

# Fick's Diffusion Experiments Revisited —Part I

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## Abstract

In this paper, we revisit Fick's original diffusion experiments and reconstruct the geometry of his inverted funnel. Part I demonstrates that Fick's experimental approach was sound and measurements were accurate despite his own claims to the contrary. Using the standard modern approach, we predict Fick's cylindrical tube measurements with a high degree of accuracy. We calculate that the salt reservoir at the bottom of the inverted funnel must have been about 5 cm in height and the unreported depth of the deepest salt concentration measurement by Fick was yet another 3 cm above the reservoir top. We verify the latter calculation by using Fick's own calculated concentration profiles and show that the modern diffusion theory predicts the inverted funnel measurements almost as well as those in the cylindrical tube. Part II is a translation of Fick's discussion of diffusion in liquids in the first edition of his three-volume monograph on Medical Physics published in 1856, one year after his seminal Pogendorff Annalen paper On Diffusion.

## Keywords

Salt Diffusion, Medical, Physics, Tube, Funnel, Experiment, Pogendorff Annalen

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## 1. Introduction

Fick's classical diffusion equation is so much a part of the scientific folklore that I decided to revisit its original derivation and the underlying experiments in a graduate course. To my surprise, Fick's own experiments turned out to be remarkably accurate and the geometry of his funnel experiments could be adequately reconstructed. While searching for Fick's original publications, a student in the class found on the Web an antique book dealer who had the first edition of Fick's handbook on medical physics, which I quickly purchased. I then asked my neighbor who is German by birth and education to help me in the translation of the relevant sections of the book and she kindly agreed. The book was written by Fick as an account of physics applicable to medicine and it

brings interesting insights into Fick's way of thinking about diffusion and osmosis, see Part II. The book section on the diffusion in liquids is more personal and somewhat different from the two famous papers published one year earlier (Fick, 1855a; Fick, 1855b).

This paper is a simple evaluation of Fick's original experiments based on the theory of diffusion presented so well in (Hirschfelder et al., 1954) and (Bird et al., 1960). For an exquisite and brief discussion of the various theories of diffusion developed over the decades by Maxwell, Stefan, Onsager, Chapman and Enskog, Eckart and Meixner, and many others, one may refer to (Truesdell, 1962).

Fick's theory of diffusion is almost as old as the theories of heat conduction by Fourier (Fourier, 1807; Fourier, 1822) and viscosity by Newton. While originally it was too primitive to reveal any ideas of principle, Maxwell soon<sup>1</sup> gave it a rational basis in his kinetic theory of gas mixtures and Stefan (Stefan, 1871) cleared away the specifically kinetic details to achieve an inclusive phenomenological theory, see (Truesdell, 1966) for further details.

## 2. Background

For convenience, a few pertinent equations describing diffusion will be listed here. A full derivation may be found in, e.g., (Bird et al., 1960). Let  $\mathbf{v}_B$  denote the velocity of constituent<sup>2</sup>  $B$  of a fluid mixture with respect to a stationary coordinate system, and define this velocity as by taking a snapshot of instantaneous velocities of the molecules of  $B$ . For a mixture of  $N_c$  constituents, we define the local mass-average velocity as

$$\mathbf{v} = \frac{\sum_{B=1}^{N_c} \rho_B \mathbf{v}_B}{\sum_{B=1}^{N_c} \rho_B} = \frac{\sum_{B=1}^{N_c} \rho_B \mathbf{v}_B}{\rho} \quad (1)$$

Thus  $\rho \mathbf{v}$  is the local rate at which mass passes through a unit area perpendicular to  $\mathbf{v}$ . Similarly, we may define a local molar average velocity as

$$\mathbf{v}^* = \frac{\sum_{B=1}^{N_c} c_B \mathbf{v}_B}{\sum_{B=1}^{N_c} c_B} = \frac{\sum_{i=1}^{N_c} c_B \mathbf{v}_B}{c} \quad (2)$$

Thus  $c \mathbf{v}^*$  is the local rate at which moles pass through a unit area perpendicular to  $\mathbf{v}^*$ .

In flow systems one is often interested in the velocity of a given constituent with respect to  $\mathbf{v}$  or  $\mathbf{v}^*$ , rather than with respect to a stationary coordinate system. This leads to the following definition of the diffusion velocities:

$$\begin{aligned} \mathbf{v}_{(D)B} &\equiv \mathbf{v}_B - \mathbf{v} = \text{diffusion velocity of } B \text{ relative to } \mathbf{v} \\ \mathbf{v}_{(D)B}^* &\equiv \mathbf{v}_B - \mathbf{v}^* = \text{diffusion velocity of } B \text{ relative to } \mathbf{v}^* \end{aligned} \quad (3)$$

These velocities measure the motion of constituent  $B$  in a fluid relative to the local mean motion of the fluid.

