

# THERMAL DIFFUSION IN CRYSTALLINE SOLIDS

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## I. INTRODUCTION

If a temperature gradient is applied to a homogeneous system of more than one component, a concentration gradient will slowly build up until a steady state is reached in which a time-invariant concentration gradient exists with a magnitude characteristic of the system. This phenomenon will first be observed by Ludwig (112) in aqueous sodium sulfate solution and was later extensively studied in other electrolyte solutions by Soret (173–175). It is generally called the Soret, or sometimes the Ludwig–Soret, effect. For a one-dimensional system Fick's law of diffusion (161, 182) must be modified thus

$$J_i = -D_i \frac{\partial n_i}{\partial x} - D_i' n_i \frac{dT}{dx} \quad (\text{Eq 1})$$

$J_i$ , the flux of species  $i$ , is the number of moles of  $i$  crossing a unit area in the  $yz$  plane per unit time in the direction of the positive  $x$  axis,  $n_i$  is the number of moles of  $i$  per liter,  $D_i$  is the isothermal diffusion coefficient, and  $T$  is the absolute temperature.  $D_i'$  is called the thermal diffusion coefficient. In the steady state ( $J_i = 0$ ), the equation yields

$$\left( \frac{d \log n_i}{dT} \right) = - \frac{D_i'}{D_i} = - s_i \quad (\text{Eq 2})$$

For dilute solutions  $s_i$ , the thermal diffusion factor, is not strongly dependent on concentration. Extensive measurements of the thermal diffusion factor in liquids (88, 182) and gases (69) have provided valuable information on molecular mechanisms of migration and intermolecular forces.

In contrast, extended thermal diffusion measurements in crystalline solids have been made only in the last 10 years. The object of this review is to give a brief account of the information available and its molecular interpretation. A recent review (96) gives references to transport through membranes of high molecular weight organic materials in which simple molecular interpretations are not feasible. These systems and all work on amorphous materials will not be considered.

The relatively late development of interest in crystalline solids can be ascribed in part to a previous lack of sufficient knowledge of the kinds and concentrations of intrinsic lattice defects, such as vacant sites and interstitial atoms, occurring in simple crystals and to even a modest amount of information on isothermal diffusion mechanisms involving such defects. A few recent studies of thermal diffusion in solids have been stimu-

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lated by technological needs. The properties of metals and alloys subjected to unusually high temperatures and temperature gradients for long periods are of particular interest in nuclear reactor technology, *e.g.*, the studies on hydrogen in zirconium reported below. Certain thermal diffusion results for ionic solids, described in section III.B.3, have led to speculations in connection with the design of thermoelectric devices (29). The meeting of such technological requirements will not be discussed.

#### A. EARLIEST MEASUREMENTS

The first Soret effect measurements in solid systems by Wessels (185) were mainly on noncrystalline materials but included one simple mixed crystal system. He found that in a solid solution of bibenzyl (98%) and azobenzene (2%) the azobenzene concentrated toward the hot end, giving a concentration gradient which was detected by the red color of the azobenzene. This remains the only observation for a simple organic mixture and the only use of a colorimetric method. The first observation for a metallic alloy was by Ballay (13) who observed a 0.6% difference in Pb content between the 200 and 300° zones of a 16-cm bar of lead (48.8%)–thallium (51.2%) alloy maintained at 360° at one end and in air at the other end for 336 hr. He later (14) observed the effect in Pt–Rh and Pb–Th alloys.

Much more extensive were measurements by Reinhold (136, 137, 145, 146) between 1929 and 1937 principally on ionic solids. The first system studied (136, 137) was a mixed crystal of CuI (0.25 mole fraction) in AgI. A cylinder 5 cm long with a 1-cm<sup>2</sup> cross section was kept with its ends at 325 and 210° for 4 days, and a 15 mole % concentration variation was found, the silver moving to the hot end. However, the experiment was later criticized (57) since the salt undergoes a phase transformation at 270°. Indeed, later experiments over a wide range of composition (57) showed that a separation was observed only if the temperature range spanned the transition temperature. Similar results were obtained for Ag<sub>2</sub>S–Cu<sub>2</sub>S and for AgBr–CuBr (145). Finally, a weak Soret effect was found in Cu–Se (146). Because of the phase transitions encountered and the smallness of the effect in their absence, and the difficulty of precise measurement with current techniques, the results of Reinhold, and the other results quoted in this section, are mainly of historical interest. An adequate review is available (57, 145).

A less direct way of studying thermal diffusion in ionic conducting solids was also pioneered by Reinhold (135, 138–144). When a crystal is placed between two metallic electrodes at different temperatures, a thermoelectric emf is produced. In general, anions and cations will migrate at different rates and the migration produced by the thermal gradient therefore tends to produce a separation of charge. However, the separation

is only incipient, since the space charge formed immediately affects the flow of ions so that bulk electrical neutrality is maintained. The measured emf is the sum of two parts. The first is called the homogeneous thermoelectric power and arises from the electric field—the diffusion field—produced by thermal diffusion within the crystal. The second is called the heterogeneous thermoelectric power and arises from the difference in contact potentials for the two electrode–crystal contacts because they are at different temperatures. Although perhaps more satisfactory than the Soret experiments, the thermoelectric measurements did not, at the time, admit to any detailed molecular interpretation, and the subject of thermal diffusion remained neglected for a number of years.

Apart from the isolated observation (100) that carbon diffused to the hot end of  $\gamma$ -Fe, no further observations on thermal diffusion in solids were published until 1954 when Soret measurements (36) for three binary alloys were published. In the same year the possible usefulness of thermal diffusion measurements in determining atomic mechanisms of diffusion in solids was debated (25, 89, 102, 164) following a suggestion by Shockley (163). It was by then known that migration of atoms is intimately connected with the properties of point defects, and, in order to understand Shockley's proposal and subsequent developments, a few pertinent facts must be reviewed.

#### B. ISOTHERMAL MIGRATION MECHANISMS IN CRYSTALS

The most thoroughly studied metals have been the face-centered cubic metals Al, Cu, Ag, Au,  $\gamma$ -Fe, Co, Ni, and Pt which have been shown experimentally to contain vacant lattice sites. At thermodynamic equilibrium, the site fraction of vacancies is given by

$$c_v = \exp(-g_v/kT) \quad (\text{Eq 3})$$

where  $g_v$  is the change in Gibbs free energy of the crystal when one vacancy is formed by removing an atom from the bulk to the surface of a perfect crystal at constant temperature  $T$  and pressure  $P$ , excluding the configurational entropy contribution, and  $k$  is Boltzmann's constant. An atom may jump into an adjacent vacancy, and as successive atoms do this the vacancy migrates through the crystal. Many substitutional impurities dissolved in small concentrations in such metals also diffuse by the vacancy mechanism. The diffusion mechanism in other metals, in particular the body-centered cubic metals, is less well established (99, 104). For the few body-centered cubic metals in which thermal diffusion experiments have been made, a vacancy mechanism is generally assumed on balance of evidence.

A crystal at thermodynamic equilibrium contains a fraction of atoms in interstitial sites, the fraction being

governed by a Boltzmann factor like that for vacancies. Matter can be transported by the interstitial jumping to a neighboring interstitial site. The concentration of interstitial atoms in the metals considered below is much less than the concentration of vacancies and can be neglected. However, impurities in solids are frequently incorporated interstitially and diffuse by an interstitial mechanism, *e.g.*, C in  $\alpha$ -Fe, H in  $\beta$ -Zr.

In strongly ionic solids (*e.g.*, alkali halides, silver halides), two kinds of lattice disorder are found. Pure alkali halides contain equal site fractions of cation vacancies and anion vacancies, denoted by  $c_+$  and  $c_-$ , respectively, governed by the relation

$$c_+c_- = \exp(-g_s/kT) \quad (\text{Eq 4})$$

where  $g_s$  is the Gibbs free energy of formation of one Schottky defect pair, *i.e.*, one cation and one anion vacancy. Self-diffusion and impurity diffusion occur by the vacancy mechanism. In pure AgBr and AgCl, however, the dominant defects are cationic Frenkel defects; equal site fractions of cation vacancies,  $c_+$ , and interstitial cations  $c_i$ , related by an analogous equation

$$c_+c_i = \exp(-g_F/kT) \quad (\text{Eq 5})$$

where  $g_F$  is the Gibbs free energy of formation of a Frenkel defect pair. The interstitial cations in AgBr are believed to diffuse by an interstitial mechanism in which an interstitial ion displaces a neighboring normal lattice ion into an interstitial site, the original interstitial taking up the vacated lattice site (50).

Frequently a divalent cation impurity is incorporated substitutionally into these ionic crystals by adding the corresponding halide, *e.g.*, CdBr<sub>2</sub> in AgBr or NaBr. Electrical neutrality means that a cation vacancy is added with every impurity molecule and that

$$c_+ = c_i + c_-, \quad c_+ = c_i + c_i \quad (\text{Eq 6})$$

for Schottky and Frenkel disorder, respectively, where  $c_i$  is the site fraction of impurity cations. Thus by doping the crystal with a concentration of impurity much bigger than the number of defects in the pure crystal, the concentration of cation vacancies can be controlled since  $c_+ \simeq c_i$  and  $c_- \ll c_+$ , as follows from Eq 4 and 6. The impurity again diffuses by a vacancy mechanism.

Reference may be made to other reviews and books (26, 88, 92, 107, 161) for the methods by which the defect concentrations and diffusion mechanisms have been established experimentally for the systems referred to here.

The expressions for defect concentrations given above assume that there are no interactions between the point defects. If interactions are present, then every site fraction  $c_k$  is multiplied by an activity coefficient  $\gamma_k$  (4) in Eq 3-5. For low defect concentrations, cluster expansion expressions for the activity co-

efficients as power series in defect concentrations are available (4). Alternatively, provided that the defect interactions are short ranged, expressions may be derived by application of the law of mass action to the equilibria between "free" (noninteracting) defects, nearest neighbor pairs of defects, triplets of defects, etc. (78, 92). The choice of method is, of course, one of convenience and depends on the details of the problem at hand (4).

### C. STATEMENT OF THE THERMAL DIFFUSION PROBLEM

In both vacancy and interstitial diffusion mechanisms, the jump between adjacent sites is a thermally activated process and occurs when a normal thermal fluctuation supplies sufficient energy and momentum for the atom to pass through the intermediate state of high energy between its initial and final positions. For an isothermal system, the probability per unit time that an atom will jump to a particular adjacent vacant site is written (107, 184)

$$\omega_0(T) = \nu \exp(-\Delta g_m/kT) \quad (\text{Eq 7})$$

where  $\Delta g_m$  is called the free energy of activation, and  $\nu$  is a vibrational frequency. Since activated processes are very familiar in chemistry, we defer to section IV detailed consideration of this formula and consider next an anisothermal system in which the migrating atom jumps between sites at different mean temperatures. The jump involves the collective motion of many atoms in planes which are now at different mean temperatures. It is plausible to expect that the probability per unit time for a jump from a plane at temperature  $T$  to one at  $T + \Delta T$ , say  $\omega(T, T + \Delta T)$ , can be written as

$$\omega(T, T + \Delta T) = \omega_0(T)(1 + \Delta\omega(T)\Delta T) \quad (\text{Eq 8})$$

The equation defines  $\Delta\omega(T)$ . The objective of the experiments reviewed is its determination. Its molecular interpretation provides a severe test of the details of the theories of the activated process so far used for  $\omega_0$ . In practice it proves convenient to express the results of theory in terms of a related parameter,  $q^*$ , whose definition in terms of  $\Delta\omega$  will now be given.

According to Eq 3, if there is a temperature gradient then there will be a concentration gradient of vacancies, and hence of atoms, provided local thermodynamic equilibrium is maintained. Consider the flux of atoms between two adjacent planes of atoms a distance  $\Delta x$  apart and at temperatures  $T$  and  $T + \Delta T$  in a pure monatomic crystal, 1. The flux of atoms in the direction of increasing temperature,  $J_1$ , is given by

$$J_1 = \alpha [c_1(T)c_v(T + \Delta T)\omega(T, T + \Delta T) - c_1(T + \Delta T)c_v(T)\omega(T + \Delta T, T)] \quad (\text{Eq 9})$$

where  $\alpha$  is a constant of proportionality which can be calculated from the lattice geometry, and  $c_1$  is the site

fraction of 1. By making a Taylor series expansion of  $T + \Delta T$  about  $T$ , one finds to first order

$$J_1 = -D_1^{(0)}N \left[ \frac{dc_1}{dx} - \frac{c_1}{c_v} \frac{dc_v}{dx} + q_1^* \frac{c_1}{kT^2} \frac{dT}{dx} \right] \quad (\text{Eq 10})$$

where  $N$  is the number of sites per unit volume and where

$$D_1^{(0)} = \alpha \Delta x \omega_0 c_v \quad (\text{Eq 11})$$

$$q_1^* = \Delta h_m - 2kT^2 \Delta \omega \quad (\text{Eq 12})$$

$q_1^*$  will be called the heat of transport for a single jump.  $\Delta h_m$  denotes the enthalpy corresponding to  $\Delta g_m$ . (Other enthalpies will not be defined if the corresponding free energy has been defined.) Note the similarity in form of Eq 1 and 10. Using Eq 3 and assuming  $c_v \ll c_1$ , the thermal diffusion flux becomes

$$J_1 = - \left( \frac{ND_1^{(0)}(q_1^* - h_v)}{kT^2} \right) \frac{dT}{dx} \quad (\text{Eq 13})$$

Clearly one part of the driving force for the flux arises directly from the vacancy concentration gradient, as was noted by Shockley (163). However, his discussion omitted the second driving force due to the heat of transport term. LeClaire (102) presented a treatment similar to that above but took  $\Delta \omega = 0$ , and Brinkman (25) made the same error. Shockley (164) pointed out that this assumption was unlikely to be correct since "the activation energy is not taken up all at the same temperature." A similar analysis for thermally produced interstitial atoms gives the equation

$$J_1 = - \left( \frac{ND_1(q_1^* + h_i)}{kT^2} \right) \frac{dT}{dx} \quad (\text{Eq 14})$$

Because of the unknown magnitude and sign of  $q_1^*$ , it is not possible to predict even the direction of the thermal diffusion or to distinguish between vacancy and interstitial transport mechanism by measurement of  $J_1$ , contrary to Shockley's original proposal (163). However, it is clear from these equations that even in a pure material thermal diffusion can cause dimensional changes, as first noted by Shockley (163), and this observation forms the basis of the "marker movement" studies described below. Thus for the vacancy mechanism, the flow of matter in one direction creates a flow of vacancies in the reverse direction, causing a deficit of vacancies at one end of the sample and an excess at the other. In order to maintain the thermal equilibrium number of defects in the crystal, new vacancies are formed by way of a source of vacancies at one end, and the excess vacancies are removed at a sink at the other end. These processes cause dimensional changes: one-half of the sample becomes shorter (or thinner) and the other half longer (or thicker), as shown in Figure 1. The sinks and sources may be dislocations exhibiting jogs which can move from one lattice point to another

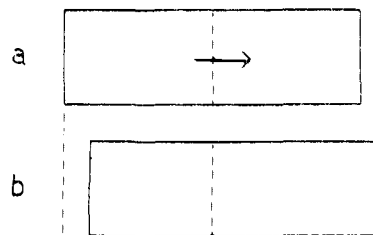


Figure 1.—Mass transport by vacancies in a pure metal: (a) before thermal diffusion, (b) after at thermal diffusion experiment. As a result of mass transport through the lattice plane indicated by the dotted line, its position changes relative to the ends of the sample.

