Mutual Diffusion in Dilute Binary Systems

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Since its inception twenty-five years ago the absolute rate theory of diffusion in liquids (5) has been frequently utilized by experimenters for data interpretation. One significant test of the theory is its ability to predict the group $(D\mu/T)$, which should be a function of the characteristic intermolecular distances in the lattice of the quasi-crystalline liquid and of the difference between the free energies of activation of the viscous and diffusive processes. There is no accepted method for evaluating the latter difference, and in all previous studies the two free energies of activation have been assumed equal. This assumption is defensible for self-diffusion, since the substances taking part in both the viscous and diffusive processes are identical. However there is no justification for the equality in mutual diffusion, even for systems in which the solute approaches infinite dilution. If the solute is present in very small amounts, the viscosity of the system is due almost entirely to the characteristics of solvent. The diffusion process on the other hand must involve the solute species, irrespective of its degree of dilution. The differences between solvent-solvent and solute-solvent interactions cannot be dismissed because of the low concentration of the diffusing species.

This study provides an approximate means for estimating the difference between the free energies of activation of the viscous and diffusion processes in dilute binary systems in terms of the properties of the pure components. When it is incorporated into absolute rate theory, this factor provides better agreement between the calculated and observed values of $(D\mu/T)$ than can be obtained by treating self and mutual diffusion as identical processes.

The latest version of Eyring's original theory indicates that the group $(D\mu/T)$ is given by (9)

$$\frac{D\mu}{T} = \left(\frac{\lambda_1}{\lambda_2\lambda_3}\right)\left(\frac{k}{\xi}\right)\exp\left\{\frac{\Delta F^*_\mu - \Delta F^*_D}{RT}\right\} \quad (1)$$

The λ's are independent of the solute species; they arise from considerations of the viscous process, which, for dilute systems is controlled almost entirely by the solvent.

If $\lambda_\mu \approx \lambda_1$, the viscosity can be expressed in terms of the molecular size parameters (5):

$$\mu = \frac{h}{\lambda_1\lambda_2\lambda_3}\exp\left\{\frac{\Delta F^*_\mu}{RT}\right\} \quad (2)$$

As indicated by Bondi (*1*) this relation should be regarded as a definition of ΔF^*_μ.

The parameter ξ in Equation (1) was taken as unity in the original Eyring theory. However Li and Chang (6) and Ree and Eyring (9) have shown that the assumption of a hexagonal packing arrangement in the liquid lattice leads to a value of 6. An empirical evaluation of ξ from mutual diffusion data yielded a value of 5.6 (9). Another indication that a factor of about 6 should be included in the Eyring model results from a combination of Equation (1) and the relation between the molar volume and the molecular size parameters:

$$\frac{V}{N_{AV}} = \lambda_1\lambda_2\lambda_3 \quad (3)$$

For self-diffusion (in which $\Delta F^*_\mu = \Delta F^*_D$) Equations (1) and (3) yield expressions for λ_1 and $\sqrt{\lambda_2\lambda_3}$ in terms the measurable quantities $(D\mu/T)$, (ξ/k), and (V/N_{AV}). Comparisons of λ_1 and $(\lambda_2\lambda_3)^{1/2}$ have been made by a number of investigators (*3, 4, 5, 8*) with the assumption that $\xi = 1$. Their results have uniformly indicated, that λ_1 is smaller than $\sqrt{\lambda_2\lambda_3}$ by a factor of 3 to 4. However if the modification of Li and Chang (6) and Ree and Eyring (9) is accepted, and ξ taken as 5.6, this discrepancy disappears.* Thus all subsequent discussion of Equation (1) will be based on the following assumptions: $\xi = 5.6$, and $\lambda_1 = \sqrt{\lambda_2\lambda_3}$.

