Separative Fluodiffusion *

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Earlier work on fluodiffusion is discussed. General phenomenological equations for fluodiffusion are given. It is shown that in a Poiseuille flow of a molecular mixture, separational fluodiffusion is expected to be much bigger in the direction of the flow than perpendicular to it. Experiments with liquid lithium are reported. They show a clear isotope effect, but it remains a question whether this effect is due to fluodiffusion or to an interaction of the lithium with the iron in which it was contained.

The application of a pressure gradient to a fluid gives rise to a tendency of its components to demix. This kind of separative transport can be subdivided into contributions arising from three different effects.

1. Pressure diffusion, which is directly related to the pressure gradient and is independent of whether the fluid flows or is at rest,

2. separative processes resulting from the inter-action of a flowing fluid with the containing walls, and

3. separative processes in the interior of a flowing fluid caused by its deformations. This effect may be called fluodiffusion or rheodiffusion.

Experiments in the Fifties

Efforts have been made by TOLLERT[1] and MÜL-LER[2] to verify fluodiffusion in the following way. The fluid is introduced into a capillary tube and is forced through it in a laminar flow. At the outlet end of the tube the stream is divided into a central stream and a peripheral stream; these being taken off separately. In this way the authors claim to have obtained partial demixing in systems such as nitro-gen-hydrogen, coppersulfate-water, sugar-water and glycerine-water. They believe that the reason for this demixing is transverse fluodiffusion whereby the heavier and larger molecules are transported towards the axis of the tube where their concentration increases.

Evidently, it has been overlooked that the demix-ing by means of such a device may also be due to longitudinal pressure diffusion and longitudinal fluodiffusion. These effects produce, as will be shown below, a difference (Δv) in the longitudinal velocities of the components of the fluid, which is constant throughout the tube. Let us suppose the local differences in the concentrations that may arise, when the fluid enters the tube, level out by diffusion during further progress of the fluid through the tube. Then despite constant concentrations in the tube, a separation factor (α) between the products delivered by the central and peripheral streams of a dilute binary mixture will result, i. e. $\alpha \neq 1$, and is given by

$$\alpha = \frac{\int\limits_0^\varrho v \, r \, \mathrm{d}r}{\int\limits_0^\varrho (v+\Delta v) \, r \, \mathrm{d}r} \cdot \frac{\int\limits_\varrho^R (v+\Delta v) \, r \, \mathrm{d}r}{\int\limits_\varrho^R v \, r \, \mathrm{d}r} \qquad (1)$$

where

$$v = v_0 (1 - r^2/R^2). \qquad (2)$$

ϱ and R are the radii of the central and peripheral streams. The linear expansion of (1) in $\Delta v/v_0$ yields

$$\alpha = 1 + 2 \left(1 - \frac{\varrho^2}{R^2}\right)^{-1} \left(2 - \frac{\varrho^2}{R^2}\right)^{-1} \frac{\Delta v}{v_0} . \qquad (3)$$

Equal amounts of liquid are transported by the central and peripheral streams if

$$\varrho^2/R^2 = 1 - 2^{-1/2} . \qquad (4)$$

In this case

$$\alpha = 1 + 4 \, (2^{1/2} + 1)^{-1} \, \Delta v/v_0 . \qquad (5)$$

Another demixing effect, not discussed by TOL-LERT[1] and MÜLLER[2] may be caused by the dis-turbances of the Poiseuille flow at the outlet end of the tube[3], where the central and peripheral streams are forced to separate. Since it is not clear where

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[1] H. TOLLERT, Z. Elektrochem. **60,** 1024 [1956].
[2] F. H. MÜLLER, Deutsches Patent 1,005,046 [1955] ; An-gew. Chemie **68,** 186 [1956] ; US-Patent 3,005,552 [1961].
[3] E. CREUTZ, J. Appl. Phys. **41,** 120 [1970].

and how the demixing really happened, little can be learned about fluodiffusion from this work. Also, the separations reported are close to the limits of observability.

