PHYSICS IN PHARMACY.

Part V, A Strip of Filter Paper or Capillary Hydrostatics, Capillary Diffusion and Capillary Osmosis.*,[1]

BY JOHN URI LLOYD, WOLFGANG OSTWALD AND HANS ERBRING.

I. PRESENTATION AND THEORY.

1. *Basic Experiment.*—About 35 years ago, the senior author, in a publication not easily accessible to physico-chemical investigators,[2] described the following experiment:

Connect two glass tubes closed below, one being filled with a salt solution, the other with water, by means of a strip of filter paper, and bring the meniscuses in

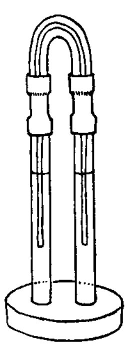

Fig. 1*a*.

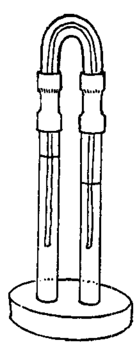

Fig. 1*b*.

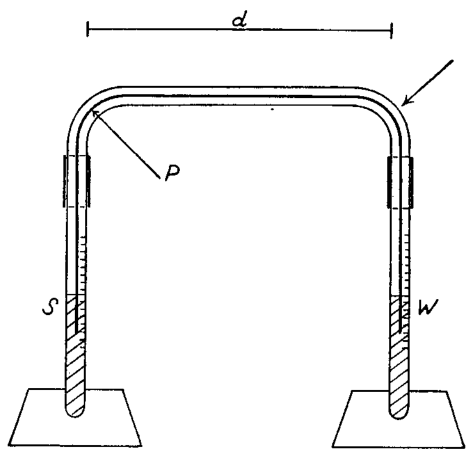

Fig. 2.—S, Salt solution; W, Water; P, Filter paper.

both tubes to the same level by raising or lowering the tubes (see *Fig. 1a,* original figure). Protect the system from evaporation by means of a connecting tube bent in U shape and two short pieces of rubber tubing.

After a few hours, more plainly after a few days, it is found that a motion of the liquid has taken place. The liquid column in the tube with the salt solution has increased, that in the tube containing water has diminished. Hence, water has passed through the strip of filter paper into the salt solution (see *Fig. 1b,* original figure).

The experiment looks very simple; its explanation, however, is not correspondingly simple. We shall see in the following study that in this apparently "spontaneous" transport of liquid, quite a series of physico-chemical principles is involved which should be of interest to the thoughtful pharmacist. In the following pages, we have taken up the problem of determining the nature of these forces in order to find an explanation of this effect.

* Translated from the German by Dr. Sigmund Waldbott.

[1] Scientific Section, A. Ph. A., Toronto meeting, 1932.

[2] John Uri Lloyd, "Etidorpha," The Robert Clarke Company, 1897, page 138.

It is evident that if this phenomenon can be seen to rest on a safe experimental and possibly also theoretical basis, it will be of interest in many a question of physical and colloid chemistry. The senior author himself (*loc. cit.*) has pointed out that such movements of liquids would affect geological and hydrological questions, *e. g.*, as to the origin of salt lakes and subterranean water courses, thereby assuming that porous materials like sand, sandstone, etc., act in the same manner as filter paper. Then the theories of "swelling" suggest themselves. Concerning this, different authors, *e. g.*, Proctor and Wilson, J. Duclaux, D. Jordan Lloyd, J. Loeb, Northrop and Kunitz, etc., have recently considered "osmotic" forces in the movement of water in the swelling of gels although the existence of "cell structure" or "semipermeable membrane" in swelling gels has not always been proved, nor is it even always considered probable.

In filter paper, also, we have movement of water without cell- or (honey) comb structure, and without membranes. Such movements of liquids "without membranes" might be of importance also in the physiological problems of movements of water in the organism.

2. *Method of Operation.*—The following method was used in these experiments. Two glass tubes, closed at one end, each 10 cm. long and of 0.5-cm. diameter, and provided with a millimeter scale, were filled to about $^3/_4$ with the solutions to be examined, and placed upon a suitable support. Through a U-shaped glass tube, also of 0.5-cm. diameter, a thin strip of filter paper, 2–3 mm. wide, was drawn, both ends of the paper projecting from the tube. The two strips of paper were introduced into the two liquid cylinders, immersed to a definite distance in the liquids, and two short pieces of rubber attached to the ends of the U tube were drawn over the edge of the cylinders. The pieces of rubber were covered with a layer of paraffin or "pizein," which protected the system quite well from loss by evaporation.

