On the Interpretation of the Heat of Transport of Substitutional Impurities in Noble Metals *

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The heats of transport of several substitutional impurities (such as Sb, Sn, In, Ag, Ni and Co) in copper and silver are discussed in terms of atomic quantities. They are considered as consisting of essentially two parts. The first one, the so-called intrinsic heat of transport, can be derived from the electrostatic potential generated by the impurity at the site of a normal lattice atom in excess over the potential of the host lattice. This interpretation is compatible with the thermodynamic definition of the heat of transport. The calculations were carried out for fcc lattices but, in principle, may be easily extended to other alloy structures. The second part, calculated by Gerl, is due to the electronic scattering potential of the impurities. From comparison of theoretical and observed data of heats of transport one finds the agreement to be very good. This is taken to be an indication of the validity of the theoretical models used and of the vacancy mechanism as the dominating mass transport mechanism in these systems, not only in a uniform temperature field but also in a temperature gradient.

1. Introduction

Thermotransport is generally understood to be the transport of matter in a temperature gradient. This effect has not yet been sufficiently investigated in condensed phases to obtain a final picture of its mechanism. The sign and magnitude of thermotransport depends on the heat of transport. Comprehension of the phenomena of thermotransport is, therefore, based on an atomistic interpretation of this quantity.

From an atomistic point of view, thermotransport arises from asymmetric jump frequencies in a temperature gradient. Among the forces responsible for these asymmetries are[1,2]

a) the "intrinsic" forces in a solid; i.e., locally variable energy content including the different chemical nature of atoms in solutions and

b) the "extrinsic" forces; i.e., interactions of moving ions with heat carriers (electrons and phonons) and extrinsic fields.

All forces superpose to give additive contributions to the heat of transport[1].

Most kinetic models to interpret thermotransport in condensed phases known from literature[3–8] consider only intrinsic forces and explain the anisotropy of jump frequencies in terms of different temperatures attributed to neighboring lattice sites between which atoms may jump back and forth. The threshold energy for such a jump can be more easily provided at sites of higher temperature than at lower temperature resulting in different jump probabilities in and against the temperature gradient. The diffusing particle collects energy at a certain temperature from its environment and releases the energy at the new site after the jump at a different temperature.

The energy carried along by the moving particle generally does not equal the threshold energy, H_m, as originally assumed[4,5] (this would mean, in contrast to the experimental results, the heat of transport of interstitials to be always positive). According to Wirtz' model[3] it is a positive or negative fraction of H_m depending on the local distribution of the activation energy of motion prior to and after the particle jump; i.e., on the way it is picked up and dissipated. Wirtz considers this energy distribution by formally dividing the activation energy of motion into three parts: an energy, H_{m1}, which must be given to the jumping atoms on the original plane, that one, which must be given to them in the intermediate plane of the jump to surpass the

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2 M. GERL, J. Phys. Chem. Sol. **28**, 725 [1967].
3 K. WIRTZ, Phys. Z. **44**, 221 [1943].
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saddle point and, eventually, an energy, H_{m3}, required to prepare the final place for the jumping atom. The last part of the energy opens up an relaxed vacancy site or an interstitial site depending upon the diffusion mechanism. In this model, the heat of transport has the form for an interstitial mechanism:

$$Q^* = H_{m1} - H_{m3} = \beta H_m \quad \text{with} \quad \beta = \frac{H_{m1} - H_{m3}}{H_m} \tag{1}$$

and for a vacancy mechanism:

$$Q^{**} = H_{m1} - H_{m3} - H_{vf} = \beta H_m - H_{vf}. \tag{2}$$

The term H_{vf}, the vacancy formation enthalpy per mole, enters because, in case of a vacancy mechanism, the mass flux is always accompanied by an oppositely directed vacancy flux. In this case, H_{m3} as defined above is relatively small compared to H_{m1}.

GIRIFALCO[8] arrives at a similar result by defining a critical distribution function of the activation energy of motion along the jump axis of two lattice sites allowing a jump to take place. The shape of this distribution function is determined by the quantity β. WEVER[9] extended the treatment to the whole concentration range of a binary alloy. The heats of transport of both components derived by him confirm Eqs. (1) and (2) but contain free energies instead of total energies.

The Wirtz model has been frequently used to interpret the heat of transport in solids, partially successfully but also revealing some discrepancies between theory and experiment. These deviations at least in part arise from the fact that the model, in principle, considers only the intrinsic part of the heat of transport and does not take into account interactions of the moving particle with electrons. On the other hand, they may also indicate weaknesses inherent to the model[10].

An important requirement to be fulfilled by any theoretical interpretation of the heat of transport is its compatibility with the definition as given by the thermodynamics of irreversible processes. This has recently been emphasized by ORIANI[10]. The heat of transport, phenomenologically introduced as a proportional factor between mass flux and temperature gradient can be shown thermodynamically to be the ratio of the reduced heat flux, I_q, and the mass flux, I_m, under isothermal conditions:

$$Q^* = \left(\frac{I_q}{I_m}\right)_{\nabla T = 0}. \tag{3}$$

In a model to describe thermotransport* the problem of introducing the notion of a temperature gradient on an atomic scale may become irrelevant. Previously, several authors[9,11] have point ed out that it may be difficult to ascribe different temperatures to neighboring lattice sites as is done in the Wirtz model.

It is the objective of this article to quantitatively estimate the heat of transport in accordance with the above stated thermodynamic requirement. In a first section, the intrinsic part of the heat of transport in dilute fcc alloys will be deduced from atomic quantities following a procedure similar to that used by DENBIGH for liquids[12]. For the evaluation of the extrinsic part, reference is made to the results of FIKS[13,14], GERL[2] and HUNTINGTON[1]. In a second section, the calculated values of the total heat of transport comprising both the intrinsic and extrinsic part are to be compared with experimental data in various dilute alloys of noble metals. Some conclusions as to how thermotransport proceeds in these systems may then be drawn.