(climb of a dislocation). Depending on the direction of climb, vacancies are either filled up or are newly formed (26). The number of dislocations in a crystal is a function of the previous treatment. Vacancies can also be filled or created at the grain boundaries or at the outer surfaces.

The usefulness of the thermodynamics of irreversible processes was finally pointed out (89) in this early discussion. The equations and methods of this formalism (59) provide the most general and satisfactory description of thermal diffusion experiments. They add additional physical significance to and provide the reason for the name of  $q_1^*$ , the heat of transport for one jump, defined by Eq 8 and 12.

The objective of the review will be amplified at this point. Although references will be given to other crystalline solids, detailed results will be quoted only for solids in which diffusion is by the simple interstitial and vacancy mechanisms outlined above. The molecular interpretation of thermal diffusion by these mechanisms will then be reviewed.

## II. PHENOMENOLOGICAL THEORY OF THERMAL AND ISOTHERMAL DIFFUSION

### A. FLUX EQUATIONS OF IRREVERSIBLE THERMODYNAMICS

The application of the methods of irreversible thermodynamics to isothermal diffusion in solids was first made by Bardeen and Herring (17); a slightly fuller discussion and an extension to thermal diffusion was later made by Allnatt and Jacobs (8). An extensive review of both topics has been recently made (78). The object of the present section is to define the basic quantities and assumptions employed and state concisely results of value for the description of thermal diffusion experiments. Detailed proofs of equations can be found in the articles quoted and in standard works on the thermodynamics of irreversible processes (58, 59).

The flux equations of irreversible thermodynamics can be written in the form

$$J_i = \sum_{k=1}^n L_{ik} X_k + L_{iu} X_u \quad (\text{Eq 15})$$

$$J_q = \sum_{k=1}^n L_{uk} X_k + L_{uu} X_u \quad (\text{Eq 16})$$

The species present (atoms and interstitials of different kinds, vacancies of different kinds) are labeled by subscripts  $i$  and  $k$  ( $= 1$  to  $n$ ). The flux  $J_i$  gives the number of atoms (or molecules, or ions, or vacancies as appropriate) of species  $i$  crossing a unit area, fixed relative to the local crystalline lattice, in unit time. The flows so defined are often called lattice flows. Note that species refer to the occupants of single lattice sites: vacancy pairs, vacancy impurity, nearest neighbor complexes, etc. are not treated as separate species.  $J_q$  is the "reduced" heat flux referred to the same axes. (An adequate discussion of the formal definition of the reduced heat flux is lengthy and can be found elsewhere (59, 182)). The thermodynamic forces  $X_k$  and  $X_u$  are defined by the equations

$$X_k = -(\nabla \bar{\mu}_k)_T - e_k \nabla \phi \quad (\text{Eq 17})$$

$$X_u = -\nabla T/T \quad (\text{Eq 18})$$

$e_k$  is the charge per atom of species  $k$ , and  $\phi$  is the electrical potential due to external fields.  $\bar{\mu}_k$  is the chemical potential of  $k$ . The abbreviation

$$(\nabla \bar{\mu}_k)_T = \nabla \bar{\mu}_k - \left( \frac{\partial \bar{\mu}_k}{\partial T} \right)_{P, N_1, \dots, N_\sigma} \nabla T \quad (\text{Eq 19})$$

has been used. The equations are the obvious generalizations to multicomponent systems of the familiar empirical linear laws of Fick and Fourier. (For simplicity we do not employ a boldface notation for vectors. We thus follow the notation of the recent comprehensive review (78) on the application of nonequilibrium thermodynamics of solids.)

The  $\bar{\mu}_k$ 's are not necessarily true Gibbs chemical potentials since some of them refer to vacancies which are not species in the strict thermodynamic sense. However, this causes no difficulty in formulating the statistical mechanics of the system. The chemical potential of a species can be written

$$\bar{\mu}_k = g_k + kT \log c_k \gamma_k \quad (\text{Eq 20})$$

where  $g_k$  is the change in Gibbs free energy on introducing one atom of  $k$  into the perfect crystal, at a particular site, keeping the concentrations of the other species and  $T$  and  $P$  fixed. At thermodynamic equilibrium the vacancy chemical potential,  $\bar{\mu}_v$ , is zero. Equation 20 then gives the vacancy concentration (Eq 3). In ionic crystals electrical neutrality requires that defects be formed in neutral pairs. Thus for Schottky disorder

$$\bar{\mu}_+ + \bar{\mu}_- = 0 \quad (\text{Eq 21})$$

which is equivalent to Eq 4. Reference to derivation of expressions for activity coefficients has been made in section I.B.

A simplification must be employed when migration occurs by the vacancy mechanism. For a region of crystal without sinks and sources of vacancies, the restriction

$$\sum_{k=1}^n J'_k = 0 \quad (\text{Eq 22})$$

expresses conservation of sites, the prime indicating that interstitial sites are omitted. In an ionic crystal, where each defect and ion appears on either the cation or anion sublattice, but not both, a similar restriction applies to the sum of the fluxes on each sublattice. In the presence of such restrictions, the flux equation can be written (8, 17, 78) as

$$J_i = \sum_{k=1}^{n-n_v} L_{ik} (X_k + Q_k^* X_u) \quad (\text{Eq 23})$$

where

$$X_k + = X_k - X_{kv} \quad (\text{Eq 24})$$

$X_{kv}$  is the thermodynamic force for vacancies on the sublattice occupied by species  $k$ . If  $k$  is an interstitial, then  $X_{kv}$  is zero. The sum is over  $n - n_v$  species that are not vacancies. The heat of transport,  $Q_k^*$ , is defined by

$$L_{iu} = \sum_{k=1}^{n-n_v} L_{ik} Q_k^* \quad (\text{Eq 25})$$

The thermodynamic forces obey the restriction generally referred to as Prigogine's theorem (59)

$$\sum_{k=1}^n N_k X_k = 0 \quad (\text{Eq 26})$$

where  $N_k$  is the number of atoms of  $k$  per unit volume.

The famous Onsager reciprocal relations (126, 127) are assumed.

$$L_{ik} = L_{ki} \quad (i, k = 1 \text{ to } n) \quad (\text{Eq 27})$$

$$L_{iu} = L_{ui} \quad (i = 1 \text{ to } n) \quad (\text{Eq 28})$$

The reciprocal relations are not quite those originally envisaged by Onsager (126, 127) because (a) the flow vectors are not time derivatives of thermodynamic-state variables, (b) "lattice fluxes" instead of fluxes relative to the local center of mass have been used, (c) linear relationships exist between fluxes (Eq 22) and forces (Eq 26). However, it has recently been shown (59) that (a) does not impair the validity of the reciprocal relations, and it has also been shown (78) that their validity is unimpaired by (b) and (c) provided that the restrictions of Eq 22 and 26 are included in the calculation. (Note that Eq 23 includes all the restrictions except Prigogine's theorem.) A review of ex-

perimental tests in other fields (121) reveals no well-established deviations, and so their use in the present context is reasonable, although no check in the solid-state diffusion field has yet been possible. Furthermore, it has been shown (3) that the kinetic model generally employed in solid-state diffusion, plus an assumption of detailed balance, suffices to verify the isothermal relations without detailed calculations of  $L$ 's for particular defect systems. This is in agreement with less general calculations on particular systems (78).

Combining Eq 16 and 23 and using Eq 27, one can derive

$$J_q = \sum_{k=1}^{n-n_v} Q_k^* J_k + (L_{uu} - \sum_{k=1}^{n-n_v} L_{ku} Q_k^*) X_u \quad (\text{Eq 29})$$

Thus in an isothermal system  $Q_k^*$  gives the heat flux consequent upon unit flux of component  $k$ . This simple physical interpretation is the reason for using  $Q_k^*$  to describe thermal diffusion rather than  $L_{tu}$ . It follows only if the reciprocal relations (Eq 27) are valid.

For a one-component system in which diffusion is by vacancy mechanism, the flux equation reduces to

$$J_1 = -D_1^{(0)} N \left( \nabla c_1 - \frac{c_1}{c_v} \nabla c_v + Q_1^* \frac{c_1}{kT^2} \nabla T \right) \quad (\text{Eq 30})$$

where

$$D_1^{(0)} = kTL_{11}/N_1 \quad (\text{Eq 31})$$

provided that vacancy-vacancy interactions can be neglected; *i.e.*,  $\gamma_1 = \gamma_v = 1$ . By comparison with Eq 10, one obtains

$$Q_1^* = q_1^* \quad (\text{Eq 32})$$

Such a simple relation is not necessarily found on comparing a thermodynamic and a kinetic equation. For example, in the present case a more elaborate kinetic treatment might include matter transport by vacancy pairs. The jump frequency and hence the heat of transport,  $q^*$ , for an atom exchanging with a vacancy which is a member of a pair might well be different from those for a jump into an isolated vacancy.  $Q_1^*$  would then be a function of the two different single jump heats of transport. The latter term appears appropriate for the quantities  $q^*$  in view of the limiting equation (Eq 32) which gives them an added physical significance. The relationship of  $Q^*$ 's and  $q^*$ 's is further considered in section IV.

The formulation of irreversible thermodynamics for solids outlined above seems satisfactory and complete. Earlier treatments of thermal diffusion in ionic solids (57, 72-74) took no cognizance of the contribution of defects to the chemical potentials, and the species appearing in the equations were species in the thermodynamic sense. In these papers for a system of  $n$  species there are only  $(n - 1)$  independent fluxes and in consequence one can derive

$$\sum_{k=1}^n N_k Q_k^* = 0 \quad (\text{Eq 33})$$

No such relationship is valid between the  $(n - n_v)$  heats of transport appearing in Eq 23 and 25 because the corresponding fluxes are independent (79). Further confusion arises in these papers by the use of arbitrary reference velocities in defining the fluxes (78), which invalidate attempts to compare the heats of transport of the two formulations (9).

Equations 23 and 26 provide the starting point for the derivation of equations for the thermal diffusion experiments. The algebraic details of these derivations have been given in recent reviews (78, 108) for the important cases. Only results will be quoted here. The isothermal coefficients,  $L_{ik}$ , are always eliminated from these results in terms of the isothermal transport coefficients of the system. The principle coefficients encountered in this connection are therefore defined below.

## B. DEFINITION OF DIFFUSION COEFFICIENTS AND TRANSPORT NUMBERS

### 1. Self-Diffusion Coefficients

A familiar tracer-diffusion experiment is to deposit a layer of tracer onto a plane surface of a homogeneous tracer-free material containing the same chemical species as the tracer (161). After a known period of anneal at a known temperature, the Gaussian diffusion profile of the tracer is determined by sectioning the specimen, weighing the slices, and measuring their tracer content. From the profile, the Fick's law diffusion coefficient for the tracer,  $D_1^*$ , defined by the equation

$$J_1^* = -D_1^* \nabla N_1^* \quad (\text{Eq 34})$$

where the asterisk denotes a radioactive tracer, can be found.  $D_1^*$  is generally called the self-diffusion coefficient. For the case where the tracer diffuses by a vacancy mechanism on a lattice containing only a different isotope of the same chemical species, the coefficient  $D_1^*$  is related to the "self-diffusion coefficient,"  $D_1^{(0)}$ , derived in section I by

$$D_1^* = f D_1^{(0)} \quad (\text{Eq 35})$$

where  $f$ , the Bardeen and Herring (17) correlation factor, is a constant for a given lattice. The reason for this correction factor is that the naive derivation of  $D_1^{(0)}$  outlined above assumed that successive jumps of a particular atom were independent of each other. For a tracer diffusing by a vacancy mechanism, this is incorrect, since a tracer that has just exchanged with a vacancy is more likely to jump back into its original site than to jump to a third site. Successive jumps of tracer, but not of vacancy, are correlated. Accurate values of  $f$  obtained from the random-walk equations, Eq 48 and 76, are available (78). If a solute is present, then a more complicated relationship (*e.g.*, Eq 44) holds

since some of the jumps of component 1 take place when the vacancy is near a solute atom, and the jump frequency will be different.