The resulting arrangement is represented in *Fig. 2.* In all experiments, the paper was immersed in the liquid to a depth of 3 cm. The filter paper was used, either dry or moistened with the solutions employed. For an account of the differences noted, see *Section 5.* Also, different grades of filter paper have been used; see *Section 6.* At the beginning of the experiment, the meniscuses must be exactly at the same height in both cylinders; this is easily attained by vertical change of position of the cylinders.

It is furthermore important that the connecting piece *d* shall always be in an exactly horizontal position.

The changes in the position of the meniscuses were read at both scales by means of the lens. The experiments were carried out at ordinary room temperature, since it was found that the use of thermostats was superfluous as the temperature factor proved to be very insignificant. Cf. *Section 10.*

3. *Repeating the Basic Experiment.*—The following is an example taken at random from the many experiments which we conducted according to the above method, in order to demonstrate that the basic experiment is reproducible, and at the same time to characterize the Effect quantitatively.

Table I shows an experiment with saturated *ferric chloride* solution. The length of the horizontal connecting piece was 9 cm. (see *d* in Fig. 2). In this experiment the filter paper was used *dry.* Upon connecting the two liquids by the filter paper, there is at first capillary rise in both tubes; in this case, salt solution and water meet on the side of the salt solution. It was only after this capillary connection was completed that the leveling of both liquid surfaces was done.

TABLE I.

System: $FeCl_3$ (saturated) *vs.* Water. $d = 9$ cm.

1. Duration of Exp., Hours.	2. Height in Cyl. S, Cm.	3. $FeCl_3$ Increase in Cyl. S, Mm.	4. Height in Cyl. w, Cm.	5. H_2O Decrease in Cyl. w, Mm.	6. Total Difference, Mm.	7. Liquid Taken Up by Paper; Col. 5 Minus Col. 3, Mm.
0	5.00	0.0	5.00	0.0	0.0	0.0
16	5.1	1.0	4.65	3.5	4.5	2.5
42	5 15	1.5	4.5	5.0	6.5	3.5
62	5.22	2.2	4.35	6.5	8.7	4.3
80	5.25	2.5	4.33	6.7	9.2	4.2
100	5.3	3.0	4.25	7.5	10.5	4.5
Days.						
8	5.35	3.5	4.15	8.5	12.0	5.0
11	5.35	3.5	4.15	8.5	12.0	5.0
14	5.35	3.5	4.15	8.5	12.0	5.0
16	5.35	3.5	4.2	8.0	11.5	4.5
20	5.3	3.0	4.25	7.5	10.5	4.5
25	5.28	2.8	4.3	7.0	9.8	4.2
40	5.2	2.0	4.35	6.5	8.5	4.5

The headings of the 7 columns in Table I are self-explanatory; the results, also represented graphically, in Figs. 3 and 4, furnish a quantitative characterization of the effect.

From *Table I* and the *diagrams*, the following results are noteworthy.

1. The principal effect takes place within about the first 8 days.
2. Upon longer duration of the experiment, the effect again decreases, the movement of the liquid becomes retrograde; however, the descent takes place more slowly than the rise.
3. The decrease in the cylinder containing water runs somewhat parallel to the increase in the salt solution, but is of much higher absolute value than the latter.

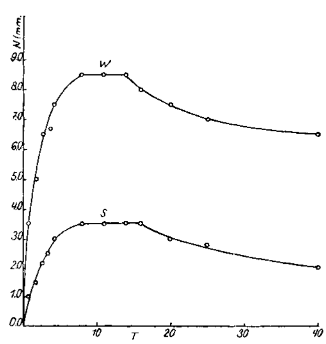

Fig. 3.—N, Difference of level in mm.; T, Time in days. Curve W shows decrease in the water cylinder; Curve S shows increase in the salt cylinder.

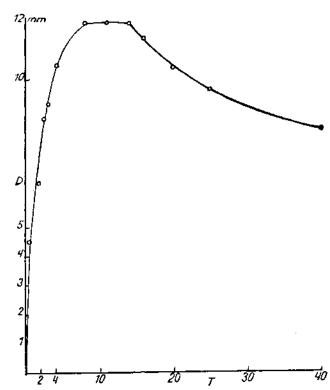

Fig. 4.—D, Total difference; T, Time in days.

