[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE SORET EFFECT

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Introduction

When a solution is maintained for some time in a temperature gradient, the upper part being warmer than the lower, a difference in concentration in the two parts is set up. This phenomenon was first observed by Ludwig.[1] Subsequently it was more fully investigated by Soret[2] and is generally known as the Soret effect.

Van't Hoff[3] attempted to account for the phenomenon on the basis of his theory of solutions. According to his views, equilibrium is attained when the osmotic pressure becomes equal throughout the solution. This leads to the expression $C/C' = T'/T$ as the criterion of equilibrium. For the temperature interval employed by Soret the ratio of concentration in the cold end to that in the warm end should therefore be 1.205. This ratio proved to be approximately correct for cupric sulfate; for potassium, sodium and lithium chlorides, however, the average observed ratios were, respectively, 1.069, 1.054 and 1.006. The supposition that these solutions might not have reached equilibrium in the time allowed is untenable since they have a higher rate of diffusion than copper sulfate.

The experiments were repeated by Berchem,[4] using aqueous hydrochloric acid and ammonia, and with more concordant results by Arrhenius,[5] who extended the investigation to dilute solutions and obtained concentration differences both greater and less than required by the van't Hoff theory. More recently a similar set of experiments has been carried out by Wereide[6] who has shown that the Soret effect occurs in aqueous solutions of non-electrolytes. He proposes a theory based on the change in rate of diffusion with the temperature, but admits that his results are not in accord with this theory.

A similar phenomenon of "thermal diffusion" in gaseous solutions has been predicted from theoretical considerations by Chapman[7] and by

[1] Ludwig, *Wien. Akad. Ber.*, **20**, 539 (1856).

[2] Soret, *Arch. sci. phys. nat.*, **2**, 48 (1879); **4**, 209 (1880); *Ann. chim. phys.*, [5] **22**, 293 (1881).

[3] Van't Hoff, *Z. physik. Chem.*, **1**, 487 (1887).

[4] Berchem, *Compt. rend.*, **110**, 82 (1890).

[5] Arrhenius, *Ofversigt Vetensk.-Akad.-Forh.*, **2**, 61 (1894); *Z. physik. Chem.*, **26**, 187 (1898).

[6] Wereide, *Ann. phys.*, **2**, 55 (1914).

[7] Chapman, *Trans. Roy. Soc.*, **216A**, 279 (1916); *Proc. Roy. Soc.*, **93A**, 1 (1917).

Enskog[8] and experimentally verified by Chapman and Dootson,[9] Ibbs,[10] and Elliot and Masson.[11]

The object of this investigation has been to study the Soret effect in a large number of typical solutions and to extend the study to more dilute solutions than have heretofore been employed. For the sake of obtaining more accurate temperature control, a temperature difference of only 10° has been used instead of the usual interval of 30° to 60° employed by earlier investigators. An added advantage of the small interval lies in the fact that changes in concentration are reduced with a corresponding reduction in the time required for the establishment of "Soret equilibrium."[12] Conductance methods have been employed to determine changes in concentration of the dilute solutions of electrolytes. It has thus been possible, with a temperature control accurate to ± 0.01°, to measure small changes in concentration with an accuracy of about 0.02%. By placing a pair of electrodes at each end of the "Soret cell" it has been possible to observe the progress of the phenomenon and to ascertain with certainty the attainment of the steady state.

Experimental Part

Thermostats.—The thermostats employed are shown in Fig. 1. The lower thermostat is of the standard type used in this Laboratory, 86 × 43 × 43 cm. Vigorous stirring is effected by the propeller stirrer A, encased in a metal cylinder which also contains the heating unit. The upper thermostat was especially constructed for this investigation. The shelf D, an integral part of the thermostat, is of double-wall construction, having 3cm. cork-board between the walls. In the bottom of this shelf are six holes about 5 cm. in diameter, through five of which the cells were in-

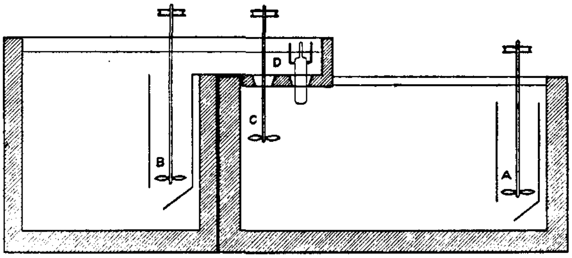

Fig. 1.—Thermostats.

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[8] Enskog, *Physik. Z.*, **12,** 538 (1911); *Ann. Physik,* **38,** 750 (1912).