2. The Heat of Transport in Dilute Binary Substitutional Alloys

It has already been pointed out that an atomistic understanding of the heat of transport requires the knowledge of a critical distribution function of the activation energy allowing an atom to jump and of the way the energy dissipates after the jump. As a first approach to this problem, an energy balance of a complete isothermal jumping process is established, referring the associated energy changes to a unit volume, V, of the crystal bounded on one side by the intermediate plane between the initial and final jumping site. If one considers the energy distribution only before and after a jumping process then, by looking at the total energy change in the volume element under consideration, one obtains the intrinsic net energy transported into or out of

[9] H. WEVER, Z. Naturforsch. **18**, 1215 [1963].
[10] R. A. ORIANI, J. Phys. Chem. Solids **30**, 339 [1969].
[11] G. SCHOTTKY, Phys. Stat. Sol. **8**, 357 [1965].

* on the basis of Eq. (3).
[12] K. G. DENBIGH, Trans. Faraday Soc. **48**, 1 [1952].
[13] V. B. FIKS, Sov. Phys. Sol. State **5**, 2549 [1964].
[14] V. B. FIKS, Sov. Phys. Sol. State **3**, 724 [1961].

this volume element and, thus, by definition the intrinsic heat of transport. However, since the heat of transport is not a function of state, one must also consider energy changes occurring in V when the particles are in the process of moving between two equilibrium sites. Such energy changes may be due to forces exerted on the moving ion in the activated state. These interaction effects give rise to another contribution to the heat of transport, Q_e^{**}, which must be added to the intrinsic part to give the total heat of trans-port, Q_e^{**}:

$$Q^{**} = Q_i^{**} + Q_e^{**}. \tag{4}$$

Initially, the second term in Eq. (4), Q_e^{**}, will be neglected and be taken into account later on. To find Q_i^{**} from the energy changes occuring in V during a jumping process under conditions of constant temperature and pressure, we consider free energies and obtain Q_H^{**} and Q_S^{**} as contributions to Q_i^{**} due to enthalpy and entropy changes respectively

$$Q_i^{**} = Q_H^{**} + Q_S^{**} \tag{5}$$

In the following treatment both contributions are determined separately.

The enthalpy contribution to the intrinsic heat of transport

For the sake of simplicity and straightforwardness, we assume each atom to be in interaction only with its nearest neighbors forming pair bonds independent from all other neighbors. In a binary alloy with two components, A and B, one must, therefore, distinguish between three different kinds of bonds, an A-A-, a B-B- and an A-B-pair. Denoting the number of pairs in a crystal by n_{aa}, n_{bb} and n_{ab}, respectively, and the corresponding binding energies — with respect to a complete separation to infinity — by u_{aa}, u_{bb} and u_{ab}, we find the potential energy of the crystal at absolute zero to be given by

$$U = n_{aa}\, u_{aa} + n_{bb}\, u_{bb} + n_{ab}\, u_{ab}. \tag{6}$$

In a random distribution of A- and B-atoms each atom, on average, has $N_a z$ nearest neighbors of type A and $N_b z$ nearest neighbors of type B, z being the coordination number of the lattice and N_a, N_b the mole fractions of the two atom species.

Upon removing an A-atom from a volume element, V, to infinity, the potential energy of the atoms in this element changes by

$$\Delta U_a^0 = -z(N_a\, u_{aa} + N_b\, u_{ab}) - P. \tag{7}$$

Here, P is the relaxation energy of the vacancy generated in the field of its surrounding ions. If the atom to be removed is located at the surface of the crystal, the energy change, ΔU_a, according to MOTT and GURNEY[15], is reduced to $1/2\,\Delta U_a$, because in this case only $1/2z$ bonds are broken. Further, if the A-atom is not removed to infinity but is placed into a neighboring position inside the crystal but outside V representing a jumping process across the border plane of the considered volume element, we again find ΔU_a to be smaller (by a factor $f<1$) than for the case of A being removed from the surface to infinity. This is because the atom, in its new position after the jump, still remains in interaction with neighbor-atoms in the original volume element:

$$\Delta U_a = \tfrac{1}{2} f\, \Delta U_a^0, \quad f<1. \tag{8}$$

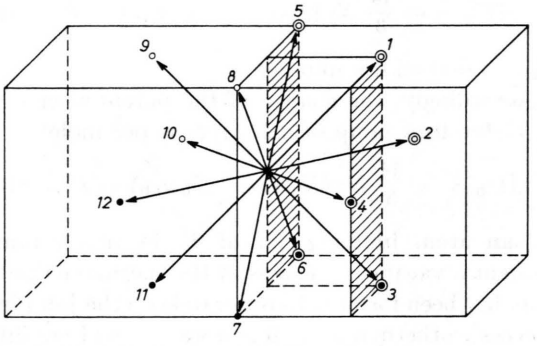

Fig. 1. Possible jumps of lattice atoms in a fcc-lattice [For explanation of factor f in Eq. (8)].

One can estimate f within the limits of the pair model adopted for this treatment. In case of a fcc-lattice ($z=12$) there are six possible atom jumps from a volume element V located at the surface leading to a position outside the crystal. In each jump six bonds are separated. For V being located in the bulk, in three, two and one of the six jumps considered above the atom remains in interaction with two, one and none of its old neighbors in V, respectively. Hence, on average, after the completion of the jumping process there are only (6−8/6) bonds broken in an fcc-lattice. In this picture, one sixth of this value may be taken to be a first approximation of the quantity f in Eq. (8):

$$f = 1/6\,(6-8/6) = 7/9 \quad \text{(fcc-lattice)}.$$

[15] N. F. MOTT, and R. W. GURNEY, Electronic Processes in Ionic Crystals, Oxford University Press, London 1948.

This is illustrated for two different jumping directions in Fig. 1. There, all twelve possible jump processes of a lattice atom in a fcc-lattice are represented by arrows. The volume element V is located such that its border plane is either a (100) step plane (marked by section lines in Fig. 1) or a (111)-step plane. In the first case, the atoms contained within V are marked by two small concentric circles, in the second example by full circles. One can see easily that the jumps # 7, 8 and 10 (# 2, 8 and 10) lead to positions outside V having two neighbors in V, the jumps # 9 and 11 (# 1 and 9) to sites still having one neighbor in V and only one jump, # 12 (# 5), leads to a position that has no neighbors in V. The numbers given in parentheses refer to the second case considered here.

