tivation energy for the glycylglycine is in fact somewhat lower, presumably owing to the electrophilic action of the $-NH_3^+$ group, but the entropy effect is predominant.

The rates of hydrolysis of the peptides formed from glycine and leucine decrease in the order: glycylglycine, glycylleucine, leucylglycine. In leucylglycine, the substituent between the charged group and the peptide bond is electron-releasing, counteracting the charged group and thus strengthening the peptide bond relative to glycylglycine. Thus the lower rate is due to an energy effect. The lower rate of glycylleucine, on the other hand, is due to a marked entropy effect. As is often the case with aliphatic compounds, substituent effects are not large; from the data in Table I the total range in the free energies of activation for the dipeptides is from 28.9 to 29.6 kcal. mole$^{-1}$.

All these reactions have large negative entropies of activation, probably because of the loss of freedom when the oxonium ion is "hydrogen bonded" to the peptide cation in the activated complex. It may be noted that the "solid acid," Dowex 50, is a more efficient hydrolyzing agent than an ordinary acid, lowering the heat of activation by about 0.5 kcal. and raising the entropy of activation by 4.6 e.u. It would appear that the adsorption of the peptide at the acid group of the resin may be accompanied by the release of a water molecule from the resin, so that the decrease in entropy caused by the activated adsorption is somewhat less than in the ordinary acid hydrolysis. It is of interest that Haskell and Hammett[14] found that the resin acid is less efficient than hydrochloric acid in the hydrolysis of a series of alkyl esters in 70% acetone solution, the lower entropy of activation being more significant than the changes in the energy of activation. Thomas and Davies,[15] using the same resin (Amberlite IR-100) and the same choice of alkyl esters, report that in aqueous media the resin is more efficient than hydrochloric acid as a catalyst.

Since it appears that dipeptides are more resistant to hydrolysis than higher peptides[2,16] the hydrolysis of diglycylglycine under the same experimental conditions as those for glycylglycine was measured. The average of the two rate constants for the splitting of the first bond in the tripeptide is four times as large as that for the bond in the dipeptide, a change in the entropy of activation accounting pri marily for the change in rate. Kuhn[4] found that in sodium hydroxide solutions at 20° the ratio for the same two compounds was 2:1. Without further study, however, which bond in the tripeptide is split first cannot be definitely decided.

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[14] V. C. Haskell and L. P. Hammett, This Journal, **71**, 1284 (1949).

[15] G. G. Thomas and C. W. Davies, *Nature*, **159**, 372 (1947).

[16] A. H. Gordon, A. J. P. Martin and R. L. M. Synge, *Biochem. J.*, **34**, 1369 (1941); H. N. Christensen, *J. Biol. Chem.*, **154**, 427 (1944).

WASHINGTON 17, D. C. RECEIVED FEBRUARY 3, 1951

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

# The Differential Soret Coefficient of Certain Electrolytes[1,2]

BY MANUEL GARCÍA MORÍN,[3] JOHN H. SAYLOR AND PAUL M. GROSS

A more rapid experimental method for investigating the Soret phenomenon is described. A distinction is made between the "integral" Soret coefficient which has been previously determined and the differential coefficient. The integral Soret coefficient of 0.100 *N* hydrochloric acid, sulfuric acid, lithium hydroxide, sodium hydroxide and potassium hydroxide is determined at different ranges of temperature which leads to the determination of the differential Soret coefficient of these substances at 25°, and of hydrochloric and sulfuric acids and sodium hydroxide at 35°. Using the "cage" model of the liquid state, the energy that opposes the departure of a "molecule" of 0.100 *N* hydrochloric acid from its cage at 25 and 35° is calculated as well as the energy necessary for the "molecule" to open a hole at the position of arrival. From these values, the heat of transport for HCl at 25 and 35° is evaluated.

While many physico-chemical quantities of value in the study of solutions are known with reasonable precision for a variety of solutions, for certain other quantities the available data are either of low precision or missing entirely. This is true of the Soret coefficient (or more properly the Ludwig–Soret coefficient).[4,5] A survey of the literature reveals wide discrepancies between the results obtained by different investigators, the existence of many gaps, and only limited data on the temperature dependence of this coefficient.

