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A HEAVY ISOTOPE IN A SOLID
DRIFTS DOWN A THERMAL ENERGY GRADIENT

R. V. HESKETH
CEGB Berkeley Nuclear Laboratories, Berkeley, Glos. GL13 9PB, U. K.

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Résumé. — La substitution isotopique est le plus simple de tous les défauts dans les solides. L'enthalpie de remplacement est souvent nulle et, pour cette raison, le signe de la diffusion thermique est important. Le signe observé constitue une contrainte sévère pour les théories couramment admises. Ici, on présente une autre possibilité.

Abstract. — Isotopic substitution is the simplest of all defects in solids. The enthalpy of substitution is commonly zero, and for this reason, the sign of isotopic thermomigration is significant. The observed sign is a severe embarrassment to currently accepted theories. An alternative is offered.

1. Introduction. — When there are alternative hypotheses from which to choose, one asks not only if each hypothesis is internally consistent, and externally consistent with the rest of scientific knowledge, but also, whether there is a crucial experiment which makes one preferable to the other. The segregation of isotopes, in solids, in the presence of a temperature gradient, seems to be a crucial test of theories of thermomigration. The emphatic title of the present paper reflects the writer's belief that the sign of the effect (the heavier isotope to the foot of the gradient, the lighter isotope to the top of the gradient) is as dependable as the second law of thermodynamics, and indeed, related to the second law; to the familiar statement that thermal energy diffuses from hot to cold we merely add the corollary even when the carriers of thermal energy are isotopic defects in solids. If isotopes segregate in the observed sense because of the thermal energy they carry, the perspective we have of the subject of thermomigration is considerably changed.

2. The thermal energy of an isotopic defect. — Consider a crystalline solid composed of one kind of atom, a perfectly regular crystal of identical atoms. At temperatures well above the Debye temperature, the thermal energy of the solid is $3NkT$, $N$ being the number of atoms, $k$ being Boltzmann's constant, and $T$ being temperature. To each atom we may ascribe a thermal energy $3kT$, provided we recognize that thermal energy is a collective property, of an assembly of atoms, and that the $3kT$ ascribed to one atom arises through interactions with its neighbours, and must be thought of as distributed energy, distributed over a volume determined by anharmonicity, by the mean free path for phonon scattering.

If we now change the mass of one atom in this solid, we have an isotopic defect. This defect has no chemical interaction with its neighbours, it does not dilate the lattice, it does not change the local elastic constants; its enthalpy of formation is zero, and this is important, a non-zero enthalpy of formation would allow conditions under which the sense of isotopic thermomigration could change (i.e. heavy isotope to hot end, light isotope to cold end).

Through interaction with its neighbours, the isotope partakes of the thermal vibrations, and because of its mass defect, it perturbs the local thermal energy. We may think of a defect thermal energy, associated with the mass defect, and centred on the isotope. At classical temperatures, the defect thermal energy is the perturbation from the value $3kT$. One may not have a negative thermal energy at a lattice site, but clearly one may have a negative perturbation; if the thermal energy is reduced to $2.7kT$, the defect thermal energy is $-0.3kT$. The defect thermal energy may be positive or negative. Its sign is determined by the sign of the mass defect; a negative mass defect produces a negative defect thermal energy.

The magnitude of the defect thermal energy is calculable by at least two methods. One may set up an array of masses connected by springs, and calculate the energy in the system. Alternatively one may consider phonons, quasi particles, moving through an elastic medium and being scattered at the mass defect. Any method of calculation, if accurate, should give but one answer. The second method seems the simpler, and it gives an answer which is recognizably
correct in that it tells us, in the general case, that if
we remove an atom from the solid, if we take it away
completely, we remove $\frac{1}{2}kT$ associated with the atom's
potential energy, and $\frac{1}{2}kT$ associated with its kinetic
energy. The correctness of this asymptotic limit [1, 2]
suggests that the answer may well be correct for
isotopes too. An isotope then has a defect thermal
ergory.

$$Q = \frac{1}{2}kT(\Delta m/m)^3,$$

where $m$ is the mass of an atom in the regular lattice
and $\Delta m$ is the mass defect of the isotope [1, 2]. Clearly
the sign of $Q$ depends on the sign of $\Delta m$. The $\frac{1}{2}kT$
in this expression represents kinetic energy, with
three degrees of freedom. Because there is no change
in the elastic forces constraining the isotope, there
is no contribution to $Q$ representing potential energy.

