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# Empirical Formula for Mass Transfer across the Boundary between Convections in a Two-layer System

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When a two-layer system which consists of water (upper layer) and an aqueous solution (lower layer) is heated from one side and cooled from the opposite side, a convection starts in each layer and a sharp horizontal boundary is formed by the two flows in opposite directions. The empirical formula for the transfer of a solute across the boundary was obtained by measuring the change in the concentration of a solute in the upper layer. The flux, $W_A$, of a solute, A, was expressed by

$$W_A = a_3(\Delta\rho_1 - \Delta\rho_0)D^{0.5}(\Delta c_I/\Delta\rho_2).$$

Here, $a_3$ is the mass-transfer coefficient; $\Delta\rho_1$, the density difference between the liquid on the heated wall and that on the cooled wall; $\Delta\rho_0$, the value of $\Delta\rho_1$ at which the convections start; $D$, the diffusion coefficient of a solute; and $\Delta c_I$ and $\Delta\rho_2$, the concentration difference and the density difference, respectively, between the solution of the upper layer and that of the lower layer.

When a two-layer system which consists of water (A) and an aqueous solution (B) is heated from one side and cooled from the opposite side, the liquid adjacent to the hot vertical surface moves upward, while that adjacent to the cool vertical surface moves downward. A convection starts in each layer, and a sharp horizontal boundary is formed by the two flows in opposite directions, as is shown in Fig. 1. Two papers[1,2] have been published on this phenomenon, but no attempts have been made to estimate the rate of transfer of a solute across the boundary. This paper will describe the empirical formula of mass transfer in our model.

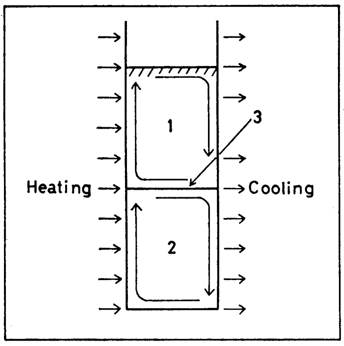

Fig. 1. Schematic illustration of the convections in two-layer system.
1: Upper layer (water), 2: lower layer (aqueous solution), 3: boundary.

## Experimental

*Materials.* All the chemicals were reagent grade and were used without further purification. The sodium chloride was dried at 280 °C for 1 h, the copper sulfate and sucrose were used without drying, and the other salts were dried at 105—110 °C for 5 h.

*Apparatus and Method.* Figure 2 shows the apparatus used for measuring convections in the two-layer system; it is made of 200×50×3 mm glass plates joined by the use of epoxide resin as adhesive. Two glass rods, 3 mm in diameter and 50 mm in length, were fixed on both sides at a distance of 7 cm above the bottom in order to make the flows of the convections stable.

Water (63 cm$^3$) was gradually poured over an aqueous solution (63 cm$^3$) previously placed in the vessel at the flow speed of 2 cm$^3$/min by the use of a micropump; the two-layer system was thus made. The temperature of the circulating water used for heating or cooling the wall was kept constant within ±0.05 °C.

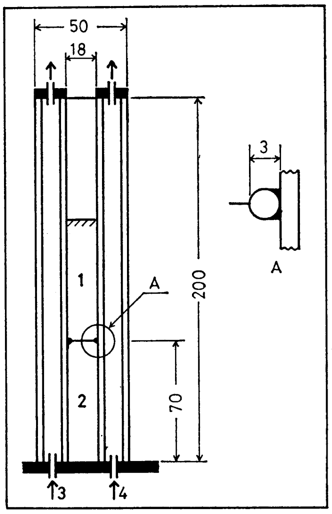

Fig. 2. Apparatus for measuring convections in two-layer system.
1: Upper layer, 2: lower layer, 3: hot water, 4: cold water.

The concentration of electrolytes was determined by the electric-conductance method. The conductance was measured with a conductometer (Toa Electronics CM-6A) equipped with electrodes formed of platinized platinum wires which were sealed at one end of a glass tube 6 mm in diameter. The electrodes were placed in the middle of the upper layer.

The concentration of sucrose was determined by colorimetry as reported by Dubois *et al.*[3] The samples (50 mm$^3$) for the determination of the solute concentration were taken out from the solution in the middle of an upper layer.