The present investigation points out the necessity of distinguishing between the "integral" Soret coefficients which have been previously determined and the more generally valid and useful differential coefficients. It also gives the preliminary results of the exploration of a more rapid and possibly a more generally applicable experimental method of investigating the Soret phenomenon.

In general, when a solution is subjected to a temperature gradient, a concentration gradient with opposite sign and direction appears in the solution. Each of these gradients gives rise to a flow of matter in opposite directions, so in time a steady state is attained characterized by zero net flow. If the temperature gradient is positive and has a vertical direction, the process is called the pure Soret effect. If the temperature gradient is applied in a horizontal direction, the thermogravitational effect of Clusius and Dickel[6] is obtained. The present paper deals with the determination of the Soret

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[1] This paper is taken from a thesis submitted by Manuel Garcia Morin to the Graduate School of Duke University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, June, 1948.

[2] Presented before the Division of Physical and Inorganic Chemistry at the 118th meeting of the American Chemical Society, Chicago, Illinois.

[3] Department of Chemistry, University of Puerto Rico, Rio Piedras, Puerto Rico. du Pont Predoctoral Fellow, Duke University, 1946–1948.

[4] C. Ludwig, *Sitzber Akad. Wiss. Wien*, **20**, 839 (1856).

[5] C. Soret, *Arch. sci. phys. et nat.* [3] **2**, 48 (1879); [3] **4**, 209 (1880), *Compt. rend.*, **91**, 289 (1880); *Ann. chim. phys.*, [5] **22**, 293 (1881).

[6] K. Clusius and G. Dickel, *Naturwissenschaften*, **26**, 546 (1938).

coefficient of aqueous solutions of electrolytes from observations on the pure Soret effect.

Following the conventions adopted by de Groot[7,8] the net flow in a binary solution subjected to a concentration and a temperature gradient can be expressed by

$$J_y = -D_n \rho \frac{\partial n}{\partial y} - D' \rho n n' \frac{\partial T}{\partial y} \tag{1}$$

or

$$J_y = -D_c \frac{\partial c}{\partial y} - D' \frac{cc'}{\rho} \frac{\partial T}{\partial y} \tag{2}$$

where $J_y$ represents the flow in the positive $y$ (vertical) direction; $\rho$ the density; $D'$ the thermodiffusion coefficient; $n$ and $n'$ the weight fractions of the components; $c$ and $c'$ the concentrations of the components in mass per unit volume; $T$ the temperature, and $D_n$ and $D_c$ the diffusion coefficients when the concentrations are expressed in weight fractions and in mass per unit volume, respectively. Equation (1) describes the flow when the concentrations are expressed in weight fractions, while equation (2) describes the flow when the concentrations are expressed in mass per unit volume. In general $D_n$ and $D_c$ are not equal.

At the steady state $J_y = 0$, and the definition of the differential Soret coefficient $s$ is obtained

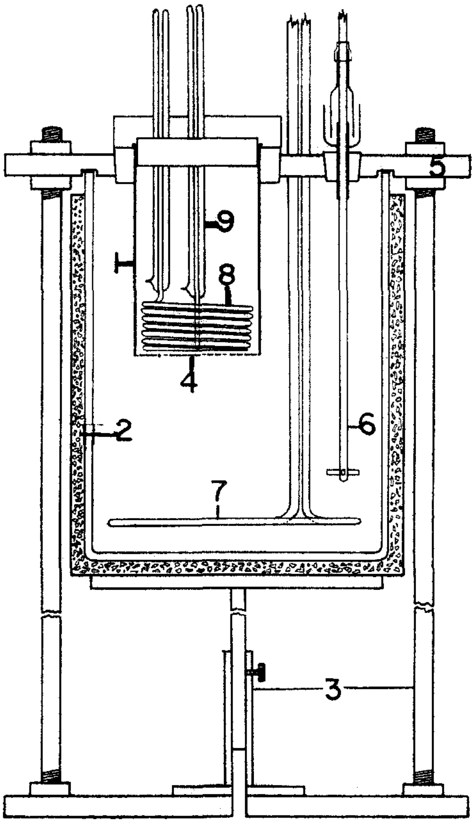

Fig. 1.—The thermodiffusion apparatus: (1) the cold chamber, (2) the hot chamber, (3) support, (4) cellophane membrane, (5) Bakelite plate, (6) stirrer, (7) heater, (8) the glass coil, (9) evacuated jacket.