[9] Chapman and Dootson, *Phil. Mag.*, [VI] **33,** 248 (1917).

[10] Ibbs, *Proc. Roy. Soc.*, **99A,** 385 (1921); **107A,** 470 (1925).

[11] Elliot and Masson, *ibid.*, **108A,** 378 (1925).

[12] The term "Soret equilibrium" will be employed to denote that state of the system in which there is no further change with time. It is not to be implied that this represents a true equilibrium in the thermodynamic sense.

serted, being supported by tightly fitting rubber stoppers. Rapid circulation of water through the thermostat and along the shelf is produced by the stirrer B and a series of baffle plates. An additional stirrer C, passing through the central hole in the shelf, serves to keep the water in the lower thermostat well stirred in the immediate vicinity of the cells. During the greater part of the investigation the temperatures of the lower and upper thermostats were maintained, respectively, at 20° and 30°. In warm weather, when it became quite difficult to maintain the lower temperature, the temperatures were changed to 25° and 35°. The temperatures were established by means of a thermometer recently calibrated by the Bureau of Standards and the variations were observed with Beckmann thermometers. Occasional variations in temperature of as much as 0.03° were observed, but by careful adjustment of the mercury regulators this was reduced to less than ± 0.01° while conductance measurements were being made. No difference in temperature could be detected between the water in the neighborhood of the cells and that in the body of the thermostats.

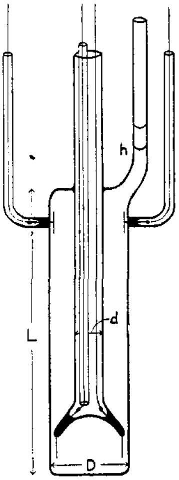

Fig. 2B.

The Cells.—Four types of cells were tried, two of which proved satisfactory. Type A was somewhat similar to B but was not of all-glass construction and was discarded after the first few trials. Type B is shown in Fig. 2B. Four electrodes of stiff platinum foil, two at each end, are sealed in by short platinum wires which are in turn welded to the copper leads. The electrodes were coated with platinum black by the method of Kohlrausch. Six cells of this type were employed; their dimensions are given in Table I. Type C was fitted with only the lower pair of electrodes, the upper half of the cell being a large bulb and the lower half a much smaller tube. Only one cell of this type was used. It required a longer time to reach equilibrium than did Type B, did not give concordant results, and finally developed a leak around the electrodes. The few results obtained with this cell seem very uncertain and will not be recorded here. Type D is shown in Fig. 2D. Samples of the solution were withdrawn from the top and bottom, respectively, and analyzed. This type of cell proved particularly useful in the work with acids and bases; for the latter, the cells were lined with paraffin.

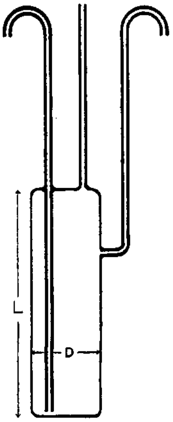

Fig. 2D.

Conductivity Set.—This was the set used by Mr. G. N. Scott in his study of the freezing points of dilute solutions. It is sufficient to note here that bridge settings could be readily duplicated within 0.005%, so

TABLE I

DIMENSIONS OF THE CELLS (SEE FIG. 2)

Type B					Type D		
No.	L, cm.	D, cm.	d, cm.	Area of electrode, cm.^{2}	No.	L, cm.	D, cm
4	13.5	3.7	1.2	1.6	2	16.5	2.9
7	15.2	3.7	1.2	1.6	3	18.0	3.8
8	14.5	4.0	1.2	0.16	4	11.6	3.8
9	13.0	4.2	1.4	.8	5	10.0	4.0
11	14.5	4.2	1.5	1.7			
12	16.3	3.4	1.5	1.6			

that the accuracy of the conductance measurements depended almost entirely upon the temperature control.

Materials.—Water was redistilled from alkaline permanganate solution and stored in resistance-glass bottles. For the very dilute solutions only freshly distilled water was used. This had on the average a specific resistance of about 10^6 ohms. The salts used were for the most part the best obtainable C. P. salts. Potassium, sodium and lithium chlorides were recrystallized once. Thallous and lanthanum sulfates were prepared from the nitrates and recrystallized. Hydrochloric and nitric acids were redistilled in an all-glass still. Potassium hydroxide was freed from carbonate by treating the concentrated hot solution with a slight excess of barium hydroxide. Lithium and thallous hydroxides were prepared from the sulfates in a similar fashion. Hydrobromic and hydriodic acids were prepared by diluting the C. P. acids. The latter was faintly colored with iodine.

