Thermal Diffusion Coefficient and its Relation to Ordinary Diffusion Coefficient of Solutions

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Though a number of theoretical formulas regarding thermal diffusion effect of solutions or the Ludwing-Soret effect have been proposed from the standpoint of kinetic theory or thermodynamics, it seems to us that they are not accepted generally. This is the reason why one of the present writers (K. H.)(1) derived a formula, adopting the cage model to the solution and applying the activated state method to the system. According to the formula, the Soret coefficient and thermal diffusion coefficient of the solute molecules whose molecular weight is 100 were calculated to be 1×10^{-3} and 6×10^{-8} respectively at 50°, if two kilocalories were assigned to the energy of activation for crossing the cage-barrier. They fall in the range of usual experimental values of aqueous electrolyte solutions (HCl, KCl, NH_4Cl, H_2SO_4, etc.). However, this successful result contained some ambiguity due not only to the absence of reliable data on the energy of activation and other quantities of such systems, but also to the inevitable occurrence of thermal diffusion potential. Because, in the case of electrolyte solutions each ion cannot behave as a perfectly independent particle hindered by their mutual electrical action as shown experimentally.(2), (3)

Considering the matter, it is desirable to check the theory with some experimental data of non-electrolyte solutions, though they are

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(1) K. Hirota, and O. Kimura, This Bulletin, **18**, 111 (1943); *cf.*, *Chem. Abst.*, **41**, 436 (1947).

(2) K. Hirota, This Bulletin, **16**, 475 (1941).

(3) G. Guthrie, J. N. Wilson and V. Schomaker, *J. Chem. Phys.*, **17**, 310 (1949).

very few in number. However, as there appeared some reliable measurement which can meet the requirement, the present research was begun again with reference to ordinary diffusion, transforming the theoretical result into the formulas which can easily be checked experimentally.

Theoretical Formulas

a) Thermal Diffusion Coefficient.—According to the transition state method, the rate of jump of a solute molecule from a cage to a neighboring one can be given by the expression,(4)

$$\overrightarrow{\mathfrak{K}} = \frac{kT}{h}\exp\left(-\frac{\Delta H^{\ddagger}}{RT}+\frac{\Delta S^{\ddagger}}{R}\right), \quad ..(1)$$

where k, h, and R denote the Boltzmann, Planck, and gas constants, respectively, while $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ denote enthalpy of activation and entropy of activation, respectively. The transmission factor was regarded to be unity as is done usually.

Now the application of the above formula, which was deduced under the condition when the whole system is kept at constant temperature, is extended to the system in which thermal gradient exists stationarily. (The relation of the energy against distance x is shown schematically in Fig. 1.) Therefore, taking the temperatures of the equilibrium positions of initial and final cages (T and $T+t$) into consideration, the rate of translation from the initial cage to the final can approximately be given by

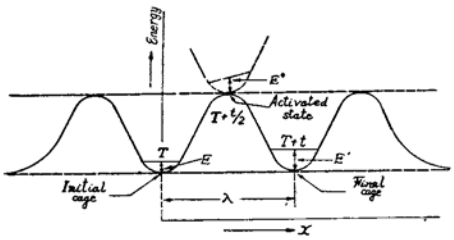

Fig. 1.—Schematic model of the cage-energy relation: Dotted lines at the activated state denotes that they are perpendicular to the plane of the paper.

$$\overrightarrow{\mathfrak{K}} = \frac{k\left(T+\frac{1}{2}t\right)}{h}\exp\left(-\frac{\Delta H^{\ddagger}}{R\left(T+\frac{1}{4}t\right)}+\frac{\Delta S^{\ddagger}}{R}\right), \quad (2)$$

because T of the exponential term can be replaced by the mean of those of T and $T+\frac{1}{2}t$, the temperature of the activated state, while kT/h in Eq. (1) is to be replaced by $k(T+\frac{1}{2}t)/h$, as it was derived from the partition function over the coordinate of the reaction path at the activated state.