3. The force on an isotopic defect in a temperature
gradient. — Temperature is a continuous field. It is
single valued and conservative. These three attributes
are not so much denied as sometimes overlooked,
within the scientific community. Thus the theory of
thermomigration in gases currently takes temperature
to be multivalued, through the premise a gas atom
takes its temperature with it, along its free path between
collisions, while the theory of thermomigration in
solids, e.g. [3] takes temperature to be discontinuous.
The mathematics with flow from these tacit assump-
tions, of multivalue and discontinuity, lead only
into error. For this reason I emphasise these three
attributes of temperature.

Given these three attributes, the force, $F$, pushing
an isotopic defect through the lattice, when the solid
is subject to a temperature gradient is

$$F = -\nabla Q$$
$$= -\frac{1}{2}kT(\Delta m/m)^3 \nabla T.$$ (2)

Eq. (2) is presented in this way, with the factor
$\nabla T$ at the end, so that we may recognize it as a
standard form of the thermodynamic literature, i.e.

$$F = -Q \nabla T.$$ (3)

This force pushing the isotope through the lattice is
of course the difference between two forces. On
every atom of the regular lattice there is a force

$$-3k\nabla T,$$ (4)

and on the isotope there is a force

$$-\frac{1}{2}k(1 +\frac{1}{2}(\Delta m/m)^3)\nabla T,$$ (5)

it is rather like trying to push your way through a
crowd at a football match, you must push just a
little harder than the others. Of course all these forces
on the atoms of the solid must be balanced by restraining
forces at the boundary of the solid, if the
solid is at rest in our laboratory frame of reference.

4. Diffusion of an isotopic defect in a temperature
gradient. — The drift velocity, $v$, of an isotopic
defect (through the lattice, in the lattice frame of
reference) is given by the Nernst-Einstein relation:

$$v = \frac{D}{kT}F,$$ (6)

where $D$ is the diffusion coefficient of the isotope.
Diffusion requires the presence of a lattice vacancy.
The isotope can only move when it has a vacancy for
a neighbour. Equally, a regular lattice atom can only
move when it has a vacancy for a neighbour.

When the isotope jumps from one lattice site to
another, it moves through a saddle point. At this
saddle point the isotope and the vacancy share two
lattice sites, though one cannot really distinguish
the isotope from the vacancy, one cannot consider
them as separate defects. There is one defect, isotope
plus vacancy. It has a fractional mass defect

$$\frac{\Delta m - m}{2m}.$$ (7)

The defect thermal energy of this diffusing entity
is, from (1):

$$Q_{\text{isotope + vacancy}} = 3kT(\frac{\Delta m - m}{2m})^3
\quad = -\frac{3}{8}kT\left(1 - \frac{3}{m}\Delta m\right).$$ (8)

If instead of an isotope, we consider a regular lattice
atom at a saddle point, we have

$$Q_{\text{atom + vacancy}} = -\frac{3}{8}kT\left(1 - 0\right).$$ (9)

Compare this with a simple vacancy at a lattice site.
In a close packed lattice, an atom which is neighbour
to a vacancy has itself eleven near neighbours, instead
of twelve. The perturbation of the elastic forces which
restrain it is thus of order $\frac{1}{2}$, and since one has to
consider the square of the perturbation [1, 2] I shall
follow Friedel [4] in choosing, as a first approximation,
to neglect the change in elastic forces at a vacancy.
Thus, for a simple vacancy, centred on a lattice site,
the defect thermal energy consists only of kinetic
energy. This has three degrees of freedom, and as
given by eq. (1),

$$Q_{\text{vacancy}} = -\frac{3}{2}kT.$$ (10)