## 2. Chemical Diffusion Coefficients and the Kirkendall Effect

According to Fick's law of diffusion, the flux of atoms of component 1 in a mixture of two substances, 1 and 2, is given by

$$J_1 = -D_1 \nabla N_1 \quad (\text{Eq 36})$$

This relation defines the diffusion coefficient  $D_1$ .  $J_1$  and  $J_2$  are defined as usual as fluxes relative to the local crystal lattice. Consider next a diffusion experiment in which plates of components 1 and 2, respectively, are placed in contact to form a diffusion couple. After an isothermal diffusion anneal, the concentration profile is measured relative to the ends of the couple where no diffusion has occurred. Clearly the experiment must yield a diffusion coefficient relating the measured concentration gradient to the flux of atoms relative to the fixed parts of the lattice at the ends of the couple. Let  $J_1'$  be the flux of atoms of species 1 relative to the fixed part of the lattice. The chemical interdiffusion coefficient  $\bar{D}$  is defined by

$$J_1' = -\bar{D} \nabla N_1 \quad (\text{Eq 37})$$

$\bar{D}$  can be determined from the measured concentration profile by the well-known Boltzmann-Matano analysis (161).  $\bar{D}$  can be related to  $D_1$  and  $D_2$  as follows. We assume that all diffusion is by vacancy mechanism so that for every jump of an atom a vacancy moves in the opposite direction. If the migration rates of components 1 and 2 are unequal, then this means that there is also a flow of vacancies, even though there is no driving force on the vacancies themselves, *i.e.*,  $X_v = 0$ ,  $J_v = -(J_1 + J_2)$ . The net result is similar to that already described for the pure metal in section I.C. Vacancies appear in some regions and are annihilated in others, for example, by dislocation climb, and dimensional changes occur. A region where diffusion flows are large (*i.e.*, near the interface) therefore moves relative to the regions where the flows are small (*i.e.*, the ends of the specimen). This is the basis of the well-known Kirkendall effect (88, 101, 170). If no pores were formed within the specimen by aggregation of excess vacancies and no bumps or kinks appeared on the surface, then the net flux of atoms,  $J_1 + J_2$ , would be just counter-balanced by a bulk movement of the lattice in the opposite direction, and the following equations would be valid.

$$J_1' = J_1 - c_1(J_1 + J_2) \quad (\text{Eq 38})$$

$$J_2' = J_2 - c_2(J_1 + J_2) \quad (\text{Eq 39})$$

From these one readily finds

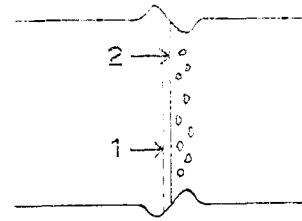


Figure 2.—Result of an isothermal Kirkendall experiment. The welding plane was at 1 before the experiment and at 2 after. Note the surface distortion and appearance of pores on the right of the interface.

$$\bar{D} = c_2 D_1 + c_1 D_2 \quad (\text{Eq 40})$$

Unfortunately, these conditions are not met in practice (68, 101), as shown in Figure 2. The phenomena encountered in the Kirkendall effect are also relevant to some of the thermal diffusion studies.

The difference  $(D_1 - D_2)$  can in principle be found by inserting inert markers into the lattice and measuring the velocity,  $v$ , relative to the fixed parts of the lattice. Then one has

$$v = (J_1 + J_2)/N = -(D_1 - D_2) \nabla c_1 \quad (\text{Eq 41})$$

Equations 40 and 41 allow the determination of  $D_1$  and  $D_2$  as functions of composition from experiment. In practice a few measurements of this kind have been successfully completed for Cu-Zn (97), U-Zr (2), Au-Pt (22), Al-Ag (67).  $D_1$ ,  $D_2$ , and  $\bar{D}$  are required for the interpretation of thermal diffusion experiments. Since direct measurements are rarely available, the relationship of these quantities to the more readily available tracer diffusion coefficients,  $D_1^*$  and  $D_2^*$ , must be considered.

Expressions for the diffusion coefficients can be obtained in terms of the phenomenological coefficients (78). For example, if one assumes  $X_v = 0$  and employs Prigogine's theorem, one can obtain from the thermodynamic flux equation the Fick's law equation for a binary mixture, Eq 36, with

$$D_1 = kT(L_{11}/N_1 - L_{12}/N_2) \left( 1 + \frac{\partial \log \gamma_1}{\partial \log c_1} \right) \quad (\text{Eq 42})$$

By similar methods the relationship between the five diffusion coefficients have been investigated (78). Kinetic expressions for the  $L_{ij}$ 's have been derived (78), and, by employing these, the relations between the diffusion coefficients have been determined for a dilute substitutional solute, 2, dissolved in a solvent, 1, when both diffuse by a vacancy mechanism in a fcc lattice. The result is (78, 80)

$$D_2 = D_2^* = c_p a^2 \omega_2 (\omega_1 + 7\omega_3/2) / 3c_2 (\omega_1 + \omega_2 + 7\omega_3/2) \quad (\text{Eq 43})$$

$$D_1 = \frac{11}{9}D_1^* - \frac{c_p a^2 \omega_2 (-2\omega_1 + 3\omega_3)}{3c_2(\omega_1 + \omega_2 + 7\omega_3/2)} \quad (\text{Eq 44})$$

Here  $c_p$  is the concentration of impurity atoms that are nearest neighbor to a vacancy, and  $c_2$  is the total impurity concentration. The frequencies  $\omega_1$ ,  $\omega_2$ , and  $\omega_3$  refer to the following vacancy jumps: from one nearest neighbor position to another *via* exchange with a solvent atom ( $\omega_1$ ); from one nearest neighbor position to another *via* exchange with an impurity atom ( $\omega_2$ ); from a nearest to a second nearest neighbor position ( $\omega_3$ ). The distance between nearest neighbors is  $\sqrt{2}a$ , and all distances are measured relative to the impurity atom. These equations have been derived on the assumption that impurities and vacancies interact at nearest neighbor separations only, and are correct to first order in the concentrations. For thermal diffusion studies, it is of particular value to obtain the ratio  $D_1/D_2$

$$\frac{D_1}{D_2} = \frac{11}{9} \frac{D_1^*}{D_2^*} - \frac{[3 - 2(\omega_1/\omega_3)]}{7/2 + (\omega_1/\omega_3)} \quad (\text{Eq 45})$$

### 3. Diffusion Potential and Transport Numbers in an Ionic Crystal

For brevity the term ionic crystal will be used for ionic crystals in which there is ionic conduction but essentially no electronic or hole conductivity. The ionic crystals discussed in section I.B. are all of this kind. The anions and cations are restricted to positions on their separate sublattices, but their migration is nevertheless coupled because of the electrical diffusion potential (Nernst potential). The diffusion potential,  $\phi_{\text{int}}$ , satisfies the equation

$$\nabla \phi_{\text{int}} = - \sum_{k=1}^{n-n_v} \frac{t_k}{e_k} \left[ \nabla (\bar{\mu}_k - \bar{\mu}_{k\nu})_T + \frac{Q_k^*}{T} \nabla T \right] \quad (\text{Eq 46})$$

$t_k$ , the transport number of  $k$ , is the fraction of electrical current carried by species  $k$ . The derivation (8), by substituting the flux equation into the condition that the total electrical current in the absence of an external field is zero, depends on use of the Onsager relation (Eq 27). A comprehensive review of the measurement of transport numbers and ionic mobilities in ionic crystals is available (107).

### C. RANDOM-WALK EQUATIONS

The theory of the Kirkendall experiment and other topics discussed above has been further clarified by the random-walk method (103), and the extension to anisothermal systems (10) is of value. Consider a system with temperature and concentration gradients in the direction of the  $x$  axis only. Let  $K_i(x_i, t|x_i + \Delta x_i, t + \Delta t)$  be the conditional probability that an atom of species  $i$  which was at  $x_i$  at time  $t$  will be at  $x_i + \Delta x_i$  at time  $t + \Delta t$ , and let  $N_i(x_i, t)$  be the concentration of  $i$  at  $x_i$  at time  $t$ . The conservation of matter requires

$$N_i(x_i, t + \Delta t) = \int N_i(x_i - \Delta x_i, t) K_i(x_i - \Delta x_i, t|x_i, t + \Delta t) d(\Delta x_i) \quad (\text{Eq 47})$$

The method is to convert this relation to a differential equation by expanding the functions in powers of  $\Delta x_i$  and  $\Delta t$  and neglecting terms of order  $(\Delta t)^2$  and  $(\Delta x_i)^2$  (10). Use of the equation of continuity then allows one to identify the flux of species  $i$  along the  $x$  axis in an  $n$ -component system:

$$J_i = N_i \left[ \frac{\langle \Delta x_i \rangle}{\Delta t} - \frac{1}{N_i} \frac{\partial N_i}{\partial x} \left( \frac{\langle (\Delta x_i)^2 \rangle}{2\Delta t} \right) - \sum_{j=1}^{n-1} \frac{\partial}{\partial n_j} \left( \frac{\langle (\Delta x_i)^2 \rangle}{2\Delta t} \right) \frac{\partial N_i}{\partial x} - \frac{\partial}{\partial T} \left( \frac{\langle (\Delta x_i)^2 \rangle}{2\Delta t} \right) \frac{\partial T}{\partial x} \right] \quad (\text{Eq 48})$$

where the mean displacement  $\langle \Delta x_i \rangle$  and the mean-square displacement  $\langle (\Delta x_i)^2 \rangle$  are defined by

$$\langle (\Delta x_i)^k \rangle = \int K_i(x_i, t|x_i + \Delta x_i, t + \Delta t) (\Delta x_i)^k d(\Delta x_i) \quad (\text{Eq 49})$$

Uses of this equation are referred to below.

## III. EXPERIMENTAL METHODS AND RESULTS

We outline the experimental methods and difficulties encountered. Detailed descriptions and diagrams of apparatus can be found in the original papers. The equations used to calculate the thermodynamic heats of transport and the values obtained are presented.

### A. MARKER MOVEMENT

#### 1. Pure Substances

Measurements have been restricted mainly to metals with relatively large self-diffusion coefficients and well-established vacancy diffusion mechanisms. The principle of these experiments is to place a pair of markers in the crystal which remain fixed relative to the crystal planes of the lattice in the region of the marker. Since, in a temperature gradient, the two markers are at different temperatures, the corresponding thermal diffusion fluxes differ in magnitude. There is therefore either a gain or loss of matter between the two markers, and their distance apart should therefore change by an amount which depends on the heat of transport as follows.

The thermodynamic flux equation for a one-component system with a temperature gradient along the  $x$  axis only can readily be shown (78) to reduce to

$$J_1 = -D_1^* N (Q_1^* - h_v) \frac{dT}{dx} / kT^2 f \quad (\text{Eq 50})$$

as also follows from Eq 13 and 35. The change in separation distance,  $\Delta x$ , after time  $t$ , for two markers on the  $x$  axis at mean temperatures  $T_1$  and  $T_2$  is given by

$$\Delta x = Kt [J_1(T_1) - J_2(T_2)] / N \quad (\text{Eq 51})$$



TABLE I  
 MARKER MOVEMENT IN METALS

Metal <sup>a</sup>	Ref	Method <sup>b</sup>	$Q_1^* - h_v$ , <sup>c</sup> kcal mole <sup>-1</sup>	$Q_1^*$ , kcal mole <sup>-1</sup>	Ref for $\Delta h_v$	$\Delta h_1$ , kcal mole <sup>-1</sup>	Ref for $\Delta h_1$	Temp gradient, °K cm <sup>-1</sup>
Zn (distorted hcp)	158	s	0 ± 0.2	9.0	52, 176 <sup>d</sup>	13.7	171	310
	178	s, l	-2.3 ± 0.7	6.7				50
	11	s, m, l	3.9 ± 0.7	12.9				705
			3.2 ± 0.5	12.2				460
Cu (fcc)	181	s, a, l	-0.2 ± 1.5	8.8	167	20.2	167	1150-1300
	120	m	3.0 ± 2.8	29.9				~400
	86	s, l	(-7.2) <sup>e</sup>	19.7				
	1	m	0	26.9				
$\alpha$ -Fe (bcc)	24	m	0 ± 2					2500
	1	m	<0					
$\gamma$ -Fe (fcc)	44		0					
	66	s, l	25-100					
Co (fcc)	70	s, a	167-633 <sup>f</sup>					500
Ni (fcc)	91		<0	<32.3	123	34.6	157	
Ag (fcc)	1	m	0	23.8	34	19.1	38	
	27	m	0	23.8				
Au (fcc)	120	m	-4.8 ± 2.8	17.8	168	18.9	156	1150-1300
	86	s, l	-8.6	14.0				~400
	1	m	0	22.6				
Pt (fcc)	71							
	Cor	s, a	15.7 <sup>f</sup>	46.4	12	34.1	28	400
	70							
Al (fcc)	179	s, l	-1.5 ± 0.3	17.5	166	14.3-16.5	179	150
$\beta$ -Zr (bcc)	45		(-115)		... <sup>g</sup>			
$\beta$ -Ti (bcc)	45		(185)		... <sup>g</sup>			
Li (bcc)	110	s, a, l	12.2 ± 0.4	21.7	113 <sup>g</sup>	4	124	~50
Pb (bcc)	181	s, a, l	(2.1 ± 4.0)	>14.3	43	<12.0	122	

<sup>a</sup> hcp = hexagonal close packed, fcc = face centered cubic, bcc = body centered cubic. <sup>b</sup> m = embedded marker, s = surface scratch or indent, a = ac heating of specimen to produce gradient, l = lateral distortions studied. <sup>c</sup> Values of  $(Q_1^* - h_v)$  regarded by workers as more doubtful are given in parentheses. <0 and >0 indicate qualitative observations only. There are also qualitative observations on W (125). <sup>d</sup> Mean value of 9.0 kcal mole<sup>-1</sup> was used but may not be very reliable (178). <sup>e</sup> Other markers at a different temperature moved in the opposite direction giving  $Q_1^* - h_v \sim 500$  kcal mole<sup>-1</sup>. <sup>f</sup> Temperature-dependent result. <sup>g</sup> A vacancy mechanism is not certain. For Li see ref 110. For  $\beta$ -Zr and  $\beta$ -Ti see ref 99, 104.

where  $K$  is the lattice accommodation coefficient (84, 86), which allows for any change in geometric proportions of the specimen and is further discussed below. Values of  $(Q_1^* - h_v)$  calculated from these equations are summarized in Table I.