Now we can define the different mass and molar fluxes. The mass or molar flux of constituent  $B$  is defined as a vector whose magnitude is equal to the mass or moles of constituent  $B$  that pass through a unit area per unit time. The motion may be referred to stationary coordinates, to the local mass-average velocity,  $\mathbf{v}$ , or to the local molar-average velocity,  $\mathbf{v}^*$ . Thus the mass and molar flux densities relative to stationary coordinates are

$$\mathbf{j}_{(m)B} = \rho_B \mathbf{v}_B \quad \text{mass}, \quad \mathbf{j}_{(n)B} = c_B \mathbf{v}_B \quad \text{molar} \quad (4)$$

The mass and molar flux densities relative to the mass-average velocity  $\mathbf{v}$  are

$$\mathbf{j}_{(m|\mathbf{v})B} = \rho_b \mathbf{v}_{(D)B} \quad \text{mass}, \quad \mathbf{j}_{(n|\mathbf{v})B} = c_B \mathbf{v}_{(D)B} \quad \text{molar} \quad (5)$$

and the mass and molar flux densities relative to the molar-average velocity  $\mathbf{v}^*$  are

<sup>1</sup>Maxwell published four important papers on gas theory, the first of which, "Illustrations of the Dynamical Theory of Gases", appeared in 1860, and contained Maxwell's first theory of diffusion. See (Garber et al., 1986) for details.

<sup>2</sup>"Constituent" denotes a chemical species or a pseudo-component.

$$\mathbf{j}_{(m|v^*)B} = \rho_B \mathbf{v}_{(D)B}^* \quad \text{mass}, \quad \mathbf{j}_{(n|v^*)B} = c_B \mathbf{v}_{(D)B}^* \quad \text{molar} \quad (6)$$

Again, one should remember that the definition of a mass flux density is *incomplete* until both the units and the frame of reference are given.

By analogy with the flux of energy in one-dimensional systems:

$$q_y = -\alpha \frac{d}{dy}(\rho c_p T) \quad (\text{Fourier's law for constant } \rho c_p), \quad (7)$$

one may *define* the mass flux of constituent 1 in a binary system 12 as

$$j_{y1} = -D_{12} \frac{d}{dy}(\rho_1) \quad (\text{Fourier's law for constant } \rho) \quad (8)$$

Note that the total mass density,  $\rho$ , of the mixture is *uniform*, i.e., constant given a constant temperature. Here  $\alpha$  is the thermal diffusivity,  $c_p$  is the heat capacity,  $D_{12}$  is the diffusion coefficient, and  $\rho_1$  is the mass density of constituent 1.

If the fluid density is *not* uniform, one defines the mass diffusivity  $D_{12} = D_{21}$  in a binary system in an analogous fashion:

$$j_{(m|v)1} = \rho D_{12} \nabla w_1 \quad \text{mass}, \quad \mathbf{j}_{(n|v^*)1} = c D_{12} \nabla x_1 \quad \text{molar} \quad (9)$$

Note that Equation (9) is purely *kinematic*, i.e., it involves only the dimensions of length and time, and it must be justified from an independent *dynamic* theory that invokes forces.

It may easily be shown (Bird et al., 1960) that the mass or molar diffusion fluxes in Equation (9) are also given by

$$\begin{aligned} j_{(m|v)1} &= \mathbf{j}_{(m)1} - w_1 \sum_{B=1}^2 \mathbf{j}_{(m)B} = -\rho D_{12} \nabla w_1 \\ \mathbf{j}_{(n|v^*)1} &= \mathbf{j}_{(n)1} - x_1 \sum_{B=1}^2 \mathbf{j}_{(n)B} = -c D_{12} \nabla x_1 \end{aligned} \quad (10)$$

These two relationships are of special importance for this paper.

Fick's experiment (Fick, 1855b) in a cylindrical tube is shown in Figure 1. At  $z = L$ , salt (1) diffuses into fresh water (2), while solid salt in a salt reservoir dissolves, replenishing the diffusing salt, and maintaining the

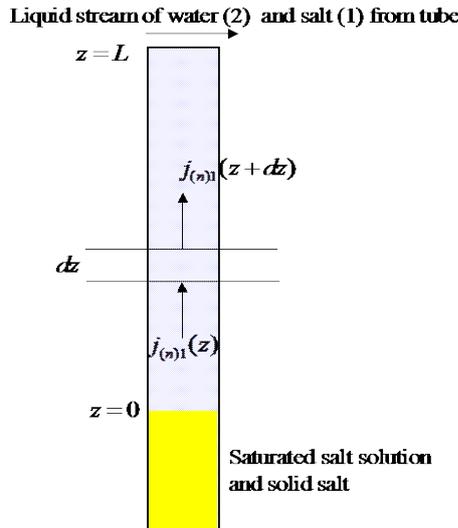


Figure 1. Fick's diffusion experiment in a cylindrical tube with a salt reservoir at the bottom and flowing fresh water at the top.

saturated salt concentration at  $z = 0$ . A stream of fresh water sweeps the salt emerging from the tube, keeping the zero salt concentration at  $z = L$ . The whole system is at constant (albeit unknown) temperature and pressure. The mixture of salt and water is assumed ideal, i.e., each component activity is equal to its mole fraction.

When this dissolving salt system attains a steady state, there is a net motion of salt away from the salt reservoir and the water in the tube is stationary. Hence we can use expression (10)<sub>2</sub> for the molar flux of salt relative to a stationary frame of reference:

$$\begin{aligned} j_{(n)1}^*(z) &= j_{(n)1}(z) - x_1 j_{(n)1}(z) - x_1 0 = -cD_{12} \nabla x_1 \\ j_{(n)1}(z) &= -\frac{cD_{12}}{1-x_1} \frac{dx_1}{dz} \end{aligned} \quad (11)$$

The salt mass balance over an incremental column height,  $dz$  states that at steady state

$$\frac{dj_{(n)1}(z)}{dz} = 0 \quad (12)$$

Substitution of Equation (11) into Equation (12) gives

$$\frac{d}{dz} \left( \frac{cD_{12}}{1-x_1} \frac{dx_1}{dz} \right) = 0 \quad (13)$$

We shall assume that  $D_{12}$  is nearly independent of concentration. Indeed the literature data show that  $D_{12} \approx 1 \text{ cm}^2/\text{day}$  for 0.1 - 1 normal salt solutions. The saturated salt concentration is about 36 g NaCl/100g of water or 26 g NaCl/100g solution at room temperatures of 10 - 20 degrees C. From **Appendix**, we can calculate the total concentration of water and salt at 20 deg C. This calculation is summarized in **Table 1**. The percent coefficient of variation is generally less than 1%; therefore, the total concentration can be assumed constant.

