Thermal Diffusion of Binary Salt Solutions. A Note on the Paper of Gillespie and Breck.

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Introduction. In previous two papers (printed in Japanese), accepted by the Chemical Society of Japan on April 17 and May 27, the present author reported the method on the determination of thermal diffusion coefficient of solutions, using an apparatus of Clusius and Dickel,(1) and discussed the data thereby obtained and also reported preliminarily an "inverse" effect found in the binary solution of NaCl–HCl.

While these papers were being translated, a journal containing a paper of Gillespie and Breck, where the similar effect (in their $FeCl_3$–HCl

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(1) K. Clusius and G. Dickel: *Naturwissenschaften*, **26** (1938), 546.

system) to that given in the author's second paper was described, came into his hand on the 3rd of June. For the purpose of comparing his result with theirs, his second paper is now translated with additional data for the HCl–NH_4Cl and a few remarks before the detailed experimental descriptions are published.

Experiments. The column consisted of two concentric boron glass tubes, having reservoirs of capacities 28 and 23 c.c. at the top and bottom ends, respectively. Width, length and volume of the annular space of the column were 1.5 mm. 94 cm. and 89 c.c., respectively. The higher temperature of the inner tube was maintained by the boiling point of carbon tetrachloride (76°C.) which was heated electrically, while the lower one of the outer tube by running water which was kept constant at 20°C. at the entrance and at 30°C. at the exit of the column, mean temperature difference thus being 51°C. The top reservoir was cooled as much as possible to protect the solution from evaporation and to circulate the solution freely.

At a fixed time after the experiment was begun, the content of each reservoirs was taken out, and the concentrations of the H^+ and Cl^- ions were analysed volumetrically, while those of the other ions were determined by the difference. The experimental results are summarised in Table 1 and 2, where every value is the mean of at least two measure-

Table 1.

$$\text{Separation Ratio}\left(=\frac{\text{Concetration at the bottom reservoir}}{\text{Concentration at the top reservoir}}\right)\text{ of HCl—}H_2SO_4\,.$$

Hours Elapsed	1			2			Infinite		
Ions	H^+	Cl^-	SO_4^{--}	H^+	Cl^-	SO_4^{--}	H^+	Cl^-	SO^{--}
1 N HCl	1.19_5	1.19_5	—	1.22	1.22	—	1.25	1.25	—
0.5 N HCl 0.5 N H_2SO_4	1.19	1.21	1.18	1.23	1.23	1.22	—	—	—
1 N H_2SO_4	1.21	—	1.21	1.23	—	1.23	1.23	—	1.23

Table 2.

Separation Ratios of HCl—NaCl and HCl—NH_4Cl.

Hours Elapsed	1			2			Infinite		
Ions	H^+	Cl^-	Na^+ or NH_4^+	H^+	Cl^-	Na^+ or NH_4^+	H^+	Cl^-	Na^+ or NH_4^+
1 N NaCl	—	1.04_3	1.04_3	1 —	1.04_7	1.04_7	—	1.04_8	1.04_8
0.5 N HCl 0.5 N NaCl	1.30_5	1.12	0.96	1.34	1.26	0.97	—	—	—
1 N HCl	1.19_5	1.19_5	—	1.22	1.22	—	1.25	1.25	—
0.5 N HCl 0.5 N NH_4Cl	1.35	1.12	0.90	1.42	1.22	0.89	—	—	—
1 N NH_4Cl	—	1.00_8	1.00_8	—	1.01_0	1.01_0	—	1.01_0	1.01_0

ments, and those of the infinite hours were estimated by extrapolation, according to the theory of Debye. It was thus observed that in the system of HCl–H_2SO_4, the separation took place additively for the component salts, and that in the systems of HCl–NaCl and HCl–NH_4Cl, the concentration of H^+ ion became larger than that in system of HCl alone, while Na^+ and $NH_4{}^+$ ions were concentrated in the top reservoir. Such an "inverse" effect occurred especially more markedly in the HCl–NH_4Cl system.

Remarks. Because the annular space was constructed larger,(*) in order to shorten the time of attainment of the stationary state, the observed effect was small when it was compared to that of Korsching and Wirtz(2) or to that of Gillespie and Breck, who used an apparatus with the annular space of 0.75 mm. and needed about one day for the attainment of the stationary state. But, as both the experimental conditions and the solutions were selected so as to be free from the ambiguity effected by creeping and hydrolysis of the solute, the "negative"(3) effect in the solutions, which contained H^+ and Cl^- ions, was confirmed without doubt.

In conclusion the author wishes to express his sincere thanks to Dr. R. Yoshimura, Director of the Department, for his interest and encouragement in carrying out this research.

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(*) The details of the reason was described in the first paper which will be translated shortly.

(2) H. Korching and K. Wirtz: *Naturwissenschaften*, **27** (1939), 367.

(3) L. J. Gillespie and S. Breck: *J. Chem. Phys.*, **9** (1941), 370.