Studies on the Thermal Diffusion of Solutions. I. Thermal Diffusion Coefficient of Some Inorganic Solutions.*

By Kozo HIROTA.

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I. Introduction. Generally speaking, when a temperature gradient exists in a solution, a concentration gradient is also set up. This phenomenon, which is known as the thermal diffusion of solution, or as Ludwig-Soret effect after the discoverers,(1) has been studied by several workers. Analogous phenomenon in gaseous solutions, is also predicted from the detailed studies in gas-kinetic theory by Enskog(2) and by Chapman,(3) and later demonstrated experimentally by Chapman and Dootson.(4)

Concerning the phenomenon for gases many experimental as well as theoretical works have been carried out, and they have afforded an important basis to our knowledge of the repulsive potential of the molecules.(5) Similarly, the studies on solutions might contribute to the elucidation of its constitution, but the systematic studies(6),(7),(8),(9) in this field are comparatively rare until recently. These circumstances might have been due to such experimental difficulties as the effect produced is extremly small and as continuous measurements for many days are required.

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* The main part of this paper has been published in Japanese [*J. Chem. Soc. Japan*, **62** (1941), 480].

(1) Ludwig: *Wien Akad. Ber.*, **20** (1856), 539; Soret: *Ann. chim. phys.*, (5), **22** (1881), 293.

(2) D. Enskog: *Phys. Zeit.*, **12** (1911), 533; *Ann. Phys.*, **38** (1912), 750.

(3) S. Chapman: *Proc. Roy. Soc.*, **A 93** (1916), 1; *Phil. Trans.*, **217** (1917), 157.

(4) S. Chapman and F. W. Dootson: *Phil. Mag.*, **33** (1917), 248.

(5) Chapman and Cowling: "The Mathematical Theory of Non Uniform Gases," Cambridge, (1939), 252–258.

(6) J. Chipman: *J. Am. Chem. Soc.*, **48** (1926), 2577.

(7) S. Arrhenius: *Z. phys. Chem.*, **26** (1898), 187.

(8) C. C. Tanner: *Trans. Faraday Soc.*, **23** (1927), 75.

(9) A. Eilert: *Z. anorg. Chem.*, **88** (1914), 1.

But in 1938 Clusius and Dickel⁽¹⁰⁾ devised an apparatus which could increase the small separation, caused by the effect in gaseous solutions, to such an extent as even chlorine isotopes could be separated perfectly. In the following year Clusius and Dickel,⁽¹¹⁾ as well as Korsching and Wirtz⁽¹²⁾ succeeded in an attempt to concentrate the liquid solutions with an apparatus constructed according to the same principle. This success opened out a new field of research in the study of the Ludwig-Soret effect.

The thermal diffusion phenomenon can be expressed quantitatively by the *thermal diffusion coefficient* D' which is defined by the equation: $f=D'n\frac{dT}{dx}$; f denots the flow of diffusion caused by the temperature gradient $\frac{dT}{dx}$ in the solution of concentration n. It has been considered to be inconvenient to measure D' directly, on account of the ordinary diffusion phenomenon superposed on it; i.e., the concentration gradient set up is opposed by the process of diffusion, tending to equalise the composition. When a stationary state is reached, therefore, the next relation holds:

$$D\frac{dn}{dx} = -D'n\frac{dT}{dx} ,$$

or

$$d\ln n/dT = -D'/D ,$$

D denotes the ordinary diffusion coefficient. As D'/D, or Soret constant (S.C.), can be obtained at once by the measurement of the concentration change and the temperature difference, there have been some measurement of D'/D in both, gaseous and liquid solutions, while those of D' have been scarcely done.

The object of the present paper is to devise an apparatus suitable for the direct determination of D' by the use of the thermal diffusion apparatus of Clusius and Dickel (II and III); to describe the experiments carried out for some inorganic solutions, using the apparatus devised (Art. 4 and 5); and to discuss the results thus obtained (Art. 6).