The coefficient of variation is defined as  $\text{C.V.} = \frac{c - \langle c \rangle}{\langle c \rangle} 100\%$

Thus, we can recast the steady state diffusion mass balance of salt, Equation (13), as

**Table 1.** Total concentration of aqueous salt solutions, see **Appendix**.

$c_1$ -water	$c_5$ -water	Total $c$	C.V.
99	55.2915	55.4635	0.5408
98	55.1087	55.4551	0.5255
96	54.7360	55.4386	0.4956
94	54.3790	55.4478	0.5123
92	53.9682	55.4133	0.4498
90	53.5350	55.3667	0.3653
88	53.0787	55.3075	0.2579
86	52.5986	55.2353	0.1270
84	52.0893	55.1446	-0.0372
82	51.5643	55.0498	-0.2091
80	51.0133	54.9405	-0.4072
78	50.4400	54.8208	-0.6243
76	49.8391	54.6856	-0.8693
74	49.2182	54.5433	-1.1273

$$\frac{d}{dz} \left( \frac{1}{1-x_1} \frac{dx_1}{dz} \right) = 0 \quad (14)$$

$$x_1(0) = 0.0976, \quad x_1(L) = 0$$

This equation can be easily solved (Bird et al., 1960) and the result is

$$\frac{1-x_1}{1-x_1(0)} = \left( \frac{1-x_1(L)}{1-x_1(0)} \right)^{\frac{z}{L}} \quad (15)$$

The density-mole concentration data from **Table 1** and **Table 2** are summarized in **Table 3**. The latter table can be used in conjunction with the excess gravities reported by Fick to convert his gravity versus depth results into the salt mole fraction versus depth. This was implemented as linear interpolation.

The results are shown in **Figure 2**. Agreement between the theory and experiment is excellent.

### Remarks

**Figure 3** shows the profile of excess gravity that would have been calculated by Fick for the cylindrical tube experiment. Note that there is a systematic deviation of the calculation from the experimental data. Fick himself said (Fick, 1855a): “That the degrees of concentration in the lower layers decrease a little more slowly than in the upper ones, is easily explained by the consideration, that the stationary condition had not been perfectly attained”. Similar excuses have been used by experimentalists ever since.

### 3. Fick’s Conical Funnel Experiment

The conical funnel data obtained by Fick (Fick, 1855a) are more difficult to decipher because of the incomplete reporting of the experiment. The most likely experiment geometry may be inferred from **Figure 6**. In an inverted

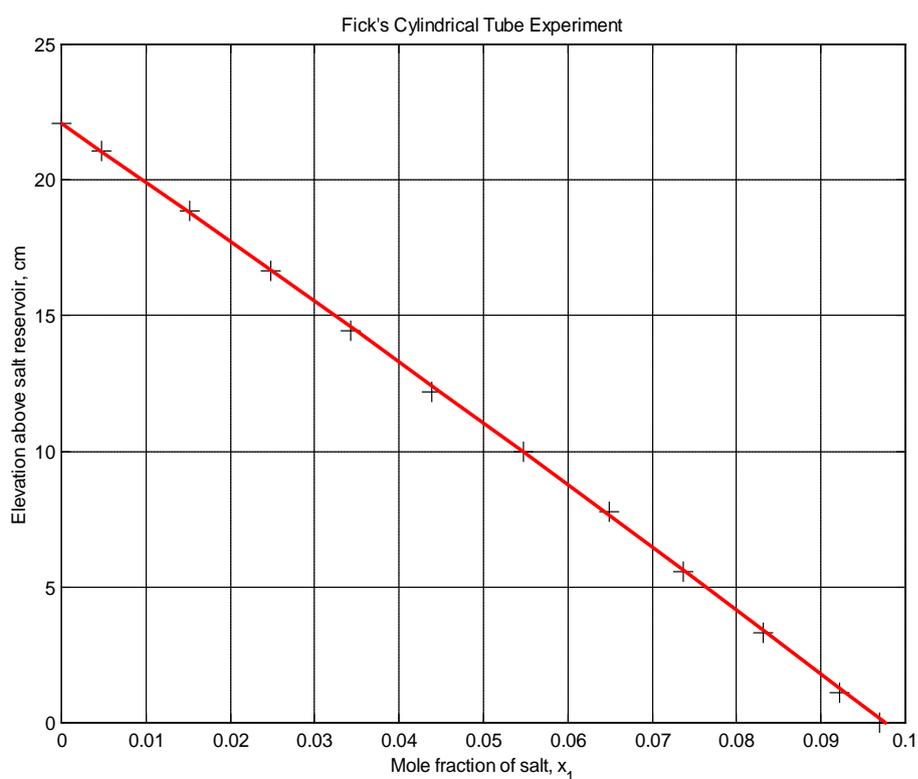
**Table 2.** Density and concentrations of aqueous NaCl solutions at 20 deg C.