Two forms of marker have been used. Shewmon (158) studied crystals and bicrystals of zinc marked using a Tukon hardness machine and a Knoop indenter. Indents were made at 1-mm intervals, and the specimen annealed to recrystallize deformed material and produce a stable grain size. The distance between markers was measured to  $\pm 0.0004$  cm while the specimen was annealed in a gradient for 20 days, but the result  $\Delta x = 0$  was found. A discussion of the precautions necessary in this experiment has been given (178). These include (a) avoidance of compressive strains on the sample through the method of holding, (b) checking that no movement due to surface tension effects occurs in an isothermal anneal, (c) maintenance of an accurately linear temperature gradient. Using an apparatus designed to overcome these difficulties and a similar indentation method, a contraction was observed for zinc (178) in disagreement with the earlier result. The latter was tentatively ascribed to non-

linearity of the temperature gradient. Another possibility is that  $Q^*$  varies with orientation relative to the crystal axes and that different orientations have been used, but later measurements have not found this effect (11). Self-diffusion in zinc is markedly anisotropic.

Other possible adverse factors have been discussed. It is perhaps possible (120) that surface diffusion effects occur which are different from volume diffusion effects. It has also been speculated (24) that the surface of indentations may act as sources and sinks of vacancies in such a way that the observed net mass transport would be appreciably less than that which actually occurred. Experiments to check these possibilities have not so far been devised.

A variation of the surface indentation procedure has been used for Pt (71) and Co (70). Fine deep marks 0.7 mm apart were made in Pt wire of 0.032- and 0.045-in. diameter. The temperature gradient was established by passing an ac current. The ends of the wire were kept at room temperature by cooling water, and one end of the wire was clamped in a small vise floating in mercury in order to avoid thermal stress. The temperature distribution was measured without disturbing the

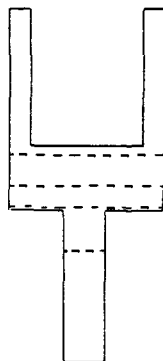


Figure 3.—Cross section of a marker experiment specimen. Dotted lines indicate marker wires (24, 120).

systems by means of an optical pyrometer. The results must be corrected for a creep effect. The method is essentially similar to that used in electromigration studies but with ac instead of dc heating (84) and has also been used for Pb, Zn (181), and Li (110).

The second type of marker consists of a thin filament of some inert material embedded in the crystal perpendicular to the temperature gradient. Kirkendall effect experiments (165) have given results independent of the form and kind of marker material, thus providing some evidence for the propriety of this method. In the first study of this kind, on  $\alpha$ -Fe (24), Pt wires of 0.0015 in. diameter were placed in square parallel grooves in a half-cylinder of iron which was covered with a complementary half-cylinder; the whole assembly was sintered and then cut at right angles to expose the wire ends. The distance apart of the ends was measured and a complementary half-cylinder sintered to the wire-containing half-cylinder. The sample was then cut down to its final size which was 0.04 in. in diameter and 0.125 in. long with a 0.25-in. diameter and 0.25-in. long top section which acted as a heat source. The sample, shown in Figure 3, was maintained in a gradient of 2500°/cm and finally sectioned, and the marker spacings were remeasured.

A very similar method has been used for Cu and Au employing 20- $\mu$  diameter silica fibers as markers (120). The outer surface of the cup and the temperature at the bottom of the stem are fixed in this apparatus, and the temperatures at the bottom of the cup and at the bottom of the stem are measured. Equations have been derived (105) to allow calculation of the temperature along the axis of the specimen from these measurements.

Experiments of this kind have proved very difficult. The major problems include obtaining sintered interfaces which are free from microscopic voids, the machining of the specimens to the correct form without distorting them, and the insertion and removal of the specimen from the annealing apparatus without bending the stem. A further difficulty sometimes met is the growth of grains or twins in the vicinity of the marker

which may perturb the progress of the markers. Pore formation has also been observed (120).

A difficulty is the value of the lattice accommodation coefficient  $K$ . If the change in dimensions, due to the change in the number of atoms between the markers, is isotropic, then  $K = 1/3$ , but if changes occur only in the direction of the temperature gradient, then  $K = 1$ . The same problem arises in Kirkendall effect studies (165) and in electromigration studies in which surface marker movement in wires subject to direct current electrical fields occurs. It would be surmised that a specimen size and shape factor is involved. Creation or destruction of vacancies to maintain local equilibrium would produce isotropic changes. However, external mechanical constraints may lead to anisotropy. For example (83), in the Kirkendall experiment with a large sample (165) lateral marker movements might be constrained by the mass of material surrounding the markers. In electromigration studies in Al (131), a transition from isotropic to uniaxial distortion occurred as the diameter of the specimens increased. Elastic-plastic theory was used to show that  $K$  is a function of the ratio of the diameter to length of the sample and is  $1/3$  for thin wires used in the Pt experiments (71). At present no generally agreed way of predicting  $K$  exists, and the small amount of information available is sometimes contradictory, perhaps partly because of this shape effect. For thin strips of gold  $K = 1/3$ , whereas for copper  $K = 1$  (86). For zinc, lateral dimension changes which increased with increasing temperature were observed (11) in one case, but no changes were found in another (178). Without supporting studies of this kind, values of  $Q_1^* - h_v$  may be appreciably in error.

The derivation of Eq 50 assumes that the vacancy sources and sinks present are efficient enough to maintain the equilibrium concentration of vacancies everywhere. It is by no means certain that this occurs in practice. If the vacancy production and destruction rate is small compared with the atom flux then the vacancy flux could be quite small (102). Indeed in a region far from sinks and sources a Soret stationary state ( $J_1 = 0$ ) would be established such that (102)

$$\nabla c_v/c_v = Q_1^* \nabla T/kT^2 \quad (\text{Eq 52})$$

Let  $J_1^0$  and  $c_v^0$  be the flux and vacancy concentration if local equilibrium were maintained, as assumed in Eq 50, and  $J_1$  and  $c_v$  be the mean values in the real crystal. These are related by the approximate equations (20, 21)

$$(c_v - c_v^0)/c_v^0 = [h_v(h_v + \Delta h_1 - Q_1^* - 2kT) - Q_1^*(\Delta h_1 - 2kT)] \left[ \lambda \frac{dT}{dx}/kT^2 \right]^2 \quad (\text{Eq 53})$$

and

$$J_1 = J_1^0 c_v/c_v^0 \quad (\text{Eq 54})$$

where  $\lambda$  is the mean free path of a vacancy between creation and annihilation. For  $Q_1^* - h_v < 0$ , a supersaturation of vacancies occurs, *e.g.*, Au, whereas for  $Q_1^* - h_v > 0$ , *e.g.*, Pt, a subsaturation is attained. Information about  $\lambda$  at high temperatures is very limited, but for well-annealed gold the value corresponds to about  $10^9$  vacancy jumps. For a gradient of  $1000^\circ\text{K cm}^{-1}$ , this gives a fractional increase in vacancy concentration at  $1000^\circ\text{K}$  of  $10^{-4}$  for Au and  $-5 \times 10^{-4}$  for Cu (20), increasing rapidly in magnitude with decreasing temperature. The error in most of the marker experiments from supersaturation would therefore appear to be negligible. Supersaturation may still manifest itself through pore formation, and it has been suggested (20) that this may be used to measure  $\lambda$ . However, until values of  $\lambda$  for actual thermal diffusion specimens are available, results should perhaps be viewed with caution.

In another calculation (24) the deviation from the flux equation, Eq 50, was derived for the situation where the only sources and sinks for vacancies are parallel grain boundaries perpendicular to the temperature gradient. As expected, the deviations are slight if the separation of sinks and sources is large compared with the lattice spacing but small compared with sample size. A three-dimensional diffusion problem has been analyzed (120) where the vacancy concentration is maintained at the boundaries of a cylinder free from sinks and sources. It was found that a vacancy concentration gradient normal to the temperature gradient along the axis of the cylinder will be established and may be of importance in experiments on geometries like that in Figure 3.

Related to the above calculations is the problem (21) of a barrier making perfect contact with the lattice and transverse to the temperature gradient and vacancy flux. It was found that the vacancy concentration deviates exponentially from that in the bulk on both sides of the barrier, the fractional change at the interface being  $\pm(Q^* - h_v)(dT/dx)/kT^2$ . A local flux between regions of high and low vacancy concentrations will be superimposed on the bulk flux. However, for a wire thicker than about  $5\lambda$  this makes a negligible change to the marker velocity.

Some final comments on Table I may be made. In view of the difficulties, it is encouraging to note the fair agreement using the two different marker techniques obtained for Au by different workers, and the agreement when both methods are used in the same specimen for Zn. There is independent evidence, section III.A.2, that  $Q_1^* - h_v$  is close to zero for Zn which may account for some of the discrepancies found here. In the marker experiments, failure to observe a movement should be viewed with caution. The temperature dependence noted for Pt (71) may be partly due to errors in  $D_1^*$ . Further measurements as a function of dis-

location content and grain size on zone-refined specimens of the materials already studied would be of interest. Purity is important since impurity atoms tend to accumulate near dislocations and grain boundaries and may well trap migrating vacancies.

The experiments on  $\beta$ -Zr and  $\beta$ -Ti were unusual in that the temperature range spanned the phase transition between low- and high-temperature forms. The vacancies generated in the high-temperature  $\beta$ -Zr were believed to be annihilated at the surface near phase boundaries which act as defect sinks. The marker intervals near the phase boundaries shortened because the lattice planes were destroyed during the anneal. The results in the table may not be correct since the departure from vacancy equilibrium in these regions will invalidate Eq 50. The situation at the interface is reminiscent of the Kirkendall experiment interface in Figure 2. The  $\alpha$ - $\gamma$  transition region has been studied in similar experiments with Fe (44).

## 2. Two Components

The variety of experiments and phenomena is much greater, but results suitable for quantitative interpretation are difficult to obtain so we shall be relatively brief. A study of marker movement in systems containing a phase boundary, *e.g.*,  $\beta$ -Zr and  $\beta$ -Ti, has been extended to a detailed study of the alloy Cu-Sn (46, 186). Both isothermal and nonisothermal Kirkendall experiments (119) have been made on diffusion couples of face-centered cubic metals (Au-Ni, Cu-Ni,  $\gamma$ -Fe-Ni,  $\gamma$ -Fe-Pd, and Ni-Pd) in which the vacancy mechanism is believed to be the dominant diffusion mechanism. The specimens of the form shown in Figure 3 were annealed in temperature gradients in the range  $2000$ – $3000^\circ\text{C cm}^{-1}$  and also under isothermal conditions. The concentration profiles were determined by microhardness and chemical etching techniques. The most satisfactory results were for the Au-Ni couple in which the Matano areas for the temperature gradients  $1900$ ,  $0$ , and  $-2300^\circ\text{C cm}^{-1}$  were in the proportion 3.8:2.8:1, showing the marked effect of thermal diffusion (the Matano area is proportional to the net number of atoms which have diffused across the Matano interface). An interesting observation was that grain boundary diffusion of Ni into Fe was strongly affected by the temperature. This appears to be the first observation of its kind.

The extension of the Kirkendall effect equations, Eq 37–41, to anisothermal systems has been given (46, 186) but not starting from the full thermodynamic flux equations, although it has been pointed out these could easily be used (78).

The temperature gradient introduces complications in the discussion of such binary couples. For example (119), the vacancy concentration varies from point to point through the presence of the temperature gradient,

but unfortunately the energy of vacancy formation also varies with composition and hence with position. According to Meechan (119), the increase in vacancy flux due to the temperature gradient in his experiments is not entirely compatible with a flux equation like that discussed for self-diffusion and taking the heat of transport as approximated by the activation energy. An interesting variant of the experiment would be to plate a layer of radioactive tracer of each component at the interface of the couple and measure the mean displacement of the tracer as is done in isothermal studies (103). In fact, the latter type of experiment would be interesting if both halves of the couple were of identical composition (either one or two component) and the mean displacement of a tracer were studied. In the absence of a temperature gradient, a symmetrical Gaussian curve with maximum at the interface results, but with a temperature gradient the maximum is displaced from the interface and the mean displacement of tracer atoms can be found. For example, for a tracer of element 1 diffusing by a vacancy mechanism in pure 1, comparison of the random-walk equation with the thermodynamic equation yields the following expression from which the heat of transport may be found (10).

$$Q_1^* - h_v = \frac{kT^2}{D_1^*} \left[ \frac{dD_1^*}{dT} - \frac{\langle \Delta x_1 \rangle}{\Delta t} \left( \frac{dT}{dx} \right)^{-1} \right] \quad (\text{Eq 55})$$

An identical equation was found (81) for an impurity atom. For reasonable values of the parameters involved, it was concluded that measurable displacement should occur. Experiments of this kind have not so far been reported.

## B. SORLET EFFECT

The earliest measurements of the unmixing of a binary mixture by a temperature gradient, the Soret effect, were outlined in section I. The more recent measurements to be described have often been on dilute solutions rather than the 1:1 mixtures of earlier work. This has been facilitated by the availability of radioactive tracers which have led to considerable understanding of isothermal diffusion mechanisms in such systems. It is convenient to express the results in terms of an "apparent heat of transport,"  $Q_{\text{app}}^*$ , defined by

$$\nabla c_2/c_2 = -Q_{\text{app}}^* \nabla T/kT^2 \quad (\text{Eq 56})$$

where the gradients are the steady values. Species 2 will be taken as the solute in a mixture of species 1 and 2. These measurements employ relatively straightforward and conventional tracer techniques. We therefore present the theoretical equations and results obtained and add remarks only on exceptional points of technique encountered.

The difference between initial and final concentra-

tions decreases approximately as  $\exp(-t/\theta)$  (57, 182) where

$$\theta = h^2/\pi^2 D_2 \quad (\text{Eq 57})$$

where  $h$  is the specimen thickness along the gradient. A time of  $5\theta$  is therefore required to bring a sample within 99.3% of the steady state.

The effects of misalignment of the crystal relative to the direction of the temperature gradient on the accuracy of determination of  $Q_{\text{app}}^*$  have been considered theoretically (6).