The difference between (9) and (10) is the thermal
energy accumulated by a lattice atom in going from
a lattice site to a saddle point. The difference,

$$\frac{3}{8}kT,$$ (11)

suggests that (9) is a reasonable approximation.
A diffusive jump occurs when the accumulated thermal
energy is comparable to the enthalpy of migration,
when \( kT \sim E_m \). The present approximation gives a jump when \( \frac{3}{8} kT \sim E_m \). The enthalpy of migration, \( E_m \), represents potential energy stored in the elastic forces, by straining the lattice to the saddle point configuration; thus the present approximation does not omit the strain energy in the lattice at the saddle point. Notice too that the value of \( -\frac{3}{8} kT \) given in (10) has good experimental support, it is close to the value measured by Simmons and Balluffi [5] in the noble metals.

The differential drift velocity of isotopic atoms, and regular lattice atoms, each exchanging places with lattice vacancies, is, from (6),

\[
\Delta v = \frac{\Delta(DF)/kT}{kT} = \frac{D \Delta F + F \Delta D}{kT}. \tag{12}
\]

From (3), (8) and (9),

\[
\Delta F = -\Delta Q \frac{VT}{T} = -9 \frac{kT \Delta m}{m} \frac{VT}{T}. \tag{13}
\]

The change in diffusion coefficient is to a first approximation given by the assumption that the diffusion coefficients of the two types of migrating atoms vary inversely as the square root of the mass, an assumption which stems from their similar energies and hence different attempt frequencies. A second approximation introduces the kinetic energy factor, \( \Delta K \), see, e.g. [6], and, for distinguishable atoms, the correlation factor, \( f \). One then has

\[
\Delta D = -f \Delta K \frac{\Delta m}{2m} D. \tag{15}
\]

Concealed within eq. (8) is the fact that the isotope and the vacancy more in opposite directions, in the act of migration. Thus the perturbation involving \( \Delta m/m \) is of the same sign in (8) as in (1), and refers to the atom. The rest of the expression, in both (8) and (9) refers to the vacancy. Thus, when we come to (12) we must ensure that all its terms refer to the isotope, or to the regular lattice atom (in the case of the second term) and not to the lattice vacancy. The quantity \( \Delta F \) is given by (14), but to obtain \( F \) (for the atom) one must use (6), (3) and (9), and change the sign. Eq. (12) then is

\[
\Delta v = -\frac{3}{8} D \frac{\Delta m}{m} \frac{VT}{T} \left(3 - \frac{1}{2} f \Delta K\right). \tag{16}
\]

The quantity \( f \Delta K \) is less than one. For sodium it is 0.36 [8]. Thus the numerical factor in (16) lies between \( \frac{1}{18} \) and \( \frac{1}{12} \), is \( \frac{1}{12} \) for sodium, and may be approximately written as one.

Thus in the frame of reference defined by the specimen boundaries, the isotope drifts with a velocity

\[
\Delta v = \frac{D}{kT} \left(\frac{-\Delta m}{m} kT\right) \frac{VT}{T}. \tag{17}
\]

Comparing (17) with (6) and (3), we see that in this experimental frame of reference the isotope behaves as if it has a thermal energy

\[
\frac{\Delta m}{m} kT. \tag{18}
\]

Eq. (17) gives the drift velocity when there is no concentration gradient. In experiments, it is customary to wait for a steady state to develop, in which there is zero drift velocity, but a steady concentration gradient; the thermal energy of (18) produces the thermomolecular pressure which supports the concentration gradient. In this steady state, one may make an Arrhenius plot of isotope concentration and temperature, along the specimen. In our model its slope is the energy (18), thus

\[
\frac{-1}{c} \frac{dc}{dT} kT^2 = \frac{\Delta m}{m} kT \tag{19}
\]

where \( c \) is the isotope concentration. Simplifying:

\[
\frac{dc}{c} = -\frac{dT}{T} \frac{\Delta m}{m}. \tag{20}
\]

5. Experimental data. — There are data on isotopic thermomigration in lithium [9, 10] (1) and beryllium [11]. I have a vague recollection of a report that isotopes of uranium were segregated, by thermomigration in the solid metal, in the Manhattan Project, but I cannot now give a reference.

