

# Fick's Diffusion Experiments Revisited —Part II (English Translation of Fick's Original Thinking)

Tad W. Patzek

Department of Petroleum and Geosystems Engineering, The University of Texas, Austin, TX, USA  
Email: [patzek@mail.utexas.edu](mailto:patzek@mail.utexas.edu)

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## Abstract

In this paper, we revisit Fick's original diffusion experiments and reconstruct the geometry of his inverted funnel. In Part I, we show 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. In Part II, we provide 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's Annalen paper On Diffusion.

## Keywords

Salt, Liquid, Diffusion, Medical, Physics, Pogendorff Annalen

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## 1. Introduction

Here we translate the pertinent fragments of Chapter 2 in *Medical Physics*, Parts I and II, by Dr. Adolf Fick, Anatomy Demonstrator in Zürich. This book was published by the Printing Press and Publishing Company of Friedrich Vieweg and Son, Braunschweig, 1856.

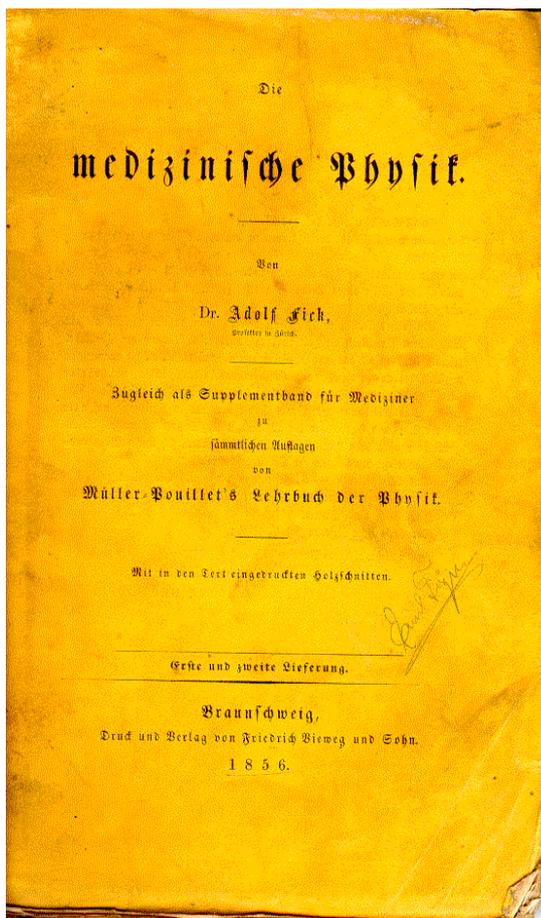
This translation of Fick's discourse on laws of diffusion in liquid mixtures in direct contact and separated by permeable membranes (Articles 23 - 39) was performed by Ms. Karin Mumford with the help from Tad W.

Patzek. The figure numbers follow Fick's book. The book was typeset in German gothic, **Figure 1**, and Fick's painfully long compound sentences did not make the translation any easier.

## 2. Laws of Diffusions

Now all that's left are those molecular movements that occur on contact with heterogeneous liquids. The essence of this is given the name *liquid diffusion*. At this point one has to remember the commonly known fact that in contrast to gases in each case of contact of heterogeneous molecular aggregates, diffusion currents will occur regardless of hydrostatic equilibrium. Liquid diffusion operates in much more heterogeneous liquids, which on contact are absolutely indifferent against each other, so that in no location flow will prevail as soon as each of the liquids by itself is in a state of hydrostatic equilibrium. Examples of these indifferent characteristics are combinations of fatty oils with water, or mercury with most other liquids. To explain this one cannot assume that the heterogeneous molecules in question reject each other entirely, rather it is sufficient to assume that the attraction between each two heterogeneous molecules is less than that between two homogeneous of one as well as of the other aggregate. If attraction between the heterogeneous molecules is stronger than between a pair of homogeneous molecules, a molecular movement happens immediately at the interface, which develops the diffusion current in a manner analogous to the gas process. Therefore, both processes have in common that none of them comes to rest and attains final equilibrium until a uniform equilibrium distribution is produced in the entire space that is occupied by both diffusing substances, meaning until in each part of this space the same condition is obtained for each of the substances.

24. In the currently still inadequate understanding of the structure of molecules, it would be useless to try to demonstrate this course of events. We have to restrict ourselves to just demonstrating here the known laws from



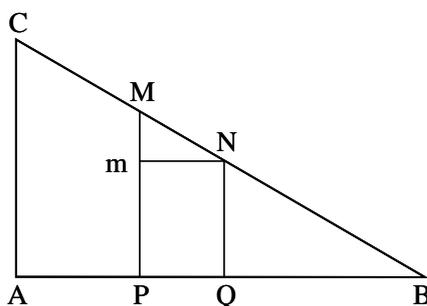
**Figure 1.** Cover of Parts I and II of Fick's Medical Physics book.