A considerable quantity of the liquid "disappears" in the experiment; this is especially noticeable in *Fig. 3.* The "vanished" liquid is contained partly in the capillary spaces of the paper and contributes in part to the swelling of the filter paper; another part is condensed in the form of droplets along the glass walls, especially that of the U tube.

The general course of the Effect may be well visualized by the aid of *Fig. 5*, in which the height of the liquid columns attained in the time periods I, II, III and IV are brought out by hatched lines.

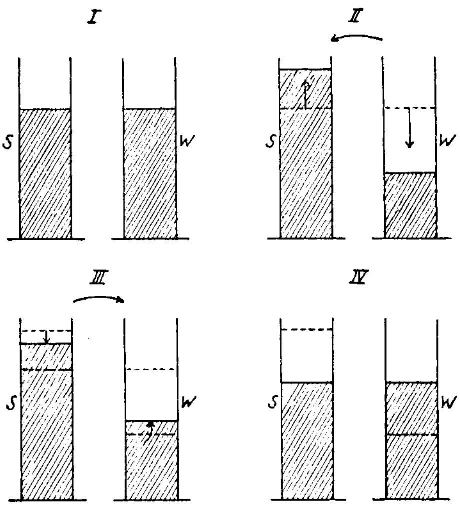

Fig. 5.

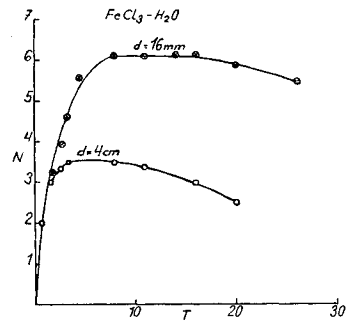

Fig. 6.—N, Increase of level in mm.; T, Time in days.

As one might be inclined to regard the numerical value of the Effect, in this case a maximum difference of 12 mm. as insignificant, we present herewith in *Table II* an example to show how large an effect may be attained under certain conditions. By merely leaving $FeCl_3$ in contact with undissolved $FeCl_3$ at the bottom of cylinder S, and conducting the experiment as before, there will be, during the same period of time, differences of level of at least 28.3 mm., the maximum not yet being reached.

TABLE II.

System: $FeCl_3$ plus undissolved $FeCl_3$ at the bottom, *vs.* Water. $d = 12$ cm. Paper wetted at start.

Duration, Hours.	$FeCl_3$—Increase, Mm.	H_2O—Decrease, Mm.	Total Difference, Mm.
2	1.0	3.0	4.0
10	5.0	7.0	12.0
18	7.0	9.0	16.0
24	9.0	11.5	20.5
Days.			
2	10.5	14.5	25.0
4	10.5	15.5	26.0
8	11.5	15.5	27.0
15	12.5	15.8	28.3

II. FURTHER EXPERIMENTAL DETAILS.

Before passing on to the theory of the phenomenon, we wish to give from our large and varied experimental material a few experimental details in order that the effect herein considered may be viewed from other angles.

4. *Influence of Length of the Capillary Connecting Piece.*—In the foregoing discussion, the capillary connecting piece, *i. e.*, the strip of filter paper, is of essential importance. It therefore became of interest to know in what manner the dimensions, particularly the length (*d*) influences the Effect. Summing up, we find a distinct *increase of the Effect with increase of length, provided,* however, that the *paper is previously moistened with the solution.* Experimental details for this are given in the following *Tables III, IV, V, VI,* and *Figs. 6* and *7;* salt solutions used against water were saturated *Ferric Chloride* and saturated *Barium Chloride* solutions.

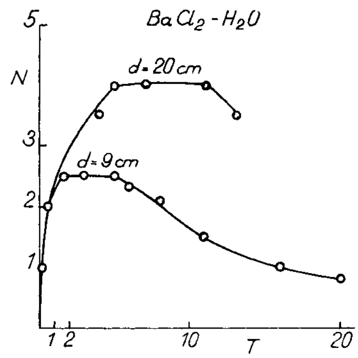

Fig. 7.—N, Increase of level in mm.; T, Time in days.

