

Thermal Diffusion of Isotopes in Pure Liquids

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A theoretical treatment is given of the recently discovered thermotransport effect in pure liquid metals. The isotope effect is related to the diffusive mass flow by a proportionality factor familiar from electrotransport. The mass flow is given primarily by the temperature dependence of the mean size or amount of density fluctuations in the liquid. Very little activation energy is required for diffusive motion, which takes place by cooperative position adjustments of neighbor atoms. The mean displacement length of the diffusing cluster is by an order of magnitude smaller than the effective cluster diameter. The liquid model suggested is coherent with models based on evidence from other experimental methods.

It was discovered two years ago¹, that a considerable de-mixing of isotopes takes place in pure liquid lithium metal, when a temperature gradient is imposed. The same effect was since found in other molten metals². In all cases the light isotope was enriched at the hot end. The maximal steady-state separation factor (i. e. the abundance ratio of the isotopes at the cold end of the cell, divided by the abundance ratio at the hot end) was for lithium (masses 6 and 7) about 1.04, corresponding to the temperature interval 350°–525 °C. In gallium (masses 69 and 71) the temperature interval 50° to 500 °C gave a separation factor of about 1.03. The same order of magnitude was obtained in the other liquid metals investigated.

As thermal diffusion (SÔRET-effect) of isotopes represents the purest possible example of thermotransport, it should be possible to draw significant theoretical conclusions.

On account of numerous evidence of close-range order in liquids and on the reasonable assumption that at any moment the percentage of particles engaged in diffusive position adjustment relative to its neighbors is small, the concept can be used of a pseudo-lattice, consisting of the bulk of momentarily ordered atoms. This, rather than the container, will serve as a reference system for atom transport motion in a liquid. With such a model, a certain analogy with a solid-state approach appears justified.

To begin with, as in solid-state diffusion³ it can be assumed that, in order to make a displacement, a particle needs an energy E_m ("activation energy for motion") to overcome a potential barrier. If the diffusion takes place by defects, e. g. vacancies, an "activation" energy E_v for defect formation is also required. Vacancies in liquids have a different meaning from those in solids, but the melt does have a great concentration of voids of various sizes^{4,5}, and generally the nearby presence of a density fluctuation will be conducive to a diffusive step. Only if the main transport mechanism is some kind of a rotation, the formation energy will be zero. The notion of activation energies in liquids has been under discussion^{6–8}. Although the temperature behavior of diffusion coefficients has shown certain deviations from the ARRHENIUS type relationship, within not too wide temperature intervals straight lines are obtained. In the present treatment, a BOLTZMANN factor dependence of displacement probabilities will be used (at worst a useful approximation). It will not be assumed, however, that diffusion necessarily takes place by single atoms making jumps of a definite length. To allow for the possibility of cooperative motion, suggested by several authors^{6,8,9}, the diffusing particles will be thought of as clusters of several atoms, and the displacement lengths as ranging from zero to several interatomic distances. It is, in fact, the purpose of

¹ A. OTT and A. LUNDÉN, Z. Naturforsch. **19 a**, 822 [1964].

² A. LODDING and A. OTT, Z. Naturforsch. **21 a**, 1344 [1966].

³ See e. g., P. G. SHEWMON, Diffusion in Solids, McGraw-Hill, New York 1963.

⁴ K. FURUKAWA, Nature **184**, 1209 [1959].

⁵ K. FURUKAWA, Sci. Rep. Res. Inst. Tohoku Univ., Ser. A, **12**, 368 [1960].

⁶ R. A. SWALIN, Acta Met. **7**, 336 [1959].

⁷ H. A. WALLS and W. R. UPTHEGROVE, Acta Met. **12**, 461 [1964].

⁸ M. H. COHEN and D. TURNBULL, J. Chem. Phys. **31**, 1164 [1959].