our experience. Until now, from all possible cases, only the ones where the touching liquid solutions of the same solid in the same solvent, which only differed in their concentrations were subject to a specific test. This is the reason for us to start this case with the governing law, but not without mentioning immediately that other cases with a probability bordering certainty are subject to the same law, if one only interprets or modifies terms of their mathematical description. To avoid unnecessary notation and at the same time deal with fixed concepts, we will simply name the dissolved solid salt and the solvent water. The governing law for the spreading of salt in a water mass is, to say it very briefly, the same as the one that rules the spreading of heat in a heat-conducting body, on which Fourier based his famous mathematical theory of heat, and that was extended by Ohm, as we know with great success, to the flow of electricity in a conductor. Avoiding the shorthand language of mathematical analysis, we must express the same as follows. One has to think of two very thin horizontal solvent layers on top of each other, the lower one contains more salt and its concentration is  $=k$ ; in the top one we will assume the lesser concentration  $k'$ . If now the separation of both layers is  $=d$ , all these quantities will somehow retain the same values during a certain time interval  $\mathcal{G}$ . The diffusion current, caused by the heterogeneity (concentration difference) between both layers during the imagined time interval, conveys a quantity of salt through the unit area of the dividing surface from the concentrated lower layer to the thinner upper one that is  $C \frac{k-k'}{d} \mathcal{G}$ . Here  $C$  is a quantity depending on the chemical nature of the relevant salt and the temperature alone, and therefore for the present consideration it is considered constant. If  $Q$  were the total surface area of both layers, the total amount of salt delivered to the upper would be  $=C \cdot Q \frac{k-k'}{d} \mathcal{G}$ . At the same time, a water mass will be added from the upper layer to the bottom layer, which occupies the same volume so that the volumes of both layers together will not be altered during the process. The special assumption of horizontal layers with constant concentration was necessary to make, because only in this case a hydrostatic equilibrium remains in the liquid mass. It also had to be assumed, as we did just now, that the change of the concentration from one horizontal layer to the other one only takes place if the upper layer is more diluted than the lower layer. Only then, meaning that always when a less dense layer rests upon a heavier one, the hydrostatic equilibrium is stabilized. Hydrostatic equilibrium must also hold in the liquid mass if the diffusion current shall be achieved untroubled by hydrodynamic currents<sup>1</sup>. One can derive through integration of the just formulated law that directly represents the elementary process, how the concentrations in a finite mass will change after elapse of a finite time, if initially they were distributed in a given manner. By comparing the thus achieved results with the observational facts, one can recognize the accuracy or inaccuracy of the assumed governing law.

**25.** At this point, we shall discuss in more detail a case that can be perceived without application of the higher analysis. We think namely of a cylinder filled with liquid whose density from bottom to top in elevation above the ground is proportionally reduced in such a way that if one looked at the concentration of a given layer as ordinate of a curve of which the abscise would be the height of the same above the lower end surface, this curve would make a straight line<sup>2</sup>. In this geometry, of course, the given concentration difference of two arbitrarily chosen layers is always proportional to their distance, and the constant proportion of these two quantities can namely be expressed through the proportion of the concentration difference between the lower- and upper-end cross-section to the length of the whole cylinder. **Figure 2** further makes this assertion graphically clear. It means namely,  $AB$  is the length of the whole cylinder and  $CB$  is a line, the ordinates of which denote the concentrations of the layers, so that for example over a distance  $AP$  from the lower end cross-section the concentration  $PM$  occurs. At  $Q$ , in comparison, the concentration  $QN$  is located. By looking at the figure, one recognizes immediately that  $PM-QN$  or  $Mm$  has a constant proportion to the distance of the layers  $PQ$  or  $mN$ . This distance is arbitrary, and specifically the latter proportion is the same as the proportion of the difference of the concentration  $A$  ( $AC$ ) and  $B$  (zero is the assumed value of the liquid concentration at the upper end of the cylinder) to the full length of the cylinder, therefore  $=\frac{AC}{AB}$ . The same ratio has to hold between the infinitely small differences of concentrations in two immediately adjacent layers at the just as infinitely small distance from each other. One may take the same proportion at whichever section of the cylinder one chooses. As to how from this proportion the salt and water exchange between consecutive layers depends on the assumed governing law. This exchange

<sup>1</sup>Text underlined by TWP.

<sup>2</sup>Hence, Fick wrote Equation (30) in Part I, text underlined by TWP.



**Figure 2.** In cylindrical geometry, the given concentration difference of two arbitrarily chosen layers is always proportional to their distance, and the constant proportion of these two quantities can be expressed through the proportion of the concentration difference between the lower- and upper-end cross-section to the length of the whole cylinder.

is just as intense in all parts of the cylinder; that means that each layer receives as much salt from the previous one during a given small time interval as it distributes to the following one. Thus, the concentration (in each layer) remains the same. If therefore the concentration  $AC$  of the lower-end cross-section and the zero concentration of the upper end during a finite time interval could be kept constant by any means, the concentration in the entire cylinder would remain constant during the entire time. This way a stationary diffusion current is formed, which moves the same amount of salt from bottom to top in each time instant through all cross-sections, which according to our law has to be  $= C \cdot Q \frac{AC}{AB}$ . In due time, the stationary distribution of the concentration in the cylinder evolves, it could have been in the beginning or otherwise, one only needs to keep the concentration of the two end cross-sections constant. This condition can be accomplished easily in an experiment. One keeps the lower-end cross-section of the cylinder temporarily filled with any saturated solution in contact with solid salt, the upper one though in contact with (fresh) water. This way the lowest layer always maintains total saturation by constantly being able to dissolve salt, the top one constantly delivers each trace of salt it receives from the bottom through diffusion immediately to the surrounding water and its concentration remains constant = zero.

Temperature during the processes <sup>3</sup>	C calculated from the amount of salt delivered		
	The longest tube	The medium tube	The shortest tube
15.8 - 14.8	9.67	9.7	9.30
15.5 - 16		9.57	
16 - 16.5		9.94	
17.5 - 18.5	10.79		
18 - 19	10.71	11.08	10.50
20	11.14		11.02
19 - 22	11.44	11.33	
20 - 21	11.89		11.12

In fact, experiments took place<sup>4</sup> in part to prove the law, and in part to determine the constant  $C$ . So far, though, only experiments with kitchen salt and water are at hand. The experimental setup is as follows. A cylinder filled with a salt solution was cemented into a salt reservoir, and the whole unit was sunk into a huge water container. The same amount of salt, which passed through each cross-section of the cylinder after achievement of the stationary condition, also had to pass through the end cross-section and pass over into the water container. The difference in the density of both end cross-sections was the value of the total saturation as the subtrahend,

<sup>3</sup>In centigrades.

