APPROXIMATE EVALUATION OF THE THERMAL DIFFUSION
CONSTANT IN LIQUID ISOTOPIC MIXTURES

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An attempt is made to derive a semiempirical dependence for the thermal diffusion constant in liquid isotopic mixtures on the basis of data available in the literature.

Since the theory available for transport in liquids does not permit a numerical calculation of the thermal diffusion constant α_{liq} for any liquid isotopic mixtures, efforts are being made to obtain empirical dependences for at least an approximate evaluation of this quantity. The very few experimental α_{liq} values which are available for liquids are shown in Table 1.

For gaseous isotopic mixtures, we have the following relation [1]:

$$\alpha_g = \frac{105}{118} \frac{M_1 - M_2}{M_1 + M_2} R_T,$$ (1)

where R_T is a function characterizing the force of the intermolecular interaction. The second factor often makes the primary contribution to the numerical value of α_g calculated from Eq. (1).

In this paper, we adopt the following dependence for liquid isotopic mixtures:

$$\alpha_{liq} = f\left(\frac{M_1 - M_2}{M_1 + M_2}\right).$$ (2)

This assumption is in agreement with the results of Wirtz [2], according to whom

$$\alpha_{liq} = f\left(\sqrt{\frac{M_1}{M_2}} - 1\right),$$ (3)

since it is easily shown that the expressions in the parentheses in Eqs. (2) and (3) are essentially identical, differing only by a factor which is essentially equal to unity. That relations of the type (2) should be sought is also confirmed by the tendency noted in [3] for α_{liq} to decrease with a decrease in the relative mass difference.

Difficulties arise in the calculation of the ratio $(M_1 - M_2)/(M_1 + M_2)$ shown in the sixth column in Table 1 when the isotopes being separated can appear in the initial compound in different combinations, and when this initial compound may contain in addition isotopes of other elements. In these cases, the elements whose isotopes are present in quantities less than 1% are treated in the subsequent calculations as monoisotopic. In ethylene trichloride, e.g., the mass numbers 130, 132, 134, and 136 should appear; for these four masses, the difference $M_1 - M_2$ should be equal to two mass units in three cases, four in two cases, and six in one case. The average value of this difference, which is the effective mass difference, is $(3 \cdot 2 + 2 \cdot 4 + 1 \cdot 6)/(3 + 2 + 1) = 3\frac{1}{3}$ mass units, and $M_1 + M_2 = 2M_{av}$, which gives the desired ratio, is equal to 0.0125. An analogous situation occurs during the melting of metals, which, as was shown in [4, 5], diffuse as aggregates containing various numbers of atoms (Table 2). It can be shown that in all such cases the relation

$$M_1 - M_2 = \frac{1}{3} \Delta (m + 1),$$ (4)

holds where Δ is the minimum difference between the mass numbers for two types of molecules, and m is the number of possible mass combinations. This procedure of calculating the effect of mass difference is,

TABLE 1. Thermal Diffusion Constants for Liquid Isotopic Mixtures

No.	Isotopes being separated	Compound	Thermal diffusion constant	Reference	$\frac{M_1-M_2}{M_1+M_2}$
1	H_2—D_2	D_2O+H_2O	0,02	[12]	0,0526
2	H_2—D_2	$C_6D_6+C_6H_6$	0,2	[13]	0,0370
3	Li^6—Li^7	Li	0,142	[4,6]	0,0360
4	Li^6—Li^7	$LiNO_3$	0,02	[15]	0,0071
					0,00384
5	Cl^{35}—Cl^{37}	C_2HCl_3	0,1	[14]	0,0125
6	Cl^{35}—Cl^{37}	n-C_4H_9Cl	0,1	[3]	0,0108
7	K^{39}—K^{41}	K	0,0596*	[4]	0,0111
8	Ga^{69}—Ga^{71}	Ga	0,038	[4]	0,00523
9	Br^{79}—Br^{81}	C_2H_5Br	0,04	[3]	0,00637
10	Rb^{85}—Rb^{87}	Rb	0,031	[4]	0,00453
11	U^{235}—U^{238}	UF_6	0,007—0,01	[11]	0,00428

*This value is found from a recalculation on the basis of the data of [4], which contained an error in the calculation of α.

TABLE 2. Minimum Number of Atoms in Aggregates in Molten Metals According to [4]*

Metal	No. of atoms in the aggregates*	Metal	No. of atoms in the aggregates*
Li	5	Ga	10
K	3	Rb	6

*Rounded to integers.

of course, based on an assumed independence of α_{liq} from the concentration; this has been confirmed by the experiments of Prigogine with D_2O –H_2O mixtures [16].

Table 1 shows two values of the relative mass difference for molten lithium nitrate, corresponding to the existence of $[Li(NO_3)_2]^-$ ions along with $LiNO_3$ molecules in the melt [7]. The data of Table 1 are also shown in the accompanying Fig. 1, from which it is evident that most of the points, except those for water (which is known to have anomalous properties), have a rather clear tendency to concentrate around a correlating line described by

$$\alpha_{liq} = 5.4 \frac{M_1-M_2}{M_1+M_2}. \tag{5}$$

The numerical coefficient in Eq. (5) can be given a certain physical meaning on the basis of the theoretical results of Dougherty and Dricamer [8], who showed on the basis of the thermodynamics of irreversible processes that the following equation holds for molecules of the same shape:

$$\alpha_{liq} = \left[\left(\varphi_1 \sqrt{\frac{U_1}{V_1}} + \varphi_2 \sqrt{\frac{U_2}{V_2}} \right) \left(\sqrt{\frac{U_1}{V_1}} - \sqrt{\frac{U_2}{V_2}} \right) \frac{V_1V_2}{x_1V_1+x_2V_2} \right] \times \left[2 \left\{ RT \right[1 \right.$$
$$\left. + x_1x_2 \left(\frac{V_1-V_2}{x_1V_1+x_2V_2} \right)^2 \right] - 2\varphi_1\varphi_2 \frac{V_1V_2}{x_1V_1+x_2V_2} \left(\sqrt{\frac{U_1}{V_1}} - \sqrt{\frac{U_2}{V_2}} \right)^2 \right\}\right]^{-1}$$

