A Theory of the Ludwig-Soret Effect.

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At present there are various theories concerning the mechanism of the Ludwig-Soret effect, i.e., the phenomenon of setting up of a concentration gradient, when a temperature gradient exists in solutions. The first theory is due to J. H. van't Hoff(1) who considered the effect purely thermodynamically and arrived at the conclusion that the effect could be expected from his well-known law of the osmotic pressure. According to this theory the concentration of the solute molecules distributes itself inversely proportional to the absolute temperature and is independent of the kind of solutions. This theory was, however, rejected both experimentally(2) and theoretically(3) by many studies. Forty years later, Eastman(4) and Wagner(5) formulated the "thermodynamics" of nonisothermal systems and tried to explain the effcet. This trial leads to plausible conclusions to some degree, but cannot be said satisfactory in the quantitative point of view, because the theory contained a quantity, heat of transfer, which was

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(1) J. H. van't Hoff, *Z. physik. Chem.*, **1** (1887), 487.
(2) S. Arrhenius, *ibid.*, **26** (1898), 187.
(3) G. S. Hartley, *Trans. Faraday Soc.*, **27** (1927), 1.
(4) E. D. Eastman, *J. Am. Chem. Soc.*, **48** (1926), 1482; **50** (1928), 292.
(5) C. Wagner, *Ann. der Physik*, [4], **3** (1928), 629; **6** (1930), 370.

hard to be determined experimentally. On the other hand, theories which can be called as molecular kinetic ones have been proposed by Chapman⁽⁶⁾ and Wereide⁽⁷⁾. These theories, however, were devoid of firm experimental evidences. Recently Wirtz⁽⁸⁾ attackd the problem, using the cage model of solutions and got to fairly reasonable results. Considering these circumstances, the present authors treated the problem after the recent theory of viscosity and diffusion of liquid, and obtained a result which was similar to that of Wirtz in some part, but was derived standing on clearer theoretical basis.

Formulation of the Theory. In our treatment it is assumed that the movement of the solute molecules are composed of random jumps from one equilibrium position to another and that some activation energy ΔE is necessary for jumping over the potential barrier as in the chemical reaction. These assumptions are similar to those of Wirtz. Then it is further assumed that the number of jumps can be given by the following rate formula:

$$\mathfrak{K} = \frac{kT}{h}\frac{Q^*}{Q}, \qquad (1)$$

according to the transition state or activated state method,⁽⁹⁾ where k and h denote the Boltzmann's and Planck's constant, respectively, and Q and Q^* the state-sums at the initial and the activated states, omitting the degree of freedom corresponding to jumps. It should be mentioned here that the last assumption includes implicitly the applicability of the above formula to such systems as the temperature is not uniform, i.e., when the temperatures of the two state-sums are different. To express the point clearer, Q or Q^* will be described hereafter as $Q(T)$ or $Q^*(T^*)$.

If we designate the distance between two adjacent equilibrium positions and the direction of the temperature gradient as λ and x, the numbers of solute molecules v passing through the y, z-plane per square centimeter in the x-direction will be given by

$$\overrightarrow{v} = c'\lambda\overrightarrow{\mathfrak{K}}, \qquad \text{or} \qquad \overleftarrow{v} = c\lambda\overleftarrow{\mathfrak{K}} \qquad (2),\ (2')$$

where c' and c denote, respectively, the number of molecules in the region before and behind the barrier, and → (and←) the sign of the crossing over it to (and against) the temperature increase t. From these equations, the following two important quantities in the Soret effect will be derived theoretically.

(1) *Soret Coefficient*. At the steady state, when the Soret "equilibrium" is reached, the number of jumps will be equal for both directions,

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(6) S. Chapman, *Proc. Roy. Soc.*, A **119** (1928), 34.

(7) T. Wereide, *Ann. des physique*, **2** (1914), 67.

(8) K. Wirtz, *Ann. der Physik*, **36** (1939), 295.

