

FICK'S INSIGHTS ON LIQUID DIFFUSION

T. N. NARASIMHAN¹

BACKGROUND

In 1855, Adolph Fick published “On Liquid Diffusion”, mathematically treating salt movement in liquids as a diffusion process, analogous to heat diffusion. Less recognized is the fact that Fick also provided a detailed account of the implications of salt diffusion to transport through membranes. A careful look at Fick (1855) shows that his conceptualization of molecular diffusion was more comprehensive than could be captured with the mathematical methods available to him, and therefore his expression, referred to as Fick’s Law, dealt only with salt flux. He viewed salt diffusion in liquids as a binary process, with salt moving in one way and water moving in the other. Fick’s analysis of the consequences of such a binary process operating in a hydrophilic pore in a membrane offers insights that are relevant to earth systems . This paper draws attention to Fick’s rationale, and its implications to hydrogeological systems. Fick (1829-1901; Figure 1), a gifted scientist, published the first book on medical physics (Fick, 1858), discussing the application of optics, solid mechanics, gas diffusion, and heat budget to biological systems.

Fick’s paper is divisible into two parts. The first describes his experimental verification of the applicability of Fourier’s equation to liquid diffusion. The second is a detailed discussion of diffusion through a membrane. Although Fick’s Law specifically quantifies solute flux, Fick visualized a simultaneous movement of water and stated, “*It is evident that a volume of water equal to that of the salt passes simultaneously out of the upper stratum into the lower.*” (Fick, 1855, p.30).

Fick drew upon Fourier’s model purely by analogy. He assumed that concentration gradient impelled salt movement, without inquiring why concentration gradient should constitute a driving force. As for water movement, he stated intuitively, “*...a force of suction comes into play on each side of the membrane, proportional to the difference of concentration, consequently a stronger force at the upper side corresponding to the saturated solution*” (Fick, 1855, p.38).

¹ Department of Materials Science and Engineering, Department of Environmental Science, Policy and Management, 210 Hearst Memorial Mining Building, University of California, Berkeley, Ca 94720-1760



Figure 1: Adolph Fick, pioneer in the application of physics, chemistry, and mathematics to biological systems (Fick, 1903; Frontispiece)

To understand double diffusion across a membrane, Fick considered a single vertical cylindrical pore with hydrophilic walls, separating solutions of differing concentrations above and below. He cited earlier observations of Brücke, and others suggesting that the substance of the partition attracted the particles of water more than the particles of salt. Fick made a clear distinction between two fundamentally different modes of water movement; diffusion of water, and “*filtration of the liquid, by virtue of their cohesion*”, driven by external pressure differences. He assumed the

radius of the pore to be sufficiently small so that filtration is prevented even at high pressure gradients, and that any differences in pressure on either side of the pore would take a very long time to equilibrate. Thus, transport across the membrane was solely attributed to diffusion.

The central theme of Fick's analysis was that water will preferentially move along the hydrophilic wall, while salt will tend to migrate along the axis of the pore. This would result in a gradual increase of concentration radially inward from the wall to the axis in any horizontal plane within the pore. In combination with the concentration differences between the upper and lower ends, the radial gradient results in a complex three dimensional concentration pattern within and in the vicinity of the pore. This complex pattern profoundly controls the nature of binary diffusion across the membrane, depending on specific combination of circumstances.

Fick's conceptualization is schematically shown in Figure 2. In this figure, $\alpha\beta\delta\gamma$ represents the cross section of a cylindrical pore of a hydrophilic membrane, whose upper and lower surfaces are shown as AA' and BB'. Within this pore, salt diffuses downward in the direction of decreasing concentration, and water moves upwards, driven by large suction forces in the concentrated solution. Because of hydrophilic forces, freshwater from below moves up along the walls, where the concentration is zero. On any horizontal plane, concentration increases radially from zero at the walls to some finite value at the center. The hatched strips ba and b'a' show the variation of concentration in a vertical cylindrical element of thickness dr , as one proceeds upwards from the bottom. The density of hatching denotes strength of concentration. Above the upper surface AA' of the membrane, concentration increases through a conical transition region to full saturation at some distance above. Downward salt diffusion is zero at the walls, and is a maximum along the axis. Clearly, two competing forces (hydrophilic and diffusive) are interacting in complex ways within and in the vicinity of the pore.