<sup>4</sup>“Ueber Diffusion”, von Dr. Adolph Fick, Annalen der Physik und Chemie, Herausgegeben zu Berlin von J. C. Pogendorff, Vol. CXIV (Vier und Neunzigster Band), Leipzig, 1855, pp. 59-86.

the concentration on the upper end was =zero. If the cylinder, the length of which was likewise known, would deliver a salt amount  $m$  during the given time interval, all remaining quantities will be known in the equation  $m = C \cdot Q \frac{AC}{AB}$ , so that  $C$  can be found from it. The numeric results for the combination of cooking salt and water are compiled in the following table. We remark that each time three tubes of different length were set up at the same time and from the delivered salt in each one  $C$  was calculated. The three values of  $C$  of course had to be the same and in fact corresponded as perfectly as is to be expected in similar experiments anywhere.

26. The bases of consideration for these units are: the time, one day (24 hours); the length, 1 mm; the area, a circle of 10 mm radius; and the concentration, complete saturation. One also recognizes from the above table that the quantity  $C$  is defined henceforth as the amount of salt that moves through the unit cross section during the unit time interval in a stationary diffusion current. This current owes its existence to a uniform concentration decrease, which, expanded over the whole length, will reduce the concentration from 1 to zero under controlled temperature increase.

The constant  $C$  is the only true constant for a given solid combination and temperature, which can be comfortably drawn from experiments in the just described order. It is quantity independent from all other conditions, which one can also fittingly name "the rule of the diffusivity of the given solid combination at the given temperature. Graham<sup>5</sup>, in his generally well-known work about the subject with which we are dealing here did not proceed to the analysis of the process. He would derive the measure of the diffusivity directly from different experiments which took place in the following manner: He filled two bottles of the same size and shape up to the neck (which has a radius of 1.25 English inches) with the solutions of the solid to be tested. The neck itself was still filled with clear water and then the whole receptacle was sunk into a water container; he determined the amount of the removed solid, which in the course of a certain time was diffused from the bottle into the water of the container. He was convinced that in this formula he had discovered the measure of diffusivity. Following these advanced discussions one may by no means expect that these numbers must be proportional to our  $C$ . In the neck of the bottle, a stationary diffusion current obviously does not develop, instead a process that would be very difficult to discuss analytically. Nevertheless, these numbers are very interesting whilst they at least grow simultaneously with the diffusivity, though not proportionally, so that in Graham's experiments a solid described by a larger number is more diffusive than one described by a smaller one. Therefore, I will here now list Graham's numerical results especially that a comparable overall view of different solids has not been reached yet in a different way.

Solution of 20 parts of dehydrated salt per 100 parts of water	Specific gravity of solution	The amount diffused during 8 days in Grains
Sodium chloride	1.1265	58.5
Magnesium sulfate	1.1265	58.87
Sodium sulfate	1.185	27.42
Aqueous sulfuric acid	1.120	52.1
	1.120	51.02
	1.108	68.79
	1.108	69.86
Cane sugar	1.070	27.74
Melted cane sugar	1.066	26.21
Starch sugar	1.061	26.94
Syrup of cane sugar	1.069	32.55
Arabian gum	1.060	13.24
Albumen	1.053	3.08

<sup>5</sup>Annalen b. Chem. u. Pharm., Vol. 77, p. 56.

The temperature for all experiments was kept between the limits of 15.5 and 17 degrees Celsius. The diffusion capability of albumen will be increased by the addition of acetic acid. The adding of egg white does not reduce the diffusivity of the salts, just as it does little to that of urea, which incidentally stands very close to that of sodium chloride.

27. Graham also conducted very remarkable experiments with combinations of different salt solutions, which he filled into his bottles, retaining all other arrangements, and let them diffuse. It was namely found that with the simultaneous presence of the other salt the diffusivity of the less soluble one became reduced. If bi-sulfuric acid potash was filled to the bottle, not only this salt diffused out but also still free sulfuric acid, so that therefore a part of this salt decomposed through the diffusion. Under these circumstances, alum will be partly decomposed just as well, whilst more sulfuric acid potash diffuses into the surrounding water than alum is built up by the simultaneously diffusing sulfuric acid aluminum oxide. If Graham mixed sulfuric acid potash (in a very diluted solution to not develop immediate concentration gradient), potassium chloride or sodium chloride with calcium water and let the mixture diffuse against calcium water, the freed alkali would diffuse and the acid would combine with the calcium, which would precipitate if it was in sulfuric acid.

28. It also still seems to follow from Graham's experiments that weak diffusion currents can cross through each other without any disturbance; because it was found that the diffusion of a 4-percent solution of sodium carbonate took place in the same manner whether the surrounding liquid was pure water or a 4-percent solution of sodium chloride. In addition, with several other different combinations of two salts, the same behavior was observed.