The change of the potential energy in V for a jump of an A-atom now can be rewritten to be per mole in a fcc-lattice

$$\Delta U_a = -\frac{14}{3} N_L (N_a u_{aa} + N_b u_{ab}) - P' \qquad (9)$$

N_L = Loschmidt's number.

Accordingly, the change of the potential energy in V due to a jump of a B-atom is per mole

$$\Delta U_b = -\frac{14}{3} N_L (N_a u_{ab} + N_b u_{bb}) - P'. \qquad (10)$$

By an atom jumping out of V, in this volume element a vacancy in excess of the thermal equilibrium has been formed. In order to keep the jumping process isothermal and to restore thermal equilibrium of the vacancy concentration another atom from outside must enter V to annihilate the newly formed vacancy. Only then, the whole jumping process of an atom is considered to be complete in the sense that isothermal conditions are maintained. This notion will be used throughout the following treatment. For the vacancy to be reoccupied, an energy, ΔU_L, must be added to V amounting to $\Delta U_L = -\Delta U_a$ for an A-atom and to $\Delta U_L = -\Delta U_b$ for an B-atom. On the average, we have

$$\Delta U_L = -(p_a \Delta U_a + p_b \Delta U_b), \quad p_a + p_b = 1 \qquad (11)$$

where p_a and p_b are the probabilities for an A- or B-atom, respectively, to jump into the vacancy.

All jumping processes discussed so far proceeded isothermally at constant pressure. To find the enthalpy changes in V, ΔH, associated with an atom jump from the energy changes discussed above, volume changes, ΔV, must be considered occurring in a diffusion process of components with different atomic radii. For an estimate of the volume work involved, $p\Delta V$, one may tentatively assume a ΔV-value in the order of the atomic volume per g-atom which is generally less than 100 cm^3/g-atom. Using this figure one finds $p\Delta V$ to be approximately 2.4×10^{-3} kcal/mole at normal pressure which is at least three orders of magnitude smaller than the ΔU-values in Eqs. (7)—(11). Since the volume work turns out to be negligible in this case, all previous ΔU-values may be simply replaced by corresponding ΔH-values without introducing an appreciable error; $\Delta U \cong \Delta H$. Differences may only become significant at high pressures.

The process of forming and annihilating a vacancy in V is now complete. The sum of all enthalpy changes involved is the net enthalpy isothermally transported per atom jump and, thus, by definition, equals the corresponding enthalpy contribution to the intrinsic heat of transport. For an A-atom we find

$$Q^{**}_{aH} = \Delta H_a + \Delta H_L \qquad (12)$$

and for a B-atom

$$Q^{**}_{bH} = \Delta H_b + \Delta H_L \qquad (13)$$

or, with the aid of Eq. (11)

$$Q^{**}_{aH} = p_b (\Delta H_a - \Delta H_b), \qquad (14)$$

$$Q^{**}_{bH} = -p_a (\Delta H_a - \Delta H_b). \qquad (15)$$

The probabilities p_a and p_b are functions of concentrations and jump frequencies of the A- and B-atoms, respectively, surrounding the vacancy. In dilute alloys where association effects between the substitutionally solved impurities and vacancies frequently play an important role[16], five types of vacancy jumps with the frequencies w_i ($i = 0, 1, 2, 3, 4$) are to be distinguished. One of them proceeds via exchange with an impurity atom B (w_2) and four of them (w_0, w_1, w_3, w_4) via exchange with a solvent lattice atom A, from an unassociated position to another unassociated position (w_0), from an associated position to another associated position (w_1), from an associated position to an unassociated position (w_3) and from an unassociated position to an associated position (w_4).

[16] See e. g., Y. QUERE, J. Phys. Soc. Japan **18**, (Suppl. III) 91 [1963].

HOWARD and MANNING[17] assign different heats of transport, q_i^* ($i = 0, \ldots, 4$) to each of those five jumps and find the following relations between the macroscopic heats of transport of solvent and solute and the q_i^* in the lattice reference system

$$Q_b^{**} = \frac{2w_1(q_2^* - 2q_1^*) + w_3(7q_2^* + 3q_3^* + 3q_4^*)}{2w_1 + 7w_3} - \left[(h - E_B)\left(\frac{-2w_1 + 13w_3}{2w_1 + 7w_3} + n\right) + \frac{3w_3}{2w_1 + 7w_3} E_B\right] \quad (16)$$

$$Q_a^{**} = q_0^* - h \quad (17)$$

and relative to fixed parts of the system (endpoint reference system)

$$Q_b^{**\prime} = Q_b^{**} - \frac{D_a}{D_b}(q_0^* - h). \quad (18)$$

Here, n is the fraction of the impurities associated with vacancies and E_B is the binding energy of an associated impurity-vacancy-pair. The diffusion coefficients of the impurities, D_b, and of the host lattice, D_a, introduced to Eq. (16) are related to the corresponding tracer-diffusion coefficients, D_b^* and D_a^*, in sufficient approximation by[18]

$$\frac{D_a}{D_b} = \frac{11}{9}\frac{D_a^*}{D_b^*} - \frac{3 - 2w_1/w_3}{\frac{7}{2} + w_1/w_3}. \quad (19)$$