Thus there are two, perhaps three, results on the sign of isotopic thermomigration. In each case the lighter isotope segregates to the hot region, the heavier to the cold. We may place particular trust in the results on the two light metals, because the authors expected the opposite sign [10, 11].

As to magnitude, the results on beryllium are still, so far as I am aware, unpublished, but we do have figures for lithium (1); the ratio \( ^6\text{Li}/^7\text{Li} \) at 400 K is greater by a factor 1.027 \( \pm 0.012 \) than the same ratio at 320 K. Since the natural abundance of \(^6\text{Li}\) is 7.4 % we have

\[
\frac{dc}{c} = 0.027 \pm 0.012, \tag{21}
\]

and of course,

\[
\frac{dT}{T} \frac{\Delta m}{m} \frac{1}{28} = 0.0357. \tag{22}
\]

The agreement is not unsatisfactory. It may even be better than indicated by (22). Lodding Mundy and Ott have measured the diffusion coefficients of $^6$Li in $^7$Li and of $^7$Li in $^6$Li [12]. On an Arrhenius plot they obtained two beautifully parallel straight lines; the respective diffusion coefficients are in the ratio $\frac{3}{2}$, over the experimental temperature range. This ratio is large. I take it to imply that a light isotope is bound to a lattice vacancy with a positive binding entropy, so that the two stay together, allowing the light isotope to diffuse more rapidly. Conversely, there is a negative binding entropy, an entropy barrier, between a heavy isotope and a lattice vacancy. The heavy isotope can only migrate when the lattice vacancy surmounts this barrier. Consequently, the diffusion velocity of the heavy isotope is reduced. Without knowing the value of $f \Delta K$ in lithium one can only estimate the binding entropy. From the experimental ratio of the two diffusion coefficients, one may estimate that the diffusion coefficients of $^6$Li and $^7$Li, both diffusing in a matrix of $^7$Li, are in the ratio $(\frac{3}{2})^{1/2}$. One may then compare this with the theoretical value given by (15). If we take the maximum possible value of $f \Delta K$, we have for the binding entropy,

$$\Delta S_B \geq 0.06 \, k,$$

which seems a credible value.

One may avoid estimating $f \Delta K$, by using (15) and (16) to put the value $\Delta D/D = (\frac{3}{2})^{1/2}$ into (16). Eq. (16) then has a numerical constant of 0.77. Thus in place of (22) we have

$$- 0.77 \frac{dT}{T} \frac{\Delta m}{m} = 0.77 \frac{28}{m} = 0.0275 .$$

The agreement with the thermomigration result of (21) is as accurate at one could wish.

6. Equation (16). — Having demonstrated that present results are of the expected sign and magnitude, we may now attach significance to eq. (16). The quantity $f \Delta K$ will not exceed one, and the sign of (16) will not change. Thus eq. (16) predicts that, in solids, isotopic impurities which are heavier than the matrix will segregate to the foot of the thermal gradient. Conversely, light isotopes segregate to the top of the gradient.

An isotope with a positive defect thermal energy, moving down a temperature gradient, carries heat from hot to cold. Equally, an isotope with a negative defect thermal energy, moving up a temperature gradient, carries heat from hot to cold. Thus the sign of (16) says that isotopic defects behave like other heat carriers. Phonons, by diffusion, carry heat from hot to cold. In metals, plasmons, by diffusion, carry heat in the same direction. As long as all these heat carriers move by diffusion the sign of isotopic thermodynamics need not perplex us, it is an aspect of the second law; diffusion is the means by which the free entropy of the subsystem (the specimen) attains a maximum.

7. Images and analogues. — In diffusion, drift velocity, and not acceleration, is proportional to the impressed force; we have Aristotelian rather than Newtonian mechanics. (The criterion that the driving forces of diffusion are strong, rather than weak, that we have non-linear rather than linear thermodynamics, is that the equations become Newtonian rather than Aristotelian [13].) The proportionality of velocity and force, and the continuity of the thermal energy field, together suggest the simple analogue of stones falling through water, or bubbles rising, as a useful parallel of isotopic thermomigration. The gravitational energy gradient corresponds to the thermal energy gradient. The stone is a region where the density is high, and it migrates to the foot of the gradient. The bubble is a region where the density is low, and it migrates to the top of the gradient. In so doing, the bubble carries mass down the gravitational gradient.