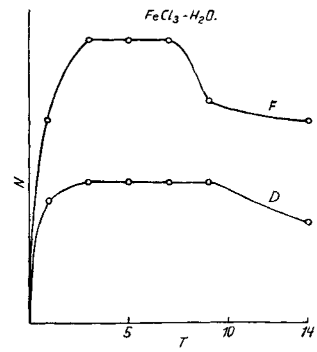

Fig. 8.—N, Increase of level in mm.; T, Time in days; F, Moist; D, Dry.

TABLE III.—INFLUENCE OF LENGTH OF *d* (d = 4 CM.).

System: $FeCl_3$ (saturated), *vs.* Water. Paper moistened with $FeCl_3$ at start.

Duration, Hours.	$FeCl_3$—Increase, Mm.	H_2O—Decrease, Mm.	Total Difference, Mm.	Liquid Taken Up by Paper, Mm.
16	2.0	4.0	6.0	2.0
42	3.0	8.0	11.0	5.0
62	3.3	8.5	11.8	5.2
80	3.5	8.5	12.0	5.0
100	3.5	8.5	12.0	5.0
Days.				
8	3.5	8.0	11.5	4.5
11	3.5	7.5	10.8	4.2
16	3.0	7.5	10.5	4.5
20	2.5	7.3	9.8	4.8

TABLE IV.

Same as Table III, except d = 16 cm. Paper moistened at the start.

Duration, Hours.	$FeCl_3$—Increase, Mm.	H_2O—Decrease, Mm.	Total Difference, Mm.	Liquid Taken Up by Paper, Mm.
48	3.2	8.0	11.2	4.8
66	3.9	10.0	13.9	6.1
80	4.6	12.0	16.6	7.4
110	5.6	13.5	19.1	7.9

Days.				
8	6.1	14.0	20.1	7.9
11	6.1	14.0	20.1	7.9
14	6.2	14.0	20.2	7.8
16	6.2	14.0	20.2	7.8
20	5.9	13.8	19.7	7.9
30	5.5	13.4	18.9	7.9

TABLE V.—INFLUENCE OF LENGTH OF *d* (d = 9 CM.)

System: $BaCl_2$ (saturated), *vs.* Water. Paper moistened with $BaCl_2$ at start.

Duration, Hours.	$BaCl_2$—Increase, Mm.	H_2O—Decrease, Mm.	Total Difference, Mm.	Liquid Retained by Paper, Mm.
8	1.0	1.7	2.7	0.7
16	2.0	3.0	5.0	1.0
42	2.5	4.0	6.5	1.5
Days.				
3	2.5	5.0	7.5	2.5
4	2.5	5.0	7.5	2.5
5	2.5	5.0	7.5	2.5
6	2.3	5.0	7.3	2.7
8	2.1	5.0	7.1	2.9
11	1.5	5.0	6.5	3.5
13	1.5	5.0	6.5	3.5
16	1.0	4.8	5.8	3.7
20	0.7	4.6	5.3	3.9

TABLE VI.—INFLUENCE OF LENGTH OF *d* (d = 20 CM.)

System: Same as in Table V. Paper moistened at start.

Duration, Hours.	$BaCl_2$—Increase, Mm.	H_2O—Decrease, Mm.	Total Difference, Mm.
22	2.0	2.2	4.2
Days.			
4	3.5	4.0	7.5
5	4.0	5.0	9.0
7	4.0	6.0	10.0
11	4.0	6.0	10.0
13	3.5	6.0	9.5

With $FeCl_3$ (*Tables III* and *IV*), we see that the fourfold length of the capillary connecting piece results in practically doubling the Effect (increase of level in cylinder S). Relatively still more pronounced is the Effect with $BaCl_2$ (*Tables V* and *VI*), where tubes with d = 9 cm. and 20 cm. are used.

In both cases, we also note a faster decline from the maximum in the shorter connecting tube. Experiments with still longer tubes have shown that the errors caused by the large quantities of the liquid retained by the paper and by condensation of liquid become so great as to render results inexact; hence longer connecting tubes cannot be recommended.

5. *Influence of Preliminary Wetting.*—In starting the experiment, we may allow both liquids to rise and meet in the dry paper, or we may first moisten the paper with the salt solution, then continue with the experiment. Moistening with water would practically have the same effect as the use of dry paper, since water

as a rule rises very much faster than the solution; in this case, both liquids would meet in cylinder S.

We found the Effect to be notably stronger and better reproducible if the solution is allowed to migrate into the filter paper, as high as into the beginning of the descending branch of the connecting tube on the water side (see arrow in *Fig. 2*). Waiving numerical data for this experiment, we show in *Fig. 8* the graphic results of such a parallel experiment with wet and with dry filter paper.