The last two terms in Eq. (16) comprise the contributions of the vacancies to the heat of transport of the impurities, which is, in general, not equal to the vacancy enthalpy of formation, h, in the pure solvent metal as in Eq. (17)[19]. To calculate the intrinsic heats of transport in terms of the Eqs. (12) and (13), it is, however, more convenient to include the proper vacancy formation enthalpy in the heat of transport of each type of vacancy jump separately; i.e., h for unassociated vacancies and $(h - E_B)$ for associated vacancies per mole. For jumps of atoms starting from associated positions (type 1, 2 and 4), the binding energy, E_B, must be included but not for those starting from unassociated positions (type 0 and 3):

$$q_i^{**} = q_i^* - h, \quad i = 0,3$$

and

$$q_i^{**} = q_i^* - (h - E_B), \quad i = 1, 2, 4.$$

Introducing the q_i^{**} into Eqs. (16) and (17), the macroscopic heats of transport of A- and B-atoms in the lattice system become

$$Q_b^{**} = \frac{2w_1(q_2^{**} - 2q_1^{**}) + w_3(7q_2^{**} + 3q_3^{**} + 3q_4^{**})}{2w_1 + 7w_3} - n(h - E_B) \quad (20)$$

and

$$Q_a^{**} = q_0^{**}. \quad (21)$$

The enthalpy parts of the q_i^{**} can now be estimated in a manner quite analogous to that one employed in Eqs. (9) to (15) by establishing an enthalpy balance for a complete atomic jumping process of type i for a certain volume element V in the crystal

$$q_{iH}^{**} = \Delta h_i + \Delta h_{iL}. \quad (22)$$

Δh_i and Δh_{iL} are the enthalpy changes per mole in V occurring along with an atom of type i jumping across the border plane of V and another atom jumping into V to fill the vacancy, respectively. Employing this method in detail for all possible jumps ($i = 0, \ldots, 4$) and assuming the impurity concentration to be so low that impurity-vacancy pairs are surrounded only by solvent atoms leads to the following results for an fcc-lattice:

a) Jumps of A-atoms of type 0

Only atoms of the solvent lattice are involved in jumps of type 0. Thus, [see Eq. (9) and (11)]

$$\Delta h_{0L} = -\Delta h_0 = \frac{14}{3} N_L u_{aa} + p \quad (23)$$

(p = relaxation term) and

$$q_{0H}^{**} = \Delta h_0 + \Delta h_{0L} = 0. \quad (24)$$

b) Jumps of A-atoms of type 1

The A-atoms remain nearest neighbors of an impurity atom B. The vacancy formed by the jump is an associated position, hence*

$$\Delta h_1 = -\frac{14}{3} N_L\left(\frac{11}{12} u_{aa} + \frac{1}{12} u_{ab}\right) - p. \quad (25)$$

The associated vacancy has as nearest neighbors four A-atoms being also nearest neighbors of the B-atom (enthalpy change for a jump of one of these A-atoms into the vacancy: Δh_1), seven A-atoms that are not nearest neighbors of B (enthalpy change for a jump into the vacancy Δh_0) and a B-impurity (enthalpy change for a B-jump into the vacancy

[17] R. E. HOWARD, and J. R. MANNING, J. Chem. Phys. **36**, 910 [1962].

[18] R. E. HOWARD, and A. B. LIDIARD, Acta Met. **13**, 443 [1965].

[19] D. HEITKAMP, Phys. Stat. Sol. **24**, 341 [1967].

* Differences in the relaxation terms for associated and unassociated vacancies are neglegted.

Δh_2). We, therefore, obtain

$$\Delta h_{1\mathrm{L}} = -\frac{7w_3\Delta h_0 + 4w_1\Delta h_1 + w_2\Delta h_2}{7w_3 + 4w_1 + w_2} \tag{26}$$

where*

$$\Delta h_2 = -\frac{14}{3} N_{\mathrm{L}} u_{\mathrm{ab}} - p. \tag{27}$$

According to Eq. (22), $q_{1\mathrm{H}}^{**}$ becomes

$$q_{1\mathrm{H}}^{**} = \Delta h_1 + \Delta h_{1\mathrm{L}} = \frac{w_2}{7w_3 + 4w_1 + w_2}(\Delta h_0 - \Delta h_2) + \frac{7w_3 + w_2}{7w_3 + 4w_1 + w_2}(\Delta h_1 - \Delta h_0) \tag{28}$$

or

$$q_{1\mathrm{H}}^{**} = -\frac{14}{3} N_{\mathrm{L}} \frac{w_2 - \frac{1}{12}(7w_3 + w_2)}{7w_3 + 4w_1 + w_2}(u_{\mathrm{aa}} - u_{\mathrm{ab}}). \tag{29}$$

c) Jumps of B-impurities of type 2

With values of Δh_0, Δh_1, Δh_2 and $\Delta h_{1\mathrm{L}} = \Delta h_{2\mathrm{L}}$ known from Eqs. (23) to (27) we obtain in accordance with Eq. (22)

$$q_{2\mathrm{H}}^{**} = \Delta h_2 + \Delta h_{2\mathrm{L}} = -\frac{7w_3 + 4w_1}{7w_3 + 4w_1 + w_2}(\Delta h_0 - \Delta h_2) - \frac{4w_1}{7w_3 + 4w_1 + w_2}(\Delta h_1 - \Delta h_0) \tag{30}$$

or

$$q_{2\mathrm{H}}^{**} = \frac{14}{3} N_{\mathrm{L}} \frac{7w_3 + 4w_1 - \frac{w_1}{3}}{7w_3 + 4w_1 + w_2}(u_{\mathrm{aa}} - u_{\mathrm{ab}}). \tag{31}$$

d) Jumps of A-atoms of type 3

The corresponding vacancy jumps occur from an associated to an unassociated position. Thus, the A-atom prior to the jump and the vacancy formed after the jump are in an unassociated position surrounded only by matrix atoms as nearest neighbors and one B-atom as a next-nearest neighbor. As a result, on average the vacancy may be occupied by 17/7 A-atoms coming from an associated position and by 67/7 atoms coming from an unassociated position

$$\Delta h_{3\mathrm{L}} = -\frac{\frac{17}{7}w_4\Delta h_1 + \frac{67}{7}w_0\Delta h_0}{\frac{17}{7}w_4 + \frac{67}{7}w_0}, \quad \Delta h_3 = \Delta h_0 \tag{32}$$