With these simplifications Equation (1) may be written as

$$Y = \left(\frac{D\mu}{T}\right)\left(\frac{\xi}{k}\right)\left(\frac{V}{N_{AV}}\right)^{1/3} = \exp\left\{\frac{\Delta F^*_\mu - \Delta F^*_D}{RT}\right\} \quad (4)$$

EVALUATION OF $\Delta F^*_\mu - \Delta F^*_D$

At low solute concentrations the viscous mechanism is determined almost completely by the strength of the interaction between solvent molecules. The process can be pictured in two stages: the formation of a hole or vacant lattice site followed by the movement of a neighboring molecule into the recently vacated site. Although the relative importance of these two processes is unknown, the free total energy of activation for viscosity and self-diffusion in a pure substance can be written as

$$\Delta F^*_\mu = \Delta F^h_{AA} + \Delta F^j_{AA} \quad (5)$$

where the first term on the right represents the contribution of the hole-making process to the total and the last term the contribution due to bond breaking or overcoming of repulsive forces by the molecule in motion.

This model is equivalent to considering ΔF^j as the free energy difference between the equilibrium and activated states and $\exp\,[-\Delta F^h/RT]$ as the probability that a vacant site is adjacent to the activated molecule. The explicit subdivision of viscosity or self-diffusion (not only their temperature-dependent parts) into kinetic and volume contributions has previously been utilized by McLaughlin (7).

In the diffusion process however the moving solute molecule can be pictured as completely surrounded by solvent molecules because the system is assumed very dilute in solute. Thus the hole which will receive the solute molecule must be formed in a medium of essentially pure A, but the forces which the diffusing molecule must overcome in order to move into the hole depend upon the nature of the interaction between the solute and solvent molecules. When one designates the solute by S, the total free energy of activation for diffusion can be written as

$$\Delta F^*_D = \Delta F^h_{AA} + \Delta F^j_{AS} \quad (6)$$

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* If ξ is 5.6 rather than unity, the computed λ_1's are increased by $\sqrt{5.6}$ while $\sqrt{\lambda_2\lambda_3}$ is decreased by $(5.6)^{1/4}$.

Equation (6) differs from Equation (5) only in that the last term depends upon $A-S$ rather than $A-A$ interactions.

Since the activation process involves passage up a potential barrier, the free energy change for this step can be written in terms of the zero point energy difference[*], and the ratio of the partition functions in the activated and initial (or equilibrium) states

$$\exp\{-\Delta F^j/RT\} = (Q^*/Q) \exp\{-e_o/kT\} \quad (7)$$

Combining Equations (4) to (7) one gets

$$Y = \frac{(Q^*/Q)_{AS}}{(Q^*/Q)_{AA}} \exp\left\{\frac{e_{oAA} - e_{oAS}}{kT}\right\} \quad (8)$$

Since no combination rules for the zero point energy difference between dissimilar species are available, e_o must be related to molecular constants for which such rules exist. McLaughlin (7) has shown that for the purpose of self-diffusion and viscosity the zero point energy can be represented by a fraction (empirically determined) of the Lennard-Jones expression for the potential energy between the central molecule and its nearest neighbors:

$$e_o \,\alpha\, \epsilon \left\{1.2\left(\frac{V_o}{V}\right)^2 - 0.5\left(\frac{V_o}{V}\right)^4\right\} \quad (9)$$

V_o is related to the collision diameter by $V_o = N_{AV}\sigma^3$. The force constants ϵ and σ are available from gas viscosity data. For the substances studied by McLaughlin (argon, nitrogen, carbon monoxide, methane, carbon tetrachloride, benzene) V_o/V varied from 0.77 to 1.25; however the bracketed term in Equation (9) remained reasonably constant, increasing from 0.54 at $V_o/V = 0.77$, passing through a maximum of 0.72 at $V_o/V = 1.1$, and decreasing again to 0.65 at $V_o/V = 1.25$. Thus the zero point energy depends primarily upon the force constant ϵ. If it is assumed that the near linear relation between e_o and • is valid for molecules more complex than those studied by McLaughlin, then the combination rule for the ϵ's, that is $\epsilon_{AS} = \sqrt{\epsilon_{AA}\epsilon_{SS}}$, yields

$$e_{oAS} = \sqrt{e_{oAA} e_{oSS}} \quad (10)$$

According to the absolute rate and free volume theories one may express the partition function ratios as (5, 7)