29. The equilibration of heterogeneous liquids still also takes place, just alike the gases, if they are separated by a porous partition wall of suitable composition, and with it still occur very strange phenomena, which are known under the names of "endosmose"<sup>6</sup> and "exosmose". Without a doubt (the membrane) is the last reason for the equilibration or the driving forces are here the same as in the simpler case of diffusion without a membrane, only the effect is modified through the physical conditions of the liquid molecules in the membrane. Therefore, above all, the attention has to be directed to these if the reason is to discover the diffusion of liquids through membranes. That means one has mainly to examine the way in which the liquids penetrate into those bodies, which used as a partition wall can cause diffusion. Actually, the idea that a substance penetrates into a space that is occupied by another substance cannot create any problems for us. We assume from the atomic picture that each space occupied by an ever so dense substance still leaves enough empty space to grant room for the atoms of another substance, which will store themselves among the atoms of the first one. The penetration of a liquid into certain solids, known by the name of "imbibition", can also be thought of in a considerably different way though. One can, 1) imagine the molecules of the imbibed liquid are among themselves in the uniform molecular interstices of the solid body distributed in the same manner. Were this opinion correct, then one might understandably assume very radical differences between the constitution of "imbibable" and not imbibable bodies; nevertheless, the same chemical substance (i.e., clay) can now have the one and then the other characteristic depending on the mechanical formation of its small (not smallest) particles. Admittedly, the imbibition of a piece of porous clay may still be different in nature from that in a piece of coagulated protein. The difference shows itself immediately if one changes the expression and says "swelling" instead of "imbibition". From a piece of clay, one cannot say that it swells. 2) It also can be thought that a body capable to imbibe is similar to a network or a spongy tissue that besides the molecular interstices also has other gaps that in mechanical sense stand far apart from the interstices, namely much surpassing them in size. These gaps, one could think then, fill themselves during the swelling with the imbibed liquid; meanwhile, no atom penetrates into the space between the molecules that constitute the solid part of the network. This idea offers the immense formal convenience that, if one takes it as a basis of the explanation of the swelling appearances as well as the one of the diffusion through separating walls, one becomes independent of each molecular hypothesis.

In fact, most of the researchers in these fields have more or less explicitly adopted the just discussed second theory. By the way, it is still to consider that these two theories do not exclude each other. In particular, Ludwig tends to connect them when he states<sup>7</sup>: "As much as we find ourselves in the dark about the special kind of fusion (of the solid substance and the imbibed liquid particles), we may yet still assert that in most of the swollen

<sup>6</sup>The general term *osmose* (now osmosis) was introduced in 1854 by a British chemist, Thomas Graham. Here we shall use the modern term *endosmosis*, which is synonymous with motion through, passage, transmission; permeation; penetration, interpenetration; infiltration; endosmose, exosmose (obs); endosmosis (Chem) (Roget's Thesaurus, Project Gutenberg, <http://promo.net/pg/>).

<sup>7</sup>Lehrbuch der Physiologie, Vol. I, p. 60.

substances the absorbed liquids partly are present in larger pores, which are existing between more or less large piles of molecules, but partly are nestling between the molecules themselves”.

**30.** The appearance of the swelling itself is now essentially that a substance capable of it absorbs a certain quantity from the surrounding liquid in the course of a more or less long time. When this happens, the process reaches equilibrium, whilst no other liquid molecule penetrates into it, may by the way, as much or as little liquid be in store. Through the comparison of the amount of the solid substance and the maximum absorbed liquid (or in the equilibrium after completion of the process), one obtains the swelling ratio. It (this ratio) obviously depends on the nature of the solid body as well as the liquid, so that the same solid body can absorb different amounts of different liquids, and that different amounts of the same liquid penetrate into different solids. Besides that, the swelling ratio varies also with temperature. No extended quantitative series of experiments are available yet on all these aspects.

Particularly important for our purposes is the imbibition of saline solutions. First, it has been shown that as far as the imbibition in the swelling body, thus the swelling ratio, is concerned, regularly less liquid is imbibed from the saline solution than from pure water, and from different solutions of the same salts even less, the more concentrated they are. After Liebig, for example, 100 weight parts of dry ox bladder take in 310 weight parts of pure water, 288 parts of a 9% sodium chloride solution, 235 parts of a 13.5%, and 219 parts of 18% solution. After Cloetta<sup>8</sup>, the swelling ratio (the imbibed weight of liquid divided by the weight of the swelling body) of the ox heart bag is 1.35 for 5.4% and 1.01 for 24.3% saline solution, respectively; it is 1.15 for a solution of 3.5% Glauber's salt<sup>9</sup>, and 0.86 for a 11.7% solution of the same salt.

Much more remarkable though is the difference in the concentration of the solution imbibed into the swelling body and that of the surrounding liquid from which it originated. Bruecke, relying on other appearances, with which we will soon become acquainted, has proposed the hypothesis that a substance that can cause diffusion of a certain saline solution and consequently is swelling-capable for the same, would exert a larger attraction towards the molecules of water than towards those of the dissolved salt. If this assumption were correct, in each of the pores in which the imbibed liquid is contained, there would be a less concentrated solution against the walls than in the center, whilst the predominant attraction of the wall molecules against the water simply in the proximity of the same has to draw together more water. Ludwig, based on this thought, and also considering that even in the most central part of the pore in any case no larger concentration could occur than in the surrounding liquid, assumed that the concentration in all of the imbibed liquid should be lower than the one in the surrounding liquid from which the imbibed one is taken. It had to be an average result of the lower concentrations in the wall layers and the higher ones in the center layers, the last of which can at best equal the concentration of the surrounding liquid. One therefore understands in one word as the concentration on the imbibed liquid the figure, which expresses the proportion of the imbibed salt amount to the total imbibed liquid mass, regardless of how water and salt are distributed in the pores of the solid body. Ludwig saw himself not deceived by his theory but confirmed it through compelling experiments. If he namely put an ox bladder in a 7.2% solution of Glauber's salt, it imbibed a liquid that contained only 4.4% salt. Did he put the same substance in a 19% kitchen salt solution, it so imbibed a 16.5% solution in its pores. Cloetta, who continued this line of experiments, ascertained the ratio of the densities of liquids imbibed in the bodies capable of swelling (animal membrane) and the surrounding ones is for kitchen salt constant, in fact =0.84:1, for Glauber's salt though it depends on the solution density of the surrounding liquid.

#### Experiments with kitchen salt.

Percent content of surrounding liquid	Percent content of solution inside swollen solid	Experiment time in hours	Temperature in deg Réaumur	Density ratio of inner and outer liquid
24.002	20.022	76	10 - 14	0.83
24.288	20.427	78	12 - 15	0.84
6.005	4.679	48	9 - 14	0.77
5.540	4.545	76	9 - 15	0.82
5.493	4.512	76	10 - 15	0.82

<sup>8</sup>Experiments with diffusion through membranes with two salts, 1851.