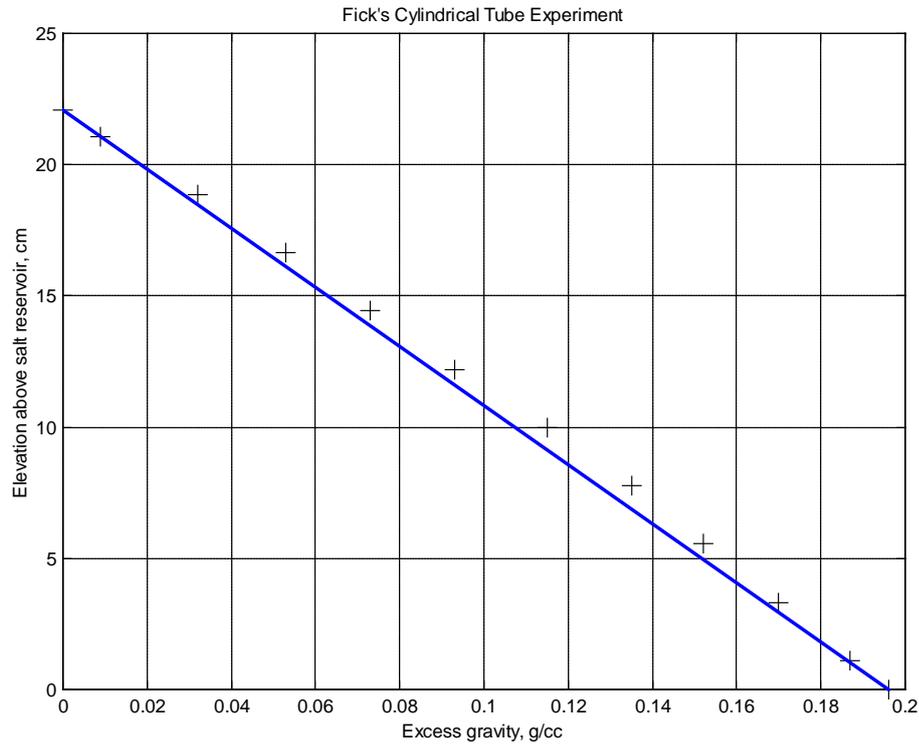
$c_1\%$	$\rho_4^{20}$ g/l	$\delta$	$c_3$	$c_5$
1	1005.3	0.22	10.053	0.1720
2	1012.2	0.24	20.250	0.3464
4	1026.3	0.28	41.072	0.7026
6	1041.3	0.31	62.478	1.0688
8	1055.9	0.34	84.472	1.4451
10	1070.7	0.37	107.070	1.8317
12	1085.7	0.39	130.284	2.2288
14	1100.9	0.42	154.128	2.6367
16	1116.2	0.44	178.592	3.0553
18	1131.9	0.47	203.742	3.4855
20	1147.8	0.49	229.560	3.9272
22	1164.0	0.51	256.080	4.3808
24	1180.4	0.53	283.296	4.8465
26	1197.2	0.55	311.272	5.3251

The concentration units are explained above. The correction  $\delta$  is as follows: if the solution density is determined at the temperature  $T_1$  in deg C, then one adds  $\delta(T_2 - T_1)$  to this density to obtain the corresponding solution density at the temperature  $T_2$ . The numeric value of specific gravity of a solution relative to the specific gravity of water at 4 degrees C is identical to the numeric value of the solution density in g/cc. Data source is (Achmatowicz et al., 1954a, 1954b).

**Table 3.** Salt solution density at 20 deg C and the mole fraction of salt.

g/cc	$x_1$
1.0053	0.0031
1.0122	0.0062
1.0263	0.0127
1.0413	0.0193
1.0559	0.0261
1.0707	0.0331
1.0857	0.0403
1.1009	0.0477
1.1162	0.0554
1.1319	0.0633
1.1478	0.0715
1.1640	0.0799
1.1804	0.0886
1.1972	0.0976

**Figure 2.** Fick's cylindrical tube excess gravities (+) have been converted to mole fractions of salt versus depth by linear interpolation of data in [Table 3](#). The theoretical curve given by Equation (15) is the solid line. Note excellent agreement between theory and experiment.



**Figure 3.** This is how Fick would interpret his cylindrical tube experiment. Note the systematic deviation between the data and the straight line drawn by Fick.

conical funnel, and in the absence of gravity, the salt concentration contours would be sections of concentric spheres centered on the salt reservoir at the funnel tip. One may argue that in the gravitational field the spherical concentration profiles of salt will be flattened vigorously by buoyancy force<sup>3</sup>. The denser salt solution near the funnel axis will sink, while the less dense solution near the walls will be buoyed. The concentration profiles will then become almost perfectly horizontal. With help of **Figure 4**, this assertion can be proven as follows. For the salt profile flattening to happen, the ratio of the characteristic time of diffusion,  $\tau_D$  spreading the salt radially, and convection,  $\tau_C$ , tumbling the more concentrated salt solution down a “hill” of height  $h$ , must be much more than one:

$$\text{Fick's Number } Fi = \frac{\tau_D}{\tau_C} \gg 1, \quad (16)$$

i.e., buoyancy flattens the constant salt concentration profiles before diffusion propagates them as sections of concentric spheres.