As the rate formula to the opposite direction $\overleftarrow{\mathfrak{K}}$ will be similarly given by

$$\overleftarrow{\mathfrak{K}} = \frac{k\left(T+\frac{1}{2}t\right)}{h}\exp\left(-\frac{\Delta H^{\ddagger}}{R\left(T+\frac{3}{4}t\right)}+\frac{\Delta S^{\ddagger}}{R}\right), \quad (2')$$

the mean distances moved per second by the solute molecule equal to or against the temperature gradient will be $\overrightarrow{\mathfrak{K}}$ or $\overleftarrow{\mathfrak{K}}$ multiplied by the distance of the neighboring cages, λ, respectively.

The flow velocity of the solute molecules, whose concentration c is so small that the flow of solvent is negligible, will be given by

$$v = c\lambda(\overrightarrow{\mathfrak{K}}-\overleftarrow{\mathfrak{K}}), \quad \ldots\ldots\ldots\ldots(3)$$

if $\mathrm{d}\Delta H^{\ddagger}/\mathrm{d}T$ and $\mathrm{d}\Delta S^{\ddagger}/\mathrm{d}T$ are assumed to be the quantities considered in the higher order of approximation.

Phenomenologically thermal diffusion coefficient D' in solution is defined by the proportional constant in the expression of diffusion flow v, which is produced by the temperature gradient $\mathrm{d}T/\mathrm{d}x$.

$$v = -D'c(\mathrm{d}T/\mathrm{d}x). \quad \ldots\ldots\ldots\ldots(4)$$

Thus from Eqs. (3) and (4),

$$D' = -(\mathrm{d}x/\mathrm{d}T)\cdot(\overrightarrow{\mathfrak{K}}-\overleftarrow{\mathfrak{K}}). \quad \ldots\ldots(5)$$

Considering that

$$\exp\frac{-\Delta H^{\ddagger}}{R\left(T+\frac{1}{4}t\right)}-\exp\frac{-\Delta H^{\ddagger}}{R\left(T+\frac{3}{4}t\right)} \simeq \frac{-t\Delta H^{\ddagger}}{2RT}\exp\frac{-\Delta H^{\ddagger}}{RT} \quad \ldots\ldots(6)$$

and

$$\frac{\mathrm{d}T}{\mathrm{d}x} = \frac{t}{\lambda}, \quad \ldots\ldots\ldots\ldots(7)$$

we obtain from Eqs. (2), (2') and (5)

$$D' = \frac{\lambda^2 k}{2h}\frac{\Delta H^{\ddagger}}{RT}\exp\left(\frac{-\Delta H^{\ddagger}}{RT}+\frac{\Delta S^{\ddagger}}{R}\right). \quad (8)$$

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(4) Glasstone, Laidler and Eyring, "Theory of Rate Processes," 1941, p. 522.

b) Relations between Thermal Diffusion and Ordinary Diffusion.—The ordinary diffusion coefficient D was derived theoretically by Eyring and others as follows:$^{(5)}$

$$D=\frac{\lambda^2kT}{h}\exp\left(\frac{-\Delta H^{\neq}}{RT}+\frac{\Delta S^{\neq}}{R}\right). \quad ..(9)$$

Differentiating Eq. (9) with respect to T, we obtain easily from Eqs. (8) and (9)

$$D'=\frac{1}{2}\left(\frac{\mathrm{d}D}{\mathrm{d}T}-\frac{D}{T}\right). \quad \ldots\ldots..(10)$$

Soret coefficient defined by D'/D, therefore, can be expressed by

$$\text{Soret Coef.}=\frac{1}{2}(\mathrm{d}\ln D/\mathrm{d}T-1/T). \quad (11)$$

For convenience sake of discussion in the last article, the corresponding formulas of Wirtz,$^{(6)}$ who also used the cage model and applied the method of elementary kinetic theory, will be cited, *i. e.*,

$$D'=\mathrm{d}D/\mathrm{d}T, \ldots\ldots\ldots\ldots\ldots\ldots(12)$$

$$\text{Soret Coef.}=\mathrm{d}\ln D/\mathrm{d}T. \ldots\ldots..(13)$$

Experimental Method of Evaluating $\Delta H^{\neq}$, $\Delta S^{\neq}$, etc.