### 1. Substitutional Solutes in Metals

Both the substitutional solute, 2, and the solvent, 1, are assumed to diffuse by a vacancy mechanism. The steady state is achieved when the flow of matter relative to the clamped ends of the specimen is zero, *i.e.*,  $J_1' = J_2' = 0$ . It has been shown (78) that substitution of the fluxes from Eq 23 into Eq 38 and 39 and use of this steady-state condition, of Prigogine's theorem (Eq. 26), and of the isothermal Onsager relations (Eq. 27), lead to the result

$$-Q_{\text{app}}^* = \frac{c_1(Q_1^* - h_v)D_1 - (Q_2^* - h_v)D_2}{\bar{D} \left( 1 + \frac{\partial \log \gamma_1}{\partial \log c_1} \right)} \quad (\text{Eq 58})$$

For the dilute solutions studied, the approximation  $\bar{D} = D_2$ , and the relationship between  $D_1$ ,  $D_2$ , and the tracer coefficients (Eq 45) can be used. The activity coefficient correction has also been neglected. The results are summarized in Table II. The result for  $Q_2^* - h_v$  is rather sensitive to the correction involving  $\omega_1$  and  $\omega_3$  in Eq 45. If  $D_1 \gg D_2$ , then  $Q_1^* - h_v$  can be determined without knowing  $Q_2^*$ . For zinc the value determined in this way agrees with the earliest marker movement measurements (158) rather than the more recent ones (11). This kind of Soret measurement is particularly valuable.

### 2. Interstitial Solutes in Metals

If it is assumed that the interstitial diffuses entirely independently of the solvent, then the cross terms,  $L_{12}$ , in the flux equation can be neglected. The steady-state condition ( $J_2 = 0$ ) then gives

$$Q_{\text{app}}^* = Q_2^* / \left( 1 + \frac{\partial \log \gamma_2}{\partial \log c_2} \right) \quad (\text{Eq 59})$$

Experimental values found using this expression are given in Table III.

Equation 59 is valid only for a one-phase system. In the case of hydrogen in  $\alpha$ -zirconium, considerable interest has centered on diffusion in the two-phase system of solid solution and precipitated zirconium dihydride, and the hydrogen distribution has been studied both experimentally and theoretically. The assumption was made (153, 159) that the local thermodynamic

TABLE II  
SORET EFFECT FOR SUBSTITUTIONAL IMPURITIES IN METALS<sup>a</sup>

Solvent <sup>b</sup>	Solute	Ref	Solute concn atom %	$Q_{app}^*$ , kcal mole <sup>-1</sup>	$Q_1^* - h_v^c$ , kcal mole <sup>-1</sup>	$Q_2^* - h_v^c$ , kcal mole <sup>-1</sup>	$Q_1^*$ , kcal mole <sup>-1</sup>	$\Delta h_1$ , kcal mole <sup>-1</sup>	$Q_2^*$ , kcal mole <sup>-1</sup>	$\Delta h_2^d$ , kcal mole <sup>-1</sup>
Zn ⊥	Tl	187	Tracer	-2.7	b	-2.7			6.3	
Zn	Tl	187	Tracer	-1.7	b	-1.7			7.3	
Zn ⊥	Ag	187	Tracer	0.4	0.03 <sup>e</sup>		9.0	13.7		
Zn	Ag	187	Tracer	0.6	0.05 <sup>e</sup>		9.0	13.7		
Zn ⊥	In	187	Tracer	-3.7	b	-3.7			5.3	11.4 <sup>f</sup>
Cu	Co	86 <sup>g</sup>	Tracer	4 ± 3	a	-8			19	23.7
Cu	Ge	86 <sup>g</sup>	Tracer	-8 ± 3	a	-8			19	18.7
Cu	Ag	86 <sup>g</sup>	Tracer	-4.8 ± 3	a	-5.4			21.5	19.9
Cu	Au	86 <sup>g</sup>	Tracer	-4.8 ± 3	a	-9.3			17.6	21.5
Cu	Au	36	26.5	>0						
Au	Ag	86 <sup>g</sup>	Tracer	-4.2 ± 0.3	a	-9.3			12.9	17.8
Au	Tl	86 <sup>g</sup>	Tracer	-8.4 ± 3	a	-7.7			14.9	
Ag	Au	86 <sup>g</sup>	Tracer	0 ± 3	b	0			23.8	
Ag	Sb	19	Tracer	-29 ± 3	b	-29			-5	~17
Ag	Ru	19	Tracer	>0						

<sup>a</sup>  $h_v$  values same as in Table I. <sup>b</sup> ⊥ denotes perpendicular to  $c$  axis, || parallel to  $c$  axis. For a Cr-Mo alloy see ref 133. <sup>c</sup> a denotes that marker movement results in ref 86 were used; b denotes  $Q_1^* - h_v = 0$  as suggested by results in Table I. <sup>d</sup>  $\Delta h_2$  values are those given in ref 86. <sup>e</sup> Calculated (78) neglecting the solute term. <sup>f</sup> Denotes  $\Delta h_2$  values calculated by the same method as other values in the table (86) using data from ref 151 and 162. <sup>g</sup> Recalculated using Eq 44 with  $\omega_1 = \omega_2$ , following the suggestion in ref 80.

TABLE III  
SORET EFFECT FOR INTERSTITIAL IMPURITIES IN METALS<sup>a</sup>

Solvent (1)	Solute (2)	Ref	$Q_2^*$ , kcal mole <sup>-1</sup>	$\Delta h_2$ , kcal mole <sup>-1</sup>	Ref for $\Delta h_2$	$dQ_2^*/dT$ , cal deg <sup>-1</sup> g-atom <sup>-1</sup>
$\alpha$ -Fe (bcc)	C	160 36*	-24 ± 1.5	24	160 <sup>b</sup>	
$\gamma$ -Fe (fcc)	C	160 111 <sup>c</sup> 36*, 100*	-2.2 ± 1.5 -2.0 ± 1.5 0 ± 1.0 -1	36	129	
$\alpha$ -Fe (bcc)	H	56	-8.1--5.6	2.7	42	11
$\alpha$ -Fe (bcc)	D	56	-7.8--5.2	2.7	42	11
$\gamma$ -Fe <sub>0.8</sub> Ni <sub>0.4</sub> (fcc)	H	56	-1.7--1.2	9.9	51	10
Ni (fcc)	H	56	-1.5--0.2	8.4	41	10
Ni (fcc)	D	56	-1.3--0.8	8.4	41	10
$\alpha$ -Fe (bcc)	N	36*	~ -18	18	160	
$\alpha$ -Zr (hcp)	H	153	6.0	9.5	171a	
				7	114	
				8.3	152	
		87,* 116,* 117*				
$\alpha$ -Zr (hcp)	D	153	6.5	8.5	171a	
$\beta$ -Zr (bcc)	H	39	6-12			10.5
[ZrH <sub>0.44</sub> and ZrH <sub>0.88</sub> ]						
$\beta$ -Zr (bcc)	O	150	>0			
Ti (bcc)	H	118	5.3 <sup>d</sup>			
"8Al-1V-Mo titanium alloy"	H	118	3.0 <sup>d</sup>			
"6Al-4V titanium alloy"	H	118	1.8 <sup>d</sup>	12.5	74a	
$\delta$ -ZrH <sub>1.89</sub> (fcc) <sup>f</sup>	H	172	1.3 ± 0.4	11.4	61	

<sup>a</sup> Earlier, generally less complete studies for which no numerical values have been quoted here are indicated by an asterisk, in the reference list. C in steel "85KhF" has been studied (190). <sup>b</sup> Reference given to unpublished work. <sup>c</sup> Recalculated (160). <sup>d</sup> Probably underestimates. Steady state not attained. <sup>e</sup> Recalculated (129). <sup>f</sup> The atoms are randomly distributed among the tetrahedral sites (74a). The relationship between the  $\delta$  and  $\epsilon$  phases in this system is complex (134a).

equilibrium between the two phases was established everywhere so that

$$c_2 = c_0 \exp(-\Delta H/RT) \quad (\text{Eq 60})$$

where  $\Delta H$  is the enthalpy change on precipitation and

$c_0$  is a constant. This was substituted into the flux equation and used to solve the equation of continuity. The calculation has been improved (154) by allowing for the previously neglected hydrogen diffusion in the precipitated phase, and solutions for distribution of

both phases as a function of time and of the interface motion were obtained numerically and compared with observed redistributions (117, 152). The values of  $Q_2^*$  in the table appear to be the most reliable of the many measurements on this system (154).

The systems for which values of  $dQ_2^*/dT$  are quoted in Table III were obtained by the thermoosmosis method (39, 56). The specimen was maintained in a temperature gradient and the hydrogen pressure determined at the hot and cold ends in the steady state. It is straightforward to obtain

$$\frac{\Delta(\log p_1)}{\Delta(1/T)} \simeq \frac{d \log p_1}{d(1/T)} = \frac{(Q_1^* - \Delta h_{\text{vap}})}{2k} \quad (\text{Eq 61})$$

where  $\Delta$  denotes the difference between the two ends, and  $\Delta h_{\text{vap}}$  is the enthalpy of vaporization per gram-atom of hydrogen from the solid to form gaseous hydrogen. This method is capable of considerable accuracy, and the temperature dependences noted in the table are real. The results for  $\beta$ -Zr appeared independent of the composition in the range quoted.

### 3. Ionic Crystals

We consider a crystal MX containing an impurity  $\text{IX}_2$ . The derivation of  $Q_{\text{I}}^*_{\text{app}}$  for the impurity ion I is similar to the calculations above for metals. Equations have been obtained (5) for (a) a substitutional impurity ion in a crystal with Schottky disorder and (b) for a substitutional or interstitial impurity in a crystal with Frenkel and Schottky disorder. These results are cumbersome and will not be quoted in full. They are available for crystals of arbitrary valence type and appear to cover the principal disorder types at present well understood. The only experimental study is for  $\text{SrCl}_2$  impurity in  $\text{NaCl}$  (6). All diffusion is by vacancy mechanism, and the transport number of anions is very small. For tracer amounts of  $\text{Sr}^{2+}$  ions in a pure crystal the result then reduces to

$$Q_{\text{I}}^*_{\text{app}} = (Q_{\text{I}}^* - 2Q_{\text{M}}^*) - h_s/2 \quad (\text{Eq 62})$$

and for a crystal doped with  $\text{SrCl}_2$  so that thermally produced disorder is negligible

$$Q_{\text{I}}^*_{\text{app}} = (Q_{\text{I}}^* - 2Q_{\text{M}}^*)(1 + p)/2 + \chi p \quad (\text{Eq 63})$$

where  $p$  is the degree of association of cation vacancies to form nearest neighbor complexes of an impurity ion and a vacancy.  $\chi$  is the enthalpy of association of such a complex. It should be emphasized that the presence of  $p$  and  $\chi$  arises from using an explicit and approximate expression for the activity coefficients. In contrast to the metal systems, the activity coefficient corrections are important even at very low defect concentrations. The results for pure and doped crystals were consistent and led to the result

$$Q_k^* = Q_{\text{I}}^* - 2Q_{\text{M}}^* + \chi = -36.0 \pm 3.5 \text{ kcal mole}^{-1} \quad (\text{Eq 63'})$$

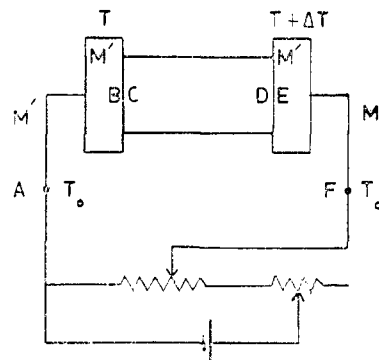


Figure 4.—Experimental arrangement for thermoelectric power of an ionic crystal MX between electrodes,  $M'$ .

in the temperature range 600 to 750°. The value of  $Q_k^*$  expected if enthalpies of activation were used in place of heats of transport for single jumps in a molecular expression for  $Q_k^*$ , Eq 79, was  $-25.3 \text{ kcal mole}^{-1}$ , and the deviation from the measured value was probably significant.

Ionic crystals suitable for such studies have been noted (5). A difficulty compared with metal systems is the relatively long diffusion times necessitated by the low diffusion coefficients encountered. Specimens 0.6 and 0.7 mm thick were therefore used. A further difficulty is the initial inhomogeneity of distribution of the tracer in the as-grown crystals (6).

Earlier measurements on  $\alpha$ -AgI-CuI,  $\alpha$ -Ag<sub>2</sub>S-Cu<sub>2</sub>S,  $\gamma$ -AgI-CuI, and  $\gamma$ -AgBr-CuBr and their unsatisfactory nature were already noted in section I. Measurements for  $\text{CeO}_2$  in  $\text{UO}_2$  (18) and  $^6\text{Li}$  in  $\text{Li}_2\text{SO}_4$  containing a mixture of  $^6\text{Li}$  in  $^7\text{Li}$  (109) do not lend themselves to molecular interpretation at present.

### C. THERMOELECTRIC POWER OF IONIC CRYSTALS WITH FRENKEL OR SCHOTTKY DISORDER

The experimental arrangement for observing the thermoelectric power of a crystal, MX, in contact with electrodes of metal,  $M'$ , is shown in the Figure 4. The thermoelectric power,  $\theta$ , is the potential difference measured at zero current flow by the potentiometer divided by the temperature difference between the electrodes,  $\Delta T$ . The contribution from the homogeneous potential differences in the electrodes and leads is always negligible.

The homogeneous thermoelectric power,  $\theta_{\text{hom}}$ , for the case of cationic Frenkel disorder can be found from Eq 5 and 46 (8, 62, 76, 130).

$$\theta_{\text{hom}} = \frac{(\phi_D - \phi_C)}{\Delta T} \simeq \frac{\nabla \phi_{\text{Int}}}{\nabla T} = -[Q_{\text{M}}^* - t_i(Q_{\text{M}}^* - Q_{\text{I}}^* - h_F)]/eT + (\nabla \mu_+)_T/e\nabla T \quad (\text{Eq 64})$$

Similar equations can be derived for anionic Frenkel disorder and Schottky disorder (8, 63, 78). This equation is valid also for crystals doped with a divalent impurity ion, of concentration  $c_I$ , since the transport number of the latter is always very small (62-64, 76, 77).