This image is useful, for one could have a ball of wood, of the same density as the water, which went neither up nor down. It would however scatter any sound waves which we were to propagate through the water. In the same way, it is possible to have a defect in a solid (not an isotopic defect) which has a zero defect thermal energy, which moves neither down nor up a temperature gradient, but which nonetheless has a thermal resistance, it scatters sound waves, it scatters phonons. The same applies to defects in an electron gas..., but this topic is too wide to be covered here.

If instead of stones, we have colloidal particles in water, they do not all sink to the bottom, they establish an exponential atmosphere. The isotopes we have discussed also form an exponential atmosphere.

This image, with its properties of fluidity and continuity allows one to see that thermomigration is a readily comprehensible subject.

A second image, which has some value in dispelling misconceptions about thermomigration, is that of the transport of people, by bus, say from Heathrow Airport to the West London Terminal. We may consider a coefficient the people of transport, by which we mean the flux of people divided by the flux of buses. Since our image is to be a parallel of thermodynamics, we must look at a statistical number of buses. May we agree that our coefficient is simply the average number of people on a bus? The properties of the image which are relevant are that the average number of people on a bus is not a function of the height of the Hammersmith flyover (the enthalpy of migration) nor of the number of Joules expended in the manufacture of the bus (the enthalpy of formation). Nor does the number of people on a bus depend
on the speed of the bus (pray God!). Stationary in a traffic jam or exceeding the speed limit, the number of people on the bus stays the same, it is a simple scalar quantity. I say scalar to emphasise the non-tensorial character (both of the people of transport and of the heat of transport); if a bus is travelling from Heathrow to West London at 40 mph its passengers are not travelling to Neasden at 50 mph.

Our image allows for irreversibility. The average number of people per bus leaving Heathrow might be 40, and the average number per bus arriving at West London might be 38.5. On every second bus three people persuade the driver to set them down at Earls Court. Despite this irreversible dissipation, the people of transport still remains quite simply the number of people on a bus — one could say that there is local thermodynamic equilibrium over a small region — from Earls Court to the West London Terminal. The point of this image is that the reduced heat of transport is as simple a concept as the people of transport.

8. Irreversibility. — An electric current, flowing through a copper wire, heats it up. Joule heating is a dissipation of energy, a creation of entropy. Thus an electric current, in an ohmic conductor, must be treated by the equations of irreversible thermodynamics. Can the driving force, for this flux of electricity, be derived from a potential? May we speak of voltage as a potential? May we use the concept of voltage gradient? in this irreversible situation.

If we may, may we also use the concept of potential, and potential gradient, for other forces of irreversible thermodynamics? May we use it, as I have done in this paper, at eq. (2), for the force of thermomigration? One of the standard texts has a chapter headed Ordinary and Thermal Diffusion Potentials [14].

There seems no reason that one should not use conservative forces, forces derivable from a potential. Conservative forces are able to generate entropy, they can provide irreversibility. Consider the electric current in the copper wire. If the electrical conductivity of the wire is \( \sigma \) and the voltage gradient is \( \nabla V \), the rate of generation of entropy, per unit volume, is

\[ \sigma \nabla V \cdot \nabla V / T. \]  

(25)

The dot product is a non-zero scalar quantity.

Seven out of ten physicists, a survey shows [15], regard the electrical conductivity of an ohmic conductor as an equilibrium parameter. They also regard it as a non-equilibrium parameter, as do the texts [e.g. 14]. In an ohmic conductor we have

\[ \sigma_{\text{equilibrium}} = \sigma_{\text{non-equilibrium}}. \]  

(26)

An ohmic conductor is one of the possible linear systems of irreversible thermodynamics and the electrical conductivity is one of the phenomenological coefficients (usually denoted by the general symbol \( L \)). It is a general rule [14] (2) in linear systems that

\[ L_{\text{equilibrium}} = L_{\text{non-equilibrium}}. \]  