In order to determine the theoretical D', it is necessary to evaluate λ, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ in Eq. (8). The most direct way to meet the requirement is to make use of the data of ordinary diffusion, because the temperature dependence of thermal diffusion is not studied yet in details. But with the exception of mannitol, there is no system whose measurement on D as well as D' has been carried out over so wide a temperature range that $\Delta H^{\neq}$ can be determined by plotting in (D/T) against $1/T$ to make use of Eq. (9).

The second way of estimating is afforded by viscosity η. According to the transition state theory, it is given by the formula

$$\frac{1}{\eta}=\frac{\lambda_x\lambda_y\lambda^2}{\lambda_z h}\exp\left(\frac{-\Delta H^{\neq}}{RT}+\frac{\Delta S^{\neq}}{R}\right), \quad (14)$$

where λ_x is the distance between the two adjacent layers of molecules (sliding each other), while λ_y and λ_z are perpendicular distances between the neighboring positions in the plane perpendicular to the shearing motion. By a number of researches viscosity has been measured over such a wide and various temperature range that $\Delta H^{\neq}$ can be determined easily, but to our inconvenience it is difficult to know the required term $\exp(\Delta S^{\neq}/R)$. Because, even if the factor independent from temperature in Eq. (14) is determined experimentally, the factors λ_x, λ_y and λ_z and therefore their product $\lambda_x\lambda_y\lambda_z^{-1}$ are hard to be estimated from the other source of data.

The third method of estimation is based on the dielectric relaxation. According to Eyring, the so-called relaxation time τ_0 is given by

$$\frac{1}{\tau_0}=\left(\frac{kT}{h}\right)\exp\left(\frac{-\Delta H^{\neq}}{RT}+\frac{\Delta S^{\neq}}{R}\right)..(15)$$

Strictly speaking, these remains an important question if $\Delta H^{\neq}$ and $\Delta S^{\neq}$ evaluated by these three methods can be identified to those of thermal diffusion, because the mechanisms of these rate processes are not the same. Actually it was shown experimentally by the studies on the relation between τ_0 and η.$^{(9)}$

However, as it seems that $\Delta H^{\neq}$ and $\Delta S^{\neq}$ can be estimated easily by the third method, the result obtained by the method will be used in the next paragraph for the check of Eq. (8). This attempt may, however, be admitted as the first approximation; because the solute molecule which rotates in the alternating electric field seems to produce as much disturbance on solvent molecules as that when the former jumps over the cage barrier, considering the situation that it is forced to rotate making the part of dipole which does not locate at the molecular center in the present ases.

Comparison of the Theoretical Diffusion Coefficient with the Observed

Recently, Higasi and Nukasawa$^{(10)}$ determined $\Delta H^{\neq}$ and $\Delta S^{\neq}$ of the solutions of cane sugar and ethyl alcohol by measuring their complex dielectric constants at 0–30°, using the electric wave of 10.45 cm. in wave length and arranging the data by the Cole-Cole method. Their results are shown in the second and third columns of Table 1. For the sake of reference, the values of $\Delta H^{\neq}$ obtained from

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(5) G., L., and E., *ibid.*, p. 524.

(6) K. Wirtz, *Naturwiss.*, **27**, 369 (1939); *Ann. Phys.*, **36**, 295 (1939).

(7) G. L. E., *ibid.*, p. 483.

(8) G. L. E., *ibid.*, p. 548.

(9) A. Bondi. *J. Chem. Phys.*, **14**, 541 (1946); Kauzmann, *Rev. Mod. Phys.*, **14**, 12 (1942); C. P. Smyth, *et al.*, *J. Am. Chem. Soc.*, **72**, 3447 (1950); **70**, 4102 (1948).