For liquid-phase isotopic mixtures, as is evident from the data in [9], the molar volumes of each component can be set equal; i.e., $V_1 = V_2$. Then

$$\alpha_{liq} = \frac{(\varphi_1 \sqrt{U_1} + \varphi_2 \sqrt{U_2})(\sqrt{U_1} - \sqrt{U_2})}{2[RT - 2\varphi_1\varphi_2(\sqrt{U_1} - \sqrt{U_2})^2]}.$$

Bearing in mind that the second term in the denominator may be neglected in comparison with the first, and that $\varphi_1\sqrt{U_1}/(U_2 + \varphi_2) \approx 1$, we find

$$\alpha_{liq} = \frac{U_2}{2RT} \left(\sqrt{\frac{U_1}{U_2}} - 1 \right)$$

(a similar result was found in [10]; the only difference was that the expression 2RT in the denominator was incorrectly replaced by $2RT\bar{V}$, where $\bar{V}$ is the average molar volume). Since the evaporation energy is related to the heat of vaporization by $U = L - RT$, we have
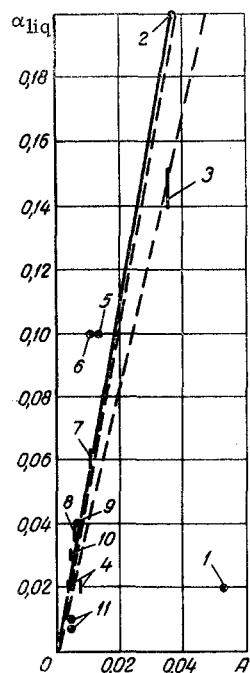
Fig. 1. Dependence of the thermal diffusion constant on the relative mass difference. The numbers near the experimental points correspond to the first column in Table 1. A $= (M_1 - M_2)/(M_1 + M_2)$.

$$\alpha_{\text{liq}} = \frac{L_2 - RT_2}{2RT} \left(\sqrt{\frac{L_1 - RT_1}{L_2 - RT_2}} - 1 \right).$$

In this equation, T should be treated as an average temperature for the process; i.e., $T \equiv \bar{T} = (T_1 + T_2)/2$.

Using Trouton's rule, according to which $L = KT$ holds at the boiling temperature, and using the approximation $T_2 \approx \bar{T}$, we finally find

$$\alpha_{\text{liq}} = \frac{K - R}{2R} \left(\sqrt{\frac{T_1}{T_2}} - 1 \right) \approx \frac{K - R}{2R} \frac{T_1 - T_2}{T_1 + T_2}. \tag{6}$$

The numerical coefficient in (6) can be easily determined when it is taken into account that $K = 20\text{-}30$ for nonpolar liquids. Then

$$\alpha_{\text{liq}} = (4.5 - 5.25) \frac{T_1 - T_2}{T_1 + T_2}. \tag{7}$$

The numerical coefficient in (5) thus characterizes the energy of the intermolecular bond in the liquid, and is approximately constant for nonpolar liquids if the following relation, which follows from (5) and (7), holds:

$$\frac{M_1 - M_2}{M_1 + M_2} = \left| \frac{T_1 - T_2}{T_1 + T_2} \right|.$$

Unfortunately, there is not sufficient experimental evidence available to check this relation.

The dashed lines in the accompanying Fig. 1 correspond to the limiting values of the numerical coefficient in Eq. (7).

The deviations from dependence (5) observed in Fig. 1 can apparently be attributed, first, to an inaccurate determination of the quantity α_{liq} itself, as was noted by Alexander [11]. Alexander pointed out that all these data for substances shown by numbers 1, 2, 5, 6, and 9 in Table 1 were not obtained on the basis of mass-spectrometric analysis, but by a pycnometric method, so the accuracy of the results is degraded. The reliability of these data is also limited by the accuracy of the viscosity coefficients and the bulk expansion coefficients which appear in the calculations for the Clusius separation column. Second, some error arises in the calculation of the mass difference from Eq. (4) for aggregates of atoms, as in melts. If, e.g., the minimum number of atoms for Li is replaced by a larger one, the corresponding point in Fig. 1 would assume a much more satisfactory position.

The discrepancy observed for Ga is due to a deviation from Trouton's rule. The data for UF_6 were obtained from the operation of a large apparatus in which the distorting effect of parasitic convection could not be exactly taken into account; these data should therefore be considered approximate.

Finally, it should also be noted that Eq. (7) was obtained for the boiling temperature, while all the experimental data in Table 1 were obtained at lower temperatures. Despite all these factors which introduce an uncertainty into calculations by Eq. (5), the latter can be used for a first approximation of the thermal diffusion constant in nonpolar liquids.

In particular, it follows from Eqs. (1) and (5) that

$$\frac{\alpha_{\text{liq}}}{\alpha_g} \approx \frac{6.3}{R_T},$$

i.e., the thermal diffusion constant for liquids is much greater than that for gases, as was first pointed out by Alexander [3].

NOTATION

α is the thermal diffusion constant;
M is the mass of the isotope or of the compound containing the isotope;
φ is the volume fraction of the component in the mixture;
V is the molecular volume of the pure component;
x is the molecular fraction of the component in the mixture;
U is the evaporation energy;
L is the heat of vaporization.

The indices 1 and 2 refer to the heavy and light components, respectively.

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