II. Theoretical Treatment of the Thermal Diffusion Apparatus. Several papers,⁽¹³⁾ in which the actions of the thermal diffusion apparatus is treated mathematically, have been published up to the present. But most of these papers, except that of Debye,⁽¹³ᵈ⁾ treated the subject from the standpoint of applying the results to gaseous solutions, and the important problem in the case of liquid solution, i.e., the problem of the degree of separation against time, has been almost put aside.

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(10) K. Clusius and G. Dickel: *Naturwiss.*, **26** (1938), 546.

(11) K. Clusius and G. Dickel: *ibid.*, **27** (1939), 148.

(12) K. Wirtz and H. Korsching: *ibid.*, **27** (1939), 110, 367.

(13) (a) W. H. Furry, R. C. Jones and L. C. Onsager: *Phys. Rev.*, **55** (1939), 1083.
(b) L. Waldman: *Naturwiss.*, **27** (1939), 230; *Z. Physik*, **114** (1939), 53.
(c) W. van der Grinten: *ibid.*, **27** (1939), 317.
(d) P. Debye: *Ann. Physik*, **36** (1939), 284.
(e) J. Bardeen: *Phys. Rev.*, **57** (1940), 35; **58** (1940), 94.

In the following paragraphs, therefore, the necessary conditions for the construction of the apparatus for measuring the thermal diffusion coefficient was discussed by the aid of the theory of Debye.

According to him, when the "equilibrium," or stationary state, is established in the solution, the concentration n' and n of the solute at the upper and the lower points, which lie apart from h vertically, are given, neglecting some small terms, by Eq. (1),

$$ln\left(\frac{n'}{n}\right)_{t=\infty} = \frac{q/120}{1+q^2/10080}\cdot\frac{D'}{D}\tau\frac{h}{a}\ , \qquad (1)$$

and

$$q = \frac{\beta g\rho\tau}{6\mu D}a^3 \qquad (2)$$

$g =$ acceleration of the gravity, $\beta =$ coefficient of expansion of the solution, ρ=density, μ=viscosity, τ=temperature difference of the wall, and a= breadth between the equidistant walls.

At time t when the stationary state is not established, n'/n can be expressed, on the conditions that $n'/n \simeq 1$ and the apparatus has no reservoirs at either end, as:

$$\frac{n'}{n} = 1+\frac{q/120}{1+q^2/10080}\cdot\frac{D'}{D}\tau\frac{h}{a}\left[1-\frac{8}{\pi^2}\sum_{\nu=0}^{\infty}\frac{exp\left\{-\frac{(2\nu+1)^2t}{\Theta}\right\}}{(2\nu+1)^2}\right], \qquad (3),$$

where Θ is defined by:

$$\Theta = \frac{h}{\pi^2 D}\frac{1}{1+q^2/10080}\ , \qquad (4)$$

and is called "Time of relaxation", which gives the order of the time of attainment of the stationary state.(14)

In case of an apparatus with reservoirs, some approximate formulae(13b)(13e) have been derived. In this paper it is assumed from the elementary consideration that, if the volume of the larger reservoir (V_l) is much larger than that of the solution flowing into the reservoir per unit time (F), Θ is enlarged by the factor V_l/F. If the relaxation time in the apparatus with reservoirs be denoted as Θ', it is expressed by the above definition as:

$$\Theta' = \Theta\cdot V_l/F\ . \qquad (5)$$

The flow velocity of the solution at a point x toward the vertical direction was given by Debye, as,

$$v = \frac{\beta g\rho\tau}{6\mu}a^2\left(\frac{x}{a}-\frac{1}{2}\right)\left[\frac{1}{4}-\left(\frac{x}{a}-\frac{1}{2}\right)^2\right], \qquad (6)$$

where the co-ordinate was selected so that the walls of the higher and the lower temperatures were the planes of $x = 0$ and $x = a$, respectively.

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(14) Numerically, Θ denotes the time when $[n'/n-1]$, attains to the value of 70.18% of $[(n'/n)_{t=\infty}-1]$ as it follows from the easy calculation.