(27)

Eq. (27) is immensely powerful, and has many consequences for the theory of thermomigration. The ordinary diffusion coefficient, \( D \), is an \( L \) coefficient. Thus ordinary, isothermal, diffusion experiments are just as much a part of irreversible thermodynamics as are thermomigration experiments. Indeed, one may go further, and say [15] that the whole of physics is non-equilibrium physics. There is no such thing as an equilibrium observable. Every experiment ever done can only be properly treated by irreversible methods. Anyone familiar with the (especially chemical) literature on irreversibility could be forgiven for being terrified by such a prospect! Such fear, though understandable, is without foundation; eq. (27) indicates that all the coefficients with which we have to deal (in the linear region of non-equilibrium) are simple equilibrium quantities. All have some place, however concealed, within the equilibrium Gibbs Function. To take a specific example, the electrical conductivity lies within the vibrational entropy.

Of present interest is the quantity \( Q \) of eq. (1). It is an equilibrium parameter, a thermal capacity multiplied by a temperature. By virtue of (27) it is also a non-equilibrium parameter, it is the reduced heat of transport of the isotopic defect.

Eq. (27) tell us also that in the linear region of non-equilibrium we have no additional parameters to deal with, other than the equilibrium ones. Clearly, if some parameter were to have a non-zero value in non-equilibrium and a zero value in equilibrium, it would not satisfy (27). Eq. (27) tell us two things, that the parameters of equilibrium continue to exist, and that no others arise. It is restricted to the linear region of irreversible thermodynamics [14], but many experiments, including isotopic thermomigration, lie within this region [13].

In summary, this section on irreversibility shows that the equilibrium quantities of eq. (1) and the simple mathematical operation of eq. (2) are necessary, sufficient, and correct, in the linear region of non-equilibrium. I note that the present view has already been adopted as a generality by Sommerfeld [16].

9. Caveat. — This paper is devoted to isotopic thermomigration in solids. The sign which it predicts is dependent on the enthalpy of formation of the isotopic defect being zero. So far as I can judge, this is a reasonable expectation, in solids, liquids, and noble gases. The polyatomic gases on the other hand

\[ (2) \] De Groot, S. R., 1972, personal communication.
can form dimers and trimers, at low temperatures (e.g. oxygen can form O$_4$ and O$_6$). These dimers have an enthalpy of formation, and therefore, at low temperatures, the sign of isotopic thermal diffusion can reverse. So far as I can judge, this complication is unlikely in solids.

The predicted sign also depends on the binding entropy between a light isotopic defect and a lattice vacancy (or equivalently, the entropy barrier between a heavy isotopic defect and a lattice vacancy) being less than a critical value. This critical value (as a multiple of $\Delta m/m$) is some five times the binding entropy observed in lithium. My own expectation is that lithium will have one of the higher binding entropies, and that the critical value is not likely to be exceeded. Binding entropies are measurable, as in the experiment of Lodding, Mundy and Ott [12].

Thus if the expected sign is, in some solid, not observed, there are two possible causes of sign reversal. Each cause is experimentally detectable, in experiments other than thermomigration. The effect of each upon thermomigration is that a non-zero enthalpy could reverse the predicted sign at low temperatures, whereas an entropy greater than the critical value would reverse the predicted sign over the whole temperature range. Since both the binding entropy between the isotopic defect and a lattice vacancy and the enthalpy of formation of an isotopic defect are measurable quantities, the situation remains well defined.

Acknowledgments. — This paper is published by permission of the Central Electricity Generating Board.

References


[2] Hesketh, R. V., in Atomic Transport in Solids and Liquids (Verlag der Zeitschrift für Naturforschung, Tubingen, ed. A. Lodding and T. Lagerwall) 1971, p. 23. Author's note: this paper contains two or three weird type setting errors, thus in the typescript and the two proof stages the first sentence reads In the absence of thermal equilibrium, the standard thermodynamic parameters continue to exist — the same point of view as presented in the present paper. In the last paragraph one should of course have In perfect insulators heat diffusion does not occur by phonons, but by phonon-phonon interaction.