Phenomenology of Fluodiffusion

Pressure diffusion is a well known phenomenon. The cartesian components of the relative velocity $(\boldsymbol{v}_a - \boldsymbol{v}_b = \boldsymbol{v}_{ab})$ of the partners a and b of a binary mixture due to pressure diffusion are

$$(v_{ab})_\mu = D\,S_{ab}\frac{\partial p}{\partial x_\mu}, \quad (\mu = 1, 2 \text{ or } 3), \quad (6)$$

where p is the pressure and D is the interdiffusion coefficient. S_{ab} is a thermodynamic property of the fluid involving the molar masses $M_{a,b}$, the partial molar volumes $V_{a,b}$, the mole fractions $\gamma_{a,b}$, and the chemical potentials $\mu_{a,b}$:

$$S_{ab} = (M_a V_b - M_b V_a) \quad (7)$$
$$\cdot (\gamma_a M_a + \gamma_b M_b)^{-1} (\partial \mu_a / \partial \ln \gamma_a)^{-1}.$$

By means of the Navier-Stokes equations

$$\frac{\partial p}{\partial x_\mu} = -\varrho\left(\frac{\partial v_\mu}{\partial t} + v_\nu\frac{\partial v_\mu}{\partial x_\nu}\right) + \frac{\partial^2 v_\mu}{\partial x_\nu\,\partial x_\nu} + (\eta_V + \tfrac{1}{3}\eta)\frac{\partial^2 v_\nu}{\partial x_\mu\,\partial x_\nu} \quad (8)$$

($\mu, \nu = 1, 2, 3$; sum – rule!; $\boldsymbol{v}$ the baricentric velocity; ϱ the density; η the viscosity) the pressure gradient may be eliminated from (6). We restrict ourselves here and in the following to the stationary state $(\partial v_\mu / \partial t = 0)$ of an incompressible fluid $(\partial v_\nu / \partial x_\nu = 0)$. The pressure diffusional transport then becomes

$$(v_{ab})_\mu = D\,S_{ab}\left(-\varrho\,v_\nu\frac{\partial v_\mu}{\partial x_\nu} + \eta\frac{\partial^2 v_\mu}{\partial x_\nu\,\partial x_\nu}\right). \quad (9)$$

Fluodiffusional terms may be added to the right hand side of (9). These terms result from deformations and therefore do not involve $\boldsymbol{v}$ itself but only its derivatives. To include all possible terms of the quadratic expansion in $\boldsymbol{v}$ involving only first and second derivatives, and observing incompressibility and stationarity, one obtains

$$
\begin{aligned}
(v_{ab})_\mu = &-D\,S_{ab}\,\varrho\,v_\nu\frac{\partial v_\mu}{\partial x_\nu} + (D\,S_{ab}\,\eta + L_{ab})\frac{\partial^2 v_\mu}{\partial x_\nu\,\partial x_\nu}\\
&+ Q_{ab}^{I}\frac{\partial^2 v_\mu}{\partial x_\nu\,\partial x_\lambda}\frac{\partial v_\nu}{\partial x_\lambda} + Q_{ab}^{II}\frac{\partial^2 v_\nu}{\partial x_\mu\,\partial x_\lambda}\frac{\partial v_\nu}{\partial x_\lambda}\\
&+ Q_{ab}^{III}\frac{\partial^2 v_\nu}{\partial x_\mu\,\partial x_\lambda}\frac{\partial v_\lambda}{\partial x_\nu} + Q_{ab}^{IV}\frac{\partial^2 v_\nu}{\partial x_\lambda\,\partial x_\lambda}\frac{\partial v_\mu}{\partial x_\nu} \quad (10)\\
&+ Q_{ab}^{V}\frac{\partial^2 v_\nu}{\partial x_\lambda\,\partial x_\lambda}\frac{\partial v_\nu}{\partial x_\mu}.
\end{aligned}
$$

If the concentrations and the temperature are not uniform, further terms have to be added. These terms, however, will not be dealt with here. The coefficients L_{ab} and Q_{ab} of the linear and quadratic terms are transport properties of the fluid. BARANOWSKI and POPIELAWSKI [4] have calculated L_{ab} for an equimolar mixture of N_2O and CO_2 at 273 K and 1 atm in a Maxwellian molecule approximation. They find

$$L_{ab}/4\,D = 8.36\cdot 10^{-11}\ \sec, \quad (11)$$

when a is N_2O and b is CO_2.