$$s_n \equiv \frac{D'}{D_n} = -\frac{1}{nn'}\frac{\mathrm{d}n}{\mathrm{d}T} \tag{3}$$

$$s_c \equiv \frac{D'}{D_c} = -\frac{c + c'}{cc'}\frac{\mathrm{d}c}{\mathrm{d}T} \tag{4}$$

where $s_n$ and $s_c$ are the differential Soret coefficients when the concentrations are expressed in weight fractions and in mass per unit volume, respectively.

When equation (3) or (4) is integrated assuming $s$ independent of $T$, or when the derivative is set equal to a ratio of finite differences, the definition of the *integral* Soret coefficient $\bar{s}$ is obtained. For dilute solutions, the differential coefficient becomes

$$s_n = -\frac{1}{n}\frac{\mathrm{d}n}{\mathrm{d}T} \tag{5}$$

or

$$s_c = -\frac{1}{c}\frac{\mathrm{d}c}{\mathrm{d}T} \tag{6}$$

from which the integral coefficient is obtained as

$$\bar{s}_n = \ln \frac{n_1/n_2}{T_2 - T_1} \text{ or } \bar{s}_n = -\frac{1}{n}\frac{\Delta n}{\Delta T} \tag{7}$$

or

$$\bar{s}_c = \ln \frac{c_1/c_2}{T_2 - T_1} \text{ or } \bar{s}_c = -\frac{1}{c}\frac{\Delta c}{\Delta T} \tag{8}$$

where the subscript 1 refers to the cold end of the gradient and subscript 2 to the hot end. This distinction between differential and integral coefficients is here proposed with the purpose of clarifying the confusion existing in the literature with respect to these quantities.

All the values of the Soret coefficients found in the literature are integral coefficients determined at different mean temperatures $(T_1 + T_2)/2$, and at different values of $\Delta T$. Since $\bar{s}$ is, in general, a function of $\Delta T$ and of the mean temperature, the values of the integral coefficients are not necessarily comparable.

A determination of the differential Soret coefficient of various electrolytes in dilute solutions has been made in the present work by determining the integral Soret coefficient at a series of different $\Delta T$'s, all having a common mean temperature. A graph of these integral coefficients against $\Delta T$ yields, on extrapolation to $\Delta T = 0$, the value of the differential coefficient, since

$$\lim_{\Delta T \to 0} \bar{s}_c = \lim_{\Delta T \to 0} \frac{1}{c}\frac{\Delta c}{\Delta T} = \frac{1}{c}\frac{\mathrm{d}c}{\mathrm{d}T} = s_c \tag{9}$$

## Experimental

The integral coefficients were determined by a modification of a method originally proposed by Riehl.[9] Two portions of a solution are separated by a thin permeable membrane across which a temperature gradient is established. Stirring of the solutions shortens the length of the gradient and the steady state is reached in a comparatively short time.

A schematic diagram of a thermodiffusion unit is shown in Fig. 1. The hot chamber consists of a 3-liter insulated Pyrex jar that fits tightly into a groove cut in a one-half inch circular bakelite top. This top holds a thermoregulator, a thermometer, a condenser, a stirrer with a mercury seal and a 600-watt heater.

The cold chamber consists of a Pyrex glass cylinder 69 mm. wide and 11 cm. long which houses a stirrer (not shown in Fig. 1), a thermometer and a refrigerating coil. Each of the outlets of the coil is surrounded by an evacuated jacket which prevents freezing of water vapor from the solution on the leads. A refrigerating machine provides

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(7) S. R. de Groot, *Physica*, **9**, 699 (1942).

(8) S. R. de Groot, "L'Effect Soret," E. V. Noord-Hollandsche Uitgevers Maatschappj, Amsterdam, 1946.