(10) K. Higasi and K. Nukasawa, unpublished result. Difference of the data between the preliminary report (*J. Chem. Phys.* **18**, 561 (1950)) and the present was brought about by the change of evaluation of their data.

viscosity data are shown in the fourth column of the table. They coincide with those obtained from relaxation time satisfactorily.

Table 1

Experimental Check of Eq. (8)

System	$\Delta H^{\ddagger}$ Calc. from τ_0, kcal.	$\Delta S^{\ddagger}$ Calc. from τ_0, E. U.	$\Delta H^{\ddagger}$ Calc. from η, kcal.	D' Calc., $\times 10^8$	D' Obs., $\times 10^8$
Ethyl alcohol (20wt%) -water	6.0	10	5.3	8	1.5 (40°C.)*
Cane sugar (10wt%) -water	5.4	9.7	4.3	7	0.34 (30°C.)**

* P. F. van Velden, H. G. P. van der Voort and C. J. Gorter, *Physica*, **12**, 151 (1946).

** J. van Dranen and F. Bergsma, *Physica*, **13**, 558 (1947).

On the other hand, thermal diffusion coefficients of ethyl alcohol and cane sugar in aqueous solution are calculated according to Eq. (8), by the use of 1.44 Å. (0°) –1.47 Å. (45°) as the distance between the two neighboring cages.(11) They are given in the fifth column of Table 1. It will be seen that the calculated value of ethyl alcohol (8×10^{-8}) is of the same order of magnitude as the experimental (1.5×10^{-8}) at 40°. However, the calculated value of cane sugar (7×10^{-8}) is larger at least by twenty times than the experimental one (3.4×10^{-9}).

A possible cause of such disagreement will be due, besides the neglect of transmission factor, not only to the use of the molecular diameter of water as λ, but also to the assumptions made in the theory, *i. e.*, substitution of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ determined from dielectric relaxation time for those of thermal diffusion. In fact, though the hindrance during diople rotation, which is brought about by electric force, may be large, the energy required seems to be less than that of making a sufficiently large hole in the neighboring cage crossing the potential barrier of the cage, while the entropy required will be also different in both phenomena. Considering the situation, the above agreement can be said to be satisfactory.

As the alternative cause of disagreement, the mechanism similar to that of ordinary diffusion must be mentioned; *i. e.*, according to Eyring the diffusion of large solute molecules is realized by the successive movement of small solvent molecules around the solute molecule. It will be shown by the discussion in the next paragraph, which is the more plausible cause of the two.

Relation of Ordinary Diffusion Coefficients with Thermal Diffusion Coefficients

First, aqueous solutions of mannitol (0.01 mole/liter) and cane sugar (10 wt %) will be discussed as the example of the non-electrolyte solution, in order to check Eq. (10). Regarding the solution of mannitol, the Soret coefficient was measured carefully over the wide concentration range down to infinite dilution, while the diffusion coefficient was determined over the temperature ranges between 0° and 60°.(12) Thus the enthalpy of activation obtained by plotting $\ln(D/T)$ is 4.2 kcal. as described in Table 2 together with $\mathrm{d}D/\mathrm{d}T$ at 35°. As the observed thermal diffusion coefficient is 0.6×10^{-8} at 35°, the one calculated according to Eq. (10) is given as 8×10^{-8}, the calculated is larger by twelve times than the observed. A similar result was obtained regarding to the cane sugar as is shown in the second system of Table 2.

Table 2

Experimental Check of Eq. (10)

System	Mean temp., °C.	D, $\times 10^5$	$\mathrm{d}D/\mathrm{d}T$, $\times 10^7$	$\Delta H^{\ddagger}$, kcal.
Mannitol	35	0.81	1.8	4.2
Cane sugar	15	0.36	1.06	4.8
Hydogen chloride	50	5.8	8.1	—
$AgNO_3$-KNO_3	400	4.3	0.96**	—

System	D' (calc.)	D' (obs.)
Mannitol	8×10^{-8}	0.6×10^{-8} (35°)
Cane sugar	4.7×10^{-8}	0.3×10^{-8} (30°)
Hydogen chloride	3.1×10^{-7}	1.7×10^{-7} (50°) *
$AgNO_3$-KNO_3	0.18×10^{-7}	1.5×10^{-7} (400°)

* Calculated from Soret coefficient and diffusion coefficient.