<sup>9</sup>Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O—crystalline hydrated sodium sulfate.

## Experiments with Glauber's salt.

Percent content of surrounding liquid	Percent content of solution inside swollen solid	Experiment time in hrs	Temperature in deg Réaumur	Density ratio of inner and outer liquid
11.692	4.623	70	8 - 13	0.39
6.500	3.578	70	10 - 16	0.55
4.831	2.744	48	10 - 13	0.56
4.803	2.755	48	8 - 12	0.57

In Cloetta's experiments with kitchen salt, the density of the surrounding liquid fluctuated between 24 and 5 percent and always turned out in the same proportion. I will place here several numeric results of Cloetta's investigation so that the reader can build his own opinion about the degree of accuracy. If one squeezes out the imbibed liquid, as far as this is possible, one receives according to Ludwig's experiments, not a solution of average concentration of the solution that was contained in the pores, but one receives one that corresponds to the density of the original surrounding liquid. Therefore, if the body swelled by dipping it into a 10% kitchen salt solution, one also squeezes out a 10% kitchen salt solution although if one uses a different way to determine the kitchen salt content in the liquid contained in the pores it results in less than 10%. This at first sight very surprising appearance has absolutely no illogicality if one only remembers that through squeezing the central liquid, mass can only be removed from those pores in which the concentration agrees with the surrounding solution. Whereas the wall layers with less concentration are held tightly by the force of attraction of the wall molecules, so that they cannot be removed by the mechanical compressive force.

**31.** If a solution containing two salts next to each other imbibes, the presence of one will modify the imbibing capacity of the other one noticeably. So in particular Cloetta discovered that a piece of ox pericardium has less capability of imbibing Glauber's salt if at the same time the solution contains kitchen salt; and the more kitchen salt it contains the less it will get Glauber's salt. The following table contains the numerical pieces of evidence according to Cloetta's experiments.

Percent content of the outer liquid	Percent content of the inner liquid	Duration of experiment	Temperature in deg Réaumur	Specific gravity of inner liquid (outer = 1)	Relation of imbibed NaS to NaCl NaCl = 100
10.81 $\left\{ \begin{array}{l} 7.838 \text{ NaCl} \\ 2.972 \text{ NaS} \end{array} \right.$	7.708 $\left\{ \begin{array}{l} 6.629 \text{ NaCl} \\ 1.079 \text{ NaS} \end{array} \right.$	72	10 -13	0.71	38
10.817 $\left\{ \begin{array}{l} 7.832 \text{ NaCl} \\ 2.985 \text{ NaS} \end{array} \right.$	7.856 $\left\{ \begin{array}{l} 6.776 \text{ NaCl} \\ 1.079 \text{ NaS} \end{array} \right.$	72	10 -15	0.7	38
15.636 $\left\{ \begin{array}{l} 10.514 \text{ NaCl} \\ 5.122 \text{ NaS} \end{array} \right.$	10.904 $\left\{ \begin{array}{l} 9.073 \text{ NaCl} \\ 1.841 \text{ NaS} \end{array} \right.$	48	11 -14	0.69	48
10.799 $\left\{ \begin{array}{l} 5.813 \text{ NaCl} \\ 4.968 \text{ NaS} \end{array} \right.$	7.030 $\left\{ \begin{array}{l} 4.646 \text{ NaCl} \\ 2.384 \text{ NaS} \end{array} \right.$	48	9 -12	0.65	85
9.93 $\left\{ \begin{array}{l} 5.312 \text{ NaCl} \\ 4.618 \text{ NaS} \end{array} \right.$	6.275 $\left\{ \begin{array}{l} 4.093 \text{ NaCl} \\ 2.182 \text{ NaS} \end{array} \right.$	46	10 -13	0.63	86
10.026 $\left\{ \begin{array}{l} 5.326 \text{ NaCl} \\ 4.700 \text{ NaS} \end{array} \right.$	6.51 $\left\{ \begin{array}{l} 4.295 \text{ NaCl} \\ 2.215 \text{ NaS} \end{array} \right.$	48	9 -13	0.64	88