Fick discussed three cases, involving different combination of concentration differences between the ends of the pore. The flow patterns inferred for each were supported by his own experimental observations, and those of others.

In the first, the pore separates a saturated solution above from fresh water below. Assuming adequate supplies of fresh water below and salt above, the steady condition would be such that the upward flux of water would be in excess of the downward flux of salt. To quantify, Fick used an endosmotic equivalent, defined as the quotient obtained by dividing the "amount of water diffused" by the "quantity of salt contemporaneously passed". Based on the expected concentration patterns,

Fick concluded that the endosmotic equivalent was smaller for larger pores. This inference was supported by his observations on animal membrane (with relatively large pores) and a collodion film (with relatively fine pores). For pig's bladder, the endosmotic equivalent varied from 4 to 6, while for collodion it was in the range of many thousands, other factors remaining the same.

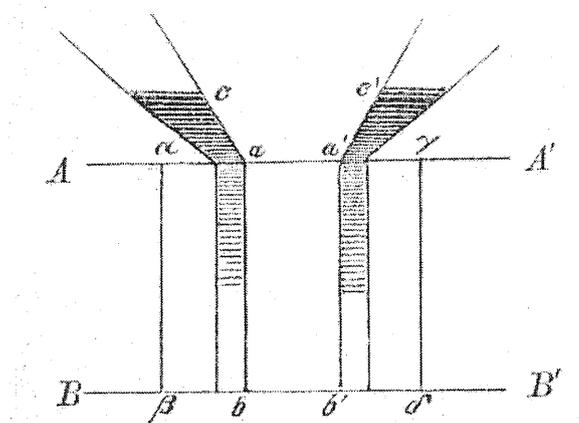


Figure 2: Fick's conceptualization of binary diffusion within a cylindrical pore, separating a saturated solution from pure water below (Fick, 1903, p. 223)

In the second case, the pore separates a saturated solution above from a solution of finite concentration below. Here, because of diminished concentration difference, the salt flux is rendered weak. Also, nearer the walls there could be vertically upward concentration gradient of salt, especially in fine pores. Hence, the endosmotic equivalent would be so high that in fine pores there would be only one current, that of water. The interesting implication is that even though the pore may be large enough to permit the passage of salt molecules, the membrane could be rendered semi-permeable because of spatial variations of concentration gradients. Fick cites his own observations as well as those of Ludwig and Cloetta in support of this inference. He found that a membrane, which gave an endosmotic equivalent of between 5 and 6 when it separated saturated solution of salt from pure water, gave an equivalent of 17.05 when pure water was replaced by a 22 per cent salt solution.

In the third case, the pore separates a solution of finite concentration above from fresh water below. Here, the fluxes of salt and water would be comparable, and the endosmotic equivalent would be relatively small, especially when the solution above is more dilute.

In summary, three findings stand out. First, Fick distinguished between pure diffusion and pressure-driven flow of water. In gas flow, Thomas Graham (1833, 1845) distinguished between these two modes with the terms diffusion and transpiration. The former involves flow resistance arising from collision among diffusing molecules while, the latter involves viscous resistance, as in the case of Poiseuille's capillary flow. Second, the mathematical statement of Fick's Law scarcely does justice to the binary diffusion process that he visualized. Mathematical analysis of binary diffusion is cumbersome, involving considerations of reference frame, magnitude of concentration, and boundary conditions. These issues have been addressed in detail, especially for binary diffusion of gases. Bird (1956) suggests that Fick's Law is valid when the molar fluxes of the two species are equal, or when one species diffuses in a stagnant second species. Cussler (1984, p.119) notes that binary diffusion in a liquid is more complex than in gases because of the many molecular interactions involved in the dense environment. Third, Fick perceptively hypothesized that the hydrophilic pore walls will force a self-organization of water and salt movement within the pore and that this self-organization could, under certain conditions, cause a membrane to behave as semi-permeable even though the pores may be large enough to permit passage of both species.