The heterogeneous thermoelectric power,  $\theta_{\text{het}}$ , arises from the temperature dependence of the contact potential,  $\Phi$ , the difference in potential between the electrode and a point inside the surface of the crystal

$$\theta_{\text{het}} = \frac{d\Phi}{dT} = \frac{[(\phi_E - \phi_D) - (\phi_B - \phi_C)]}{\Delta T} \quad (\text{Eq 65})$$

For the case that  $M' = M$  it is assumed that the cations of  $M$  are in thermodynamic equilibrium at the interface so that, by equating electrochemical potentials, one obtains

$$e\Phi = [\bar{\mu}(M^+/MX) - \mu(M^+/M)] - \bar{\mu}_+ \quad (\text{Eq 66})$$

where  $\mu(M^+/M)$  denotes the chemical potential of a cation  $M^+$  in metal  $M$ . By differentiation with respect to  $T$  and the use of an explicit expression for  $\bar{\mu}_+$ ,  $\theta_{\text{het}}$  has been found. The result for  $\theta$  is (62-64, 76, 77)

$$\theta = [t_M(h_F - Q_M^*) - t_i Q_i^*]/eT - \frac{k}{e} \log \xi - \frac{s_i}{e} + \frac{1}{e} s(M^+/M) + \frac{k}{e} \log c_{i0} \quad (\text{Eq 67})$$

$s_i$  is the entropy of an interstitial ion,  $\xi = c_+/c_{+0}$ , and  $c_{+0}$  and  $c_{i0}$  are defect concentrations in the pure crystal. The  $c$ 's should strictly be taken as activities if there are interactions between the defects.

Application of these results to AgBr (32), AgCl (30), and TiCl (31) has been made. There is good agreement between the various experimental studies for AgBr (32, 130, 135) and AgCl (30, 135, 177). We consider first the silver halides.

The transport numbers,  $t^0$ , for pure crystals are known from conductivity measurements (107), and, if it is assumed that the mobilities are independent of defect concentration, then transport numbers for doped crystals can be calculated from them if  $\xi$  is known. Since an accurate value of  $s_i$  is not available, the difference in thermoelectric power,  $\Delta\theta$ , between a doped crystal and a pure crystal was analyzed.

$$\Delta\theta = [(\xi^2 - 1)/(\xi^2 t_M^0 + t_i^0)] [t_M^0 t_i^0 \times (Q_i^* - Q_M^* + h_F)/eT] - \frac{k}{e} \log \xi \quad (\text{Eq 68})$$

It was assumed that there were no interactions between vacancies and impurity ions so that  $\xi$  is a simple known function of  $c_I$  and  $c_{+0}$  and a least-squares fit made with  $t_i^0$ ,  $c_{+0}$ , and  $(Q_i^* - Q_M^* + h_F)$  as adjustable parameters. The results (30) for  $Q_i^* - Q_M^*$  are shown in Table IV.

TABLE IV

THE DIFFERENCE OF HEATS OF TRANSPORT FOR NORMAL AND INTERSTITIAL SILVER IONS,  $Q_M^* - Q_i^*$ , FROM THERMOELECTRIC POWER MEASUREMENTS (30)<sup>a</sup>

Temp. °C	$Q_M^* - Q_i^*$ , kcal mole <sup>-1</sup>	
	AgBr	AgCl
150	13.8	14.2
175	13.5	15.2
200	14.3	15.6
225	15.3	16.3
250	16.2	17.2
275	17.4	18.3
300	18.9	19.4
325	20.1	20.5
350	21.8	21.7
375	23.7	23.0
400	...	24.4

<sup>a</sup> Activation energies for jumps:  $\Delta h_m = 8.5$  kcal mole<sup>-1</sup>,  $\Delta h_i = 3.9$  kcal mole<sup>-1</sup> for AgBr (180);  $\Delta h_m = 7.6$  kcal mole<sup>-1</sup>,  $\Delta h_i = 3.5$  kcal mole<sup>-1</sup> for AgCl (40).

The values of  $t_i^0$  and  $c_{+0}$  agreed well with those found from conductivity measurements using the same model. At low temperatures the concentration dependence of  $\theta$  was consistent with the model adopted rather than the more common one, widely employed in conductivity work (107), that allows for nearest neighbor interactions between vacancy and impurity ions. The equilibrium between nearest neighbor complexes of vacancy and impurity ions and defects not members of complexes is there treated by the law of mass action, and  $c_+$  in the equations above refers to the concentration of vacancies not in complexes. However, very similar results for  $(Q_M^* - Q_i^*)$  have been obtained for AgCl using this kind of analysis and a different set of experimental results (177). It has also been shown that inclusion of Debye-Hückel interaction effects between defects not in complexes in the mass action equilibrium has very little effect on the final results (63).

The temperature dependence of  $Q_i^* - Q_M^*$  in silver halides should probably be viewed with caution. In spite of the consistency of the analysis already noted, the need to neglect defect interactions is very unexpected and may indicate a failure of theoretical understanding of Coulomb interactions between defects (98). The assumption that mobilities are concentration independent may also be incorrect for this reason (98). It is also noticeable that an anomalous decrease in  $\theta$  during the experiments has been found for pure AgCl (177). The theory predicts that  $\theta$  is the same immediately after the temperature gradient is established and after the establishment of Soret equilibrium for impurities (76), but this has apparently not been checked. These points merit further study.

Because of the unexpectedly strong temperature dependence found in silver halides, the details of the theory have been critically studied (98). It was noted that the assumption of thermodynamic equilibrium in Eq 66 is not trivial. Indeed, it has been stated (60)

that it is impossible to define thermodynamically any contact electrical potential difference in the case of a nonosmotic contact equilibrium in which the surface of separation is, in effect, permeable to one ion common to both phases but impermeable to all others. An attempt was made (98) to show that in consequence  $\theta_{\text{het}}$  depends on the transport numbers, just as does the liquid junction contact potential for a cell with transference. In the electrode reaction for transport of M into MX, a fraction  $t_{\text{M}}$  was placed substitutionally and a fraction  $t_{\text{i}}$  interstitially in MX, and the free-energy changes per mole for the two processes were said to be different. However, if vacancies and interstitials are in equilibrium, it appears to the reviewers that it is possible to reduce these equations to those of the conventional theory. We therefore do not consider them further.

The thermoelectric power of pure AgBr has also been interpreted (130) using an earlier theory of the contact potential due to Wagner (183). If the defect contribution to the contact potential is neglected, then it follows from Eq 65 that  $\theta_{\text{het}}$  is

$$\theta_{\text{het}} = -[s(\text{M}^+/\text{MX}) - s(\text{M}^+/\text{M})]/e \quad (\text{Eq 69})$$

$s(\text{M}^+/\text{M})$  may be taken as the total entropy of the metal since the electronic contribution is negligible, and  $s(\text{M}^+/\text{MX})$  was taken as one-half the total entropy of MX. Combining Eq 64 and 69, the results for pure AgBr could be fitted by  $Q_{\text{M}}^* = 0.385$  ev, and  $Q_{\text{i}}^* = 0.017$  ev for temperatures in the range 667 to 455°K. The value of  $Q_{\text{M}}^* - Q_{\text{i}}^*$  differs from that in Table IV. This presumably illustrates the importance of the defect terms included in later theoretical studies (62-64, 76, 77). The physical reason for the defect term  $-\bar{\mu}_{\text{i}}$  in Eq 66 is that it represents the potential difference across the space charge layer at the surface of the crystal which arises whenever the energies of formation of oppositely charged defects differ (77). The importance of the defect term is also amply confirmed by the measurements of concentration- $\Delta\theta$  isotherms for doped crystals.

The thermoelectric power of TlCl and TlCl doped with PbCl<sub>2</sub> has been measured with Tl electrodes (31). TlCl has the CsCl structure and contains Schottky disorder. The data was analyzed using the Schottky analog of Eq 68. The best fit was found if no defect interaction was assumed. The result obtained was then

$$Q_{\text{Tl}^+}^* + Q_{\text{Cl}^-}^* = 38 \text{ kcal mole}^{-1} \quad (\text{Eq 70})$$

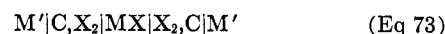
independent of temperature between 275 and 400°. The corresponding enthalpies of activation for migration are

$$\begin{aligned} \Delta h_{\text{m}}(\text{Tl}^+) &= 11.5 \text{ kcal g-ion}^{-1} \\ \Delta h_{\text{m}}(\text{Cl}^-) &= 4.6 \text{ kcal g-ion}^{-1} \end{aligned} \quad (\text{Eq 71})$$

If it was assumed that the  $Q^*$ 's were independent of temperature, then using a Debye value for  $s(\text{M}^+/\text{M})$ , it was found

$$\begin{aligned} Q_{\text{Tl}^+}^* &= 22 \text{ kcal g-ion}^{-1} \\ Q_{\text{Cl}^-}^* &= 12 \text{ kcal g-ion}^{-1} \end{aligned} \quad (\text{Eq 72})$$

For the sake of completeness we mention other theoretical and experimental studies which have not so far yielded additional thermodynamic heats of transport but may be relevant for those studies. The following arrangement has been studied experimentally (135)



where C denotes a carbon rod containing gaseous halogen X<sub>2</sub>. It is assumed that its junction with the crystal, saturated with X<sub>2</sub>, forms a reversible electrode. If this is the case, then the thermopower of the cell,  $\theta_{\text{X}}$ , may be related to that of a cell with reversible electrodes of metal M,  $\theta_{\text{M}}$ , by (63)

$$\theta_{\text{X}} - \theta_{\text{M}} = s_{\text{MX}} - s_{\text{M}} - s_{\text{X}_2}/2e \quad (\text{Eq 74})$$

where  $s_{\text{MX}}$ ,  $s_{\text{M}}$ ,  $s_{\text{X}_2}$  are the entropies of 1 mole of salt MX, of pure metal M, and of the halogen gas X<sub>2</sub>, respectively. This has been verified (63) for AgBr, AgCl, and PbBr<sub>2</sub> using Reinhold's results (135, 141). A further check on the consistency of the results is provided by the equation (139)

$$\left(\frac{\partial E}{\partial T}\right)_{\text{M}, \text{X}_2} = \theta_{\text{X}} - \theta_{\text{M}} \quad (\text{Eq 75})$$

where  $(\partial E/\partial T)_{\text{M}, \text{X}_2}$  is the temperature coefficient of the emf of the isothermal cell M|MX|X<sub>2</sub>, C.

Cu<sup>+</sup> can be incorporated interstitially in AgCl and it has been shown (64) that  $(Q_{\text{Cu}^+}^* - Q_{\text{Ag}^+}^*)$  could be obtained from thermoelectric power measurements on this system. This has not yet been done.

The thermoelectric power of CuCl and (CuCl + CdCl<sub>2</sub>) with Cu electrodes gives results similar to those for AgBr and AgCl (82), but heats of transport could not be derived because of the limited solubility of the impurity. The defect structure of this substance is not yet properly established but the results are consistent with Frenkel defects. Indeed it is unfortunate that the number of ionic crystals with well-established defect structures which also form reversible electrodes is severely limited. Studies have therefore been made for the alkali halides using Pt electrodes (9, 33, 35, 85) but the theory of the heterogeneous thermoelectric power is still not fully understood. Recent results for NaCl do not seem to be in accord with any of the proposals so far (7), and unambiguous heats of transport cannot be obtained. The use of cells like that in Eq 73 may perhaps circumvent this difficulty (63).



Measurements of  $\theta$  for other ionic conducting solids with reversible electrodes are available. Unfortunately, these are for materials in which the defect structure may perhaps be simple but is at present not well enough studied to allow detailed interpretations, *e.g.*, PbCl<sub>2</sub> (135), PbBr<sub>2</sub> (135), PbI<sub>2</sub> (141), CuI (94), CuBr (141), or in which the structure is such that interpretation in terms of simple vacancy or interstitial mechanisms is not possible, *e.g.*, AgI (93, 95), Ag<sub>2</sub>SO<sub>4</sub> (95), and AgNO<sub>3</sub> (169).

#### IV. MOLECULAR INTERPRETATION OF RESULTS

##### A. THE CORRELATION PROBLEM

The preceding section has described the experimental determination of the heats of transport defined by irreversible thermodynamics. The molecular interpretation of these parameters involves two distinct stages in just the same way as does the molecular theory of isothermal diffusion coefficients. The random-walk expression, Eq 48, shows that the tracer diffusion coefficient measured in a homogeneous system, so that  $\langle \Delta x_1 \rangle = 0$ , is given by the Einstein expression

$$D_1^* = \langle (\Delta x_1)^2 \rangle / 2\Delta t \quad (\text{Eq 76})$$

For the case of a substitutional vacancy mechanism, evaluation of this expression involves solution of a nontrivial correlation problem first clearly formulated by Bardeen and Herring (17). After the vacancy has exchanged with the tracer, it may diffuse right away from the tracer or it may return after a few jumps and displace the tracer a second time. The direction of the second tracer jump is clearly correlated with that of the first since the vacancy is more likely to return from the side of the tracer that it was on at the end of the first jump. Evaluation of the mean-square displacement leads to the expression already quoted in Eq 35. Equation 76 can also be used to evaluate the tracer diffusion coefficient of an impurity in a homogeneous solvent. In this case the Bardeen and Herring correlation problem is more complicated because the jump probability of the vacancy differs according to whether it exchanges with the impurity or a solvent atom. An approximate result derived from Eq 76 has been quoted in Eq 43. The second stage of the molecular theory is the interpretation of the jump probabilities determined using such theoretical expressions and the experimental results.

As an alternative to the use of the random-walk expression, kinetic methods have been devised to evaluate the flux of atoms in nonuniform systems and hence to evaluate the coefficients  $L_{ik}$  and the diffusion coefficients in terms of jump probabilities. The kinetic method (78, 106) essentially involves the study of the pair distribution functions in the steady state. Another review (78) gives an account of results of these calculations

and complete references. More recently it has been shown (3) that a correlation formula can be derived for each  $L_{ik}$  which is essentially a generalization of the familiar Einstein expression for  $D_1^*$  and involves the correlation of successive jumps of an atom of  $i$  and an atom of  $k$ . This provides in a sense a bridge between kinetic and random-walk methods.

A similar pattern arises for thermal diffusion. For the first stage, the correlation calculation, the random-walk expression for  $Q^*$ , *e.g.*, Eq 55, has not so far been used, but the kinetic method has been extended (53–55, 75, 81). The correlation problem involves no problems peculiar to thermal diffusion once the form for the jump probabilities is assumed. It is therefore appropriate merely to quote the results available and to devote the rest of the review to molecular interpretation of the single jump heats of transport,  $q^*$ , appearing in these results.