$$\frac{Q^*}{Q} = \frac{h}{(2\pi\, m\, kT)^{1/2}\, v_f^{1/3}} \quad (11)$$

In order to estimate the pre-exponential factor of Equation (8) consider the following mechanistic picture of the free volume in a liquid. The volume available to the central molecule is approximately the difference between the size of the cell without the central molecule and the dimensions of the central molecule. Unless the solute molecule is large enough to distort the normal cell dimensions of the solvent molecule, the cell size will be the same in viscosity and mutual solvent molecule by a solute molecule diffusion. Replacement of the central solvent molecule by a solute molecule of different size will increase the free volume if the solute molecule is smaller than the solvent, or decrease it if the solute molecule is larger. However the effect is counterbalanced by the molecular mass term in Equation (11); a small solute molecule increases $v_f^{1/3}$ but decreases $m^{1/2}$. It will be assumed that the replacement of a solvent central molecule by a solute molecule leaves the product $m^{1/2}\, v_f^{1/3}$ essentially constant, or that the pre-exponential term in Equation (8) is unity.

The zero point energies in the exponential term of Equation (8) can be related to pure component values by Equation (10). Since the difference must ultimately be related to the calculable total free energies of activation by Equation (2), two additional relations are needed: a link between ΔF^j and ΔF^* and some information concerning the partition function ratios for pure substances. The latter represents one of the major inadequacies of absolute rate theory; fortunately, for this discussion, absolute values of Q^*/Q are not required. If for the moment Eyring's relation between the free volume in terms of the energy of vaporization is accepted, calculated values of Q^*/Q from Equation (11) are quite insensitive to the particular substance involved. For example cyclohexane and n-tetradecane differ by 35%, while ethyl, ether, carbon tetrachloride, toluene, and the lower normal hydocarbons fall in between these two. Furthermore the discrepancies between the natural logarithms of the partition function ratios are roughly one half as large. Thus the predominant variable on the right-hand side of Equation (7) is the exponential term; compared with variations in $\Delta F^j/RT$, $\ln(Q^*/Q)$ can be considered essentially constant for the liquids investigated here. Furthermore all free volume theories, no matter how sophisticated, must result in a ratio

$$\beta = -\frac{\ln(Q^*/Q)}{(\Delta F^j/RT)} \quad (12)$$

which is less than unity. Otherwise the zero point energy difference would be negative, and the activated state would represent a lower energy level than the equilibrium position.

Substituting Equations (7) and (10) into (8), and assuming all partition function ratios to be equal, one obtains

$$\ln Y = \left(\frac{\Delta F^j{}_{AA}}{RT}\right)\{1 - \alpha\sqrt{r}\} \quad (13)$$

where

$$r = \frac{\Delta F^j{}_{SS}}{\Delta F^j{}_{AA}} \quad (14)$$

and

$$\alpha = \frac{[(1-\beta_A)(r-\beta_A)]^{1/2} + \beta_A}{\sqrt{r}} = 1 - \frac{\beta_A}{2}\left(\frac{1}{\sqrt{r}} - 1\right)^2 - \frac{\beta_A{}^2}{8}\left(\frac{1}{r} - 1\right) + \ldots. \quad (15)$$

β_A is given by Equation (12) with $\Delta F^j{}_{AA}$ instead of ΔF^j.

The series expansion of Equation (15) shows that since β_A must be less than unity or r (whichever is smaller), and for the substance studied here $0.6 \leqq r \leqq 1.6$, all terms but the first are negligible, and $\alpha \approx 1$ (for example if $\beta_A = 0.75$, $r = 1.6$, $\alpha = 0.96$).

Although the relative importance of the two terms in Equation (5) is not known, it will be assumed that the kinetic part constitutes a constant fraction f of the total free activation energy:

$$f = \frac{\Delta F^j}{\Delta F^*} \quad (16)$$

The factor f is assumed to be the same for all pure substances. The validity of this assumption, and an estimate of the value of f, can be obtained from Bondi's study of the isobaric and isochoric temperature coefficients of the viscosity of a number of pure liquids (*1*). Such data yield the energy contributions to the kinetic and volume components, which can be expressed as the ratio $\Delta H^j/\Delta H^*$. (See Table 1 of reference *1*.) The magnitude of ΔH^j compared with ΔH^* depends upon the restricted external rotation of the molecules in the liquid state; hence it is smaller than average for relatively spherical molecules such as carbon tetrachloride and toluene and slightly larger than average for normal paraffin hydrocarbons. The high value for the alcohols is due to the strong field created by the presence of hydroxyl groups, which oppose the motion of

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[*] The amount of energy which the molecule must acquire at 0°K. in order to reach the activated state, or the barrier height.