## Results and Discussion

*Phenomenon of Mass Transfer.* In a previous paper[2] it was shown that the concentration in each layer is uniform. Therefore, the rate of mass transfer across the boundary can be calculated from the incre-

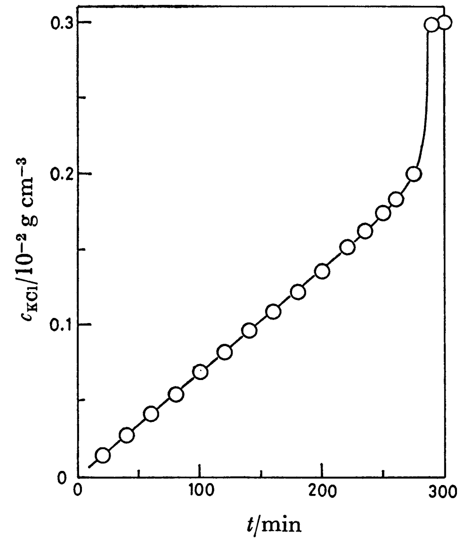

Fig. 3. Variation of the concn $c_{KCl}$ in the upper layer with time $t$.
Concn of the lower layer at the start of the convections: 0.6 g/(100 cm$^3$), temps of heating and cooling water: 36 and 26 °C.

ment in the concentration of a solute in the upper layer. Figure 3 shows the variation in the concentration of a solute in the upper layer with the lapse of time. Within ten minutes from the beginning of the convections, each convection becomes a steady current; then the concentration in the upper layer increases linearly with the time. When the time has elapsed, the concentration difference between the two layers becomes small and the boundary unstable. Then, the boundary is destroyed and the two-layer system changes into a one-layer system. The flux (g cm$^{-2}$ min$^{-1}$), $W_A$, of a solute, A, across the boundary was calculated by means of

$$W_A = \frac{V}{100S}\frac{\Delta c_A}{\Delta t}. \tag{1}$$

Here, $c_A$, $S$, $t$, and $V$ are the concentration {g/(100 cm$^3$)} of a solute, A, in the upper layer, the area (cm$^2$) of the boundary, the time (min), and the volume (cm$^3$) of the upper layer, respectively.

Figure 4 shows the relation between $W_{KCl}$ and the concentration in the lower layer at the start of the convections. It can be seen that $W_{KCl}$ is independent of the concentration difference.

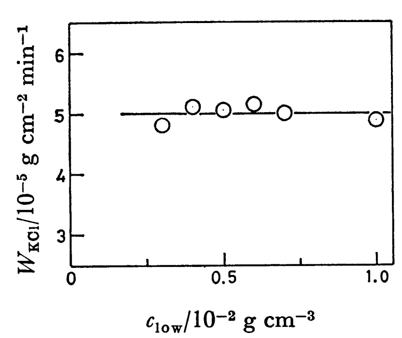

Fig. 4. Relation between $W_{KCl}$ and concn $c_{low}$ of KCl in the lower layer at the start of the convections.
Temps of heating and cooling water: 30 and 20 °C.

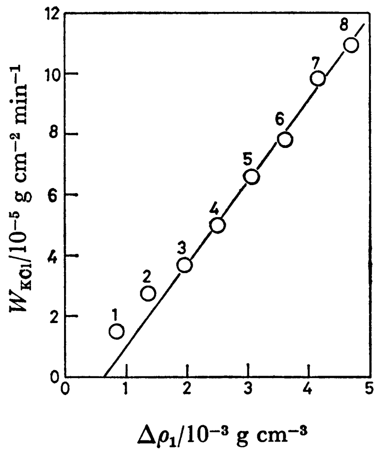

Fig. 5. Dependence of the flux $W_{KCl}$ on the density difference $\Delta\rho_1$ between the liquids on the heated and the cooled wall.
Concns in the lower layer at the start of convections: 0.2—1.0 g/(100 cm$^3$).
Temps of heating and cooling water—1: 29 and 26 °C, 2: 30 and 25 °C, 3: 31 and 24 °C, 4: 32 and 23 °C, 5: 33 and 22 °C, 6: 34 and 21 °C, 7: 35 and 20 °C, 8: 36 and 19 °C.

*Effect of Density Difference Caused by the Temperature.* Figure 5 shows the dependence of $W_{KCl}$ on the density difference, $\Delta\rho_1$, between the liquid on the heated wall and that on the cooled wall. This plot shows a straight line except for small values of the density difference. The value of $\Delta\rho_0 = 0.63 \times 10^{-3}$ g cm$^{-3}$ was obtained by extrapolation of the linear portion of the plot to $W_{KCl} \rightarrow 0$. The convections in our two-layer system can be considered to occur above this value of $\Delta\rho_0$. Therefore, the following equation can be obtained:

$$W_A = a_1(\Delta\rho_1 - \Delta\rho_0). \tag{2}$$

Here, $a_1$ is the mass-transfer coefficient.