(9) H. Eyring, *J. Chem. Phys.*, **3** (1935), 107. J. Horiuti, this Bulletin, **13** (1938), 210. K. Hirota and J. Horiuti, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **34** (1938), 1174.

$$\overrightarrow{v} = \overleftarrow{v}$$

or

$$c'/c \fallingdotseq Q(T)\,/\,Q(T+t) \tag{3}$$

Adopting the approximations that the entropy term of Q's at both temperatures is equated, equation (3) is simplified as

$$c'/c = \exp\left\{\frac{\varDelta E}{R}\left(\frac{1}{T}-\frac{1}{T+t}\right)\right\}. \tag{4}$$

Considering that

$$t \ll T\,, \tag{5}$$

$$c'/c = \exp\left\{\frac{\varDelta E}{RT^2}\,t\right\}. \tag{4'}$$

The above relation holds between each successive layers. As there are L/λ layers in the interval L, the contraction ratio N'/N caused by the temperature difference ΔT between the interval will be.

$$\frac{N'}{N} = \left(\frac{c'}{c}\right)^{\frac{L}{\lambda}} = \left[\exp\left\{\frac{\varDelta E}{RT^2}\,t\right\}\right]^{\frac{L}{\lambda}} = \exp\left\{\frac{\varDelta E}{RT^2}\,\frac{t}{\lambda}\,L\right\} \tag{6}$$

Approximating that the temperature gradient is constant,

$$t/\lambda = \varDelta T/L\,.$$

Then we have,

$$\frac{N'}{N} = \exp\left\{\frac{\varDelta E}{RT^2}\,\varDelta T\right\}, \tag{6'}$$

or by definition,

$$SC. = \frac{1}{\varDelta T}\,\frac{N'-N}{N} = \frac{\varDelta E}{RT^2}\,. \tag{7}$$

It is remarkable that the result obtained here coincides with that of Wirtz.

(2) *Thermal Diffusion Coefficient.* Usually thermal diffusion coefficient D' is defined in solutions by the following equation,

$$v = -D'c\,\frac{dT}{dx}\,, \tag{8}$$

while by the equations (2) and (2′),

$$v = +(c'\overrightarrow{\mathfrak{R}} - c\overleftarrow{\mathfrak{R}})\,\lambda \fallingdotseq +c(\overrightarrow{\mathfrak{R}} - \overleftarrow{\mathfrak{R}})\,\lambda \tag{9}$$

From equations (1), (8) and (9), we obtain

$$D' = \frac{\lambda}{dT/dx}\,(\overleftarrow{\mathfrak{R}} - \overrightarrow{\mathfrak{R}})\,. \tag{10}$$

According to Eyring, following relations can be derived,⁽¹⁰⁾

$$\overrightarrow{\mathfrak{R}} = \frac{kT}{h}\,\frac{Q^*(T^*)}{Q(T)} \doteqdot \left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} \frac{1}{v_f^{\frac{1}{3}}}\, e^{-\frac{\Delta E}{RT}} \tag{11}$$

$$\overleftarrow{\mathfrak{R}} = \frac{k(T+t)}{h}\cdot\frac{Q^*(T^*)}{Q(T+t)} \doteqdot \left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} \frac{1}{v_f^{\frac{1}{3}}}\, e^{-\frac{\Delta E}{R(T+\frac{1}{2}t)}} \tag{11'}$$

where v_f denotes the free volume and m the molecular weight of the solute⁽¹¹⁾. Then we have

$$D' = \frac{-\lambda}{dT/dx}\left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} \frac{1}{v_f^{\frac{1}{3}}}\left(e^{-\frac{\Delta E}{RT}} - e^{-\frac{\Delta E}{R(T+\frac{1}{2}t)}}\right) \tag{12}$$

considering that

$$\exp\left\{-\frac{\Delta E}{R}\left(\frac{1}{T} - \frac{1}{T+\dfrac{1}{2}t}\right)\right\} \doteqdot \frac{\Delta Et}{2RT^2}\exp\left\{-\frac{\Delta E}{RT}\right\},$$

and $$dT/dx = -t/\lambda\,,$$

equation (12) can be simplified into

$$D' = \left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} \frac{\lambda^2}{v_f^{\frac{1}{3}}}\,\frac{\Delta E}{2RT^2}\, e^{-\frac{\Delta E}{RT}}\,, \tag{13}$$

