in which the holes diffuse to the impurity atoms, displace them, and move on, is clearly in disagreement with the values of Q_x in Table II of SSN, not essentially because those values are *markedly* smaller than Q_0, but because they are *at all* smaller than Q_0. The alternative mechanism of molecule-motion, which avoids this limitation, is developed in the next section.

5. FORMATION AND DRIFT OF SOLUTE-HOLE MOLECULES

The holes in their equilibrium distribution (which they will attain relatively rapidly, since they diffuse rapidly) will not be scattered at random in the lattice, but will tend (1) to cluster around x atoms if these are not so tightly bound to their neighboring a atoms as a atoms are bound to one another, and will tend (2) to avoid contiguity with x atoms if the $x-a$ binding is more firm than $a-a$ binding. This is readily seen either by considering the probable moves of a hole in the vicinity of an x atom or by using the Boltzmann theorem to find the average local equilibrium concentration of the holes. Case (2), in which the holes detour around x atoms, yields a slower diffusion for x than for a atoms and hence is without practical interest. In case (1), where x atoms are more likely than a atoms to have holes associated with them, it is convenient and legitimate to speak of xo molecules as statistically present in the lattice. In the simplest situation, where the disturbing influence of an x atom extends not far beyond its nearest neighbors, the fraction of the sites adjacent to x atoms which will in equilibrium be vacant is

$$\exp[-W/RT],$$

where W is the energy necessary for removing an a atom from one of these sites. The fraction of the x atoms instantaneously associated with holes to form a diatomic xo molecules is therefore approximately

$$z \exp[-W/RT],$$

where z as before is the number of nearest neighbors.

It remains only to notice that an xo molecule can travel, unassisted by additional holes, through the a lattice. A typical cycle which restores the molecule to its original configuration and orientation but leaves it displaced by one lattice-spacing is shown in Fig. 1, the lattice being approximated by a plane square array. The diagonal orientation of the molecule in this simple array (Fig. 1 (3) and (5)) is a sort of excited state—in a more complicated lattice so wide a separation between x and o might never have to occur in the course of a cycle (for example, it would not occur in a plane hexagonal array).

The rate of diffusion by this mechanism can be estimated very roughly as follows: Consider first the case in which inversion of the molecule requires less energy of activation than does re-orientation—that is, the x atom is more likely than an a atom to move into the trapped hole. Suppose that m moves of the hole are necessary for completing a displacement-cycle, and that each move can occur in q directions only one of which contributes to completion of the cycle. The probability that a given sequence of m moves will complete a cycle and so advance the molecule by one lattice-spacing is $1/q^m$. In the time required for n moves of a trapped hole ($n \gg m$) the molecule will have moved a distance S_d given by

$$\langle S_d^2 \rangle_{\text{Av}} = np^2/mq^m,$$

where p as before is the lattice-spacing. The diffusion constant for xo molecules is therefore

$$D_d = \nu p^2/mq^m \exp[-S/RT],$$

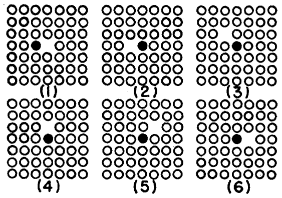

FIG. 1. A cycle of inversion (1–2) and reorientation (2–6) which moves a solute-hole molecule one lattice-spacing.

where S is the activation energy for moving an a atom into an adjacent hole, both the a atom and the hole being in the immediate neighborhood of an x atom. Correspondingly, the diffusion constant for x atoms generally, whether associated with holes or not, is

$$\begin{aligned} D_x = z\nu p^2/mq^m \exp[-(W+S)/RT] \\ = A^* \exp[-Q_x/RT]. \end{aligned}$$

With this mechanism Q_x again appears as the sum of two interpretable terms, but neither of these is directly related to the work necessary for forming a hole in the a lattice, nor to the activation energy for moving a hole about in the a lattice, nor to the activation energy for moving an x atom into an adjacent hole. It is plausible (though not essential) to suppose that if $W < H_0$, then also $S < J_0$. At any rate, Q_x is left largely unrestricted, and it is entirely reasonable that Q should generally be larger for self-diffusion than for the diffusion of any solute whose solubility increases with increasing temperature. Since z, q and m are all of the same order, evidently A^*, with this mechanism, should be significantly less than the corresponding A for self-diffusion, calculated on the basis of the other mechanism.

In the second possible case, where the activation energy for passage of the x atom into the trapped hole exceeds that for passage of an a atom into the hole, the rate of diffusion would be limited by the rate of inversion of molecules rather than by the rate of re-orientation. S as defined above would then be replaced by the activation energy for inversion, and A would be larger than A^* estimated above. This case seems less likely to occur than does the alternative discussed in detail in the two preceding paragraphs.

6. Range of Application of the Mechanism

None of the discussion has involved the ratio of the concentration of holes to that of x atoms. Either of these may far outnumber the other. In particular, the concentration of impurity atoms may increase from zero up to the point where interactions among the impurity atoms become appreciable. The arguments, in short, apply to the same range as do the usual "infinite dilution" theories.

No use has been made of the periodicity of the lattice. For this reason it seems that the foregoing considerations ought to apply without change to dilute liquid solutions, wherever the hole theory of diffusion is at all applicable. It is uncertain from the data[3] whether the solute-hole molecule mechanism is commonly suitable for accounting for diffusion in liquids—that is, whether Q_0 commonly exceeds Q_x.

I am indebted to Dr. C. W. Hewlett, Mr. C. G. Found and Dr. W. Shockley for several discussions on this subject.

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[3] H. S. Taylor, J. Chem. Phys. **6**, 331 (1938).

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Transport Phenomena in Mixtures of Gases

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The theory of transport in gases taking into account the full effect of quantum statistics is extended to include mixtures as well as one-component gases. The method of Lorentz, Hilbert, and Enskog, which was used previously in the development of the quantum theory of transport in a single component gas, is used again in this more general case. As is to be expected, all transport equations have formally the same dependence on velocity, temperature, and pressure gradients as in the classical statistics, the effects of diffraction and interference introduced by the quantum statistics appearing only in the coefficients themselves. Expressions for the viscosity, heat conductivity, pressure diffusion, and thermal diffusion coefficients into which assumptions with regard to the interaction laws may be introduced have been obtained. It is expected that these expressions may form the basis for calculation based on plausible assumptions as to the interaction that will provide a relatively good test of these laws as well as of the theory itself.

Introduction

The study of transport phenomena in gases has been recognized as a most promising field of investigation having as its objective the determination of intermolecular forces. The study of viscosity, heat conductivity and diffusion by numerous early investigators together with the rigorous analytical treatments of the subject given by Enskog and Chapman have demonstrated fully the sensitivity of the method and the practicality of the calculations which lead to the possibility of detailed comparisons between theoretical results and experimental observations.

With the introduction of the quantum statistics, the study of transport phenomena in gases took on a further significance, which was to be found in the possibility of an experimental test of these statistics. Certain discrepancies between observational data and the results of calculations based on the classical theory of Chapman and Enskog had already appeared. These discrepancies, which were observed for all transport coefficients, were at first attributed to the assumption of incorrect interaction laws on the basis of which the theoretical results were obtained. That this interpretation of the discrepancies was inadequate was demonstrated by Massey and Mohr[1] for the case of viscosity and heat conductivity in single component gases. The considerable improvement in the theoretical results obtained by these authors when quantum-

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[1] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. **A141**, 434 (1933): **A144**, 188 (1934).