and $q_{3\mathrm{H}}^{**}$ becomes

$$q_{3\mathrm{H}}^{**} = -\frac{17w_4}{17w_4 + 67w_0}(\Delta h_1 - \Delta h_0) = -\frac{7}{18} N_{\mathrm{L}} \frac{17w_4}{17w_4 + 67w_0}(u_{\mathrm{aa}} - u_{\mathrm{ab}}). \tag{33}$$

c) Jumps of A-atoms of type 4

Prior to the jump the A-atom is a neighbor of B as well as the vacancy formed after the jump. The expression, obtained for $q_{4\mathrm{H}}^{**}$ is, therefore, similar to that shown in Eq. (29)

$$q_{4\mathrm{H}}^{**} = q_{1\mathrm{H}}^{**}. \tag{34}$$

Inserting all values of the $q_{i\mathrm{H}}^{**}$ derived above into Eq. (20) one obtains the macroscopic heat of transport of the impurities due to intrinsic enthalpy changes

$$Q_{\mathrm{bH}}^{**} = \frac{14}{3} N_{\mathrm{L}} \left[\frac{2w_1(7w_3 + 4w_1 + 2w_2) + 7w_3(7w_3 + 4w_1 - \frac{3}{7}w_2)}{(2w_1 + 7w_3)(7w_3 + 4w_1 + w_2)} - \frac{4w_1(14w_3 + 2w_1 + w_2) - 3w_3(7w_3 + w_2)}{12(2w_1 + 7w_3)(7w_3 + 4w_1 + w_2)} - \frac{51w_3w_4}{(17w_4 + 67w_0)(2w_1 + 7w_3)}\right](u_{\mathrm{aa}} - u_{\mathrm{ab}}) - n(h - E_{\mathrm{B}}). \tag{35}$$

In this expression the last two fractions within the brackets amount to at maximum 4 percent of the first term and, generally, are of no significance. To determine the difference between the potential energies of an AB- and AA-pair, $u = u_{\mathrm{ab}} - u_{\mathrm{aa}}$, it is not necessary to know the absolute interatomic potentials but only the potential generated by the impurity at the site of a normal lattice atom in excess over the potential of the host lattice:

$$u = e\Phi.$$

The excess potential, Φ, can be obtained from a solution of the Poisson-equation[20–22] with the boundary conditions $\Phi = Ze/r$ for $r \to 0$ and $\Phi = 0$ for $r \to \infty$

$$\Phi = \frac{Ze}{r} \alpha \exp(-qr) \tag{36}$$

and, hence

$$u_{\mathrm{aa}} - u_{\mathrm{ab}} = -\frac{Ze^2}{a} \alpha \exp\{-qa\} \tag{37}$$

(a = atomic distance).

[20] N. F. Mott, Proc. Cambridge Phil. Soc. **32**, 281 [1936].
[21] L. C. R. Alfred, and N. H. March, Phys. Rev. **103**, 877 [1956].
[22] H. Fujiwara, J. Phys. Soc. Japan **10**, 339 [1955].

The difference $Ze=(Z_b-Z_a)e$ of the charges of the solvent, $Z_a e$, and the solute, $Z_b e$, generates a potential that is increasingly screened by the conduction electrons with growing distance r from the site of the impurity (α, q = screening constants).

With the aid of relation (37), Eq. (35) can now be rewritten in its final form

$$Q_{bH}^{**} = -\frac{14}{3} N_L g \frac{Z e^2 \alpha}{a} \exp\{-aq\} - n(h - E_B) \tag{38}$$

where

$$g = \frac{2\frac{w_1}{w_0}\left(7\frac{w_3}{w_0}+4\frac{w_1}{w_0}+2\frac{w_2}{w_0}\right)+7\frac{w_3}{w_0}\left(7\frac{w_3}{w_0}+4\frac{w_1}{w_0}-\frac{3w_2}{7w_0}\right)-\frac{w_1}{3w_0}\left(14\frac{w_3}{w_0}+2\frac{w_1}{w_0}+\frac{w_2}{w_1}\right)+\frac{w_3}{4w_0}\left(7\frac{w_3}{w_0}+\frac{w_2}{w_0}\right)}{\left(2\frac{w_1}{w_0}+7\frac{w_3}{w_0}\right)\left(7\frac{w_3}{w_0}+4\frac{w_1}{w_0}+\frac{w_2}{w_0}\right)} - \frac{51}{12}\frac{\frac{w_3}{w_0}\frac{w_4}{w_0}}{\left(17\frac{w_4}{w_0}+67\right)\left(2\frac{w_1}{w_0}+7\frac{w_3}{w_0}\right)}. \tag{39}$$

In this expression all quantities except n can be calculated. The screening constants α and q have been estimated by FUJIWARA[22] and ALFRED and MARCH[21] in copper and silver for Z values of -3 to $+4$. The potential Φ mentioned above and being the essential part of Eq. (38) has been successfully used by LAZARUS[23] and LE CLAIRE[24] in their theoretical treatment of isothermal impurity diffusion in metals. On this basis, Le Claire calculates the binding energy for Z-values of -3 to $+4$ as well as the differences, ΔH_i, between the activation enthalpy of motion of atoms of type 1, 2 and 3 and that of type 0

$$\Delta H_i = H_i - H_0, \quad i = 1,2,3. \tag{40}$$

With the aid of the ΔH_i the ratios of the jump frequencies in the factor g of Eq. (39) can be estimated

$$\frac{w_i}{w_0} = \exp\left\{-\frac{\Delta H_i}{RT}\right\}, \quad i = 1,3$$
$$\text{and} \quad \frac{w_2}{w_0} = \frac{\nu_2}{\nu_0}\exp\left\{-\frac{\Delta H_2}{RT}\right\} \tag{41}$$

assuming the vibration frequencies, ν_i, in a first approximation, to be equal for all A-atoms

$$\frac{\nu_i}{\nu_0} = 1, \quad i = 1,3. \tag{42}$$

The relative vibration frequency of the B-atoms, ν_2/ν_0, however, according to Le Claire, may be calculated from the pre-exponential factors, D_{0a} and D_{0b}, of lattice and impurity diffusion coefficients and from the corresponding correlation factors f_0 and f_2:

$$\frac{\nu_2}{\nu_0} = \frac{D_{0a}}{D_{0b}}\frac{f_0}{f_2}\exp\left\{\frac{C}{RT}\right\} \quad \text{with} \quad C = R\frac{\partial \ln f_2}{\partial (1/T)}. \tag{43}$$

So far, on the basis of Eq. (6) only enthalpy changes at absolute zero have been considered. This procedure, however, is a fair approximation and is justified from the fact that the vibration energies at relatively high temperatures ($h\nu/kT \ll 1$) become independent of lattice frequencies and proportional to the absolute temperature. As a result, in isothermal jump processes of lattice atoms the contribution of vibrational energy to the enthalpy is negligibly small.