For a dilute suspension of spheres of radius a and density ϱ_a (component a) in a liquid of viscosity η_b and density ϱ_b (component b), hydrodynamic calculations by STOKES [5], SIMHA [6] and SAFFMAN [7] give

$$D\,S_{ab}\,\eta = \frac{2}{9}\frac{\varrho_a - \varrho_b}{\varrho_b}a^2, \quad (12)$$

$$L_{ab} = \frac{1}{6}a^2, \quad (13)$$

$$Q_{ab}^{II} + 2\,Q_{ab}^{V} = -0.214\frac{\varrho_b}{\eta_b}a^4. \quad (14)$$

The energy dissipation per unit of volume and time, due to the viscosity η, is

$$\Phi = \tfrac{1}{2}\eta\left(\frac{\partial v_\nu}{\partial x_\lambda} + \frac{\partial v_\lambda}{\partial x_\nu}\right)^2. \quad (15)$$

If the tendency to minimize Φ were the only driving force for fluodiffusion, then $(v_{ab})_\mu$ would be proportional to

$$\partial \Phi / \partial x_\mu = 2\,\eta\left(\frac{\partial^2 v_\nu}{\partial x_\mu\,\partial x_\lambda}\frac{\partial v_\nu}{\partial x_\lambda} + \frac{\partial^2 v_\nu}{\partial x_\mu\,\partial x_\lambda}\frac{\partial v_\lambda}{\partial x_\nu}\right). \quad (16)$$

Clearly, Eq. (10) is a more general expression for fluodiffusion.

For a Poiseuille flow in a tube of radius R

$$v_z = v_0(1 - r^2/R^2), \quad v_r = 0, \quad v_\varphi = 0, \quad (17)$$

and Eq. (10) reduces to

$$(v_{ab})_z = -(D\,S_{ab}\,\eta + L_{ab})\frac{4\,v_0}{R^2}, \quad (18)$$

$$(v_{ab})_r = (Q_{ab}^{II} + 2\,Q_{ab}^{V})\frac{4\,v_0^2}{R^4}r, \quad (19)$$

$$(v_{ab})_\varphi = 0. \quad (20)$$

From Eqs. (12), (13), (14), (18), and (19) it can be seen that $(v_{ab})_z$ is proportional to $(a/R)^2$

[4] B. BARANOWSKI and J. POPIELAWSKI, Acta Physica Polonica **30**, 821 [1966].
[5] G. G. STOKES, Camb. Phil. Trans. **9**, 8 [1851].
[6] R. SIMHA, Kolloid-Z. **76**, 16 [1936].
[7] P. G. SAFFMAN, J. Fluid Mechanics **1**, 540 [1956].

and $(v_{ab})_r$ is proportional to $(a/R)^4$. Therefore, if a is of molecular, and R is of macroscopic order of magnitude, the transverse effect (19) can be neglected in comparison with the longitudinal effect (18). In principle it should be possible to determine the longitudinal fluodiffusion coefficient L_{ab} on the basis of Eq. (18) by measuring $(v_{ab})_z/v_0$ in a capillary of radius R, provided D, S_{ab} and η are known, which is the case for many systems.

When a binary mixture A forces a fluid B (immiscible with A) out of a capillary, then, as a result of pressure- and fluodiffusion, the faster moving component of A accumulates at the interface. This process is multiplicative, i. e. the obtainable enrichment is larger than the elementary effect, the magnitude of which is given by

$$v_{ab}/\bar{v}\,, \quad \left(v_{ab} = (v_{ab})_z\,, \ \bar{v} = v_0/2\right).$$

The zone of enrichment spreads from the migrating interface into the fluid A an average distance[8] $(\pi D_{eff}\, t)^{1/2}$, where t is the time elapsed since the entrance of the interface into the capillary, and[9]

$$D_{eff} = D + (\bar{v}^2\, R^2/48\, D)\,. \quad (21)$$

The amount of components transported out of, and into, the zone of enrichment is proprtional to t. Therefore the enrichment at the boundary is proportional to $t^{1/2}$.