(9) N. Riehl, *Z. Elektrochem.*, **49**, 306 (1943).

constant temperature refrigerant which can be circulated through the coil at different rates. A capillary vent in the cold chamber ensures atmospheric pressure and avoids evaporation or condensation of moisture. The membrane that separates the cold and the hot chambers is wrapped around the cylinder and held in place by means of a few turns of strong cotton thread. Vigorous stirring is accomplished by means of variable speed motor stirrers. It was found that the thermodiffusion is independent of the rate of stirring above a minimum value.

Several types of membranes such as parchment paper, gold beater's skin, sintered-glass of different porosities and thicknesses and different samples of cellophane were investigated. It was found that the membrane should possess the following characteristics: (a) mechanical, thermal and chemical resistance; (b) fine porosity to avoid gross streaming; (c) thickness less than 0.1 mm. in order to attain equilibrium in a short time; (d) the membrane potential between the two sides of the membrane should be the same as the thermodiffusion potential that would exist in the absence of the membrane.

Cellophane was found to be the most satisfactory. While no direct data are available as to a possible membrane effect, investigation of cellophane of different thicknesses and brands gave essentially the same results. This indicates that a membrane effect, if present, must be very small. For the isothermal case, the membrane potential and the diffusion potential for dilute solutions of HCl and KCl have been measured and found to be the same.[10]

All the measurements reported were made using non-water-proof 600-gage (0.04 mm. thick) cellophane sheets with the same sample number manufactured by du Pont de Nemours Co. All the solutions were prepared from C.P. chemicals. Sodium and lithium hydroxide solutions were prepared from concentrated carbonate free stock solutions. Potassium hydroxide solutions were prepared without removal of the carbonate, since it was shown that the small amount of carbonate present in these solutions did not affect the value of the Soret coefficient obtained. The initial concentration of these solutions was adjusted to the desired value with a precision of 5 parts per 1000 at room temperature which never varied more than ±5°. Therefore, the initial concentration was known with a precision of 1% which produced a negligible error in the Soret coefficient.

The cold and hot chambers were filled with solution to be investigated until the levels in both chambers were the same. The hot chamber was sealed tight against the bakelite top and the cold chamber was sealed with paraffin. The stirrers were turned on and the temperature gradient established by heating the hot chamber and circulating refrigerant through the coil at the proper rate. Preliminary experiments have shown that the steady state is reached in 6 to 12 hours; therefore, the system was allowed to thermodiffuse for about 24 hours to ensure the attainment of the steady state. Then samples were taken from the cold and hot chambers, brought to room temperature and analyzed. By means of the appropriate percentage–density data, the concentrations at the temperature of the cold and hot chambers were calculated and equation (8) used to find $\bar{s}_c$. Analyses of the acid and alkaline solutions were made volumetrically using calibrated apparatus.

The maximum variation in temperature throughout the cells during the course of an experiment was ±0.2° for the hot cell and ±0.3° for the cold cell. The uncertainty in the concentration was ±1 part per 1000. From these values, the probable error in the calculated integral coefficient can be estimated to be about ±3%, or approximately $\pm 0.1 \times 10^{-3}$ for the substances investigated. The average values may have a somewhat smaller error.

## Results

Five electrolytes were studied at an initial concentration of 0.100 $N$. Hydrochloric and sulfuric acid and sodium hydroxide were studied at two mean temperatures, 25 and 35°. Lithium hydroxide and potassium hydroxide were studied at a mean temperature of 25° only. Table I shows the results obtained. Columns 4 and 6 show the ratio of the normalities $N$ and molalities $m$, respectively, of the solutions in the cold and hot chambers at equilibrium. Columns 5 and 7 give the average values of the integral Soret coefficients $\bar{s}_n$ and $\bar{s}_m$ in terms of normalities and molalities, respectively. The number $n$ of experiments averaged in each case is indicated in the last column. Within the experimental errors, the values of $\bar{s}_m$ reported are the same as for $\bar{s}_n$, the integral coefficient in terms of weight fractions.