Consider a fcc crystal which is a very dilute alloy of solute, species 2, in a solvent, species 1. Five types of vacancy jump are distinguished as in section II.B.2. A vacancy which is nearest neighbor to an impurity may exchange with the impurity ( $\omega_2$ ), or it may exchange with a solvent atom which is nearest neighbor to the impurity ( $\omega_1$ ), or it may exchange with a solvent atom not a nearest neighbor to the impurity ( $\omega_3$ ). The reverse of a  $\omega_3$  jump is assigned a jump probability ( $\omega_4$ ). All other jumps have frequency  $\omega_0$ . The results of the kinetic analysis (81) yields an expression for the Soret effect equivalent to the thermodynamic result (Eq 58), if the identification is made

$$Q_2^* - h_v = [2\omega_1(q_2^* - 2q_1^*) + \omega_3(7q_2^* + 3q_3^* + 3q_4^* - 3\chi) + (h_v - \chi)(2\omega_1 - 13\omega_3)] / (2\omega_1 + 7\omega_3) - p(h_v - \chi) \quad (\text{Eq 77})$$

and the denominator of Eq 58 is approximated by  $D_2$ .  $q_i^*$  denotes the heat of transport corresponding to the jump  $\omega_i$  ( $i = 1, 2, 3$ , or  $4$ ) defined above.  $p$  is the fraction of impurities which are nearest neighbor to vacancies calculated by the law of mass action assuming that the energy of binding is zero at all greater separation.  $\chi$  is the binding enthalpy for this equilibrium.

Clearly one must attempt to select systems for which some simplification allows a reduction in the number of parameters. Two cases of interest are (a) all vacancy exchanges with the solvent have the same jump parameters, say  $\omega_0$  and  $q_0^*$ . This gives

$$Q_1^* = q_0^*, \quad Q_2^* = q_2^* \quad (\text{Eq 78})$$

This may be appropriate for Tl in Zn (81), given in Table II. (b) The "tight binding" approximation,  $\omega_3$ , is negligible compared with all other jump frequencies and may be put as zero in Eq 77. This assumption has been made for SrCl<sub>2</sub> in NaCl (6) and leads to the identification

$$Q_k^* = q_2^* - 2q_1^* \quad (\text{Eq 79})$$

where  $Q_k^*$  is given in Eq 63'.

For the systems in Tables I, III, and IV, only one kind of jump for each species need be identified and so

$$Q^* \equiv q^* \quad (\text{Eq 80})$$

#### B. THEORIES OF THE HEAT OF TRANSPORT FOR A JUMP

The proposal  $q^* = \Delta h_m$  noted in section I may be compared with the experiment. For the vacancy mechanism the results for metals fall into two groups, namely, those in which it is difficult to decide whether the small deviations are significant, and the remainder in which  $q^*$  is largest, as for Co, Zr, and Ti. The two temperature-dependent results, for Pt and Co, fall into this class but it seems fair to say the remaining experiments are not extensive enough to detect a temperature dependence in most cases. The results for ionic crystals, TlCl (31) and SrCl<sub>2</sub> in NaCl (6), are both consistent with  $q^* > \Delta h_m$  and essentially independent of  $T$ . By contrast the results for interstitials indicate  $q^* < \Delta h_m$  and  $q^*$  is often negative. Furthermore the linear temperature dependence of  $q^*$  is well established for H and D in  $\alpha$ -Fe and Ni, and for H in  $\gamma$ -Fe<sub>0.6</sub>Ni<sub>0.4</sub>. Unfortunately, the temperature dependence for AgBr and AgCl in Table IV cannot be separated into vacancy and interstitial contributions, but it is striking that the temperature dependence of the sum is not linear.

The theory of the isothermal jump frequency due to Rice (147) has been useful in discussions of the nature of the heat of transport (10, 128, 129, 155). The isothermal frequency,  $\omega_0$ , is taken as a product  $\omega_a \omega_b$ .  $\omega_a$  is the frequency with which the jumping atom attains a critical configuration in which it has a large amplitude of vibration properly oriented toward the adjacent vacancy.  $\omega_b$  is the frequency with which the shell atoms adjacent to the jumping atom and vacancy attain a critical configuration such that the jumping atom can pass from its initial site to the vacancy without its path being blocked.  $\omega_b$  is much greater than  $\omega_a$ , and it is thought that the separation into the product of probabilities is valid if the displacements of the shell atoms are not too large. This particular approximation is avoided in a slightly different formulation of the theory (115).

To calculate  $\omega_a$  the harmonic approximation is assumed, and displacement of the jumping atom is written as the superposition of contributions from the normal modes of vibration. It is assumed that if the critical configuration is attained, then a jump will occur and the motion becomes irreversible. However, the necessary elements for irreversibility are not included in the formalism but are introduced by fiat just as in the transition-state formulation (147) and as they must be in the harmonic approximation. The result is

$$\omega_a = \nu_a \exp(-U_0/kT) \quad (\text{Eq 81})$$

where the frequency,  $\nu_a$ , can be calculated from the normal mode analysis, and  $U_0$  is the minimum energy required for the atom to achieve the critical configuration.  $\omega_b$  is calculated by assuming that the distribution function for the probability of finding the shell atoms in their critical configuration is given by the equilibrium value. In the harmonic approximation the result is

$$\omega_b = A \prod_j [\exp(-U_j/kT)] \prod_{k>l} g_{kl} \quad (\text{Eq 82})$$

where  $U_j$  is the energy to displace atom  $j$  to its critical configuration, and  $g_{kl}$  is the pair correlation for atoms  $k$  and  $l$  in the critical configuration.  $A$  is a normalization parameter. The outstanding criticisms of the theory are the method of introducing irreversibility and the use of the harmonic approximation, particularly for  $\omega_a$ . However, the physical picture is very clear and not dependent on these limitations. Although the formulation appears rather different from the transition-state approach used for the same problem (107, 184), the relationship between the results is quite close (78), at any rate as far as final results are concerned.

Equations 81 and 82 may be combined to yield the traditional activated process formula (Eq 7) in which all the parameters can be fully defined by the Rice theory. With this model in mind we review the theories of  $q^*$ .

An intuitive generalization of the rate process formula (Eq 7) has been extensively discussed. Wirtz (188) first proposed that  $\Delta g_m$  may be decomposed into three parts:  $\Delta g_1$ ,  $\Delta g_2$ , and  $\Delta g_3$ . These energies are respectively supplied (i) at the initial position of the atom; (ii) at the plane of normal atoms between the initial and final positions of the jumping atom; (iii) at the final position of the atom where the atoms surrounding the vacancy must be pushed back to accommodate the jumping atom. The component energies are said to be supplied at slightly different temperatures in an anisothermal system so that one has, in the notation of section I

$$\omega(T, T + \Delta T) = \nu \times \exp\left(-\frac{\Delta g_1}{kT} - \frac{\Delta g_2}{k(T + \Delta T/2)} - \frac{\Delta g_3}{k(T + \Delta T)}\right) \quad (\text{Eq 83})$$

where  $\Delta T$  is the difference in jumping between final and initial positions of the jumping atom. By expanding in powers of  $\Delta T$ , retaining only leading terms, and comparison with Eq 8 and 12, one arrives at

$$q^* = (\Delta h_1 - \Delta h_3) \quad (\text{Eq 84})$$

A similar discussion can be made for an interstitial. The enthalpies  $\Delta h_1$  and  $\Delta h_3$  are not unambiguously defined and have occasionally been interpreted in different

ways by different workers. For example, the identification  $\Delta h_3 = h_v$  has been made (10) but appears incorrect since the energy refers to the enlargement of an already existing vacancy. The identification  $\Delta h_1 = U_0$  may be tentatively made (10).

A similar discussion of thermal diffusion in binary liquids has been given (189), and attempts have been made to calculate the energy quantities involved for such systems with nearest neighbor interactions (37, 132).

The Wirtz model makes one quantitative prediction,  $q^* \leq \Delta h_m$ . It is not obvious that this is a reasonable prediction. The local fluctuation by which the migrating atom acquires the energy  $U_0 \simeq \Delta h_1$  might be expected to involve the acquisition of energy from neighbors predominantly on the side of the atom far from the vacancy in order that the migrating atom is impelled in the right direction. But, if the vacancy is on the high-temperature side, then the relevant neighbors will be undergoing fewer fluctuations than they would in an isothermal system. In the language of the Wirtz model,  $\Delta h_1$  is not necessarily supplied at the mean temperature of the initial site of the jumping atom since the atoms involved are asymmetrically disposed about the site and probably at a lower mean temperature. It is readily seen that this will tend to make  $q^*$  more positive, so that the prediction mentioned above does not seem very certain. Furthermore, from the remarks at the beginning of this section, there are experimental results in disagreement with the prediction for the vacancy mechanism.

The relationship between  $\Delta h_1$  and  $U_0$  has been clarified by Schottky's theory (155) which makes a formal extension of the Rice model for a one-dimensional chain with a vacancy. Let  $\epsilon_k$  be the energy of normal mode  $k$ , of wavenumber  $k$ , and frequency  $\omega_k$ . In the presence of a temperature gradient, the mean phonon energies,  $\epsilon_k$ , are approximated by

$$\epsilon_k = kT - k\tau \frac{d\omega_k}{dk} \frac{dT}{dx} \quad (\text{Eq 85})$$

where  $\tau$  is a measure of the relaxation time for a non-equilibrium phonon distribution to return to equilibrium and is determined by the phonon-phonon interactions. This approximation is familiar in discussion of the lattice thermal conductivity,  $\kappa$ , which requires solution of the Boltzmann equation for phonon numbers. At high temperatures  $\kappa$  is given in a similar approximation by

$$\kappa = k\tau v_s^2 N \quad (\text{Eq 86})$$

where  $v_s$  is the mean sound velocity. Employing these phonon energies in the Rice equation and remembering that for a linear chain  $\omega_0 = \omega_a$  and  $\Delta h_m = U_0$ , the Schottky result (155) is

$$\Delta\omega \simeq +U_0\tau\omega_1/akT^2 \quad (\text{Eq 87})$$

(from his Eq 9 with  $\omega_1 \simeq \omega_2$ ), and hence

$$q^* = U_0(1 - 2\tau\omega_1/a) \quad (\text{Eq 88})$$

but the term  $U_0$  on the right was omitted by Schottky.  $\omega_1$  is an averaged phonon velocity which can be (155) explicitly expressed in terms of the force constants for the chain. Note that  $(-\tau\omega_1)$  is essentially the mean free path,  $\lambda_0$ , of the phonons which contribute to the energy of the jumping atom. The coupling of heat and matter fluxes expressed by  $\Delta\omega \neq 0$  arises from the asymmetry of the phonon scattering at the jumping atom due to the applied temperature gradient. (This aspect has been emphasized elsewhere (56)). Suitable thermal conductivity measurements allow an estimate of  $\tau$ . Since  $\tau \sim T^{-1}$  and  $\omega_1$  is negative, the heat of transport decreases with increasing temperature whereas the variations found are in the opposite direction for Pt, Co, AgBr, and AgCl. Explicit calculations yield the following results at the melting point:  $q^*/U_0 = 3.3-3.8$  for Cu, 4.7-4.9 for Ag, and 3.2 for Au. The higher values are for the approximation that  $\tau$  is independent of wavenumber,  $k$ , as assumed above and the lower values for  $\tau(k) = A\omega_k^{-2}$ . These values cannot be compared directly with experiment since the factor  $\omega_b$ , which accounts for the contribution of the shell atoms to  $\omega_0$ , is omitted in a one-dimensional approach. In the isothermal Rice theory the distribution function for the shell atoms is approximated by the equilibrium value. In the Wirtz analysis, this is essentially extended by assuming that the local equilibrium value with local mean temperatures is sufficient, which is perhaps plausible for  $\omega_a < \omega_b$  but difficult to assess.  $q^*$  would then be reduced by  $\Delta h_3$  as in Eq 84. The result of the Schottky calculation does therefore not necessarily disagree too severely with experiment although the apparently incorrect temperature dependence arising from  $\tau$  is disturbing. Note that in this theory  $q^*$  can be bigger than  $\Delta h_m$ , in agreement with results for ionic crystals, AgBr, AgCl (30), TlCl (31), NaCl + SrCl<sub>2</sub> (5), which are most suitable for comparison because of the absence of perturbing effects of conduction electrons (see below).

A less detailed theory has been studied in which the effect of scattering of phonons by an atom in the activated state was considered (48).

Theoretical treatments of  $q^*$  may be classified as isothermal or anisothermal calculations. In the latter the jump frequency in an anisothermal is calculated and  $q^*$  then found from Eq 8 and 12, as in the methods described above. However, for an isothermal system, Eq 29 yields

$$J_q = \sum_{k=1}^{n-n_r} Q_k^* J_k \quad (\text{Eq 89})$$

which forms the basis of isothermal calculations. Indeed this could be taken as the definition of the heat of

transport. It is identical with that previously employed (Eq 25) provided the Onsager relation

$$L_{tu} = L_{ut} \quad (\text{Eq 90})$$

is valid (9). Unfortunately the heat fluxes in solid-state diffusion processes are too small to measure directly so that experimental verification of the Onsager relation is not possible. Measurements for gases and liquids have not provided any evidence of the invalidity of the relation which is therefore always assumed in practice.

To use the macroscopic Eq 89 as the basis of a molecular calculation, we recall the Kirkwood transport theory (90, 149). The flow of heat must be described over a period of time macroscopically short, but longer than the time,  $\tau$ , of the basic dynamical event, *i.e.*, the jump of one atom. What is important is not merely the distribution of thermal energy "just before" and "just after" the jump, but the process of gathering and dissipation of the energy of all the atoms involved in the jump over a period of time,  $\tau$ , long enough that the motions of the atoms at the beginning and end of  $\tau$  are essentially uncorrelated. In addition the assumption  $\tau \ll \omega_0^{-1}$  is always made in the calculation of the correlation factor,  $f$ , and in the discussions of the heat of transport (129), but *direct* evidence for this is not available. The self-consistency of interpretations based on it and semiquantitative arguments (148) are available.