In order to determine $v_{ab}/\bar{v}$, the flow is stopped when the interface reaches the outlet end of the capillary. The binary mixture A is then subdivided into sections, the weights N_i and the compositional ratios $(\gamma_a/\gamma_b)_i$ of which are determined. If these ratios do not differ appreciably from the ratio $(\gamma_a/\gamma_b)_0$ prevailing in the reservoir at the inlet end of the capillary, then $v_{ab}/\bar{v}$ can be calculated by means of the formula

$$v_{ab}/\bar{v} = \sum_i N_i\{1 - [(\gamma_a/\gamma_b)_0/(\gamma_a/\gamma_b)_i]\}/\sum_i N_i\,. \quad (22)$$

The summations must take account of all the material that has flown into the capillary.

Experiments with Liquid Lithium

According to (18) $v_{ab}/\bar{v}$ is proportional to R^{-2}. Consequently fluodiffusion could only be detected using prohibitively narrow capillaries. First experi-

ments[10] along these lines have been performed with a tight packing of iron beads, 2 μm diameter, in a steal tube, 2 mm inner diameter and 110 cm length. Molten lithium, a binary mixture of ^{6}Li and ^{7}Li, was pressed into this packing with a piston at a speed of $\bar{v} = 10^{-1}$ cm/sec. The displaced fluid was argon. After the interface had moved 90 cm, the melt was frozen and analyzed mass-spectroscopically. At the front the ^{6}Li/^{7}Li-ratio was found to have increased by 7%, and $v_{67}/\bar{v}$ as calculated from Eq. (22), to be $(4.3 \pm 1.0) \cdot 10^{-3}$. The iron beads did not show any corrosion after the experiments.

For an isotopic binary mixture, Eq. (7) becomes

$$S_{ab} = \frac{\Delta M}{M}\, \frac{V}{R'\, T}\,. \quad (23)$$

In the case of lithium ($\Delta M/M = 1/6.94$, $V = 13.9$ cm^3/mol, $R' = 8.31 \cdot 10^7$ g K^{-1} mol^{-1}, $T = 483$ K) $S_{ab} = 5 \cdot 10^{-11}$ cm sec^2 g^{-1}. Putting $D = 10^{-5}$ cm^2 sec^{-1}, $\eta = 10^{-2}$ g cm^{-1} sec^{-1} and $R = 10^{-4}$ cm one finds that the contribution of pressure diffusion to $v_{67}/\bar{v}$ is only of the order $4 \cdot 10^{-9}$. The separative effect, therefore, must have been longitudinal fluodiffusion, or a separative process resulting from the interaction of the lithium with the surface of the packing.

In an attempt to clarify this, some more experiments have been performed at our Institute which shall be reported here. The device used is shown in Fig. 1. Instead of pressing with a piston, as in the earlier work, the lithium was introduced into the packing by means of pressurized argon. The iron bead diameters ranged from 1.8 to 2.1 μm. The packing fraction was $.58 \pm .02$. Solid lithium, protected by pure argon and freed from oxide with a knife, was brought into the upper reservoir, fitted in with a pounder and melted. The temperature was kept at 210 °C. The outlet end of the tube was submerged in paraffin oil and could be observed through the glass tubings. The argon pressure was manipulated in such a way that the argon displaced by the lithium in the packing emerged steadily at at the outlet end of the tube by passing along the thread of the screw shown in Fig. 1. For better control of the speed, the argon was collected in an inverted U-tube as shown in Fig. 1. When the first lithium appeared at the outlet end of the steel tube,