Experimental Procedure.—The cell was filled to the level h (Fig. 2) and connected to the vacuum line for a short time to remove the greater part of the dissolved air. The solution was then covered with a layer of clear paraffin oil to prevent evaporation, and placed in the lower thermostat. Conductance measurements were made on the lower pair of electrodes until constant readings were obtained (generally one to two days). The cell was then transferred to the upper thermostat and constant readings were obtained on the upper pair of electrodes. The cell was placed in the temperature gradient in such a way that the supporting rubber stopper was equidistant from the two pairs of electrodes rather than exactly midway of the cell. The electrodes were in all cases not less than 3 cm. below and above the near edge of the stopper. Conductance measurements were made from time to time on both pairs of electrodes until the readings were constant for a period of at least 24 hours for the rapidly-diffusing solutes, or 48 hours for those which diffuse less rapidly. The time required for the attainment of the steady state varied from 1 to 36 days, depending on the length of the cell, the rate of diffusion and the magnitude of the Soret effect. The initial readings were then checked as follows. The cell was placed in a half-submerged position in the upper thermostat so that its upper half was at room temperature. Convection currents accomplished the work of stirring the solution to a uniform composition in a few hours. The cell was then entirely submerged, and constant readings were obtained on the upper electrodes. After transferring the cell to the lower thermostat, several days sometimes elapsed before the conductance at the lower electrodes became constant. This phenomenon is caused by "Soret diffusion" toward the outer, colder portions of the solution which settle to the bottom, thus establishing a difference in concentration at the two ends. Several days may be required for this difference to be removed by ordinary diffusion. Failure to allow a sufficient time may have caused an appreciable error in some of the earlier results.

For the Type D cells the time allowed was in general somewhat longer than was estimated to be necessary from the behavior of the Type B cells. That sufficient time was allowed is evidenced by the results in hydrochloric acid and in 0.1 *M* potassium hydroxide solution. In the latter case the shorter cell was allowed the longer time, yet the two determinations are in excellent agreement. Analyses were conducted by weight titration. Solutions of non-electrolytes were analyzed by means of the Zeiss water-interferometer, the "zero" method recommended by Adams[13] being employed.

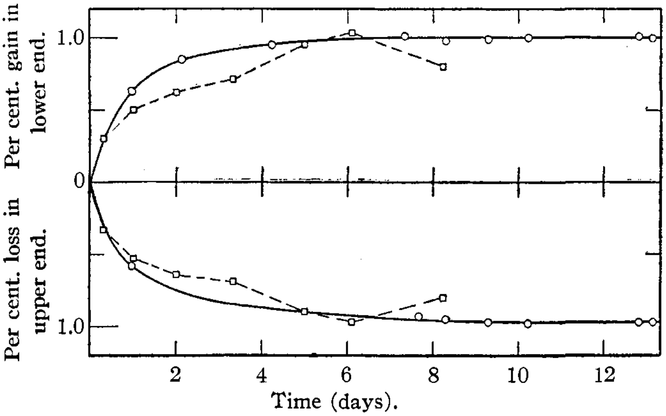

Fig. 3.—Soret effect in 0.1 *M* hydrochloric acid.

Results.—Two time-graphs are shown in Fig. 3. The upper branches represent the percentage increase in conductivity in the lower part of the cell; the lower, the decrease in the upper part. Both graphs are for 0.1 *M* hydrochloric acid in Cell 7. In obtaining the broken line, the supporting stopper in the temperature gradient was 1.6 cm. in thickness, in the other case 2.5 cm. In other experiments as well it was observed that the thicker stopper gave the more constant final value. In all the following experiments the thickness of the stopper was 2.5 cm. unless otherwise noted. Other time-graphs are shown in Fig. 4. These are of the ordinary type generally encountered, the amount of separation of the components gradually approaching a definite limiting value. These will be designated

[13] Adams, This Journal, **37**, 481 (1915).

as Type A curves. The break in the curve for sulfuric acid was caused by the breaking of the stirrer belt of the upper thermostat and the consequent fluctuations in temperature. Another type, B, was obtained when the solution reacts with the glass or is slowly adsorbed by the electrodes; for example, bases and very dilute acids. Examples of this type are given in Fig. 5. Here the ordinates are bridge-settings, the change in bridge-setting being proportional to the fractional change in conductivity. In