An adequate dynamical description is not available, but attempts have been made to relate  $q^*$  to  $\Delta h_m$ ,  $h_v$ , heats of solution, etc. The validity of the calculations is therefore uncertain.

Shewmon (158) proposed that there are two major contributions to  $q^*$ . In order for an atom to jump, the activation energy must be absorbed. A fraction,  $\beta$ , of this excess energy is absorbed by the jumping atom at its first site and is transported to and dissipated at the second site, thereby contributing  $\beta\Delta h_m$  to  $q^*$ . The fraction  $1 - \beta$  is absorbed by the lattice atoms surrounding the saddle point and is given up by them after the jump. It is not transported. Let  $E_L$ , the "localized heat of solution," be the decrease in energy when a vacant site is filled by an atom from outside some small region of the crystal containing the vacancy. There will be a contribution to  $q^*$  of  $E_L$ , and for vacancy diffusion this is approximated by  $h_v$ . The result is therefore

$$q^* - h_v = \beta\Delta h_m \quad (\text{Eq 91})$$

and independent evidence suggests  $\beta \simeq 0$  (158). This analysis agrees with the Wirtz theory that the part of  $\Delta h_m$  associated with the saddle point atoms does not contribute to  $q^*$ . Presumably  $\beta\Delta h_m$  is essentially the same as  $\Delta h_1$  of Wirtz. However, the energy of vacancy formation can be written approximately as  $h_v = h_v' - \Delta h_s$ , where  $h_v'$  is the energy to form a vacancy around

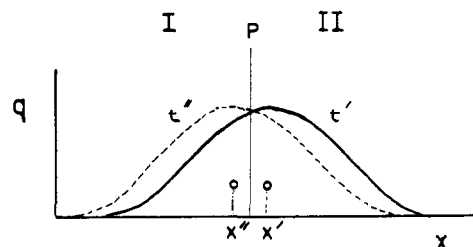


Figure 5.—Excess thermal energy,  $q$ , as a function of distance for the sphere surrounding vacancy-atom pair at times  $t'$ , just before interchange, and  $t''$ , just after interchange.

which the atoms have not relaxed.  $h_v'$  contributes to  $q^*$  in Shewmon's analysis but not in that of Wirtz.

A similar argument for interstitial diffusion yields

$$q^* = -\bar{H}_i + \beta\Delta h_m \quad (\text{Eq 92})$$

where  $\bar{H}_i$  is the partial molar heat of solution of the interstitial atom. Thus with  $\beta \simeq 0$ , the sign of  $q^*$  should be the opposite of that of  $\bar{H}_i$ , in agreement with the results for N in  $\alpha$ -Fe, C in  $\alpha$ -Fe, C in  $\gamma$ -Fe, and H in  $\alpha$ -Zr (36, 100, 111, 116). A similar result was suggested by others (134).

The Rice model has been used to clarify the isothermal calculations (128, 129). Figure 5 represents the excess thermal energy  $q$  as a function of distance for a small sphere surrounding the jumping atom and vacancy at times  $t'$  and  $t''$  just before and just after the jump. Let  $\bar{q}'$  and  $x'$  be the coordinates of the centroid of the curve at  $t'$  and  $\bar{q}''$  and  $x''$  be those at  $t''$ . If the jump is adiabatic as far as the sphere is concerned, then  $\bar{q}' = \bar{q}''$  and

$$q^* = \bar{q}'(x'' - x') \quad (\text{Eq 93})$$

The heat flux may conveniently be referred to the plane  $P$  which bisects  $x'' - x'$ . A part of the energy, say  $E_c^L$ , of the  $q(x, t')$  curve on the left of  $P$  must be converted to "chemical energy," *e.g.*, electronic energy, representing, for example, the energy of formation of the hole created by the atom jumping into the adjacent vacancy. Let  $E_{vib}$  be the amount of vibrational energy transferred from the  $q(x, t')$  curve on the left of  $P$  to the other side of the plane. The result is then

$$q^* = E_{vib} + E_c^L \quad (\text{Eq 94})$$

The division of energy is not very different from that given by Shewmon (158), but a more detailed discussion of the factors has been given emphasizing the role of the localized normal modes around the defect.

If a chemical or structural impurity is introduced into a lattice and the impurity is either a substitutional vacancy or an atom of smaller mass than the normal lattice atom, then the frequencies of the continuum of normal modes are displaced slightly downward,  $0(N^{-1})$ , and some normal modes have their frequencies displaced upward out of the band. The latter frequencies correspond to localized normal modes decreasing ex-

ponentially with distance from the defect. The higher the frequency of the localized mode, the faster is its exponential decay with distance. The localized modes associated with impurities are either symmetrical or antisymmetrical about the impurity; *i.e.*, the atoms to the left are either in phase or antiphase with those to the right of the impurity. Whereas a vacancy produces antisymmetric localized modes, an interstitial or substitutional impurity produces both types. This may be of some importance for the jump process, which is presumably favored by the symmetric mode. Consider  $q^*$  for an interstitial impurity. The smaller the ratio of the mass of the impurity to that of the normal atom, and the larger the ratio of the effective force constant between the impurity and a host atom relative to that between two host atoms, the greater will be the localization of the localized symmetrical normal modes produced and the higher will be their frequencies. For very small mass ratios, almost all of the vibrational energy of the impurity atom and its neighbors reside in the localized modes, and the number of atoms whose motions are correlated is very small. In these circumstances there is a positive contribution to  $E_{\text{vib}}$ , and one expects that the impurity takes with it a sizeable fraction of the activation energy, which is dissipated in the final position. At the other extreme, as the mass ratio increases, the dominance of the localized mode decreases and the diffusive motion of the impurity, described for example in Rice's theory, consists more and more in the superposition of the phases of many spatially extended normal modes. Most of the activation energy comes from a relatively large region of the lattice, and once the atom has jumped most of  $\Delta h_m$  is dissipated behind it making a negative contribution to  $q^*$ .

For a vacancy jump,  $E_c^L$  is not quite equal to  $h_v$  because the vacancy to be created in I is at a position adjacent to the already existing vacancy in II so that on a nearest neighbor basis it is approximately  $h_v(z-1)/z$ , where  $z$  is the number of nearest neighbors per atom. The marker movement experiments available at the time of Oriani's paper (24, 158) suggested that  $q^* \simeq h_v$  so that  $E_{\text{vib}}$  would be between 0 and  $0.1h_v$ . According to Oriani, this might have been expected in the absence of a localized normal mode effect.

For interstitial solutes like N or C in  $\alpha$ -Fe, where  $q^*$  is negative, since  $E_{\text{vib}}$  is positive or a small negative quantity it follows that  $E_c^L$  is negative. The nature of  $E_c^L$  can be clarified by a thermodynamic cycle. When an impurity atom in its normal thermodynamic standard state is added interstitially to the solvent lattice, the enthalpy change is  $\bar{H}_i$ . We may reach the state of solution so formed in two steps. The first step is to take the atom from its standard to its as-dissolved state in the lattice, and this requires an energy  $E_{\text{met}}$  for "metallizing" the solute species from the standard state.

The second step is to add the "metallized" atom to its position in the solid solution. From the cycle performed one has

$$q^* = -\bar{H}_i + E_{\text{met}} + E_{\text{vib}} \quad (\text{Eq 95})$$

For the interstitial solutes considered, Oriani assumed  $E_{\text{vib}} \simeq 0$  and used the experimental results to calculate the approximate values for  $E_{\text{met}}$ , *e.g.*, C in  $\alpha$ -Fe  $\sim 0$ , H in  $\alpha$ -Fe  $\sim -43$  kcal, but no interpretation was made and independent values are not at present available. The expression for  $q^*$  may be compared with Shewmon's result. The kinetic parts,  $E_{\text{vib}}$  and  $\beta\Delta h_m$ , are both claimed to be small, although as a result of rather different analyses, and  $-\bar{H}_i$  appears in the thermodynamic part of both expressions. The results differ by the term  $E_{\text{met}}$  whose origin is quite clear from Oriani's analysis. The principal difficulty with this analysis was noted by Oriani himself. The central assumption is that no thermal energy "leaks" between regions I and II after  $t''$ . In fact, as emphasized above, the whole process of energy gathering and dissipation must be described by the theory, and there seems no good reason to suppose that this involves no leakage, particularly if the vibrations are appreciably anharmonic. The connection of the analysis with the Schottky (155) dynamical calculation is not at all clear at present, particularly in the occurrence of the thermodynamic terms  $\bar{H}_i$  and  $h_v$ . In addition the temperature dependence of certain interstitial solutes is not explained. In another isothermal theory an attempt has been made to discuss  $q^*$  within the framework of the transition-state theory (65).

Another semiempirical approach has been proposed by Girifalco (53-55) in which a picture of the spatial energy distribution similar to that in Figure 5 is used to calculate the flux in an anisothermal system. Two temperatures  $T_+$  and  $T_-$  are defined by

$$\omega(T, T + \Delta T) = \nu \exp(-\Delta g_m/kT_+) \quad (\text{Eq 96})$$

$$\omega(T + \Delta T, T) = \nu \exp(-\Delta g_m/kT_-) \quad (\text{Eq 97})$$

Consider next an Oriani diagram of the spatial energy distribution when the jumping atom moving from left to right has reached the critical configuration. Let the origin of the  $x$  axis in the diagram now be at the center of the jumping atom and let  $\delta$  be the distance of the maximum in the energy curve from the origin. If  $\delta < 0$ , atoms to the left of the initial site of the atom impart energy to the solute atom; if  $\delta > 0$  then atoms to the right of its final position exert an attractive force. If  $\delta < 0$ , then  $\omega(T, T + \Delta T) < \omega(T + \Delta T, T)$  since the probability of the jump from  $T$  to  $T + \Delta T$  across the plane at  $x = 0$ ,  $T + \Delta T/2$  is controlled by an energy fluctuation with maximum in the region  $x < 0$ , while a jump in the reverse direction is controlled by a fluctuation with maximum in the region  $x > 0$ . Thus

for  $\delta < 0$  the temperature difference  $\Delta T_0 = T_+ - T_-$  is negative. A "critical configuration separation distance"  $x_0$  is defined by the equation

$$\Delta T_0 = x_0 \frac{dT}{dx} \quad (\text{Eq 98})$$

and is clearly approximately  $2\delta$ . By expanding  $\omega(T, T + \Delta T)$  in powers of  $\Delta T_0$ , an analysis similar to that in the Introduction leads to

$$q^* = -(x_0/\lambda)\Delta h_m \quad (\text{Eq 99})$$

where  $\lambda$  is the jump distance. The method is therefore an approximate way of determining the position of the maximum in the energy distribution of the critical configuration. For an interstitial jump of C in  $\alpha$ -Fe,  $x_0/\lambda \simeq 1$  indicating that local expansion at the final site of the jumping atom is the most important contribution  $q^*$ , whereas for vacancy mechanisms, where  $q^* \simeq \Delta h_m$ , the centroid of energy is near the initial site. The method is in a sense a generalization of the Wirtz method, but the latter was limited to  $x_0/\lambda$  values in the range  $\pm 1$ .

Phonon transport studies of the kind first made by Schottky (155) presumably contain some of the essential elements of a description of  $q^*$  applicable to non-metals. However, to account for the large  $q^*$  values for the elements Pt, Co,  $\beta$ -Zr, and  $\beta$ -Ti and the sign of  $q^*$  for interstitial solutes in Fe and Ni, an additional mechanism of energy transport has very recently been considered (56, 70). Conduction electrons in metals furnish the major mechanism for carrying heat. It is therefore natural to inquire if the jumping atom in such systems may acquire energy from the electron flux caused by the temperature gradient. That this is possible is suggested by the phenomenon on electromigration (mass transport caused by an electric field). Electromigration in solid metals has been observed in both electron conductors (Cu, Ni, Au, Pt, Al, In, Sn, Ag) and hole conductors (Co,  $\gamma$ -Fe, Cd, Zn, Pb). The diffusing species are ions rather than neutral atoms and a diffusing ion near the saddle point of a jump experiences both an electrostatic force (field-ion interaction) and an electron wind force due to ion-electron interactions. The total force,  $F_t$ , on an ion of valence  $Z$  in a field  $E$  can be approximated by (83)

$$F_t = eEZ^* = eEZ \left( \frac{1 - N\rho_d m^*}{2\rho N_d |m^*|} \right) \quad (\text{Eq 100})$$

where  $m^*$  is the effective mass of the charge carriers, and  $\rho_d$  and  $\rho$  are the resistivities due to scattering from defects ( $N_d$  per unit volume) and lattice atoms ( $N$  per unit volume), respectively. The direction of mass transport and the sign of the effective charge  $Z^*$  therefore depend on the sign of the charge carriers which can be either electrons or holes. (Two other theoretical

treatments (23, 47) yield closely similar expressions and predictions.)

The form of irreversible thermodynamics reviewed in section II might be less convenient for the discussion of electromigration and thermal diffusion than a modification (15, 16) in which the species of a metal or alloy are taken as electrons and ions rather than neutral atoms. This discussion so far (16) has not treated vacancies as a separate species.

The effect of electron drag on the ions in the presence of a temperature gradient has been treated (49), but no quantitative calculations have been made for systems of interest. Nevertheless, empirical correlations between the Soret effect and electromigration have been noted (56, 70). Metals in which electrons are charge carriers and which have relatively simple electronic structures (Ag, Au, Cu, Al) have large electromigration effects toward the anode and relatively small Soret effects, whereas the large Soret effects are associated with complex electronic structures and sometimes hole carriers, *e.g.*, Co. There is also a correlation between the signs of  $q^*$  and  $Z^*$  for interstitial solutes, and an attempt has been made to relate these quantities (56).

It appears plausible that electron drag effects are important at least in some transition metals and that theoretical studies are required. The actual separation of any given experimental  $q^*$  into electron drag and phonon transport contributions may be rather difficult. Measurements in nonmetallic systems such as ionic crystals should therefore prove valuable in allowing the phonon transport problem to be studied alone. In this connection the generalization of the Schottky analysis (155) to three dimensions and its connection with the isothermal calculations are of immediate interest.

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