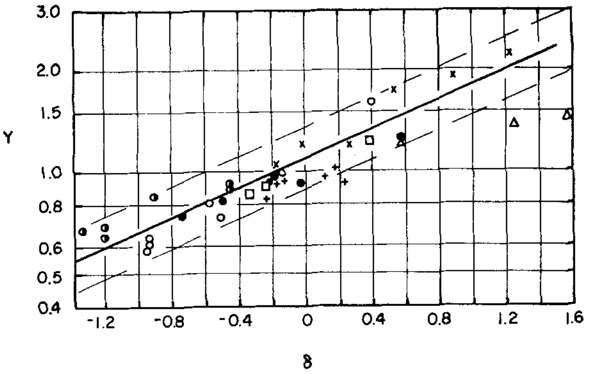

Fig. 1. The effect of differences between free energies of activation for viscosity and mutual diffusion as estimated by Equations (17) and (18). Open circle, bromoform solute; open square, benzene solvent; x toluene solute; open triangle, *n*-heptane solute; solid circle bromobenzene solute; half solid circle, α-bromonaphthalene solute; + Caldwell and Babb data (2).

the molecule from its equilibrium site. Although $\Delta H^j/\Delta H^*$ and $\Delta F^j/\Delta F^*$ are not identical, they both depend upon the relative importance of the kinetic or bond-breaking component in the overall viscous process. The average value of $\Delta H^j/\Delta H^*$ for nine liquids was 0.54; thus a reasonable value of f seems to be $\sim \frac{1}{2}$, although marked deviations from this value for particular types of liquid are to be expected.

By means of Equations (14) and (16), and the assumption that $\alpha \approx 1$, Equation (13) can be written as

$$Y = e^{f\delta} \tag{17}$$

where

$$\delta = \left(\frac{\Delta F^*_{AA}}{RT}\right)\left[1-\left(\frac{\Delta F^*_{BB}}{\Delta F^*_{AA}}\right)^{1/2}\right] \tag{18}$$

ΔF^* can be computed for solvent and solute from Equation (2). Comparison of Equation (4) and (17) shows that the difference in the free energies of activation for viscosity and mutual diffusion is $RTf\delta$.

Since the parameters required for Y and δ are experimentally obtainable, a plot of Equation (17) offers a test of method used for computing $\Delta F^*_\mu - \Delta F^*_D$ and provides a method of estimating f. Treatment of representative binary diffusion data in this manner is presented in Figure 1.* The data cover a range of Y values from 0.6 to 2.2. The best line through the points has a slope of 0.5, which suggests that approximately one half of the total activation energy of the viscous and diffusion processes is used in hole formation and the remainder in enabling the jumping molecule to overcome the potential barrier of its neighbors. This value is reasonable in view of the previous discussion of the estimate of $\Delta H^j/\Delta H^*$.

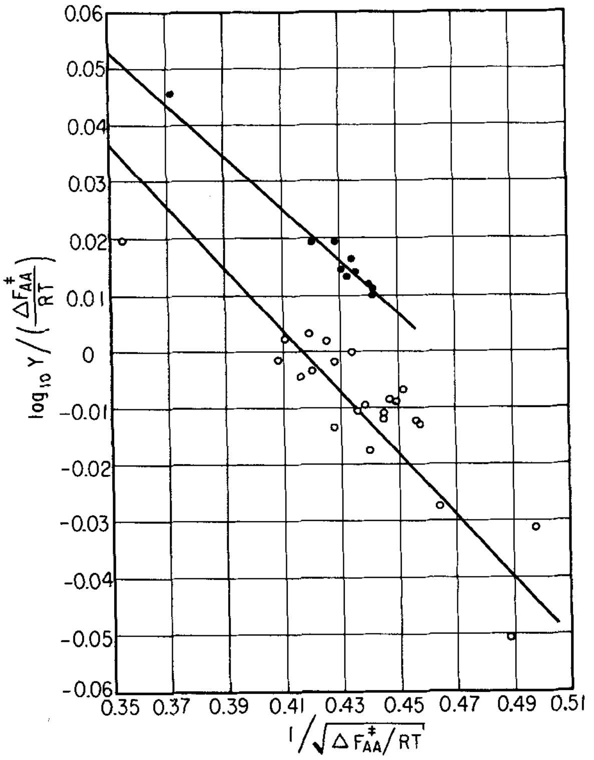

Fig. 2. Diffusion of iodine in various solvents. ● normal paraffin solvents; ○ all other solvents. Data from reference 9.