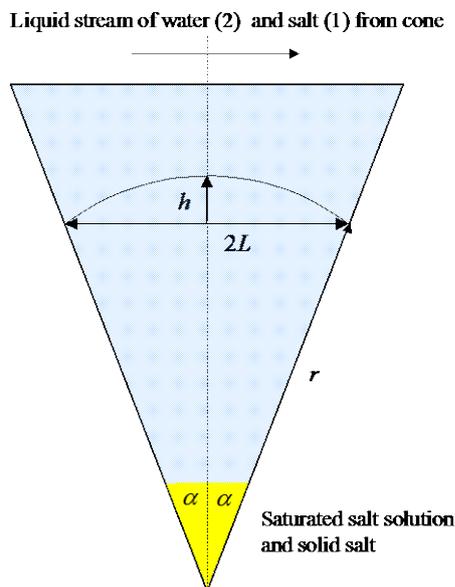
The characteristic diffusion time scale can be obtained from the diffusion coefficient,  $D_{12}$ , and the distance,  $h$ :

$$\tau_D \approx \frac{h^2}{D_{12}} \quad (17)$$

Assuming no viscous dissipation, the shortest convection time scale can be obtained from the balance of potential and kinetic energy:

$$\begin{aligned} \Delta\rho gh &= \frac{1}{2} \rho v_{C,\max}^2 \\ v_{C,\max} &\approx \sqrt{2\Delta\rho/\rho gh} \\ \tau_C &\approx \frac{L}{v_{C,\max}/2} \end{aligned} \quad (18)$$

<sup>3</sup>Fick was aware of this phenomenon; see the underlined sentences in **Part II**, Section 24.



**Figure 4.** Geometry of flattening of diffusion front.

From elementary geometry, it also follows that

$$\begin{aligned} L &= r \sin \alpha, \\ h &= r(1 - \cos \alpha) \end{aligned} \quad (19)$$

By combining Equations (16)-(19), one obtains the following criterion

$$\begin{aligned} \text{Fi} &\approx \frac{h^2/D_{12}}{2L/\sqrt{2g'h}} = \frac{r^{3/2}(1-\cos\alpha)^{5/2}}{2\sin\alpha} \frac{\sqrt{2g'}}{D_{12}} \gg 1, \quad g' \equiv \frac{\Delta\rho}{\rho} g \\ r &\gg r_{\text{crit}} \equiv \left[ \frac{2D_{12}\sin\alpha}{\sqrt{2g'(1-\cos\alpha)^5}} \right]^{3/2} \end{aligned} \quad (20)$$

The plot of the critical distance from the salt reservoir with the most conservative  $g' = 0.01g$  is given in **Figure 5**. It is obvious that at distances of more than 1 mm above the salt reservoir, the salt concentration profiles are essentially flat.

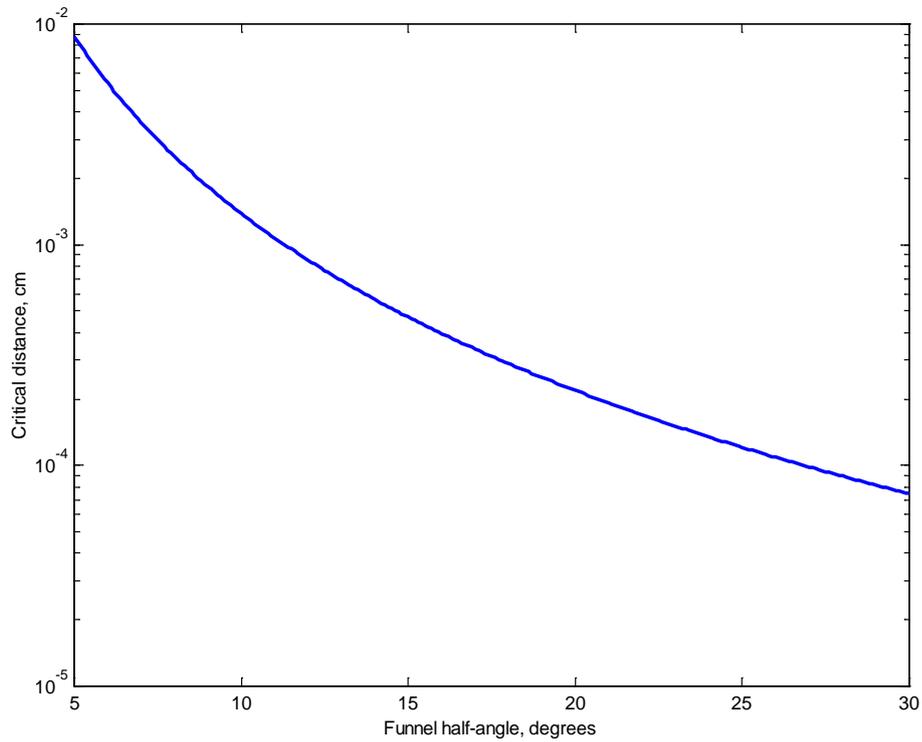
The geometry of Fick's cemented funnel experiments is shown in **Figure 6**. The junction between the funnel and the salt reservoir is at an unknown elevation  $z_1$  at which the salt solution is saturated. Because the deepest reported salt density is far from the density of the saturated salt solution, there is an unknown offset  $\delta z$  between  $z_1$  and the deepest measurement.