The entropy part of the intrinsic heat of transport

Both mixing entropy and vibration entropy contribute to the heat of transport of a binary alloy. WEVER[9] has pointed out that mixing entropies need to be considered for a quantitative interpretation of the heat of transport of both components in concentrated alloys. However, the entropy of mixing being concentration dependent may be neglected in dilute solutions ($N_b \ll 1$). To estimate the entropy of vibrations, S_s, we proceed on the basis of the Einstein approximation treating all lattice atoms as independent oscillators with one discrete frequency, ν_E, per degree of freedom. In this approach, S_s for a pure metal can be taken to be per mole

[23] D. LAZARUS, in Solid State Physics **10**, 71 [1960], and Phys. Rev. **93**, 973 [1954].

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$$S_s = S_0 + 3kN_L \left\{ \frac{h\nu_E}{kT[\exp\{h\nu_E/kT\} - 1]} - \ln[1 - \exp\{-h\nu_E/kT\}] \right\} \quad (44)$$

(S_0 = entropy at absolute zero) and for very high temperatures ($h\nu_E/kT \ll 1$)

$$S_s = S_0 + 3kN_L[1 - \ln(h\nu_E/kT)]. \quad (45)$$

The same result is obtained for ν_E being defined as the geometrical mean of a frequency spectrum characteristic of the lattice atoms. Since the atomic oscillators are considered independent one finds the entropy of vibration of an alloy simply by summing up the contributions of both components.

To find the vibrational entropies associated with jumps of both A- and B-atoms and their contributions to the heats of transport, Q_{sa}^{**} and Q_{sb}^{**}, we follow a procedure which is quite analogous to that employed above to calculate the enthalpy contributions. This includes evaluating the entropy changes involved in a complete jumping process referring to a certain volume element V in the crystal. In accordance with Eqs. (8), (14) and (15) we obtain

$$Q_{sa}^{**} = -p_b T(\Delta S_{sa}^0 - \Delta S_{sb}^0)\frac{f}{2} = -p_b T(\Delta S_{sa} - \Delta S_{sb}), \quad (46)$$

$$Q_{sb}^{**} = p_a T(\Delta S_{sa}^0 - \Delta S_{sb}^0)\frac{f}{2} = p_a T(\Delta S_{sa} - \Delta S_{sb}). \quad (47)$$

Here, ΔS_{sa}^0 and ΔS_{sb}^0 are the changes of vibrational entropy per mole upon removing an A- and B-atom, respectively, to infinite and ΔS_{sa} and ΔS_{sb} are the corresponding values for the jump of A- and B-atoms, respectively, to a neighboring position outside V:

$$\Delta S_s = \tfrac{1}{2} f \Delta S_s. \quad (48)$$

As already pointed out, in dilute alloys different types of atomic jumps are distinguished. To determine the changes of vibrational entropy associated with these jumps, Δs_i ($i = 0, \ldots, 4$), the respective mean frequencies of A- and B-atoms, ν_0 and ν_2, are defined such that they are, for simplicity, independent of whether the position of an matrix atom is associated with an impurity atom. Using Eqs. (45) and (48) we then have per mole

$$\Delta s_0 = \Delta s_1 = \Delta s_3 = \Delta s_4 = \tfrac{3}{2} f k N_L[1 - \ln(h\nu_0/kT)], \quad (49)$$

$$\Delta s_2 = \tfrac{3}{2} f k N_L[1 - \ln(h\nu_2/kT)]. \quad (50)$$

For the jumps of type 0 and 3, the entropy change in filling up the vacancy is

$$\Delta s_{0L} = -\Delta s_0 \quad (51)$$

and for the jumps of type 1, 2 and 4,

$$\Delta s_{0L} = \frac{(7w_3 + 4w_1)\Delta s_0 + w_2 \Delta s_2}{7w_3 + 4w_1 + w_2}. \quad (52)$$

Analogous to Eq. (22), the heat of transport due to entropy changes in a complete jumping process of type i now becomes

$$q_{is}^{**} = -T(\Delta s_i + \Delta s_{iL}) \quad (53)$$

or, in detail

$$q_{0s}^{**} = q_{3s}^{**} = 0,$$
$$q_{1s}^{**} = q_{4s}^{**} = -\frac{w_2}{7w_3 + 4w_1 + w_2} T(\Delta s_0 - \Delta s_2), \quad (54)$$
$$q_{2s}^{**} = \frac{7w_3 + 4w_1}{7w_3 + 4w_1 + w_2} T(\Delta s_0 - \Delta s_2),$$

where, according to Eqs. (49) and (50) and with $f = 7/9$ in a fcc-lattice, $\Delta s_0 - \Delta s_2$ is given by

$$\Delta s_0 - \Delta s_2 = \frac{7}{6} k N_L \ln \frac{\nu_2}{\nu_0}.$$

Introducing the above q_{is}^{**}-values into Eq. (20) gives the total macroscopic entropy of the B-impurities per mole

$$Q_{bs}^{**} = \frac{7}{6} g' RT \ln \frac{\nu_2}{\nu_0}. \quad (55)$$

The factor g' is given by the first fraction within the brackets of Eq. (35), (R = gas constant).