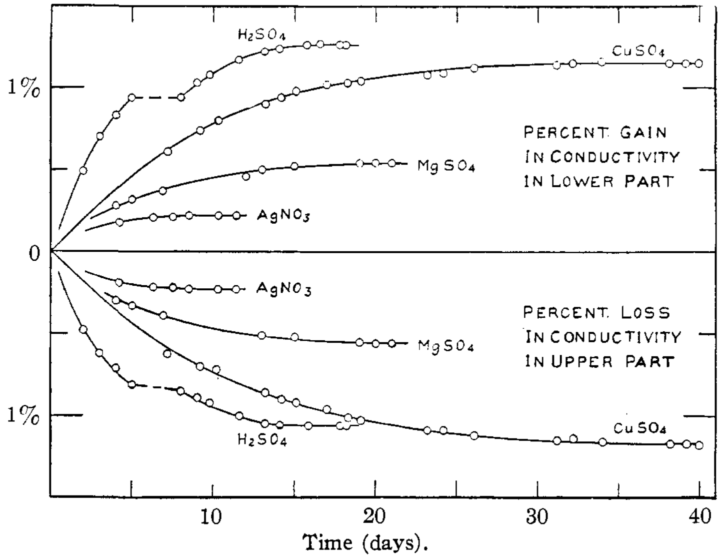

Fig. 4.—Type A curves.

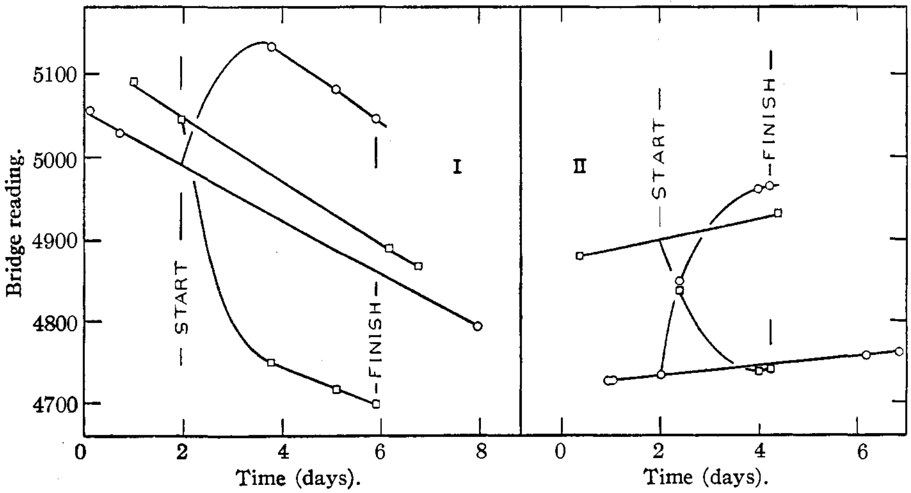

Fig. 5.—Type B curves.

Curve I (for 0.00025 *M* hydrochloric acid) there is a gradual drop in conductivity due to reaction with the glass or adsorption on the electrodes or both. In II (for 0.0002 *M* hydrochloric acid) the increase in conductivity is due to de-sorption of acid from the electrodes, the cell having been just previously used for a more concentrated solution of the same acid. For calculating the Soret effect the initial reading is interpolated between that obtained at the start and the final "check." It will be observed that the curve is approximately parallel with the interpolation line after a certain time. A third type, C, is that represented by the broken line of Fig. 3. Using a supporting stopper of 2.5 cm. thickness this type of curve was never obtained except in the more dilute solutions, and here a further increase in thickness failed to establish a more constant final value. The curves of Fig. 6 are all for 0.005 *M* sulfuric acid in Cell 12. Curves I and II were obtained under apparently identical conditions except for minor variations in the position of the cell; for Curve III the thickness of the stopper was 3.5 cm. The symmetry of the two branches precludes the possibility that the phenomenon is due to errors in measurement. Attempts to correlate the shape of the curve with vibration of the building or rate of stirring of the thermostat were unsuccessful. Moreover, in every case in which this phenomenon was observed, there were other cells in the gradient at the same time which were behaving in a perfectly normal manner. The phenomenon is doubtless to be ascribed to the accidental setting up of convection currents at the temperature boundary. In cases such as these we may say with certainty only that the