IMPLICATIONS TO HYDROGEOLOGICAL SYSTEMS

Fick's Law is widely used to analyze hydrogeological systems in which waters of contrasting chemical composition may occur in mutual proximity. Examples include sedimentary brines in oil fields, abnormally high-pressured zones in active sedimentary basins, interaction of fresh-water aquifers with sea water, and chemically contaminated aquifers. Such systems may be under hydrostatic, steady-state or transient conditions. In hydrostatic systems with little pressure-driven water movement, counter diffusion of salts and water will be the primary mechanism driving the system towards uniform concentration. In these, the disposition of the interface between brines and freshwater bodies will need to be understood in terms of binary diffusion, modified by gravity. In steady-state systems with time invariant flow velocities, advection associated with pressure-driven flow and binary diffusion will occur in conjunction. In transient systems, such as an advancing and retreating sea-water front, binary diffusion will occur in conjunction with periodical reversal of flow

directions.

It is common practice in hydrogeology to use Fick's Law to estimate salt flux, and effectively ignore diffusion of water. Only recently has there been a move to account for diffusive water movement in multi-component simulators, using methods developed in the chemical engineering. These efforts are severely limited in practice because of non-availability of data on interacting diffusion coefficients, and other complexities such as high concentrations, multiple components, heterogeneity, and transient flow. In the field of soil physics, water movement in soil solutions is conceptualized in terms of a "total water potential" (Baver et al., 1972, p.293), which is defined to be a sum of a capillary potential, a pressure potential, an osmotic potential, and other potentials. Of these, the first two are associated with water flow involving viscous resistance. By combining osmotic potential with the other two, the soil physics idealization ignores the purely diffusive mode of water transfer in solutions, and effectively treats such a flow as viscous flow.

CONCLUDING REMARKS

Fick formulated his insightful ideas three decades before van't Hoff's theory of osmotic pressure, Arrhenius' theory of electrolyte dissociation, and Nernst's theory of ionic current. Yet, Fick's intuitive interpretation of binary diffusion and its consequences are remarkably persuasive. A century and half later, comprehending water diffusion in hydrogeological systems remains challenging at all levels; theoretical, experimental, and field observations. Even under controlled laboratory conditions, theoretical analysis of molecular diffusion in water entails a multiplicity of difficult-to-measure coefficients. Further complexity arises with the introduction of hydrophilic forces. Despite the reality of water diffusion, very little experimental information is available about the nature of this mode of liquid motion. Perhaps the availability of sophisticated tools such as the Advanced Light Source may help shed new light on the nature of water diffusion in solutions. As the theoreticians and the experimentalists strive to generate precise understanding of water diffusion, the field geologist who is intrigued by anomalous interfaces between brines and groundwater may very well find Fick's intuitive approach helpful in comprehending the significance of such observations. Regardless of where Fick's ideas may lead, it is certain that they are well worth the efforts of earth scientists to explore.

ACKNOWLEDGMENTS

Thanks to Mary Anderson, Jeffrey Hanor, Yousif Kharaka, Curt Oldenburg, and Jozsef Toth for thoughtful critique. This work was supported partly by the Director, Office of Energy Research, Office of Basic Energy Sciences of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 through the Earth Sciences Division of Ernest Orlando Lawrence Berkeley National Laboratory.

REFERENCES

- Baver, L. D., Gardner, W. H., and Gardner, W. R., Soil Physics, John Wiley and Sons, New York, 1972, 498 pages
- Bird, R. B., Theory of Diffusion, Advances in Chemical Eng., 1, 156-239
- Cussler, E. L., Diffusion, Mass Transfer in Fluid Systems, Cambridge University Press, Cambridge, 1984, 525 pages
- Fick, A., On liquid diffusion, Phil. Mag. and Jour. Sci., 10, 31-39, 1855
- Fick, A., Die medizinische Physik, Braunschweig: Vieweg, 1858
- Fick A., Gesammelte Schriften, I. Band, Stahel'sche Verlags-Anstalt, Würzburg, 1903
- Graham, T. H., On the law of diffusion of gases, Phil. Mag. and Jour. Sci., 2, 175-191, 269-276, 351-358, 1833
- Graham, T. H., Of the motion of gases, Part I, Phil. Trans., iv. 573-632, 1846