⁹ A. OTT and A. LODDING, Z. Naturforsch. **20 a**, 1578 [1965].



this treatment to show that experiments indicate that the mean displacement length is considerably less than the mean distance between nearest neighbor particle centers.

a) Isothermal Diffusion

Let the binary liquid isotope mixture consist of components 1 and 2. With the pseudo-lattice model in mind, denoting by \bar{l} the positive root mean square displacement, one can derive the diffusion coefficient D_i of the component i ($i=1$ or 2) by taking the difference of the forward and backward fluxes between two planes a distance \bar{l} apart (cf. ref. ³):

$$j_i^+ = -(n_i) \gamma v_i \bar{l} \exp[-(E_m + E_v)/RT], \quad (1a)$$

$$j_i^- = -(n_i + \bar{l} \nabla n_i) \gamma v_i \bar{l} \exp[-(E_m + E_v)/RT] \quad (1b)$$

Here γ is a term containing i. a. a geometrical constant and an entropy term; v_i is a (mass dependent) frequency term. The energy E_m denotes, as discussed above, the "activation" energy necessary for one atom to overcome a barrier, whereas E_v decides the likelihood of a suitable void (or other defect necessary for motion) being in a nearby position. Both E_m and E_v are counted per mole of atomic species. If motion takes place by clusters, E_m thus denotes the necessary energy at the particle site, but E_v represents an energy pertaining to a configuration at the "outskirt" of the cluster. With this point in mind, one can nevertheless see that under isothermal conditions the Eqs. (1a) and (1b) are valid quite independent of whether single atoms or clusters are the diffusing species.

The flux difference is

$$j_i = j_i^+ - j_i^- = -(\nabla n_i) \gamma v_i \bar{l} \exp[-(E_m + E_v)/RT] \quad (2)$$

and the diffusion coefficient follows from comparison with FICK's 1st law, such that

$$D_i = f \gamma v_i \bar{l}^2 \exp[-(E_m + E_v)/RT], \quad (3)$$

where also the BARDEEN-HERRING correlation factor f has been taken into account. It can be shown⁹ that

the experimental inter-diffusion coefficient of isotopes in a binary liquid mixture is given by

$$D = c_1 D_2 + c_2 D_1, \quad (4)$$

where $c_{1,2}$ are the relative particle concentrations.

From the measurements of the temperature dependence of D , the self-diffusion activation energy $E_m + E_v$ can evidently be obtained.

The dependence of D_i on isotope mass M_i may be estimated by comparison with experimental isotope mass dependence of ionic mobilities u_i in molten salts^{10,11}, via the equation

$$D_1/D_2 \cong u_1/u_2 = (M_1/M_2)^a, \quad (5a)$$

$$\text{or} \quad \partial \ln D_i / \partial \ln M_i \cong a. \quad (5b)$$

It has been found¹⁰ that the isotope factor a (which would be $-1/2$ if single atoms could be considered as jumping from one rigid cage to another) is in liquid salts satisfactorily represented by $a \cong -0.1$. The qualitative justification of using this assessment also to liquid metals has been shown when explaining the phenomenon of isotope electromigration in metals ("HAEFFNER-effect")^{12,13}.

b) Thermal Diffusion

Neglecting the temperature dependence of density and of v_i , one can express the velocity (relative to the pseudo-lattice) of an atom of isotope i (or of a cluster containing it), in a temperature gradient, as the difference of the forward and the backward velocity, analogously with Eqs. (1) (using $j_i = n_i v_i$), such that

$$v_i^+ = \gamma v_i \bar{l} \exp[-E_m/RT] \cdot \exp[-E_v/RT(1 + \varphi \bar{l} \cdot \nabla \ln T)], \quad (6a)$$

$$v_i^- = \gamma v_i \bar{l} \exp[-E_m/RT(1 + \varphi \bar{l} \cdot \nabla \ln T)] \cdot \exp[-E_v/RT]. \quad (6b)$$

Hence, using also Eq. (1) for $i=1, 2$ and assuming the same transport mechanism for self-diffusion and thermal diffusion,

$$v_1 - v_2 = -\frac{\varphi}{f} \cdot (D_1 - D_2) \cdot \nabla \ln T \frac{E_m - E_v}{RT}. \quad (7)$$

The energy difference $E_m - E_v$ is usually called

¹⁰ A. KLEMM, J. Chim. Phys. **60**, 1-2, 237 [1963]; also new results quoted in personal communication.