Further contributions to the heat of transport

The intrinsic part of the heat of transport so far discussed was based on the consideration of the Gibb's free energy of the equilibrium states prior to and after a complete jump of a lattice atom under isothermal conditions. The interaction between the jumping particle in the intermediate states and its surrounding were not taken into account but, as already mentioned, this also generally contributes to the heat of transport. These effects stem from several different causes, such as the influence of the thermoelectric field on the moving ion with the effective charge Z and the ion's interaction with heat carriers, electrons and phonons.

Assuming that the phonons can transfer their pseudo-momentum directly to the jumping atom,

FIKS[14] has first quantitatively estimated the contribution of phonon-scattering to the heat of transport of liquids. The force acting on the impurity atom that results from the momentum transfer is proportional to the scattering cross-section of the impurity atoms and the thermal conductivity of the lattice. SCHOTTKY[11] obtained a relatively large cross section for a vacancy in a linear chain which may appreciably affect the local temperature gradient[1]. However, since it is very difficult to extend this one dimensional result to three dimensions where the vacancy is not likely to perturb the lattice as strongly, no exact conclusions as to the amount of these effects can be drawn.

As shown by Fiks, Gerl and Huntington, electron scattering, may also appreciably influence the heat of transport in pure metals and dilute alloys as well. For the discussion of details, we refer to these authors[1,2,13,14]. The numerical results obtained by GERL[2] for Q^{**}_{be} are discussed in the next section.

3. Discussion

After having determined enthalpy- and entropy-contributions in the preceding sections the intrinsic heat of transport of impurities in fcc metals is completely deduced from atomic quantities. The calculation model is based on an isothermal jumping process of a lattice or impurity atom which is compatible with the thermodynamic definition (3) of the heat of transport. It is further based on the assumption that the potential energy of an alloy may be expressed in terms of pair-interaction energies of nearest neighbors. Although the energy transport model has been exclusively used for fcc lattices, in principle, it also applies to other alloy structures in all concentration ranges. Calculations and measurements in concentrated fcc alloys are being made to study the effect of concentration on the heat of transport of solutes in noble metals.

To find the total heat of transport, the contribution from ion-electron interaction must be added as discussed previously

$$Q^{**}_{b} = Q^{**}_{bH} + Q^{**}_{bS} + Q^{**}_{be}.$$

The the main objective of this section is to compare these theoretical values with experimental data and discuss the results. To do this, the well known fcc lattices of the noble metals are most convenient as solvents. In copper, silver and gold the heats of transport of several impurities have been measured. In Table 1 the available data are compiled.

Table 1. Experimental and theoretical heats of transport of impurities in copper, silver and gold.

Solvent	Impurity	Excess Valence Z	$\overline{T}^{c}$ [°K]	Calculated Values[a]					Observed Values[a]	
				Q^{**}_{bH}	Q^{**}_{bS}	Q^{**}_{be}	$Q^{**\prime}_{b} - Q^{**}_{bf}$	Q^{**}_{b}	$Q^{**\prime}_{b}$	Ref.
Cu	Sb	4	1271,5	− 6,84	− 5,84	− 3,54	− 3,72	− 16,22	− 16, 4 ± 1,4	25
	Sn	3	1276	− 5,69	− 4,25	− 3,83	− 3,74	− 13,77	− 13, 7 ± 1,0	25
	Ge	3	1260						− 8 ± 3	28
	In	2	1295	− 5,82	− 5,02	− 2,09	− 1,96	− 12,93	− 12, 8 ± 1,0	25
	Ag	0	1271,5	~ 0	− 0,73	− 0,23	− 0,87	− 0,96	− 1, 6 ± 1,1	25
	Ag	0	1284						− 4, 8 ± 3	28
	Au	0	1284	~ 0	− 2,0	− 0,11	− 2,8	− 2,1	− 4, 8 ± 3	28
	Co	(− 0,5)	1283,2	+ 3,34	+ 3,63	− 18,98[b]	− 19,57	− 12,0	− 12, 6 ± 2,8	25
	Ni	(− 0,75)	1281,6	+ 5,66	+ 4,32	− 18,98	− 22,08	− 9,0	− 12, 1 ± 4,4	25
Ag	Sb	4	1142,8	− 5,54	− 5,34	− 11,52	− 18,12	− 22,4	− 29 ± 3	30, 31
	Sn	3	1089	− 4,44	− 3,72	− 9,22	− 6	− 17,38	− 14 ± 4	32
	In	2	1166,5	− 3,41	− 2,0	− 4,61	− 3,49	− 10,02	− 8, 9 ± 2	32
	Au	0	1178	~ 0	− 0,87	− 0,46	+ 0,87	− 1,33	0 ± 3	28
	Ru	(− 3)	1180,2						> 0	30, 31
Au	Sb	4	1066,2						− 69, 1 ± 5,3	33
	Tl	2	1200						− 8, 4 ± 3	28
	Ag	0	1261						− 4, 2 ± 3	28

[a] All energies in kcal/mole; [b] Taken from Ni; [c] Mean value of temperature interval.

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Table 2. Important quantities for the determination of the intrinsic heat of transport in silver [All energies in kcal/mole; $D_{0a} = 0{,}40$ cm²/sec and $Q_a = 44{,}09$ kcal/mol (Ref. [34])].

Impurity	Z	D_{0b}	Q_b	Ref.	C for $RT = 2,3$	ΔH_1	ΔH_2	ΔH_3	f_2	$\frac{v_2}{v_0}$	$\frac{w_1}{w_0}$	$\frac{w_2}{w_0}$	$\frac{w_3}{w_0}$	g	α
Sb	4	0,17	38,32	[35]	− 5,79	0,82	−10,15	0,23	0,456	0,056	0,70	4,61	0,90	0,67	0,52
Sn	3	0,25	39,3	[36]	− 4,93	0,67	− 8,35	0,21	0,434	0,114	0,74	5,11	0,91	0,655	0,57
In	2	0,41	40,63	[36]	− 3,72	0,50	− 6,25	0,17	0,436	0,347	0,80	5,25	0,93	0,67	0,64
Au	0	0,85	48,3	[37]	~ 0	~0	~ 0	~0		0,74	1	0,74	1	0,90	
Ru	(− 3)	180	65,8	[38]	~ 0		38,8		1	335					2,65