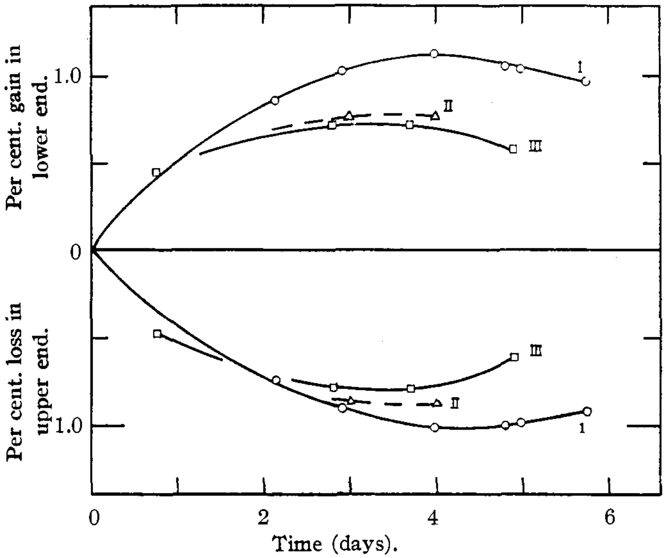

Fig. 6.—Type C curves.

true Soret effect is at least as great as that corresponding to the maximum of the curve.

Complete rate curves were not obtained in all experiments. In nearly every case, however, enough points were obtained to determine with no uncertainty the manner of behavior of the solution. In a few cases, especially where the Soret effect is small, it cannot be said with certainty whether the behavior has been normal or like Curve II of Fig. 6.

The percentage change in molality is calculated from the change in conductivity as follows. If we represent the fractional change in conductivity as $\delta L/L = \delta \ln L$, then the corresponding fractional change in molality is $\delta m/m = \delta \ln m = (\mathrm{d} \ln m/\mathrm{d} \ln L)\, \delta \ln L$. The value of the coefficient, $\mathrm{d} \ln m/\mathrm{d} \ln L$, is determined graphically with sufficient accuracy for the present purpose from the measurements of Kohlrausch and others. In general it may be said that this coefficient varies but slightly with the concentration and is nearly independent of temperature except in the case of partially ionized solutes such as sulfuric acid and cadmium chloride.

Table II contains a summary of all the determinations. Col. 2 gives the concentration expressed as gram equivalents per 1000 g. of water. Col. 3 is the percentage gain in conductivity at the lower temperature; Col. 4, the corresponding percentage loss at the higher temperature. Col. 5 is the total percentage difference in concentration under conditions of "Soret equilibrium" for the 10° interval. This column may be read as the Soret coefficient, $-\mathrm{d} \ln m/\mathrm{d}T \times 10^3$. Col. 6 is the cell number. Col. 7 is the number of days during which the cell was in the temperature gradient. Col. 8 is the number of days during which the conductivity readings were constant within the limits of experimental error. All results are for the interval 20–30° unless otherwise noted.

TABLE II

SORET EFFECT FOR 10° INTERVAL; SUMMARY OF ALL EXPERIMENTS

1	2	3	4	5	6	7	8	9	10
		Change in conductivity, %		Change in concn., %		Time, days			
Solute	Concn. N	Upper	Lower	Total	Cell	Total	Const.	Rate type	Notes
CsCl	0.1	0.10	0.12	0.23	7	24	2	C	[a]
	.1	.10	.11	.22	7	4	2	A	
KCl	.5	.07	.05	.14	8	4	..	..	
	.2	.08	.10	.19	9	24	..	B	[a]
	.1	.08	.09	.18	4	11	10	A	[a]
	.1	.05	.09	.15	7	14	..	..	[a]
	.01	.055	.07	.13	4	6	..	..	
	.002	.09	.09	.18	4	3	1	A	
NaCl	.1	.16	.13	.31	11	5	3	A	
	.1	.06	.07	.14	7	7	4	A	
	.01	.08	.09	.17	4	3	1	A	
	.002	.11	.13	.24	4	3	1	A	

TABLE II (*Continued*)