¹¹ A. KLEMM, E. LINDHOLM, and A. LUNDÉN, Z. Naturforsch. **7a**, 560 [1952].

¹² A. LODDING, in Encyclopedia of Electrochemistry, Reinhold, New York 1964, p. 491; also J. Phys. Chem. Solids, in press.

¹³ A. KLEMM, Z. Naturforsch. **9a**, 1031 [1954].

"heat of transport"¹⁴. The factor φ , important in the present reasoning, gives the distance $\varphi \bar{l}$ between the center of the cluster and the center of the particular void which makes cluster displacement by a distance \bar{l} possible.

As long as $\Delta M = M_1 - M_2 \ll M$, one can put

$$(v_1 - v_2)/(M_1 - M_2) \cong \partial v / \partial M.$$

From Eq. (5 a) it is obvious that $\partial \ln v = \partial \ln D$, and, using also Eq. (5 b)

$$v_1 - v_2 = - \frac{a D}{f} \frac{\Delta M}{M} \frac{\varphi(E_m - E_v)}{R T} \nabla \ln T. \quad (8)$$

c) Interpretation of Experiments

The entity obtained in thermal diffusion measurements is the steady-state separation factor

$$Q_{\max} = \frac{(c_2/c_1)_C}{(c_2/c_1)_H}, \quad (9)$$

where the suffixes C and H refer to the "cold end", respectively the "hot end" of the cell.

In the steady state,

$$v_1 c_1 = D_{\text{eff}} (\partial c_1 / \partial x) = -v_2 c_2, \quad (10)$$

where x is the length coordinate of a cylindrical capillary cell and D_{eff} is the effective self-diffusion coefficient, equal to $(D + D')$, D' denoting the convective term. Eqs. (9) and (10) lead to

$$v_2 - v_1 = D_{\text{eff}} (\partial \ln Q / \partial x). \quad (11)$$

Combining this with Eq. (8), and integrating from T_H , $Q = 1$, to T_C , Q_{\max} , one obtains

$$Q_{\max} - 1 = - \frac{\Delta M a D}{M f D_{\text{eff}}} R^{-1} (T_C^{-1} - T_H^{-1}) \varphi(E_m - E_v). \quad (12)$$

In a liquid the defects are "blurred out", so that the BARDEEN-HERRING correlation factor f is probably very near to unity (as a lowest limit one can use the solid-state approximation³ $f = 1 - 2/Z$, where Z is the coordination number, about 10 in liquids, making $f = 0.8$). It can also be presumed that D' is small, as special precautions were taken² to limit convection. Assuming therefore $f \cong 1$, $D/D_{\text{eff}} \cong 1$ and, as motivated above, $a \cong -0.1$, one can obtain the "heat of transport" from Eq. (12), expressed as

$$\varphi(E_m - E_v) = -20(M/\Delta M) \frac{Q_{\max} - 1}{T_C^{-1} - T_H^{-1}}^{-1}. \quad (13)$$

When the experimental results for lithium and gallium are substituted into RHS of Eq. (13), $\varphi(E_m - E_v)$ becomes -13.5 kcal/mole for Li and -11.5 kcal/mole for Ga. This is to be compared with the self-diffusion activation energies $(E_m + E_v)$, 2.8 kcal/mole⁹ for Li and 1.1 kcal/mole¹⁵ for Ga. The negative values of the "heat of transport" indicate that E_v is considerably greater than E_m ; if it is assumed, for simplicity and in accordance with a very relaxed model, that $E_m \cong 0$, one finds $\varphi_{\text{Li}} = 4.8$ and $\varphi_{\text{Ga}} = 10.5$. If $E_m \neq 0$, these values naturally become even greater. The mean displacement length is thus considerably smaller than the distance between the centre of the diffusing species and that of the void. The latter can consequently be thought of as situated at the "outskirt" of the cluster, and the mean displacement of the cluster turns out to be in Li about 10.4%, in Ga about 4.8% of its "diameter".