Then F is given by the definition as,

$$F = \frac{s}{a}\int_{\frac{a}{2}}^{a} v dx = s\frac{\beta g \rho_T}{6\mu} a^2 \frac{1}{64} \tag{7}$$

where s is the area of the horizontal cross section between the walls.

It should be borne in mind here that the important approximations included in the derivation of these equations are the constancy of β, μ, D' and D against the change of temperature and of concentration and that q is a dimensionless quantity.

III. On the Construction of the Thermal Diffusion Apparatus.

Among the quantities which are contained in Eqs. (1) and (4), ρ, μ and β, except D and D', are all easily measurable and a and τ determinable from the apparatus used. Therefore, the measurement of Θ and of n'/n may give us both D and D' simultaneously in principle, though we must take account of the following difficulty in carrying out the above plan practically in case of a liquid solution.

It can be shown easily from Eqs. (1), (2) and (4) that n'/n becomes maximum, when $q \simeq 100$, and in case of a liquid solution Θ becomes very large, if n'/n takes its maximum value. For example, if we assume $D = 10^{-5}$ cm^2./sec., and $h = 100$ cm., Θ will be 5.5×10^2 days (*cf.* Debye, *l.c.*). Moreover, if the apparatus with reservoirs is used, it requires more time to attain the stationary state. This conclusion was confirmed qualitatively by the experiments of Wirtz and Korsching.(12) Such being the case, it seems practically impossible to measure D' by the use of the thermal diffusion apparatus of Clusius and Dickel, even if the concentration change produced be by no means small.(15)

We can also derive, however, from Eq. (4) that in case of large q, Θ becomes small, and that in such a case Eqs. (1) and (4) are modified into simpler forms as;

$$ln\left(\frac{n'}{n}\right)_{t=\infty} = \frac{504}{\beta g \rho}\frac{\mu h}{a^4}D', \tag{1a}$$

or

$$\left(\frac{n'}{n}\right)_{t=\infty} = 1 + \frac{504}{\beta g \rho}\frac{\mu h}{a^4}D' \quad \text{if } n'/n \simeq 1, \tag{1a'}$$

and

$$\Theta = \frac{h^2}{\pi^2 D}\frac{7680}{q^2} = \frac{h^2}{\pi^2 a^6} \times 7680\left(\frac{6\mu}{\beta g \rho_T}\right)^2 D. \tag{4a}$$

As it can be derived from Eqs. (1a), (4a), (6) and (5) that $ln(n'/n)$, Θ and Θ' are proportional to $1/a^4$, $1/a^6$ and $1/a^8$,(16) respectively, we can make Θ and especially Θ' very small without making n'/n small to the same degree, by increasing a slightly. Besides, we find the following

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(15) In water solution and with temperature difference of 60°C., q takes the value of 100, when $a \simeq 0.1$ mm. Therefore, there exists a technical difficulty, besides, to use an apparatus which produces a large separation.

(16) It is assumed that s is constant.

three important advantages in making the wall distance of the apparatus small:

(a) As D' and D appear in Eqs. (1a) and (4a) separately, these can be determined independently from each other.

(b) As τ does not appear in Eq. (1a), only small errors arise in the D' values, even if the temperature of the solution at the walls cannot be measured accurately owing to the existence of the temperature gradient in the walls as well as the existence of a fluid film adhered to the wall surface.

(c) The small degree of separation, or $n'/n \simeq 1$, favours the approximation included that β, μ, D and D' are constant against the concentration change.

From these reasons the author constructed an apparatus made of glass with a wall distance of 1.50 mm. and was able to measure the D' of liquid solutions directly, attaining the stationary state in a few hours.