In the cylindrical-polar coordinate system in **Figure 6**, the vertical diffusion flux is

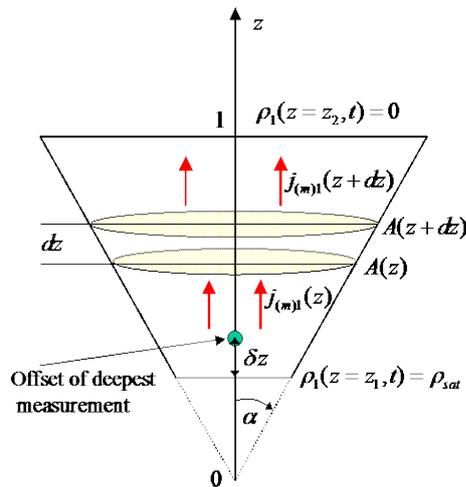
$$\begin{aligned} j_{(n)v}^*(z) &= j_{(n)1}(z) - x_1 j_{(n)1}(z) - x_1 0 = -cD_{12} \nabla x_1 \\ j_{(n)1}(z) &= -\frac{cD_{12}}{1-x_1} \frac{dx_1}{dz} \end{aligned} \quad (21)$$

The salt mass balance over a cylinder with the base of  $\pi r^2(z)$  and height  $dz$ , states that at steady state

$$\begin{aligned} \frac{d}{dz} (r^2(z) j_{(n)1}(z)) &= 0, \\ \frac{d}{dz} (z^2 j_{(n)1}(z)) &= 0. \end{aligned} \quad (22)$$



**Figure 5.** The critical distance from the salt reservoir at the tip of an inverted conical funnel versus the funnel half-angle. At distances much greater than the critical distance, the salt concentration profiles will be essentially flat.



**Figure 6.** Geometry of Fick's funnel experiment.

Substitution of Equation (21) into Equation (22) and assumption of constant  $cD_{12}$  give

$$\frac{d}{dz} \left( z^2 \frac{1}{1-x_1} \frac{dx_1}{dz} \right) = 0, \tag{23}$$

$$x_1(z_1) = 0.0976, \quad x_1(z_2) = 0.$$

Equation (23) can be readily solved (Bird et al., 1960) and the result is

$$\frac{1-x_1(z)}{1-x_1(z_1)} = \left( \frac{1-x_1(z_2)}{1-x_1(z_1)} \right)^{\frac{1/z_1-1/z}{1/z_1-1/z_2}} \quad (24)$$

To match Fick's results with the theoretical curve (24), one needs to find the lower elevation  $z_1$  and the measurement offset  $\delta z$ . Then  $z_2 = z_1 + \delta z + (155.4 - 27.7)/10$  cm. The resulting two-parameter optimization problem has been solved using the Nelder-Mead amoeba algorithm and the solution is:

$$\begin{aligned} z_1 &= 4.985 \approx 5 \text{ cm}, \\ \delta z &= 3.0848 \approx 3 \text{ cm}, \\ z_2 &= 20.84 \approx 21 \text{ cm}. \end{aligned} \quad (25)$$

Without invoking a nonzero offset, Fick's experimental results cannot be matched. Thus, the funnel-salt reservoir junction corresponds to the elevation of 5 cm above the funnel tip and the deepest gravity measurement was performed 3 cm above that junction. The resulting fit of Fick's funnel data is shown in **Figure 7**. A little bit of scientific sleuthing has resulted in excellent agreement with Fick's experimental data—a handsome reward indeed!

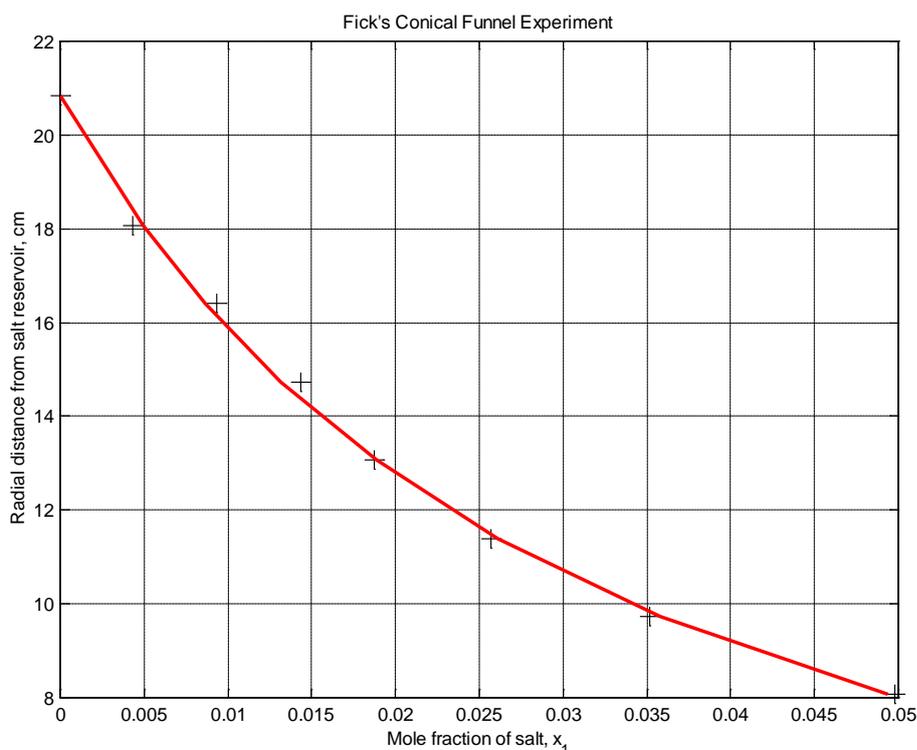
#### 4. Discussion of Fick's Equation

On *no basis* beyond an asserted analogy to Fourier's analysis of the flow of heat, Fick proposed that in a binary mixture the diffusion mass flux density vector is proportional to the gradient of mass density:

$$\dot{j}_{(mv)B} \equiv \rho_B \mathbf{v}_{(D)B} = -D \nabla \rho_B, \quad B = 1, 2, \quad D > 0, \quad (26)$$

where  $D$  is a phenomenological coefficient which may depend upon the densities and the temperature.