1	2	3	4	5	6	7	8	9	10
		Change in conductivity, %		Change in concn., %		Time, days			
Solute	Concn. N	Upper	Lower	Total	Cell	Total	Const.	Rate type	Notes
LiCl	.5	.02	.01	.03	9	9	3	..	
	.1	.01	.02	.03	7	7	3	A	
NH_4Cl	.1	.00	.00	.00	4	4	4	A	*a*
KBr	.1	.07	.07	.15	4	6	2	A	
	.01	.10	.13	.23	4	7	3	A	
KI	.1	.04	.04	.08	4	12	..	B	*f*
KNO_3	.1	.01	.03	.04	7	8	..	..	
$LiNO_3$	.1	.00	.00	.00	7	6	3	A	
$KClO_3$	.1	.045	.05	.10	4	4	2	A	
$MgCl_2$	.1	.09	.08	.19	11	5	2	A	
	.01	.06	.11	.18	11	5	3	A	
$BaCl_2$	.1	.14	.13	.29	11	6	..	..	
	.1	.18	.16	.36	11	26	15	A	*b,d*
	.01	.19	.15	.36	11	3	1	A	
$CdCl_2$	.1	.07	.07	.19	11	5	2	A	
$AgNO_3$	.1	.22	.23	.51	11	11	4	A	
$TlNO_3$	.1	.25	.24	.54	9	10	3	A	
$Ba(NO_3)_2$	.1	.42	.44	1.01	11	19	7	A	*c*
$Cu(NO_3)_2$	.1	.17	.19	0.40	11	7	1	A	*b,c*
$Pb(NO_3)_2$	.1	.38	.36	.90	4	8	0	A	
$La(NO_3)_3$	.1	.20	.21	.47	7	14	2	A	*c*
K_2SO_4	.1	.14	.18	.36	4	9	5	A	
Tl_2SO_4	.1	1.13	1.24	2.8	14	16	2	A	*g,c*
$MgSO_4$	.1	0.54	0.56	1.40	11	21	3	A	
	.02	.17	.20	0.45	11	5	..	C	
	.02	.18	.19	.45	11	9	6	A	
	.01	.18	.19	.44	11	8	..	..	
$CdSO_4$	.1	.97	1.07	2.66	4	34	3	A	*d*
$CuSO_4$	.1	1.15	1.17	2.97	7	40	6	A	
$La_2(SO_4)_3$	.1	1.48	1.44	3.97	7	42	4	A	*d*
HBr	.1	1.45	1.41	3.0	9	10	..	B	*f*
	.1	1.77	1.47	3.3	9	12	..	B	*c*
	.01	0.57	0.54	1.13	7	4	..	B, C	
HI	.1	1.22	1.32	2.66	9	9	..	B	*c*
HNO_3	.1	0.87	0.65	1.60	9	10	..	B	
H_2SO_4	.1	1.27	1.04	2.60	9	18	3	A	
	.01	1.11	1.01	2.20	12	6	..	C	*c*
KOH	1.0	..	..	6.2	D4	26	..	..	
	0.1	..	..	5.3	D3	10	..	..	
	.1	..	..	5.22	D4	18	..	..	
LiOH	.1	..	..	2.40	D4	21	..	..	*c*
NH_4OH	.11	..	..	0.00	D3	12	..	..	*h*
TlOH	.1	..	..	9.2	D4	30	..	..	*d*
$Ba(OH)_2$	.1	..	..	14.5	D3	14	..	..	
	.1	4.3	5.1	10.0	9	22	..	B	
Urea	.1	..	..	0.0	D5	22	..	..	*b,c*
Sugar	.1	..	..	.0	D5	30	..	..	*b,d*
HCl	13.16	..	..	.15	D6	7	..	..	

TABLE II (*Concluded*)

1 Solute	2 Concn. N	3 Change in conductivity, % Upper	4 Lower	5 Change in concn., % Total	6 Cell	7 Time, days Total	8 Const.	9 Rate type	10 Notes
	9.37	..	..	.34	D5	16	..	..	
	6.93	..	..	.52	D4	15	..	..	
	3.97	..	..	1.28	D2	24	..	..	
	2.286	..	..	2.04	D2	24	..	..	
	1.003	..	..	2.94	D2	14	..	..	
	0.76	..	..	2.17	D5	16	..	..	
	.50	..	..	2.80	D2	14	..	..	
	.20	..	..	2.27	D2	14	..	..	
	.20	0.94	0.90	1.90	9	10	..	B	f
	.10	1.03	.97	2.10	7	11	..	C	a
	.10	1.00	.97	2.07	7	13	6	A	
	.05	0.96	.76	1.76	9	11	..	B	
	.01	.73	.65	1.40	4	32	7	A, C	a
	.01	.85	1.01	1.88	4	10	..	C	
	.01	1.06	0.93	2.00	12	8	2	A	
	.005	0.58	.57	1.15	12	4	..	C	
	.001	.68	.45	1.13	11	19	..	C	a
	.001	.63	.67	1.30	11	4	..	C	
	.001	.47	.56	1.03	4	9	..	B, C	
	.00026	.83	.84	1.67	12	4	..	B	
	.00026	.70	.67	1.37	12	3	..	B	
	.0002	.88	.76	1.64	12	2	..	B	
	.00016	.35	.35	0.70	11	10	..	C	
	.00008	.85	(.80)	(1.65)	11	4	..	B	
	.00002	.55	.80	1.35	12	1	..	B	

[a] Supporting stopper, 1.8 cm. or less in thickness.