IV. Performance of the Experiments. (a) *Apparatus*:—Thermal diffusion column of the type, as shown in Fig. 1, was used. The column was made of Terex glass (Boron glass) except the cooling mantel. Carbon tetrachloride (b.p. 76°C.) put in the innermost tube was boiled by electrical heatings, so that the wall of the tube served as the hotter wall, while the outer tube was kept cool at 25°C. (the mean value) from outside, thus the temperature difference is 51°C. The temperatures in the cooling mantel are regulated so as to be 20°C. and 30°C. at the entrance and at the outlet of the mantel, respectively, by the adjustment of both, the flow velocity of cooling water and the degree of the heating. These temperatures could be made constant within ±0.5°C.

The internal diameter of the outer tube and the outer one of the inner tube were 1.78 and is 2.08 cm., respectively; thus the annular breadth of the equidistant walls is 1.50 mm. The length of the walls which have the annular space (89 c.c.), is 94 cm., while the volumes of the reservoirs at the top and the bottom of the column were 100 and 23 c.c., respectively. In the experiments, the solution was introduced to the mark M, so that 28 c.c. of the solution was contained in the top reservoir.

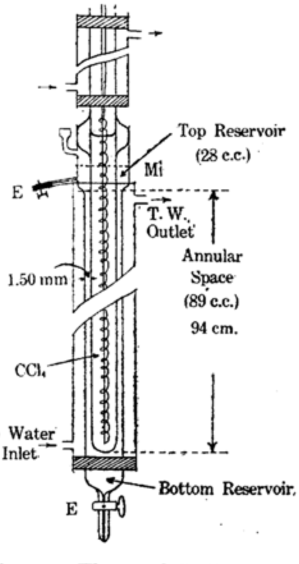

Fig. 1. Thermal Diffusion Apparatus.

The solution in the top reservoir was inclined to become warm and to interrupt the counter flow in the column there. This could be prevented by cooling it from the outside with tap water through a coil made of lead (not shown in the figure).

(b) *Samples*:—Materials, as described in Table 1, were diluted with, or dissolved in destilled water.

(c) *Procedures*:—After the sample was introduced to the mark of the apparatus, and the temperature of the cooling water was regulated at 20°C., the heating of carbon tetrachloride in the innermost tube was started; the temperature distribution in the apparatus became stationary in several minutes. At a fixed time from the beginning of heating, it was stopped, and the contents of the reservoirs were taken out from the outlets E′ and E″. After they gained the room temperature, several c.c. of samples were pipetted out and were titrated or dried up to determine the concentration in accordance with the methods as described in Table 1.

(d) *Experimental Results*:— Observed values were expressed by the separation ratio n'/n, or a ratio of the concentration at the bottom reservoirs to that at the top. Plots of the measured $(n'/n-1)$ values against the hours elapsed and lines representing the theoretical ones which were determined according to the process as described in V (b), are all shown in Fig. 2, where the ordinate of NaOH is half scaled.

Table 1. Experimental Results.

No.	Solute (conc.)	Materials Used	Analytical Method	θ'_s (hr.)	$\left(\frac{n'}{n}\right)_{t=\infty}$	$D' \times 10^{-7}$ (cm².‍/sec. deg.)
1	HCl (1 N)	Commercial pure subst. purified by destil.	Alkalimetry	0.75	1.24_8	$1._7$
1a 1b	HCl (0.1 N) ,, ,,	"de Häen" Fixanol	,, ,,	0.7	1.19_8	$1._5$
2	H_2SO_4 (1 N)	Commercial pure subst.	,,	0.5	1.23_0	$1._7$
3	NaCl (1 N)	"Shika" Extra pure	Precipitation Analysis	0.5	1.04_8	0.4
4	KCl (1 N)	"Shika" Extra pure	,,	0.9	1.04	0.3
5	NH_4Cl (1 N)	"Shika" Extra pure	,,	0.6	1.01_0	0.08
6	Na_2SO_4 (1 N)	"Shika" Extra pure	Gravitation Analysis	0.75	1.14_5	$1._1$
7	$CuSO_4$ (1 N)	"Merck" Extra pure	Iodimetry	0.5	1.12	0.7
8	Na_2CO_3 (1 N)	"Shika" Extra pure	Acidimetry	1	1.17	$1._2$
9	NaOH(17) (1 N)	"Shika" Guaranteed	,,	0.5	1.3_7	$2._6$