From Equation (9) we now know that Equation (26) holds *only* if the solution density is *constant*:



**Figure 7.** Fick's conical funnel excess gravities (+) have been converted to mole fractions of salt versus by linear interpolation of data in **Table 3**. The theoretical curve given by Equation (24) is the solid line. Note excellent agreement between the theory and Fick's experiment.

$$j_{(m)v}B \equiv \rho_B \mathbf{v}_{(D)B} = -\rho D \nabla w_B = -\rho D \nabla (\rho_B / \rho) = -D \nabla \rho_B, \quad (27)$$

$$B = 1 \text{ (salt)}, \quad B = 2 \text{ (water)}, \quad D > 0, \quad \rho = \text{const}$$

Because densities of Fick's salt solutions varied by 20%, Fick in fact was mistaken in asserting Equation (26). His subsequent diffusion equation was derived from a shell mass balance between two horizontal planes  $dz$  apart.

Based on the mass balance shown in **Figure 6**, Fick derived the following equation:

$$A(z) dz \frac{\partial \rho_1}{\partial t} = j_{(m)1}(z, t) A(z) + j_{(m)1}(z + dz, t) A(z + dz)$$

$$\frac{\partial \rho_1}{\partial t} = -\frac{1}{A(z)} \frac{\partial}{\partial z} (A(z) j_{(m)1}(z, t)) \quad (28)$$

Instead of inserting the salt mass flux density from Equation (10) (he did not know this equation), Fick asserted Equation (26), and obtained the following equation:

$$\frac{\partial \rho_1}{\partial t} = D \left( \frac{\partial^2 \rho_1}{\partial z^2} + \frac{1}{A(z)} \frac{dA}{dz} \frac{\partial \rho_1}{\partial z} \right). \quad (29)$$

At steady state, and in the conical funnel whose radius is given as  $r(z) = (\tan \alpha)z$ , Fick simplified Equation (29) and solved it:

$$\frac{d^2 \rho_1}{dz^2} + \frac{2}{z} \frac{d\rho_1}{dz} = 0$$

$$\rho_1(z) = C_1 - \frac{C_2}{z}, \quad (30)$$

The two constants  $C_1$  and  $C_2$  "... are to be so determined, that for a certain  $z$  (where the cone is cut off and rests upon the salt reservoir<sup>4</sup>)  $\rho_1$  is equal to perfect saturation; and for a certain value of  $z$  which corresponds to the base of the funnel<sup>5</sup>,  $\rho_1$  becomes = 0". Thus

$$\rho_1(z = z_2) = 0, \quad \rho_1(z = z_1) = \rho_{sat} = 0.196 \text{ g/cc}. \quad (31)$$

If Fick knew about Equation (10), then instead of Equation (30) he would have probably written:

$$cD \frac{d}{dz} \left( A(z) \frac{1}{1-x_1} \frac{dx_1}{dz} \right) = \frac{d}{dz} \left( z^2 \frac{1}{1-x_1} \frac{dx_1}{dz} \right) = 0, \quad (32)$$

and he would have obtained Equation (23).

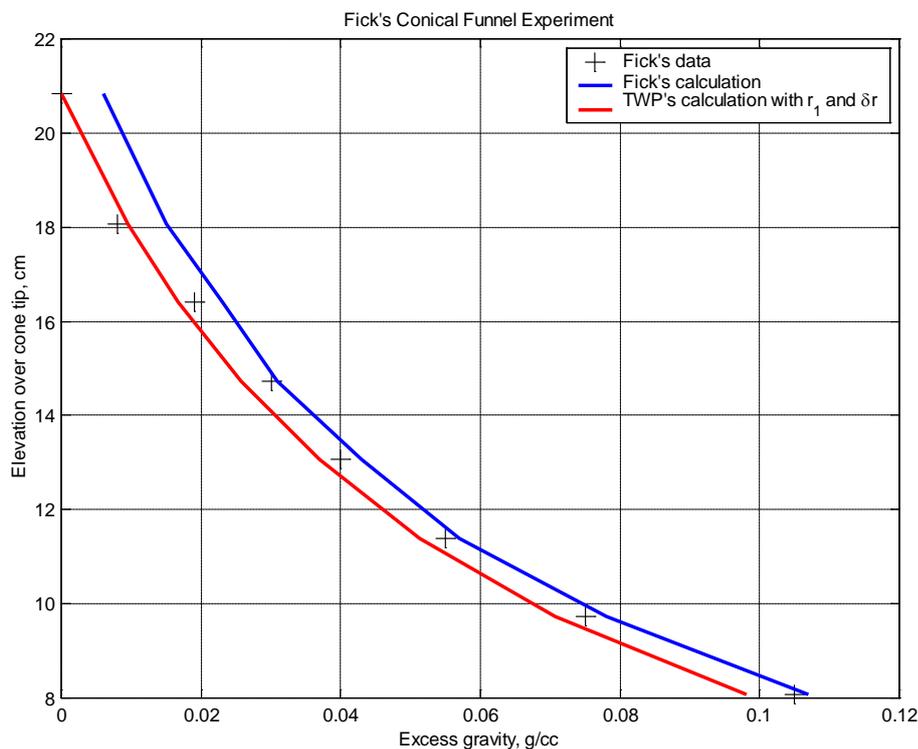
Because Fick does not report these "certain values of  $z$ ", to obtain the two constants we must use the elevation of the funnel base, and the offset of the deepest measurement calculated above. The two constants in Equation (30) are then readily calculated as  $C_1 = -0.0616$ ,  $C_2 = 1.2843$ . In the paper, however, Fick lists his calculated salt density profile! The raw data, Fick's calculation and the present calculation are shown in **Figure 8**. Agreement between the *reconstructed* solution and Fick's "*exact*" calculation is very good indeed. The latter comparison confirms validity of the elevations (or axial distances) listed in Equation (25). Of course, because of the incorrect form of the governing equation, the solutions shown in **Figure 8** are nowhere nearly as good as the solution shown in **Figure 7**.