[b] Supporting stopper, 3.5 cm. in thickness.

[c] Temperature interval 23–33°.

[d] Temperature interval 25–35°.

[e] C. P. NaCl; this contained a trace of acid. For other experiments NaCl was recrystallized from the boiling solution.

[f] Experimental error larger than usual due to changes in electrode.

[g] No final check on initial reading.

[h] Zero value in this case does not indicate that there is no tendency for ammonium hydroxide to concentrate in the lower end; since the more concentrated solution has the lower density the Soret effect would be obscured by convection.

Discussion of Results

Reproducibility.—The experimental results in the very dilute solutions, especially acid solutions, are quite erratic. The 0.1 N solutions, however, show a fair degree of reproducibility. It is believed that the Soret effect is independent of the dimensions of the cell except in so far as these affect the steadiness of the final value and the occurrence of the phenomenon represented by the Type C curves. Duplicate determinations on potassium chloride and hydroxide using different cells are in good agreement. For barium hydroxide the agreement is not so good, but the variations are in the expected direction. Thus, in the all-glass cell, 9, the observed value is doubtless small on account of the rather rapid reaction on the glass; while in the case of the paraffin-lined cell, D3, it is certain that an error occurred in the opposite sense, due to the settling of a small amount of suspended barium carbonate and its consequent inclusion in the titration of the lower solution. The best indication of the independence of the Soret effect on the diameter of the cell is given by the fact that the value for 0.2 *N* hydrochloric acid in the very narrow cell, D2, lies on the same smooth curve with that for the 0.1 *N* solution in cells of much greater diameter (see Fig. 7).

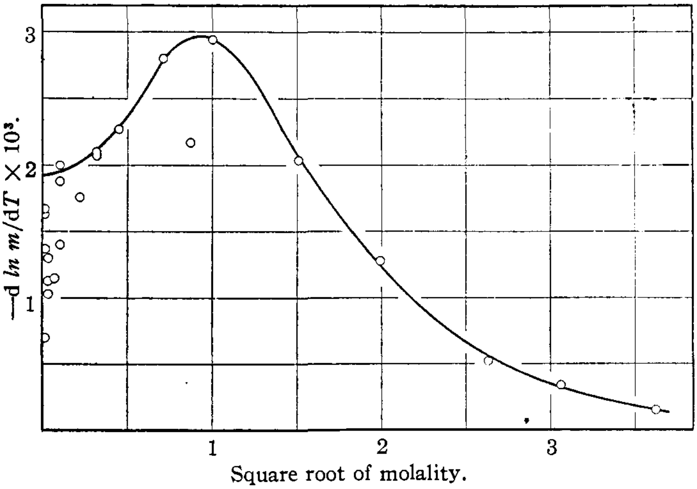

Fig. 7.—Soret coefficient in hydrochloric acid.

Effect of Concentration.—The Soret effect in hydrochloric acid was studied over a very wide range of concentration, from the very dilute solutions up to 13.16 *M*. The results are shown in Fig. 7. The Soret coefficient, $-\mathrm{d}\,ln\,m/\mathrm{d}T$, passes through a maximum at about 1 *M*. Below 0.01 *M* the results are extremely erratic; the position of the curve is, therefore, based on the result in the 0.01 *M* and 0.1 *M* solutions. It seems very probable that the limiting value of the Soret coefficient in the infinitely dilute solution has about the value shown by the curve, namely, 1.9×10^{-3}. This belief is supported by the fact that values as high as 1.65×10^{-3} were obtained at concentrations below 0.0001 *M*. The results in these dilute solutions are complicated by a reaction between acid and glass and the products of the reaction probably have a much lower Soret coefficient than has the acid itself.

Comparison of Different Solutes.—The experimental results for the 0.1 *N* solutions are collected in Table III.