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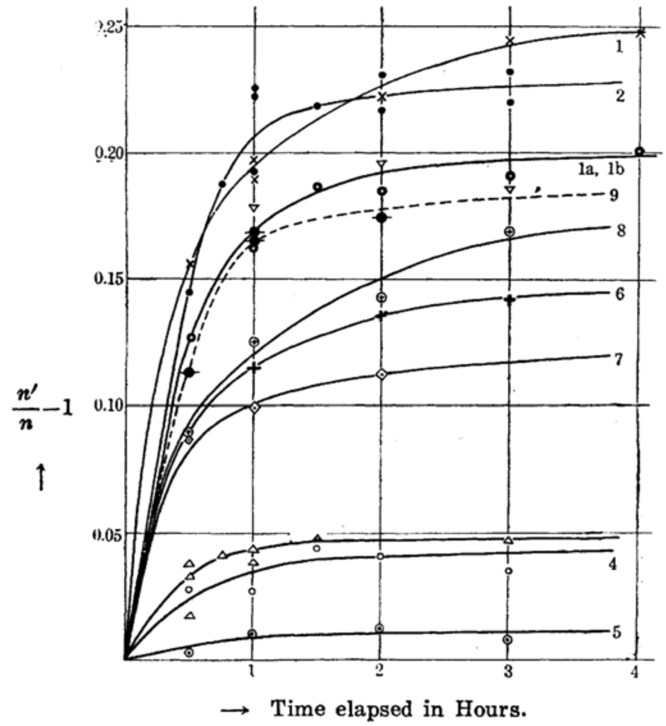
(17) The accuracy of $(n'/n)_{t=\infty}$ is worse than that of the other solutes, but that of D' is not so, because of the large value of the separation. However, there is another source of errors, i.e., the existence of a small quantity of Na_2CO_3 (0.03N) mixed in the material used. The error thus produced may not be negligible [cf. ref. (21)].

V. Discussions. (a) It was observed that in every solutions, the stationary state was reached in such a short period of few hours, as was predicted theoretically in III. The separation ratios were, however, small comparing with that of Korsching and Wirtz⁽¹²⁾, who continued their experiment for one or two days using an apparatus with a wall distance of 0.25 mm., a wall length of 90 cm. and with no reservoirs. Although the values of n'/n were smaller in this experiments, they were large enough to determine the D' values. It was thus shown that the apparatus was suitably constructed for the object.

(b) We are now going to examine the experimental results obtained with respect to the systems of 1 N HCl, 0.1 N HCl and 1 N H_2SO_4 in details before D' values are calculated for every solution.



1 × HCl, 2 ● H_2SO_4, 3 △ NaCl, 4 ○ KCl, 5 ⊙ NH_4Cl, 6 + Na_2SO_4,
7 ◈ $CuSO_4$, 8 ⊕ Na_2CO_3, 9 ● NaOH, 1a ○ HCl (0.1 N), 1b ▽ HCl (0.1 N).
Concentrations are all one normal, if otherwire stated.

Fig. 2. Experimentral Values.

To begin with, q's which were defined by Eq. (2) were calculated by taking the viscosity of pure water as 0.00549 at 50°C. and by the use of the constants as described in Table 2, and was found to be much larger than 100 as shown in Table 3. So, by Eq. (4a) instead of Eq. (4), Θ''s, the time of relaxation in case of an apparatus without reservoirs, were calculated and found to be 90,59, and 45 sec. for 1 N HCl, 0.1 N HCl and 1 N H_2SO_4, respectively. These were smaller by the factor 10^2 than the value observed, though it was natural to get such a result.