The dashed lines on either side of the line represent 25% deviations. All but three points fall in this range. In principle the line should pass through the $\delta = 0$, $Y = 1$, but in fact it lies 10% above this point. This is probably due to the selection of $\xi = 5.6$, which was based upon the estimate of Ree et al. (9). If ξ had been selected as 5, the line would have passed through $Y = 1$ at $\delta = 0$. Despite the appreciable scatter of the plot and the approximations required to estimate δ, the trend is quite clear. These systems for which the computed $\Delta F^*_\mu - \Delta F^*_D$ is positive exhibit Y values greater than unity, and vice versa. (A positive value of $\Delta F^*_\mu - \Delta F^*_D$ is usually reflected by a solvent which is more viscous and has a greater molar volume than the solute). If ΔF^*_μ and ΔF^*_D had been assumed equal, all of the points should have fallen about the horizontal $Y = 1$. The magnitudes of the calculated differences between ΔF^*_μ and ΔF^*_D lie between -0.8 and $+0.9$ kcal./mole.

An explanation of the major discrepancies from the line of slope ½ of Figure 1 can be found in Bondi's interpretation of the ΔH^j term and its relation to the factor f. For those systems which contain an alcohol as one component the difference between Y and unity would be expected to be greater than that represented by the line, since f is greater than ½ for this class of substances. This is found to be the case for the diffusion of bromoform in methyl, ethyl, and *n*-amyl alcohol. Since cyclohexane is more spherical than the normal paraffins (and consequently should exhibit an f value less than ½), the calculated Y values for the former should be and are closer to unity than those of the latter. The points representing Caldwell and Babb's (2) diffusion data for the systems bromobenzene-chlorobenzene, chlorobenzene-toluene, and carbon tetrachloride-benzene should yield Y values closer to unity than the line with $f = \frac{1}{2}$ predicts, since these systems represent combinations of fairly spherical molecules. Except for the diffusion of carbon tetrachloride in benzene, this trend is borne out by Figure 1.

In most cases marked deviations can be reasonably attributed to either hydrogen bonding or spherical shape effects, both of which lead to $\Delta H^j/\Delta H^*$ and f values different from the value of ½ which is represented by the line of Figure 1. The only unexplained deviations are those of the *n*-heptane diffusions, which are considerably below the line. This may be due to an orientation phenomenon (since both solvent and solute are normal hydrocarbons) which significantly influences both the value of f and the estimation of δ by Equation (18).

To illustrate the effectiveness of the

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* The data upon which Figure 1 is based are summarized in Table 1, which has been deposited as document 7416 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or for 35-mm. microfilm.

method for cases in which there is a marked difference in the solute and solvent, consider the diffusion of oleic acid in *n*-decane. This solute was one of many organic acids singled out by Ree and Eyring (*9*) because of the suspected difference in the activation energies for viscosity and diffusion. From the reported viscosities and molar volumes of the two substances at 30°C. and Equation (2), $\Delta F^*_{AA}/RT = 6.0$ and $\Delta F^*_{SS}/RT = 9.9$ (A = decane, S = oleic acid). From Equation (18) $\delta = -1.7$ kcal./mole; if one assumes that $f = ½$, the calculated value of Y is 0.42, which is in good agreement with the observed value of 0.40 obtained from the diffusion data. This is not surprising since the $\Delta H^j/\Delta H^*$ value for oleic acid is 0.48 (*1*). If the interactions are specific and strong, as would be the case for the methanol-water system, the method underestimates the deviation of Y from unity. However for the case of the diffusion of *n*-amyl alcohol in water (*9*) the calculated value of Y is 0.50, while from the diffusion data $Y = 0.40$ is obtained.