TABLE I

INTEGRAL SORET COEFFICIENT OF ELECTROLYTES IN 0.100 $N$ SOLUTIONS

| Substance | Mean temp., °C. | $T$, °C. | $N_1/N_2$ | $\bar{s}_n \times 10^3$ degrees$^{-1}$ | $m_1/m_2$ | $\bar{s}_m \times 10^3$ degrees$^{-1}$ | $n$ |
|---|---|---|---|---|---|---|---|
| HCl | 25 | 8 | 1.026 | 3.22 | 1.024 | 2.95 | 2 |
| | 25 | 14 | 1.045 | 3.15 | 1.042 | 2.92 | 2 |
| | 25 | 20 | 1.066 | 3.22 | 1.061 | 2.98 | 4 |
| | 25 | 26 | 1.083 | 3.05 | 1.076 | 2.81 | 2 |
| | 35 | 8 | 1.030 | 3.75 | 1.028 | 3.41 | 2 |
| | 35 | 14 | 1.054 | 3.74 | 1.049 | 3.41 | 2 |
| | 35 | 20 | 1.074 | 3.55 | 1.067 | 3.22 | 2 |
| | 35 | 26 | 1.098 | 3.59 | 1.088 | 3.25 | 2 |
| $H_2SO_4$ | 25 | 8 | 1.030 | 3.70 | 1.028 | 3.42 | 2 |
| | 25 | 14 | 1.048 | 3.37 | 1.045 | 3.13 | 2 |
| | 25 | 20 | 1.073 | 3.52 | 1.068 | 3.27 | 6 |
| | 25 | 26 | 1.090 | 3.33 | 1.083 | 3.07 | 3 |
| | 35 | 8 | 1.032 | 3.99 | 1.030 | 3.65 | 4 |
| | 35 | 14 | 1.060 | 4.13 | 1.055 | 3.80 | 2 |
| | 35 | 20 | 1.080 | 3.86 | 1.073 | 3.52 | 2 |
| | 35 | 26 | 1.102 | 3.73 | 1.092 | 3.38 | 2 |
| LiOH | 25 | 8 | 1.031 | 3.79 | 1.029 | 3.53 | 2 |
| | 25 | 14 | 1.053 | 3.67 | 1.049 | 3.41 | 4 |
| | 25 | 20 | 1.078 | 3.75 | 1.072 | 3.50 | 4 |
| | 25 | 26 | 1.100 | 3.66 | 1.093 | 3.40 | 3 |
| NaOH | 25 | 8 | 1.041 | 5.05 | 1.039 | 4.80 | 6 |
| | 25 | 14 | 1.072 | 4.96 | 1.068 | 4.70 | 6 |
| | 25 | 20 | 1.100 | 4.76 | 1.094 | 4.50 | 8 |
| | 25 | 26 | 1.132 | 4.77 | 1.124 | 4.50 | 6 |
| | 35 | 8 | 1.043 | 5.27 | 1.040 | 4.92 | 4 |
| | 35 | 14 | 1.077 | 5.32 | 1.072 | 4.97 | 2 |
| | 35 | 20 | 1.106 | 5.04 | 1.098 | 4.68 | 2 |
| | 35 | 26 | 1.134 | 4.83 | 1.123 | 4.47 | 2 |
| KOH | 25 | 8 | 1.039 | 4.75 | 1.037 | 4.50 | 4 |
| | 25 | 14 | 1.067 | 4.66 | 1.064 | 4.41 | 4 |
| | 25 | 20 | 1.097 | 4.63 | 1.091 | 4.37 | 8 |
| | 25 | 26 | 1.127 | 4.60 | 1.120 | 4.35 | 6 |

In Fig. 2 the integral coefficients, rounded to the nearest $0.05 \times 10^{-3}$, are plotted against $\Delta T$. The differential coefficients are obtained from these graphs as the value of the intercept at $\Delta T = 0$ and are shown in Table II. In the last column of this table are given the values of the thermodiffusion coefficient $D'$ calculated from values of the diffusion coefficients ($D_N$) taken from the literature. In this calculation the definition of $s_c$, equation (4), has been used. The value of $D_N$ used in the calculation of $D'$ for hydrochloric and sulfuric acids has been obtained from the data of Gordon and represents a differential diffusion coefficient determined at the same conditions of temperature and concentration as the corresponding $s_N$. The data used for the calculation of $D'$ for the hydroxides corre-

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[10] E. B. R. Prideaux, *Trans. Faraday Soc.*, **38**, 121 (1942).