Comparison with the Experimental Values and Discussion. According to Eyring⁽¹²⁾ and Polissar⁽¹³⁾, ΔE lies between 1–5 kcal. for most of the solutions, 2 kcal. is adopted as the mean value of ΔE, while other constants such values:

$$T = 50°\text{C}, \quad \Delta T = 10°, \quad \lambda^2/v_f^{\frac{1}{3}} = 2\times10^{-8}, \quad m = 100,$$

are adopted preliminary. Then Soret coefficient and thermal diffusion coefficient thus calculated according to equations (7) and (13) are found to be 1×10^{-2} and 6×10^{-8}, respectively. In Tables 1 and 2, the experimental values of $SC.$ and D', principally of electrolytes, by various authors are given. Though the magnitudes of these values are diversified, the calculated values are about of such order that the coincidence can be regarded quite satisfactory. Considering that some complexity must be caused by the electrical interaction between ions as comfirmed by one of the present

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(10) H. Eyring and others, *J. Chem. Phys.*, **5**(1937), 726; **4**(1936), 283.

(11) Approximately the temperature of the activated state will be the mean value of the initial and the final state from the reason of symmertry.

(12) R. H. Ewell and H. Eyring, *J. Chem. Phys.*, **5**(1937), 726.

(13) M. J. Polissar, *J. Chem. Phys.*, **6**(1938), 833.

authors(14), the above coincidence may be rather too fortuitous. As the theory will hold more strictly for non-electrolyte solutions, comparison in such cases is desirable, though the experimental data are lacking now.

Table 1. Soret Coefficient.

Concentration: about one mole per 1000 c.c. of solution.

Solute	Solvent	Authors	Temperature (°C.)		S. C. $\times 10^{+3}$
			Cold	Hot	
KCl	Water	Soret(15)	20	80	1.
		Eilert(16)	10	68	1.4
		Chipman(17)	20	.30	0.2
		Tanner(18)	14	38	0.9_4
		Hiby, Wirtz(19)	30	80	6.3
HCl	Water	Eilert	10	68	1.9
		Arrhenius(20)	27	67	2.3
		Tanner	26	40	5.5_7
		Chipman	20	30	2.1
		Hirota(21)	25	76	2.9
$CuSO_4$	Water	Soret	20	80	3.5
		Arrhenius	27	67	11.4
		Chipman	20	30	$3._0$
		Tanner	24	38	10.
Glycerin	Water	Wereide(22)	21	51	2
		Tanner	24	49	2.6
Cane Sugar	Water	Weriede	21	51	3
		Tanner	25	49	1.4_5
Acetic Acid	Nitrobenzene	Eilert	11.5	70	0.4_2
Benzil	Benzene	Eilert	12	75	1.7*)

(*) 0.6 g. equivalent of benzil was dissolved in 1000 g. of benzene.

Table 2. Thermal Diffusion Coefficient D'.(21)

Concentration: formula weight per one liter of solution.

Solute	HCl	KCl	NH_4Cl	H_2SO_4	$CuSO_4$	NaOH	Na_3CO_3
$D' \times 10^{+7}$	$1._7$	0.3	0.08	$1._7$	0.7	$2._6$	$1._2$

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(14) K. Hirota, this Bulletin, **16**(1941), 232; *J. Chem. Soc. Japan*, **63**(1942), 105; **64**(1943), No. 1, 2.

(15) C. Soret, *Ann. chim. et phys.*, [5] **22**(1881), 293.

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

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

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

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

(20) S. Arrhenius, *Z. physik. Chem.*, **26**(1898), 187.

(21) K. Hirota, *this Bulletin*, **16**(1941), 475.

(22) T. Wereide, *Ann. des phys.*, **2**(1914), 55.

Summary.

A mechanism of the Ludwig-Soret effect has been proposed and formulated after the recent theory of viscosity and diffusion. The important assumption therein adopted is that the reaction rate formula can be applied even in the systems which have a temperature gradient.

Soret coefficient and thermal diffusion coefficient have been calculated theoretically and the coincidence of the calculated values with the observed has been shown quite satisfactory.

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