**32.** Now we will imagine two different liquids, which in direct contact would actually balance out their differences through diffusion currents, separated from each other through a partition wall that dipped into each of the two would swell, which means that its pores could accommodate each of the two liquids. Then we would have all the conditions under which the phenomenon of the endosmosis appears. It is furthermore tacitly assumed that the pores are so tight that filtration is avoided through the attraction between the membrane and the liquid in connection with the cohesion. In addition, even if both sides of the partition wall are moistened, equilibration of the hydrostatic pressure if at all is only possible over a disproportionately long time interval, so that finally within a pore mixing currents through specific gravity differences cannot be produced. When these conditions are met, the heterogeneous solutions will obviously come in direct contact with each other within the partition wall pores and equilibrating diffusion currents will occur immediately. These, of course, cannot come to a stop until each inhomogeneity of the solutions is balanced and so we then see in fact that even with the inclusion of a partition wall between the two solutions the process will not end until all differences are balanced out. During the process, though, fundamental modifications will be caused by the existence of the partition wall. The important difference between the free diffusion and the diffusion through partition walls is mainly because in the former the equal volumes of the same substances are exchanged between two consecutive layers without any difficulty, so that two equally strong currents in opposite directions are constantly moving. In the latter, as a rule, both currents are not equally strong so that after some time the volume on one side of the partition wall has become larger and on the other side it has become smaller. A theory of the endosmosis has therefore first to be based on explaining how the modification of the diffusion current can be created by the presence of the partition wall. Bruecke carried out the first experiment in this direction, which is already based on the aforementioned idea of the distribution of removed substances in the pores of a body capable of swelling. By going into that in more detail now, it has to be remarked beforehand, that here again we can only rely on the case where solutions of the same salt of different density balance their differences through diffusion. The case is that different mixtures of originally liquid masses (for example alcohol and water) diffuse in one another. However, without hesitation, one can go back to the case that a salt in solution is to be regarded as a liquid itself; its molecules are undoubtedly just as easy to rearrange as the ones of a certain amount of alcohol distributed in water. It therefore actually will be a shortcut expression when we talk about salt and water. If now, in fact, the material of the partition wall has a stronger force of attraction to the water than to the salt, and as a result of that a wall layer of pure water surrounds a central liquid thread within the pores, which can adopt the density of the surrounding solution, the latter one will cause a diffusion current the same way as in the pores which we have imagined previously (see #25). That will distribute as much salt to one side as water to the other side, whereas salt will never be able to penetrate into the wall layer, which can be brought into motion by the attraction of the salt solutions with which it is in touch on both sides. From the side of the concentrated solution, however, works an obviously stronger attraction than from the other side, as here in the same area more attracting salt molecules are facing it. Through the continuing currents, the dilute layer at the wall therefore will be in the process of moving towards the concentrated solution, by replenishing itself constantly from the less concentrated one. Thus, to the amount of water, reaching through the central thread the concentrated solution (which is the same as the amount of salt traveling to the other side), an additional amount of water is added to the concentrated solution through the peripheral layer for which no salt equivalent travels to the other side. More water therefore has to travel each time from the more dilute solution to the denser one than salt travels in the opposite direction. The volume of the concentrated solution has to grow through the endosmosis. In fact, the success has been observed regularly. In one case, Bruecke was able to substantiate this theoretical analysis by an unambiguous experiment. Turpentine oil has a substantially stronger attraction to glass than tree oil as it forces out completely the latter from a glass surface; therefore a wall layer of turpentine oil and a central layer of a mixture of both liquids will be found in a glass capillary if both can force their way into it. Bruecke manufactured such a capillary surface, which on one side bordered turpentine oil and on the other side tree oil, and discovered according to the theory that more turpentine oil diffused through the capillary to the tree oil than tree oil in the opposite direction.

**33.** The idea that Bruecke had can be displayed a little farther so that several conclusions of quantitative nature can be drawn out of this. We think about the pores as being cylindrical, and the rectangular cross-section of the separating wall straight through the axial plane would be  $aa'bb'$  (see [Figure 3](#)). If now the separating wall were surrounded by a totally saturated salt solution, according to the above findings, an also saturated solution would only be found in the proximity of the axis of the inner pore (if the pore were extremely tight, probably not

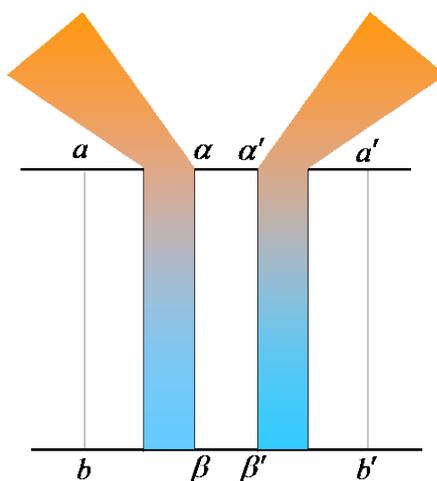


Figure 3. Axial cross-section of a cylindrical pore.

even there). Towards the wall, the concentration would be reduced so that directly at the wall it would be zero. Of course, one concentration would dominate due to the symmetry in a concentric cylindrical layer. The cross-section of such in the plane of the figure should be, e.g.,  $a\beta$  and  $a'\beta'$ . The saturated solution beneath the separating wall (thought as being horizontal) would now be replaced with pure water, diffusion would start, and we could observe what must happen in particular in the cylindrical volume with the cross-section  $a\beta$  and  $a'\beta'$ . At its lower end, the concentration is kept at the zero level through constant contact with the water. At its upper end, though, the concentration maintains the highest possible level through the contact with the saturated solution. Immediately the stationary concentration distribution occurs in this space. The concentration will grow in proportion to the height above the lower end area ( $\beta\beta'$ ). This distribution of the concentration is indicated in the figure by the hatching. Due to the smallness of this volume, stationary condition occurs almost immediately; thus, we can restrict ourselves to its consideration. The concentration distribution now necessitates a stationary diffusion current that moves just as much salt to the bottom as water to the top. One should even be able to calculate the amounts following the above principles (see 26) if the dimensions of the small volume and the maximum possible concentration in it were known. Now, though, the water passing to the top demands a special consideration as well. If the concentration in the small volume (what yet in general has to be presupposed), on which we now have our eyes, has to be lower by a finite amount than the absolute saturation, then a density jump will occur at  $\alpha$  and  $\alpha'$  from the possible maximum in the small volume to the absolute saturation above the separation wall. This jump would cause an almost infinitely strong diffusion current on the spot, which means almost infinitely large amounts of salt would be driven into the pores and just as large amounts of water would be expelled. Let us suppose for a moment that this has actually happened. The salt amounts could not penetrate because the highest concentration in this particular area already exists at the upper end; they must somehow slip off sideways. Larger amounts of water though can be delivered from the bottom than the diffusion current, already thought of as established in the cylindrical volume, delivers. A certain water amount is in a way simultaneously being drawn through. This changes the solution density, whilst the water distributes itself generally in the upper liquid, up to a certain distance noticeable from the upper pore opening. In this way, water creates an upward extending conically widening zone (its two cross-sections are shown in simplification in Figure 3 above  $\alpha$  and  $\alpha'$ ), in which the concentration grows from bottom to top up to the total saturation of the upper solution. Immediately, also here a stationary condition comes into effect and causes a diffusion current of the same strength, which brings just as much water to the top as can be distributed in the same time from the upper end of the imagined volume into the reservoir of saturated solution without altering the concentration. Because obviously the imagined zone would extend itself upwards (and through that the intensity of the diffusion current would be reduced) as soon as more water climbed up in this way, the concentration at the upper end of the zone could still be altered. On the other hand, if less water went up, a jump in the concentration increase would occur at some point, which immediately would cause an infinitely strong diffusion current and this way again absorb the relevant

water amount.