The theoretical values of Q_{bH}^{**} and Q_{bS}^{**} in copper and silver calculated by use of Eqs. (38) and (55) as well as Q_{be}^{**} as taken from GERL's theory[2] are also included in Table 1. For gold as solvent a calculation was not possible for lack of suitable data. All important quantities entering the calculation of Q_{bH}^{**} and Q_{bS}^{**} in the silver system are listed in Table 2. Similar quantities for copper as solvent and the details of the calculation procedure are published elsewhere[25]. But it should be noted here that the ratios w_i/w_0 entering the calculation of the factors g and g' and the correlation factor f_2 have been determined by use of Eq. (41). To keep the model free of ambiguity, ΔH_i-values were used that were calculated, according to Le Claire's theory, on the basis of the same potential Φ [see Eq. (36)] that also served to determine the enthalpy part of the intrinsic heat of transport. For large effective valences, Z, however, values of w_i/w_0 obtained deviate from those determined empirically from LIDIARD's relation[26]

$$f_2 = 1 - \frac{4 f_0}{b + 18} \frac{D_b}{D_a} = \frac{w_1 + 7/2\, w_3}{w_1 + w_2 + 7/2\, w_3} \qquad (56)$$

(b = characteristic constant to describe the concentration dependence of D_b).

In order to be able to compare the theoretical heats of transport that have been evaluated with respect to the lattice reference system with the experimental data measured with respect to the endpoints of the specimens, the heats of transport need to be transformed from one reference system to the other using Eqs. (17) and (18). However, according to the equations of transformation, experimental and theoretical heats of transport may be compared directly to each other if the heat of transport, Q_a^{**}, of the solvent lattice is negligibly small or the impurity atoms diffuse much faster than the matrix atom. Data from literature on the heat of transport of copper are somewhat ambiguous. Positive (4 kcal/mole[27]) as well as negative values (− 7.2 kcal/mole[28]) are reported. Recently ADDA et al.[29] failed to measure any marker movement in silver and copper in a temperature gradient and conclude Q_a^{**} to be zero for both metals. Accordingly, it seems justified to put

$$Q_b^{**} \cong Q_b^{**\prime} \qquad (57)$$

in these cases.

Comparison of experimental and theoretical heats of transport of several impurities in the silver- and copper system made on the basis of Eq. (57) shows considerable agreement in almost all instances. This result holds true not only for the total heats of transport. Also, the difference between the experimental value and the theoretical intrinsic heat of transport, $Q_b^{**\prime} - Q_{bi}^{**}$, in most instances just equals the anticipated contribution of electron scattering, Q_{be}^{**}. In the Ag-Co system such an agreement is only reached if the unknown Q_{be}^{**} value for cobalt in silver is taken to be the same as for nickel in silver[25].

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In the silver-antimony system we notice a small but clear difference between $Q_b^{**\prime}$ (obs.) and Q_b^{**} (theor.) beyond the stated limits of experimental error. This may have different causes. As already mentioned, there is an uncertainty as to how to determine the jump frequencies w_i which, in turn, may considerably affect the entropy of transport and the enthalpy of transport as well via the correlation quantities f_2 and C and the factors g and g'. According to Le Claire's theory[24] there is only a weak binding between the impurities considered here and the vacancies (i.e., w_1 and w_3 do not differ very much). Assuming a stronger vacancy binding for antimony impurities leads to a decrease of the w_3/w_1 ratio and an increase of the g-factor. This, in turn, results in an increased theoretical value for the heat of transport of Sb in Ag thereby approaching the measured value.

Recently, HEHENKAMP[39] found the heat of transport of antimony in copper to be -28 kcal/mole. The absolute value of this quantity is markedly larger than previously reported[25]. If this value is confirmed, arguments similar to those outlined for the silver-antimony system may apply to explain this finding.

When assessing the good agreement for almost all impurities considered thus far, one must bear in mind the simplifying assumptions that have been made in deriving the final theoretical expressions and also the approximations involved in numerically evaluating the various atomic quantities that enter the theory. This is true for both the intrinsic and the electronic part of the heats of transport of the impurities.

At this point it may be noted that the model adopted for the intrinsic part assumes that size differences between solute and solvent may be ignored for impurity diffusion in copper and silver. However, a more refined treatment should include strain effects. Particulary for impurities with no excess valence, the elastic term may be relatively significant.

The numerical evaluation of Gerl's equations to find Q_{be}^{**} — which has been extensively discussed elsewhere[25] for copper and was done accordingly for silver — requires the knowledge of some electrical properties of dilute alloys at high temperatures such as the electric resistance, the electric thermopower and their concentration dependencies. Most of these physical properties have been measured only at room temperature and applying these values to high temperature conditions may imply possible errors.

As far as the numerical evaluation of the intrinsic heat of transport of the impurities is concerned, most of the atomic data required are taken from isothermal diffusion measurements. Thus far, there are no reliable data for the impurity diffusion of In and Sn in Cu. The diffusion coefficients of these systems were estimated from theory. Therefore, further measurements need to be done, to supplement and ensure the results obtained in this work.

However, apart from some uncertainties regarding numerical calculations in some instances, the remarkable agreement reached so far between experimental and theoretical values of the heats of transport of various impurities in copper and silver has some interesting consequences. First of all, it is an indication that the assumptions made to estimate the intrinsic heat of transport in dilute alloys as well as those of Gerl's theory are not unreasonable. The effective valence Z turns out to be the dominating quantity of thermotransport in noble metals from theoretical and experimental evidence. This confirms experimental results obtained previously be JAFFE and SHEWMON[28]. Further, it appears in accord with WEVER[9] that the heat of transport if calculated from an isothermal process should be considered associated with free energies rather than total energies. In all instances considered in this work enthalpy and entropy part of the intrinsic heat of transport are comparably large. Finally, some conclusions may be drawn concerning the mechanism of thermotransport. The calculation models being based on an impurity transport via vacancies, the vacancy mechanism is likely to be the dominating mechanism of the investigated impurities in copper and silver.

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