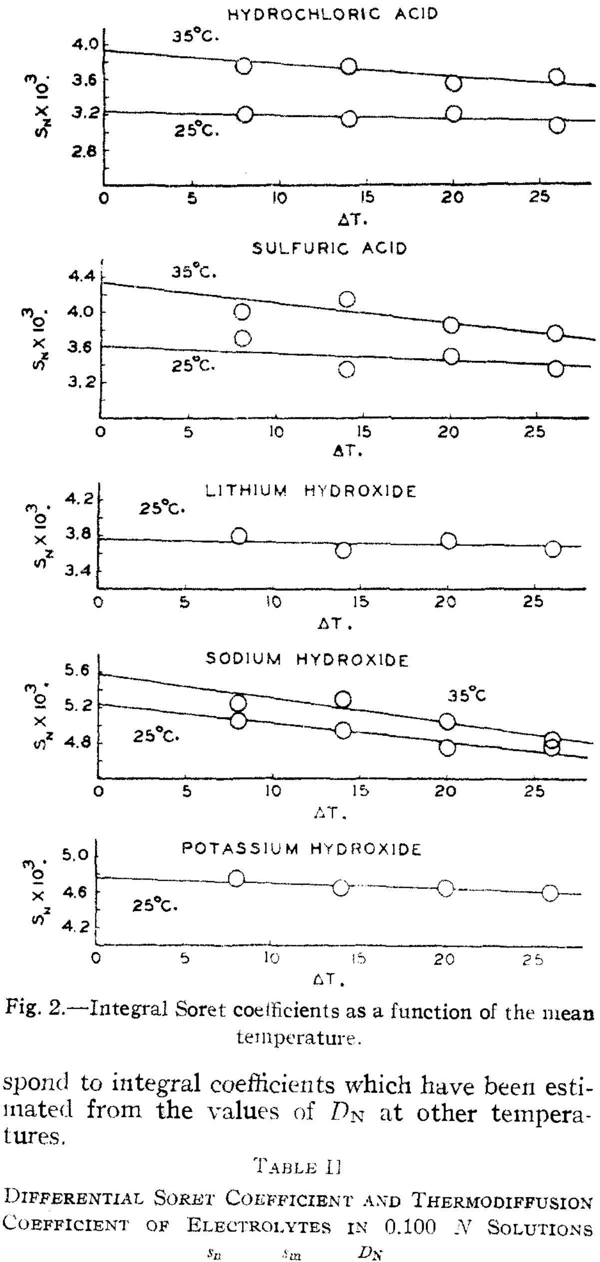

Fig. 2.—Integral Soret coefficients as a function of the mean temperature.

spond to integral coefficients which have been estimated from the values of $D_N$ at other temperatures.

TABLE II

DIFFERENTIAL SORET COEFFICIENT AND THERMODIFFUSION COEFFICIENT OF ELECTROLYTES IN 0.100 $N$ SOLUTIONS

| Substance | Temp., °C. | $s_n \times 10^3$ degrees$^{-1}$ | $s_m \times 10^3$ degrees$^{-1}$ | $D_N \times 10^5$ cm.$^2$ sec.$^{-1}$ | Ref. | $D' \times 10^8$ cm.$^2$ sec.$^{-1}$ deg.$^{-1}$ |
|---|---|---|---|---|---|---|
| HCl | 25 | 3.2 | 3.0 | 2.9 | 11 | 9.3 |
| | 35 | 3.9 | 3.6 | 3.6 | 11 | 14.0 |
| $H_2SO_4$ | 25 | 3.6 | 3.3 | 1.8 | 12 | 6.5 |
| | 35 | 4.3 | 4.0 | 2.3 | 12 | 9.9 |
| LiOH | 25 | 3.8 | 3.5 | 1.4 | 13 | 5.3 |
| NaOH | 25 | 5.2 | 5.0 | 1.8 | 14 | 9.4 |
| | 35 | 5.6 | 5.3 | 2.2 | 14 | 12.3 |
| KOH | 25 | 4.8 | 4.5 | 2.5 | 14 | 12.0 |