Then, F was calclulated by Eq. (7), assuming that s equals to $2\pi r$ times a, where r is the mean of the outer radius of the inner tube and the inner radius of the outer one. As it was shown that F was smaller by the same factor than V_l, Θ' was calculated by Eq. (5), as shown in Table 3, i.e., 2.1×10^2, 1.3×10^2 and 1.0×10^2 min., respectively. The agreement of Θ' with experiments was fairly good.

Table 2. Constants of Solutions (50°C.)

(Taken from Int. Crit. Tables and Landolt-Börnstein's Tables.)

No.	Solution	Specific Viscosity μ^*	Coefficient of Expansion β	Density	Diffusion(18) coefficient D
1	1 N HCl	1.10	4.5×10^{-4}	1.006	5.8×10^{-5}
1a, b	0.1 N HCl	1.00 *	4.5 *	1.002	4.6
2	1 N H_2SO_4	1.19	5.0	1.019	3.2
3	1 N NaCl	1.01	4.8	1.03	—
4	1 N KCl	1.04 **	4.8	1.03	—
5	1 N NH_4Cl	1.02	4.5	1.00	—
6	1 N Na_2SO_4	1.23	4.9	1.05	—
7	1 N $CuSO_4$	1.40 **	4.2	1.08 **	—
8	1 N Na_2CO_3	1.31 **	5.1	1.04 **	—
9	1 N NaOH	1.24	4.9	1.03	—

* The value of the pure water was substituted.
** Extrapolated values from the lower temperatures.

Table 3. Calculated Values.

	q	Θ (sec.)	F (c.c.)	Θ' (min.)	D (cm².sec.)
Eqs. used in the calculation.	(2)	(4a)	(6)	(7)	(4a), (7)
1 N HCl	3.6×10^4	90	0.20	2.1×10^2	1.2×10^{-5}
0.1 N HCl	5.0	59	0.22	1.3	1.6
1 N H_2SO_4	6.9	45	0.21	1.0	1.0

Then the thermal diffusion constant was calculated from the experimental data according to the following procedures, assuming that Θ' could be substituted for Θ: (i) to select Θ so as to give a straight line if n'/n were plotted against $\left\{1-\frac{8}{\pi^2}\sum_{\nu=0}^{\infty}\frac{\exp.[-(2\nu+1)^2t/\Theta]}{(2\nu+1)^2}\right\}$, (ii) to extrapolate the n'/n values at $t/\Theta=\infty$ from Eq. (3); (iii) to determine D' by Eq. (1). D' thus determined was shown in Table 1, together with the selected value of Θ' (denoted as Θ'_s).

As there exist no available data of D' for comparison at present, the calculated values of D'/D, or S.C., were compared with the ones calculated from the data of various workers(6),(7),(8) in Table 4, where D values used for the calculation were extrapolated from the recent measurements of Gordon and co-workers(18). Considering that temperatures are not perfectly coincident, the agreement can be said to be satisfactory.

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(18) W. J. James and A. R. Gordon: *J. Chem. Phys.*, **7** (1939), 963 [HCl]; E. A. Hollinshead and A. R. Gordon: *ibid.*, **8** (1940), 423 [H_2SO_4].

Table 4. Soret Constants.

Solute	Concentration	Temperature		Soret Const. $\times 10^{-3}\left(\frac{1}{\text{deg.}}\right)$	Author
		Range	Mean		
HCl	1 N	20~30°C	25°C	2.94	Chipman
	,,	27~67	47	2.3	Arrhenius
	,,	26~41	33	5.6	Tanner
	,,	25~76	50	2.9	The present author
HCl	0.1 N	20~30	25	2.1	Chipman
	,,	25~76	50	3.3	The present author
H_2SO_4	1 N	26~41	33	9.9	Tanher
	,,	25~76	50	5.6	The present author

Experimentally, Θ' could also be determined by the time when $(n'/n-1)$ was 70.18% of $(n'/n-1)_{t=\infty}$(19). The values, denoted as Θ'_0, were 0.7, 0.6 and 0.55 hour for 1 N HCl, 0.1 N HCl and 1 N H_2SO_4, respectively.