**34.** It is now apparent that through all those cylindrical elementary layers, which are so close to the pore wall that totally saturated solution can no longer exist within them, more water moves to one side than salt moves to other side. As now in a tighter pore proportionally more parts are lying closer to the wall than in a larger one, considerably more of water will be flowing in a tighter pore than in a wider one. One can hardly hope to strongly substantiate this assertion through experiment, as one will hardly find two separation walls that only distinguish themselves from each other by the width of the pores. In any case, though, the following fact speaks for the just established assertion. One has obviously some reason to assume that in the glassy colloidal membrane the pores are disproportionally tighter than in one produced from animal connective tissue (heart pericardium or bladder), so that all other differences against this one are only insignificantly effective. However, it is shown that in fact with a colloidal separation wall, the quantity of water that diffuses towards the concentrated solution is much larger than with an animal bladder. Whilst with the bladder wall approximately 3 to 6 times more water moves into the solution as salt into the water, approximately 20 times more water moves through a colloidal separation wall as salt. In most of my experiments only traces of salt had moved through the colloid, while substantial water quantities made it through in the opposite direction.

**35.** According to the aforementioned idea, the excess of the water above the salt diffusing in the opposite direction must still grow with the increasing mobility of the particles in the saturated solution above the membrane. The amount of absorbed water, which could spread itself in the reservoir without alteration of the saturation, will be even larger the easier movable the particles are. To prove this theory, I mixed solid particles with the upper solution, which interfered with the mobility; received a positive result though, while the proportion of the diffusing salt and water amounts was not changed.

Let us now imagine that instead of the pure water, a solution of the same salt is located underneath the membrane. Above it there is a completely saturated solution at a certain density  $c$ . Counting from the pore wall a number of cylindrical elementary layers will immediately inactive; namely all those in which no higher concentration than that  $c$  is possible. Naturally they fill themselves with a uniformly saturated solution, each one with possibly the most concentrated, and on both their ends the absorbing power will be, proportionally to the difference, between the concentration in the solution contained in it and the respective solutions above and under it. As the upper solution is totally saturated, the difference at the upper end and consequently the absorbency is higher, that is why now only water moves from bottom to top through all these characterized elementary layers. The more central layers in which a larger concentration than  $c$  is possible are making way for a bilateral diffusion current which will produce itself in the afore described manner even though in less intensity. As in doing this, to the contrary of the first described case, some elementary layers have become passive (dormant) for the salt movement, the surplus of the continuing water flow has to grow. If  $c$  were larger than the possible maximum of concentration in the central liquid thread of the pore, the endosmotic current would become unilateral and now only water would be able to move from the thinner solution to the thicker one. In fact, I found out that 11.05 times as much, in a different experiment even 17.05 times as much, water as salt went through a membrane, if the same separated absolutely saturated kitchen salt solution from 22% one. Only 5 or 6 times as much water as salt went through if the membrane separated the saturated kitchen salt solution from pure water. (Other pieces of evidence are in the following table).

**36.** Finally we will imagine that there is again pure water below the membrane, above it though, instead of a saturated solution, there is a solution of the concentration  $c$ . Assume that  $c$  is not as large as the highest concentration, which is still possible at the axis of the pore. Starting from here a series of elementary layers will now show at their upper ends the concentration  $c$ ; namely, all up to the one lying so close to a wall that in it the concentration  $c$  is no longer possible. In the indicated concentric elementary layers now a completely free two-way diffusion current will develop which will carry the same amounts of salt and water to opposite sides. At the upper end the density jump no longer develops and therefore no reason exists to absorb more of the water. Parts of the pores, which in the first case delivered more water, do not deliver it in this one. One can therefore expect that if an unsaturated solution is present above the membrane, the water surplus will be smaller and even much smaller the more diluted the solution is. Ludwig's experiments on the diffusion of kitchen salt confirm this forecast. Things stand different though with his experiments performed with Glauber's salt. In the following table, the numerical results of his experiments have been put together.

## Experiments with kitchen salt.

Membrane name	Temperature deg Réaumur	Concentration of originally surrounding liquids		Ratio of transported salt to transported water
		Upper, %	Lower, %	
XIX	6	Sat.	14.329	1:4.2
XIX	8.25	Sat.	0.0	1:3.2
XIX	8	4.920	0.0	1:1.4
XX	6	Sat.	14.329	1:4.5
XX	8.25	Sat.	0.0	1:4.3
XX	8	4.920	0.0	1:1.4
XXI	8	Sat.	14.34	1:4.5
XXI	8	Sat.	0.0	1:3.5
XXI	8.25	4.920	0.0	1:1.6
X	9	Sat.	22.6	1:7.0
X	9.75	2.006	0.0	1:3.1
XVI	8	Sat.	5.0	1:3.6
XVI	8.75	2.006	0.0	1:1.1

## Experiments with Glauber's salt.

Membrane name	Temperature deg Réaumur	Concentration of originally surrounding liquids		Ratio of transported salt to transported water
		Upper, %	Lower, %	
XI	6.5	Sat.	0.0	1:5.9
XI	8	5.358	0.0	1:8.2
XI	8.5	1.028	0.0	1:24.3
XII	6.5	Sat.	0.0	1:5.5
XII	8	5.359	0.0	1:8.0
XII	8.5	1.028	0.0	1:23.5
XVI	6	Sat.	0.0	1:5.8
XVI	7	5.084	0.0	1:10.5
XVI	8	1.028	0.0	1:21.6

37. Jolln believed to be able to prove that the proportion between the salt and water amounts moved back and forth for one particular salt, one particular membrane, and one particular temperature should be a certain constant, might the concentration of the solution above and below the membrane be what it may. He called this proportion the “endosmotic equivalent”.