SOLID SOLUTES

The method utilized here for evaluating $\Delta F^*_\mu - \Delta F^*_D$ is applicable only to solutes which are liquids at the temperature under consideration, since ΔF^*_{SS} is computed from the viscosity of the pure liquid by Equation (2). However there is a large body of data for solid solutes to which the proposed calculation should apply if ΔF^*_{SS} were available. The diffusion data for solute iodine have been treated by assuming $f = ½$ and calculating ΔF^*_{SS} from the measured diffusion coefficients. A combination of Equations (17) and (18) shows that a plot of $\overline{(\ln Y)/}$ $(\Delta F^*_{AA}/RT)$ against $1/\sqrt{\Delta F^*_{AA}/RT}$ should yield a straight line with a slope of 0.5 $\sqrt{\Delta F^*_{SS}/RT}$ and an intercept of ½. A plot of this type is shown in Figure 2. One could draw the lines through the two sets of points by assuming $f = ½$ and anchoring the line in each cluster of points. The slopes of the two lines yield $\Delta F^*_{SS}/RT = 4.66$ for the paraffin hydrocarbon solvents, and $\Delta F^*_{SS}/RT = 5.78$ for all other solvents. This is to be compared with the figure of $\Delta F^*_{SS}/RT = 5.95$ computed from viscosity and molar volume data for liquid iodine at 110°C. While the two lines merely show that the preceding development is not inconsistent with iodine diffusion data, the clear separation of the paraffin hydrocarbon solvent points from all others is of interest. The existence of two distinct ΔF^*_{SS} values for iodine (where there should only be one) indicates that the simple geometric mean averaging of the pure component interactions of solute and solvent it not applicable to iodine. This solute apparently interacts less strongly with saturated hydrocarbons than with all others. Such behavior is consistent with the frequently observed tendency for iodine to form complexes with many solvents, except paraffin hydrocarbons. Contrary to the investigation of Stokes and co-workers (*10*) the data for solvents carbon tetrachloride and benzene fell on the lower line, which suggests that these solvents form complexes with iodine.

CONCLUSIONS

The object of this study has been to demonstrate the possibility and necessity of accounting for the difference between the free energies of activation of viscosity and diffusion when one considers the transport properties of dilute systems. The method of estimating the difference is quite crude, but it suffices to demonstrate that the predictions of the absolute rate model are improved by considering $\Delta F^*_\mu - \Delta F^*_D$ values other than zero. The effect of this term is most noticeable when the solute and solvent have widely differing viscosity-molar volume products. Because of the approximate nature of the method the calculated fraction of the total activation energy required for hole formation (one half) should be considered only as a rough, although reasonable, estimate. The scatter of the points about the line of Figure 1 is attributed to the varying values of f characteristic of hydrogen-bonded and spherical molecules.

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NOTATION

D = diffusion coefficient, sq. cm./sec.
e_o = zero point energy difference, erg.
f = fraction of the total free energy of activation due to the bond-breaking or kinetic component
ΔF = change in free energy, cal./mole
ΔH = change in enthalpy, cal./mole
h = Planck's constant
k = Boltzmann constant
m = molecular mass, g.
N_{AV} = Avogadro's number
Q^*/Q = ratio of partition functions in the activated and equilibrium states
R = gas constant, cal./mole °K.
r = defined by Equation (14)
T = absolute temperature, °K.
V_o = equal to $N_{AV}\,\sigma^3$
V = molar volume, cc.
v_f = free volume in the liquid phase, cc.
Y = defined by Equation (4)

Greek Letters

ξ = average number of nearest neighbors with respect to which the solute species moves
ϵ, σ = force constants in the Lennard-Jones equation
μ = viscosity, poise
α, β = defined by Equations (15) and (12)
δ = defined by Equation (18)
$\lambda_1\lambda_2\lambda_3$ = molecular dimensions, cm.
λ_μ = jump distance for viscosity, cm.

Subscripts

μ = viscosity or self-diffusion in pure solution
D = mutual diffusion in a binary system
AA = interaction between solvent molecules
AS = interaction between solvent and solute molecules
SS = interaction between solute molecules

Superscripts

h = volumetric or hole-forming part of the viscous process
j = the kinetic or bond-breaking part of the viscous process
$*$ = total free energy or enthalpy of activation defined by Equation (2) for pure substances

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