The ordinary diffusion coefficient could also be calculated from Eqs. (4a), (5) and from the selected Θ'_ss (or Θ'_0s), but it gave only the order of magnitude, as shown in Tables 2 and 3; this is perhaps due to the approximation included in Eq. (5). Notwithstanding, there is still some promise in applying this method, if we use an apparatus with no reservoirs, to the determination of D which is also difficult to be measured by the methods hitherto adopted.

It seems to be confirmed that the experimental results obtained are reasonable from both, the theoretical and the experimental points of view, but taking the several approximations included in consideration, this method might not give rigourously the absolutely correct values of D', although it would give the relative ones.

(c) As q's were also found to be much larger than 100 in case of other solutions, D' values were calculated according to the same procedure as described in (b), and were shown in the last column of Table 1. However, a comparison of the results in S.C. cannot be attempted, because there are no sufficiently accurate data of D at 50°C. for most of the salts at present.

Generally speaking, it was observed, (i) that a NaOH solution has very large D', (ii) that the solutions (HCl and H_2SO_4) which contain H^+ ion have comparatively larger D' values, and (iii) that the solutions (NaCl, KCl, and NH_4Cl) which contain Cl^- ion and univalent cation have smaller values. The above tendencies were known already by many workers(6),(7),(8) with respect to the Soret effect. However, this coincidence is more or less to be expected, because the difference of D of inorganic substances is not so large as that of D' (from each other). Intermediate values were observed for sulphates and carbonates (Na_2CO_3, Na_2SO_4 and $CuSO_4$), while S.C. of $CuSO_4$ did not always accord so exactly to the measurement of some workers, e.g., an extraordinarily large value was observed by Arrhenius(7),(1).

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(19) See the footnote at II.

While these results suggest, at least, that the thermal diffusion is a characteristic property of irons, an attempt to relate the degree of separation with the hydration of the ions in the solutions seems to be difficult, because the D' values of Na_2CO_3 is comparable to that of Na_2SO_4, which is more hydrated. Similarly, Hiby and Wirtz,⁽²⁰⁾ who measured the S.C. by use of the thermal diffusion apparatus (wall distance: 0.25 mm.; wall length. 10 cm.) and indicated that their method also gave reasonable S.C. values in magnitude, pointed out the same difficulty from the experimental ground; S.C. of all lithium salts used was not large, though they were known to be much hydrated in the solution, and that the opposite result would be obtained, if there was any correspondence between S.C. and the degree of hydration.

Conspicuously large D′ value of NaOH seems to be noteworthy, as acids are usually more anomalous than bases in the other properties, e.g., electrical conductivity.

Now, a series of measurements is being carried out in order to study the nature of the Ludwig-Soret effect further, and a part of the result with mixed electrolytes has been already published.⁽²¹⁾

Summary.

(1) It has been shown that the thermal diffusion apparatus of Clusions and Dickel with a comparatively large wall distance is suitable for the determination of the thermal diffusion coefficient of liquid solutions.

(2) The separations of some inorganic solutions (HCl, H_2SO_4, NaCl, KCl, NH_4Cl, Na_2CO_3, Na_2SO_4, $CuSO_4$ and NaOH) have been carried out.

(3) The observed results have been shown to be in concordance with the theory of Debye and to give reasonable Soret constants if compared with those, hitherto, directly measured.

(4) The thermal diffusion coefficient of each solution has been determined, and from these values the nature of the thermal diffusion has been discussed to some extent.

In conclusion, the author wishes to express his hearty thanks to Dr. Y. Yoshimura, Director of the Department, for his encouragements and interest throughout this research.

Department of Inorganic Chemistry, Central Laboratory,
South Manchuria Railway Company,
Dairen, Japan.

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(20) J. W. Hiby and K. Wirtz: *Phys. Zeits.*, **41** (1940), 77.

(21) K. Hirota: *J. Chem. Soc., Japan,* **62** (1941), 568; *Bull. Chem. Soc., Japan,* **16** (1941), 232.