[8] A. KLEMM, Z. Physik **123**, 10 [1944].
[9] J. W. WESTHAVER 1947; cf. A. LODDING and A. KLEMM, Z. Naturforsch. **17 a**, 1085 [1962].
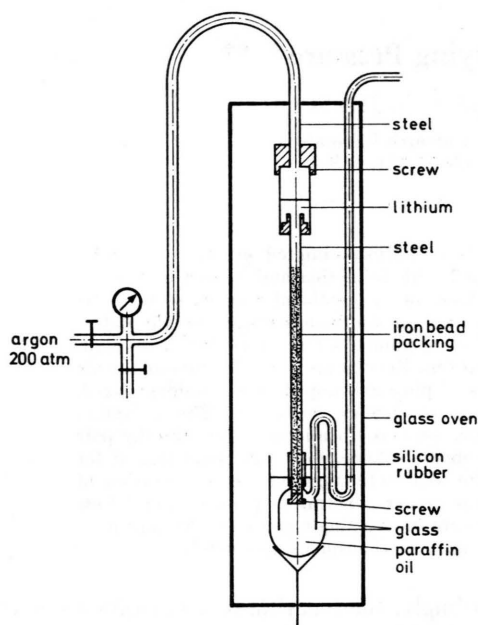
[10] A. KLEMM, Z. Naturforsch. **18 a**, 775 [1963].

Fig. 1. Apparatus to press liquid lithium through a packing of iron beads having 2 μm ϕ.
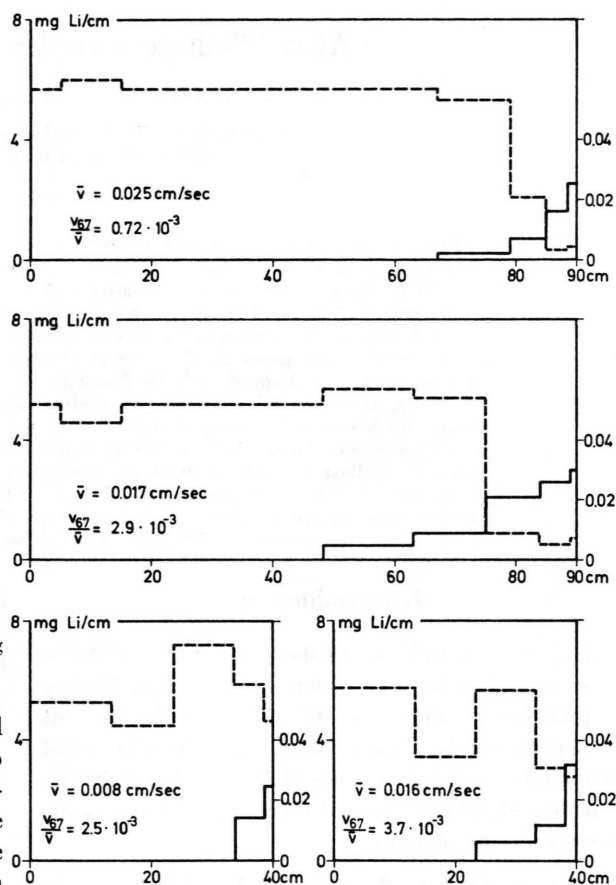

Fig. 2. Results of four runs. Abscissa: Position in column. Left ordinate and dashed line: Amount of lithium per cm of column. Right ordinate and full line: Separation factor minus one. The mean velocities $\bar{v}$ and the isotope effects $v_{67}/\bar{v}$ are indicated in the figure.

the flow was stopped and the apparatus cooled down. The whole length of the tube was cut into sections and their lithium contents determined chemically and analyzed with a mass-spectrometer. The results of four runs, out of twenty carried out, are indicated in Fig. 2. The mean velocities $\bar{v}$ were a factor between 4 to 12 smaller than in the earlier experiments where the lithium was moved with a piston. Also, contrary to the earlier experiments, the filling of the packing with lithium, which should have amounted to ≈ 7.1 mg Li/cm, was irregular and not complete (see Fig. 2). This was even more so in 10 of the 16 runs not shown in Fig. 2. For this reason, it was not possible to determine characteristic dependences such as that of $v_{67}/\bar{v}$ on $\bar{v}$. Nevertheless, in all runs the concentrations of ^{6}Li increased towards the front of the lithium column, as is characteristic for a multiplicative separation process, and $v_{67}/\bar{v}$ was found to be of the order 10^{-3}.

These more recent experiments confirm the earlier findings without clarifying the situation regarding the physics underlying this separation process.

I thank Dipl.-Phys. J. BERZEN for having performed the last mentioned experiments on liquid lithium.