## Discussion of Results

For the substances studied, the results show that the differential Soret coefficient is a function of the temperature, increasing as the temperature increases in the range of temperature 25–35°. For lithium and potassium hydroxides at 25° the integral Soret coefficient shows small dependence upon the magnitude of $\Delta T$ in the range $8° \leqq \Delta T \leqq 26°$, provided the $\Delta T$'s have a common mean temperature For these substances, therefore, the values of the differential and integral coefficients do not differ greatly. For the other substances studied, especially sodium hydroxide, a much greater dependence upon the integral coefficient and the magnitude of $\Delta T$ is observed. This demonstrates the importance of the determination of the differential coefficients.

Due to this dependence of $s$ and $\bar{s}$ on $T$ and $\Delta T$, it is difficult to compare the values obtained in this work with the values in the literature. Since this work was done Huse, Trevoy and Drickamer[15] have described a somewhat similar type of apparatus with a fritted glass disc. They obtain somewhat higher results for 0.100 $N$ HCl but the agreement with our data is better than with that of previous investigators. In general the values found in the present work are higher than the values of Chipman,[16] but lower than those of Tanner.[17] The method used by Chipman is such that low values would probably be obtained. In this method attainment of the steady state observed requires from 4 to 6 weeks (and sometimes much more) and is investigated for only one day to check for its constancy; in the present method, however, a much longer time, proportionally, is allowed, since attainment of the steady state takes about 6 to 12 hours and is then investigated for 12 to 18 hours for its constancy. The values reported by Tanner are consistently higher than all the other values in the literature.

As an illustration of the potential value of Soret effect data, the results of the present investigation can be used in connection with the data of Gordon on the diffusion coefficient of hydrochloric acid at different temperatures, to evaluate certain activation energy terms that appear in one theoretical interpretation using the "cage" model of the liquid state. According to the treatment of Wirtz and Hiby,[18] the activation energy of diffusion $q$ can be divided into two parts: (a) $q_D$, the energy that opposes the departure of a particle from its cage; and (b) $q_A$, the energy necessary for the formation of a hole in the new position where the molecule arrives. Then

$$q = q_D - q_A \qquad (10)$$

For a 1-1 electrolyte, Wirtz and Hiby obtain

$$s_c = (q'_D - q'_A + q''_D - q''_A)/2RT^2 \qquad (11)$$

where the primes and double primes refer to each ion in the electrolyte. With this notation, $\alpha$, the temperature coefficient of diffusion, becomes

$$\alpha = \frac{1}{D_c}\frac{dD_c}{dT} = \frac{q}{RT^2} = \frac{q'_D + q'_A + q''_D + q''_A}{RT^2} \qquad (12)$$

The evaluation of each of these four activation energy terms will require an equal number of inde-

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(11) W. A. James and A. R. Gordon, *J. Chem. Phys.*, **7**, 963 (1939).

(12) E. A. Hollingshead and A. R. Gordon, *ibid.*, **8**, 423 (1940).

(13) F. Voightlander, *Z. physik. Chem.*, **3**, 316 (1889).

(14) L. W. Öholm, *ibid.*, **50**, 309 (1905).

(15) Huse, Trevoy and Drickamer, *Rev. Sci. Instruments*, **21**, 60 (1950).

(16) J. Chipman, THIS JOURNAL, **48**, 2577 (1926).

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

(18) K. Wirtz and J. W. Hiby, *Physik. Z.*, **44**, 369 (1943).

pendent equations which are not available. Evaluation of each term could be made if both $s_c$ and $\alpha$ are known for four 1–1 electrolytes containing all four different ions, since a system of eight equations with eight unknowns could be written from equations (11) and (12). Another method to evaluate these quantities, perhaps more adaptable to experimental application, would be the determination of both $s_c$ and the thermoelectric coefficient at infinite time for four 1–1 electrolytes containing four different ions. A system of eight equations with eight unknowns very similar to the above could be established.[18]

There are not enough data in the literature to perform such calculations. However, it is possible to group the unknowns in equations (11) and (12) in such a way that

$$\begin{aligned} q_D' + q_D'' &= q_D \\ q_A' + q_A'' &= q_A \end{aligned} \qquad (13)$$

where $q_D$ means the net energy that opposes the departure of the anion and cation of the electrolyte, and $q_A$ the energy necessary for the formation of the holes at the new positions where they arrive. From a knowledge of $s_c$ and $\alpha$ for a 1–1 electrolyte $q_D$ and $q_A$ could be determined.