Jolln has let the density of the solution vary within too narrow limits; therefore he could easily fail to notice the variations of the endosmotic equivalent observed by Ludwig. From the start, by the way, constancy of the endosmotic equivalent was not actually probable. Apart from the particular picture we have drawn ourselves on the basis of Bruecke's hypothesis that we explained previously, it is yet this much without a doubt that in endosmosis one does not have to deal with a fundamental phenomenon in which the actual constants, which rely only on the innermost unchanging nature of the participating substances, come out that uncomplicated. Endosmosis is in any case a course of events fundamentally modified much more through complicated conditions,

through the fundamental strength of the matter, though in last instance mechanically caused like all others.

**38.** I have noticed that for one particular membrane the equivalent came out differently if I brought saturated kitchen salt solution above and pure water underneath it than if I poured saturated kitchen salt solution underneath and pure water over the membrane. In the last case, the endosmosis equivalent was smaller and more salt went through during the time unit than in the first case. Whether the density plays a role in this case or whether the different sides of the membrane which were facing the water were the actual cause, I do not dare to decide after my not adequately numerous experiments. It is known that already Cima and Matteucci have observed phenomena that favor the last interpretation.

Very important (especially for the organic process) are the diffusions that occur when solution mixtures take the place of simple solutions. Theoretically, one can hardly suspect anything about this object. Contrary to that, though, we have an exact and extensive experimental investigation from Cloetta on the diffusion of mixtures of kitchen salt and Glauber's salt solution. This investigation has resulted in the following laws: First, the diffusion equivalent for each of these two salts is, if it diffuses as the mixture, just as large as if it separately diffuses through the same membrane under the same circumstances (particularly therefore in the same solution density). The deviations from this law in the different experiments are insignificant. If for example  $n$  and  $n'$  were the endosmotic equivalents of the two salts for a certain membrane and concentration, and if it were found in an experiment with the mixture that during any given time the amount  $a$  of the first salt, and the amount  $b$  of the second salt moved across. Then, for the first one a water amount  $=na$ , and for the second one a water amount  $=nb$  must have moved across. Therefore the equivalent of the mixture  $=\frac{na+n'b}{a+b}$  should result from it. Thus this quotient should express the proportion of the entire water amount moved in this experiment counter currently to the simultaneously moved entire salt amount.

Furthermore, it produced also certain relations between the diffusion velocity of the different salt in itself and in a mixture. If one talks about diffusion velocity, for the moment one must distinguish between the salt and the water current. The velocity of the first would be measurable in each single case by the salt amount that moved through the surface unit of the membrane during a given time. The velocity of the water current would evidently find its measure in the related water amount moved to the opposite side. During experiments with each of the two salts separately, it has become obvious that the salt current for kitchen salt "ceteris paribus" has approximately twice the velocity as the one for Glauber's salt. The velocity of the water current is for both salts approximately the same. It now became clear that within the mixture the velocity of the salt current remained unchanged while that of Glauber's salt was reduced. The velocity of the total salt current was therefore larger than the one of a mere kitchen salt current, nevertheless it not quite reached the value of the sum of the velocities of a kitchen salt current and a Glauber's salt current. The water current occurs for both salts in the mixture also with the same velocity; understandably, though, the sum of each of the two speeds in itself cannot combine to the velocity of the total water current because the diffusion velocity of the Glauber's salt is reduced in the mixture. When in this manner the diffusions of the two mixed salts are independent of each other, so of course the salt endowed with a higher velocity (or larger diffusion current against water) will remove itself from the container, leaving behind the other one. From these conclusions can be founded about occurrences in the animal body, about which one should read the quoted treatise by Cloetta.

**39.** In the chronological evolution of the diffusion phenomena, only very few sentences can be expressed with certainty. Furthermore it is plausible that the equilibration of chemical differences of two liquid masses must take place in a shorter time frame when these masses are contacting each other directly than if they were separated by a porous separation wall. The wall must due to the necessary tightness of the pores, offer delayed resistance to the currents, which cause the equilibration. It can also be asserted with the same evidence that everything else being equal, the time required for equilibration increases with the thickness of the separation wall (length of the pores). Furthermore, the equilibration time depends on the size of the endosmotic equivalent. In fact, the equilibration happens even faster, the smaller the value of the endosmotic equivalent is (same velocity of the water current presupposed), in other words the more its value approaches unity. If, for example, the equivalent is very large then this means that the water current dominates the opposite salt current by far and will therefore quickly dilute the thicker solution. But the reversed current will hardly thicken the thinner solution; while this would be the case in a more similar measure if the equivalent would not differ so much from unity, i.e., if the strength of both currents would not differ so much. Furthermore, as illuminated from our consideration about the nature of the phenomena (but, apart from this, also would be concluded from every other theo-

retical idea) and already determined through older experiments (Vierordt<sup>10</sup>): The liquid amounts exchanged in the same time frame are larger, everything else set equal, the larger is the chemical difference of the masses separated by the membrane. With application of water on one and salt solution on the other side, the transported mass will grow with the salt amount in the solution. Different salts contained in a solution mixture equilibrate themselves with pure water in almost the same amount of time as if they were taken separately with water. The equilibration period of the already less diffusive salt seems to become longer by mixing it with the other one.

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<sup>10</sup>In the article “Endosmosis” in the Dictionary of Physiology (Handwörterbuch der Physiologie).

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