** Landolt-Börnstein, "Phys.-Chem. Tabellen," II Erg. Band, p. 199.

It is noteworthy that the above disagreement is the same in tendency as was found in the check of Eq. (8) regarding cane sugar, the molecule of which is large. Therefore, the second mechanism suggested in the last paragraph seems to be held to such systems, but it must be abandoned because the effect ascribable to the movement of small solvent

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(11) These values were determined by the self-diffusion coefficient. Eyring, *J. Chem. Phys.*, **4**, 283 (1936).

(12) Landolt-Bornstein, "Phys. Chem. Tabellen," II Erg. Band, p. 190.

molecules occurs in the case of an ordinary diffusion as well as in the case of a thermal diffusion, giving no net effect to the check of Eq. (10).

Second, hydrochloric acid will be utilized for our purpose, as the example of electrolyte solution. As shown in Table 2, the measured thermal diffusion coefficient of 1 N HCl is given to be 1.7×10^{-7} at 50°, while the calculated is 3.1×10^{-7} by the use of $\mathrm{d}D/\mathrm{d}T$ (8.1×10^{-7}), and D extrapolated at 50° (5.8×10^{-5}).(1) Such an unexpectedly good theoretical result seems to be due to the cancellation of the effect of a thermal diffusion potential by that of an ordinary diffusion potential, because both effects are included in the observed values. However, the above good coincidence could not be obtained in the last system of Table 2, *i. e.*, molten $AgNO_3$($AgNO_3$, 3%); the observed value (1.5×10^{-7}) is about seven times larger than that of the calculated.(13) The result obtained here may not be strange, considering that the system consists entirely of ions and electrical interaction is very large.

In concluding our discussion, it will be added that the calculated value by the use of Eq. (12) will become larger at least by two times than the above in every case, making the discrepancy increase by the same factor. Secondly it must be mentioned that Eq. (11) derivable from Eq. (10) was proposed already by Wereide(14) from the standpoint of the elementary kinetic theory of solution, taking the motion of solvent molecules into account. However, according to this theory, the formula can be applied only when the size of a solute molecule is much larger than that of solvent molecules, while Soret coefficient is to be negligibly small when the size of both molecules is of the same order of magnitude. The conclusion cannot be supported by the experimental result of Hirota and Kimura(15); *e. g.*, they confirmed by means of a Clusius-Dickel's thermal diffusion apparatus that though the separation of some sols (gelatine and hydrogen sulfide) was larger than that of usual electrolyte solutions, the separation of other sol (ferric hydroxide) was not observed definitely. Therefore, it is not wonderful that Wereide could not confirm his own formula experimentally regarding electrolyte solutions. According to the present theory, thermal diffusion coefficient will be given by Eq. (11) in the system whose molecule is not extremely large if compared with solvent molecules, while in the systems of large solute molecules it may become smaller than the value calculated by Eq. (11).

Summary

Theoretical formulas of thermal diffusion coefficient D' and its relation to ordinary diffusion coefficient D have been derived by applying the activated state method to the solution in which stationary thermal gradient exists. Regarding the solution of small solute molecules, whether it is electrolytic or non-electrolytic, the agreement with experimental result is good, while, regarding the solution of large solute molecule or molten salt, the discreparcy amounts to one order of magnitude.

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(13) K. Hirota and others, *J. Chem. Soc. Japan*, **64**, 811 (1943).

(14) T. Wereide, *Ann. de physique*, **2**, 55 (1914).

(15) O. Kimura and K. Hirota, *J. Chem. Soc. Japan*, **65**, 113 (1944).