From the data of James and Gordon[11] for 0.100 $N$ HCl at 25°

$$q = q_D + q_A = 4.0 \text{ kcal. per mole}$$

and from equations (11) and (13)

$$q_D - q_A = 2(s_N)RT^2 = 2(3.2)(1.99)(298)^2 \times 10^{-3} = 0.113 \text{ kcal.}$$

from which $q_D = 2.06$ kcal. and $q_A = 1.94$ kcal.

Similar computation for HCl 0.100 $N$ at 35°, for which James and Gordon report $q = 3.8$ kcal., yields $q_D = 1.98$ kcal. and $q_A = 1.82$ kcal.

These values indicate that the energy that opposes the departure of the cation and anion of HCl from their cages is greater, but almost equal to the energy required to open holes at their positions of arrival. It is this small difference, called the heat of transport, which bears directly proportionality to the Soret coefficient. The net heat of transport $Q^*$ for the ions of HCl in 0.100 $N$ solution is found to be 120 cal. at 25° and 160 cal. at 35°.

DURHAM, N. C.

RECEIVED FEBRUARY 12, 1951

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

# The Photolysis of Acetone: Diffusion of Methyl Radicals from the Light Beam and the Activation Energy of Hydrogen Abstraction

BY A. J. C. NICHOLSON[1]

The photolysis of acetone has been studied over a wide range of temperature, pressure and light intensity. The existing theory of methane and ethane production has been shown to be valid provided the temperature is above 100°, the acetone concentration is above $10^{18}$ molecules/cc.. and the absorbed light intensity is above $10^{12.5}$ quanta/cc./sec. Under these circumstances an activation energy of 9.6 kcal. can be identified as the difference between the activation energy with which the methyl radical abstracts hydrogen from acetone and half the activation energy of the methyl–methyl recombination. Below 100°, the existing theory is inadequate and gives a false low value for this activation energy. The effect of diffusion of radicals out of the light beam, in experiments in which the light beam does not fill the reaction cell, has been investigated. The magnitude of the correction that has to be made for this effect has been established under certain specific geometrical conditions. Although it is in the right direction, this correction is too small to bring the low temperature value of the "activation energy" up to its high temperature value.

For any system containing methyl radicals and a molecule from which they can abstract hydrogen, a function, $R$, may be defined as the ratio of the rate of formation of methane to the square root of the rate of formation of ethane. Dorfman and Noyes[2] showed that, at constant temperature and pressure, $R$ was independent of the absorbed light intensity for the acetone photolysis under the conditions of their experiments. (These authors expressed this result in a different but equivalent notation.) This independence makes $R$ convenient to measure experimentally and important theoretically because a simple mechanism can be postulated to explain it. Dorfman and Noyes postulated (a) that the *only* methane and ethane producing reactions are

$$CH_3 + CH_3 \longrightarrow C_2H_6 \quad d(C_2H_6)/dt = k_1(CH_3)^2 \quad (1)$$

$$CH_3 + CH_3{\cdot}CO{\cdot}CH_3 \longrightarrow CH_4 + CH_2{\cdot}CO{\cdot}CH_3$$
$$d(CH_4)/dt = k_2(CH_3)(A) \quad (2)$$

and (b) that these two reactions are exclusively homogeneous and bimolecular and hence that

$$R/(A) = k_2/k_1^{1/2} \qquad (3)$$

Equation (3) gives the required intensity independence to $R$, enables absolute values of $k_2/k_1^{1/2}$ to be calculated, and from measurements at different temperatures gives an activation energy that should correspond to $E_2 - 1/2E_1$. It further follows that at constant temperature $R$ should vary linearly with acetone pressure. This prediction has been only partially tested experimentally.

Trotman-Dickenson and Steacie[3] have used this

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