The most outstanding feature of the table is that the results are not addi-

TABLE III

SORET EFFECT IN 0.1 N SOLUTIONS

(0.1 equiv. per 1000 g. of water) % per 10°, or $-\mathrm{d}\, ln\, m/\mathrm{d}T \times 10^3$

	Cl^-	Br^-	I^-	NO_3^-	ClO_3^-	SO_4^{--}	OH^-
H^+	2.1	3.1	2.7	1.6	..	2.6	...
Li^+	0.03	..	..	0.00	..	..	2.4
Na^+	.14	..	..	..	..	..	...
K^+	.17	0.15	0.08	.04	0.10	0.36	5.25
Cs^+	.23	..	..	..	..	..	...
NH_4^+	.00	..	..	..	..	..	0.00
Ag^+	..	..	..	.51	..	..	...
Tl^+	..	..	..	.54	..	2.8	9.2
Mg^{++}	.19	..	..	..	..	1.40	...
Cd^{++}	.19	..	..	..	..	2.66	...
Ba^{++}	.36	..	..	1.01	..	..	12.2
Cu^{++}	..	..	..	0.40	..	3.0	...
Pb^{++}	..	..	..	.90	..	..	...
La^{+++}	..	..	..	.47	..	4.0	...

tive. That is to say, it is not possible to assign to the ions individual Soret coefficients whose sum shall equal the coefficient for the compound. Whether or not this condition will persist in extremely dilute solutions the experiments are incapable of deciding. It seems probable, however, that the values obtained in 0.1 N solution do not differ greatly from the limiting values in the case of substances of high activity coefficient. In other cases there is doubtless considerable change in Soret effect with concentration as was observed for magnesium sulfate. It is significant that the ions can in some cases be arranged in order of increasing Soret tendency. Thus the order, NH_4^+, Li^+, Na^+, K^+, Cs^+, Ag^+, Tl^+, H^+, seems to hold, except for the sulfates of the last two. Similarly, we have the order, NO_3^-, ClO_3^-, Cl^-, I^-, Br^-, OH^-. The presence of a polyvalent ion apparently renders the situation more complicated. It is to be observed, however, that in general such salts have a higher Soret coefficient than the uni-univalent compounds, except acids and bases. Considering the general trend of the results, the coefficients for barium chloride and copper and lanthanum nitrates seem surprisingly low.

In a recent paper Eastman[14] has shown that the Soret effect cannot be predicted from the ordinary thermodynamic properties of the solution. The writer is in accord with the view expressed in this paper that the Soret coefficient is at present determinable only empirically.

Comparison with Previous Observations.—The present experiments cover a much larger number of solutions than have heretofore been investigated. In general, the Soret coefficients are of the same order of magnitude as those observed by earlier workers in this field. Some noteworthy exceptions, however, are to be pointed out. The Soret coeffi-

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[14] Eastman, THIS JOURNAL, **48,** 1482 (1926).

cients in sodium, potassium and barium chlorides are much smaller than the earlier values. Wereide reports a large Soret effect in cane sugar solutions. My experiments, on the contrary, show no appreciable effect, although a change of 0.1% could have been readily observed by the interferometer.

The Soret coefficients of thallous and barium hydroxides are the largest that have ever been recorded.

The writer desires to acknowledge his indebtedness to Professor G. N. Lewis, who suggested the investigation and under whose supervision the work was carried out. He also wishes to express his thanks to Professor E. D. Eastman for the helpful interest he has taken in the investigation.

Summary

When a solution is maintained for some time in a temperature gradient, a concentration gradient is set up. This is known as the Soret effect.

The conductance method is used to determine the fractional change in concentration at the two ends of a cylindrical vessel, the upper end being maintained at a temperature 10° higher than the lower.

The Soret coefficient, defined as the fractional change in molality per degree, or d $\ln m/dT$, has been determined for a large number of solutions. This coefficient is found to vary from zero in the case of lithium nitrate and ammonium chloride to —1.2% per degree for barium hydroxide.

No explanation of the phenomenon is offered. The Soret coefficient is regarded as being determinable only empirically.

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[CONTRIBUTION FROM THE PHYSIKALISCHES INSTITUT DER EIDGENÖSSISCHEN TECHNISCHEN HOCHSCHULE, ZÜRICH, SWITZERLAND]

THE FREE ENERGY OF HYDRATION OF IONS AND THE ELECTROSTRICTION OF THE SOLVENT

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1. Introductory

The evaluation of the free energy of hydration of an ion depends essentially upon a calculation of the difference in its potential energy in a vacuum and in water. This difference in the case of ions that do not combine chemically with water, is given practically entirely by the difference in the energy of the electrical fields that surround the ion in the two states,[2] that is, by the electrical work to be obtained at constant temperature and pressure from discharging the ion in a vacuum and subsequently charging

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[2] There is a comparatively small energy change corresponding with the compression of the solvent in the vicinity of the ion, which, however, may not be neglected. (Compare Part 3.)