Thus as the result of this treatment of thermal diffusion data of pure liquid metals, a transport mechanism is suggested, where particles ("clusters") composed of several atoms move into relatively small voids, without any or with a very small activation energy of motion.

d) Free Volume and Cluster Size

According to a model based on X-ray evidence⁴, a simple liquid (at its m.p.) can be considered as a quasi-b.c.c. array of atoms, with a little less than 10% of the volume consisting of statistically dispersed voids, or "free volume". Other authors⁸ have also stressed the importance of free volume as the typical feature of fluidity.

One can hence imagine the liquid as a mixture of close-packed clusters, loosely bound single atoms and multishaped voids. Normally the voids are not localized at lattice-places. However, a statistical density fluctuation, squeezing an amount of atoms into a close-packed cluster, may simultaneously create the possibility for the cluster to move, by localizing the corresponding free volume. If a mean size void is created by the close-packing of n atoms, its volume will be

$$n V_t / N = A \delta, \quad (14)$$

¹⁴ cf. K. WIRTZ, Z. Naturforschg. 3 a, 672 [1948].

¹⁵ J. PETIT and N. H. NACHTRIEB, J. Chem. Phys. 24, 1027 [1956].

where V_f is the molar free volume, N Avogadro's number, A the void cross-section, δ its depth. The cluster with the volume

$$n(V_m - V_f)/N = A\varphi\bar{l} \quad (15)$$

(where V_m is the mole volume) will be able to move freely a distance $\bar{l} \cong \delta$ into the void, so that

$$\varphi \cong (V_m - V_f)/V_f. \quad (16)$$

This is in qualitative agreement with free volume data from X-ray evidence quoted above, and also with "activation volume" values as obtained¹⁶ by diffusion studies of liquids under pressure.

It is reasonable⁸ to assume, that the opening up of an atomic size void will enable a neighbor atom to drift into it. The amount of atoms which must cooperate to liberate such a suitable void volume is then

$$n = N \cdot \pi d^3 / 6 V_f = (V_m - V_f) / V_f, \quad (17)$$

or $n \cong \varphi$.

Admittedly such an estimate assumes the cluster to be composed of cooperating atoms moving through distances ranging from $+d$ down to comparable ne-

gative values. It has not, however, been postulated in the preceding treatment, that \bar{l} is necessarily the displacement of *all* the atoms of the cluster; \bar{l} can equally well be conceived as a mean value, and the cluster as a kind of moving micro-whirl.

Assuming accordingly about 10 atoms to cooperate along the diffusion path, one finds that $\varphi\bar{l}$ is between 2.2 and 3 atomic diameters, depending on whether the cluster is spheric or prolate. Thermal diffusion experiments then indicate that the mean diffusive displacement is between some 10% and 30% of an atomic diameter.

It has been noted above, that the present results are compatible with evidence obtained by other experimental means^{4, 10, 16}. It should be mentioned that the existence of clusters is also suggested by a model based on neutron scattering data¹⁷. According to this model, the cluster size should decrease slowly with rising temperature. This can be seen to agree with Eq. (17) above; n goes down as V_f increases with thermal expansion.

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¹⁶ N. H. NACHTRIEB, in *Liquid Metals and Solidification*, Amer. Soc. Metals 1958, p. 49.

¹⁷ P. A. EGELSTAFF, *Advan. Phys.* 11, 203 [1962].