*Effect of the Kind of Solute.* The values of $W_A$ may depend on the kind of solute through a variety of factors: (1) the diffusion coefficient of the solute; (2) the density difference between the liquid in the upper layer and that in the lower layer; and (3) the viscosity of the fluid. However, the rate of mass transfer may be expected to be practically unaffected by the viscosity, because this experiment was performed in dilute solutions. Therefore, the results were discussed from the viewpoints of the diffusion coefficient, $D$ (cm$^2$ s$^{-1}$), and the density difference, $\Delta\rho_2$ (g cm$^{-3}$). The rate of mass transfer may be proportional to the $x$-th power of $D$ with $0 \leq x \leq 1$, because the solute is transported across the boundary by eddy or by molecular diffusion.[4] The concentration difference, $\Delta c_I$ {g/(100 cm$^3$)}, should be a driving force for this mass transfer. However, it has already been described that $W_A$ is independent of $\Delta c_I$. $\Delta c_I$ is proportional to $\Delta\rho_2$, so that the $\Delta c_I/\Delta\rho_2$ ratio should be constant for a given solute. Therefore, it is likely that $W_A$ is proportional to $\Delta c_I/\Delta\rho_2$, and that, thus:

$$W_A = a_2 D^x \frac{\Delta c_I}{\Delta\rho_2}. \tag{3}$$

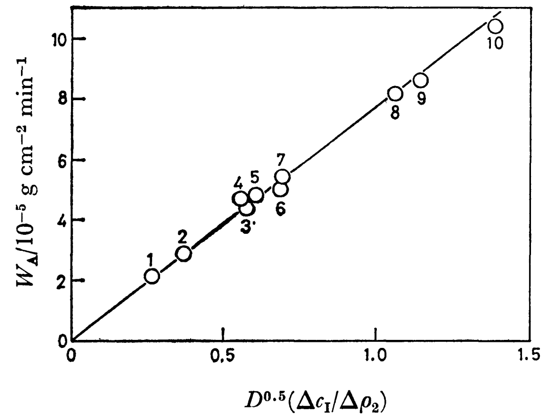

Fig. 6. Relation between $W_A$ and $D^{0.5}(\Delta c_I/\Delta\rho_2)$.
Temps of heating and cooling water: 30 and 20 °C.
Solutes—1: $CuSO_4$, 2: $Na_2SO_4$, 3: CsCl, 4: NaCl, 5: sucrose, 6: KCl, 7: $KNO_3$, 8: $NH_4NO_3$, 9: HCl, 10: $NH_4Cl$.

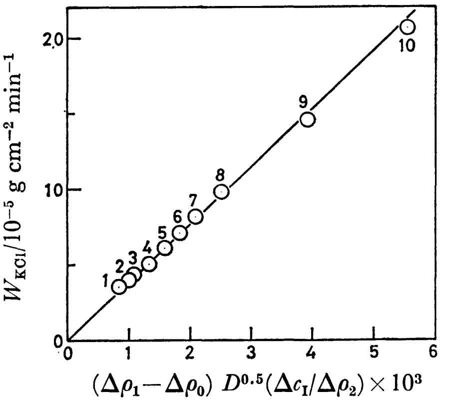

Fig. 7. Relation between $W_{KCl}$ and $(\Delta\rho_1-\Delta\rho_0)D^{0.5}\cdot(\Delta c_I/\Delta\rho_2)$.
Concn in the lower layer at the start of convections: 0.25—1.00 g/(100 cm$^3$).
Temps of heating and cooling water—1: 24 and 14 °C, 2: 16 and 26 °C, 3: 27 and 17 °C, 4: 30 and 20 °C, 5: 23 and 33 °C, 6: 26 and 36 °C, 7: 29 and 39 °C, 8: 20 and 35 °C, 9: 20 and 40 °C, 10: 20 and 45 °C.

Here, $a_2$ is the mass-transfer coefficient. The value of $\Delta c_I/\Delta\rho_2$ was calculated approximately from

$$\frac{\Delta c_I}{\Delta\rho_2} = \left(\frac{\Delta\rho_2}{\Delta c_I}\right)^{-1} \approx ((d_4{}^t)_s-(d_4{}^t)_w)^{-1}, \tag{4}$$

where $(d_4^t)_s$ is the specific gravity of the solution of 1 wt %, $(d_4^t)_w$ that of water, and $t$ the mean temperature in the upper layer. For a number of solutes we measured $W_A$ and made a plot of log $\{W_A/(\Delta c_I/\Delta\rho_2)\}$ *vs.* log $D$, from the slope of which we obtained $x=0.5$. Thus, $W_A$ was found to be proportional to $D^{0.5}(\Delta c_I/\Delta\rho_2)$, as be shown in Fig. 6.

*Empirical Formula for Mass-transfer Rate.* Combining Eq. 2 with Eq. 3 yields the following final expression for $W_A$:

$$W_A = a_3(\Delta\rho_1-\Delta\rho_0)D^{0.5}\frac{\Delta c_I}{\Delta\rho_2}. \tag{5}$$

Here, $a_3$ is the mass-transfer coefficient. Figure 7 shows the plot of $W_{KCl}$ *vs.* $(\Delta\rho_1-\Delta\rho_0)D^{0.5}(\Delta c_I/\Delta\rho_2)$ at different pairs of temperatures. This plot is linear except for the points obtained at low temperatures.

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