## 5. Conclusion

In general, Fick's Equation (29) is not entirely correct. For the concentrated salt solutions, one may not assert that mass density  $\rho_1$  is the appropriate unit of concentration, and that  $\rho = \text{const}$ . As it stands, after the sign correction, Fick's original equation can only be applied to dilute solutions and to such tubes of variable cross-section whose walls are orthogonal to the surfaces of constant concentration. This does not detract however from

<sup>4</sup>Fick used  $y$  instead of  $\rho_1$  and  $x$  instead of  $z$ . So his "certain distance  $x$ " becomes  $z = z_1$  in our notation.

<sup>5</sup>Equal to the outer elevation  $z_2$  in our notation.



**Figure 8.** Fick's excess gravity data (+) in the conical funnel, his calculated salt density profile (upper curve), and the profile reconstructed here with use of the previously obtained values of  $z_1$  and  $\delta z$ .

Fick's great physical insight, and from his creative and quite accurate<sup>6</sup> experimental technique!

## Acknowledgements

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## References

- Achmatowicz, O. et al. (Ed.) (1954a). *Chemical Calendar*. Vol. I. Warsaw: PWN. (in Polish)
- Achmatowicz, O. et al. (Ed.) (1954b). *Chemical Calendar*. Vol. 2, Part II. Warsaw: PWN. (in Polish)
- Bird, R. B., Stewart, W. E., & Lightfoot, E. N. (1960). *Transport Phenomena*. New York: John Wiley & Sons, Inc.
- Fick, A. (1855a). On Liquid Diffusion. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 10, 30-39.
- Fick, A. (1855b). Ueber Diffusion (On Diffusion). *Annalen der Physik und Chemie von J. C. Pogendorff*, 94, 59-86.
- Fourier, J. B. J. (1807). *Théorie des mouvements de la chaleur dans le corps solides*. French Academy.
- Fourier, J. B. J. (1822). *Theory of Heat (Théorie Analytique del la Chaleur)*. Paris: F. Didot.
- Garber, E., Brush, S. G., & Everitt, C. W. F. (Eds.) (1986). *Maxwell on Molecules and Gases*. Cambridge, Massachusetts: MIT Press.
- Hirschfelder, J. O., Curtiss, C. F., & Bird, R. B. (1954). *Molecular Theory of Gases and Liquids*. New York: John Wiley & Sons, Inc.
- Stefan, J. (1871). Über das Gleichgewicht und die Bewegung, insbesondere die Diffusion von Gasmengen. *Wiener Sitzungs-*

<sup>6</sup>Fick remained modest about his approach: "... This method (of weighing an immersed glass bulb to determine density) creates little confidence at first sight, nevertheless preliminary experiments showed it to be sufficiently accurate".

*berichte*, 63, 63-124.

Truesdell, C. (1962). Mechanical Basis of Diffusion. *The Journal of Chemical Physics*, 37.

Truesdell, C. (1966). *The Elements of Continuum Mechanics*. New York: Springer-Verlag.

## Appendix—Different Units for Salt Concentrations

There are several ways of expressing salt concentrations (Achmatowicz et al., 1954a, 1954b):

- 1) Number of grams of salt per 100 g of solution,  $c_1$ ;
- 2) Number of grams of salt per 100 g of water,  $c_2$ ;
- 3) Number of grams of salt per 1 liter of solution, mass concentration,  $c_3$ ;
- 4) Number of moles of salt per 1000 moles of water,  $c_4$ ;
- 5) Number of moles of salt per 1 liter of solution, molar concentration,  $c_5$ ;
- 6) Number of moles of salt per 1 kg of water, molality,  $c_6$ ;
- 7) Mole fraction of salt in water,  $c_7$ ;

Let  $\gamma$  denote the specific gravity of solution, and  $M$  the molecular weight of salt:

$$c_1 = \frac{c_3}{10\gamma} = \frac{100c_2}{100 + c_2} = \frac{c_3 M}{10\gamma}$$

$$c_2 = \frac{100c_1}{100 - c_1} = \frac{100c_3}{1000\gamma - c_3} = \frac{c_6 M}{10}$$

$$c_3 = 10c_1\gamma = \frac{1000c_2\gamma}{100 + c_2} = c_5 M$$

$$c_4 = \frac{180.2c_2}{M}$$

$$c_5 = \frac{c_3}{M} = \frac{10\gamma c_1}{M}$$

$$c_6 = \frac{10c_2}{M}$$

$$c_7 = \frac{c_4}{1000 + c_4}$$

(A1)

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