6. *Influence of the Quality of Paper.*—Filter papers are usually characterized by their transversal permeability, *i. e.*, according to the average diameter of their pores. A paper with very small-sized pores is, *e. g.*, that of Schleicher and Schüll No. 602 (hard); the size of pores is about 2.2μ.[1] Again, filter papers may be characterized by their "imbibing ability," *i. e.*, by the speed of capillary rise of water in them. This is a longitudinal property of the paper, caused by an especially numerous aggregation of narrow capillaries. Such a paper is that of Schleicher and Schüll No. 604 (soft); it has considerably larger transversal pores than the hard paper No. 602. The paper used in the preceding experiments was intermediate between these two extremes.

TABLE VII.—INFLUENCE OF QUALITY OF PAPER. PAPER WETTED AT START.

System: $FeCl_3$ (saturated), *vs.* Water. $d = 12$ cm.

Duration, Hours.	$FeCl_3$—Increase, Mm.	H_2O—Decrease, Mm.	Total Difference, Mm.	Liquid Retained by Paper, Mm.
	Paper No. 604 (Soft).			
22	5.0	8.5	13.5	3.5
70	7.0	10.5	17.5	3.5
Days.				
5	7.0	10.5	17.5	3.5
7	7.0	13.0	20.0	6.0
9	5.5	16.0	21.5	10.5
14	5.0	18.5	23.5	13.5
Weeks.				
8	2.0	16.0	18.0	14.0
	Paper No. 602 (Hard).			
Hours.				
70	1.0	4.0	5.0	3.0
Days.				
5	1.5	6.5	8.0	5.0
7	2.5	7.5	10.0	5.0
9	3.5	8.5	12.0	5.0
14	3.0	8.5	11.5	5.5
Weeks.				
8	1.5	7.5	9.0	6.0

Table VII and *Fig. 9* show considerable difference existing in the activity of the soft, felt-like paper, compared with that of the hard and dense paper No. 602. The Effect is of much greater magnitude with the former than with the latter. With No. 604, the maximal increases of level are more than twice as much as with

[1] Cf. Wo. Ostwald, "Kleines Praktikum der Kolloidchemie," 7th Edition, page 26 (Steinkopff, Dresden).

No. 602. The kinetics of rise are likewise different; with No. 604, the rise takes place far much faster than with No. 602.

There is also a notable and plausible difference in the quantities of liquid retained in the filter paper; cf. the last column in *Table VII.*

7. *Clogging of the Capillaries by Formation of a Precipitate.*—In a systematic study on the relation of size of pores in unglazed porcelain and osmotic activity by *L. Bigelow* and *F. E. Bartell* (see later), Bartell found, for example, that porcelain

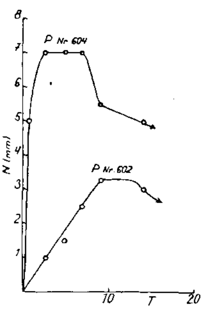

Fig. 9.—N, Increase of level in mm.; T, Time in days; P, Filter paper.

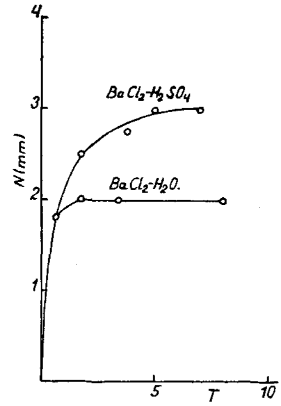

Fig. 10.—N, Increase of level in mm.; T, Time in days.

with pores smaller than 0.4μ is of direct use as an osmotic cell. He also diminished the width of the pores by precipitating $BaSO_4$, S, $PbCrO_4$, CuS, etc., within the capillaries of the pores; this likewise caused an increase of the capillary effect.

Although a piece of filter paper longitudinally soaked with liquid is evidently different from a transversally soaked wall of a porcelain cell, we may believe that in both cases a narrowing of the capillaries, resp., the pores will act in the same direction. Accordingly we have also tried to diminish the width of the fibrillary capillary spaces by depositing within them finely divided precipitates.

TABLE VIII.

System A: $BaCl_2$ (saturated) *vs.* Water. $d = 4$ cm. Paper dry at the start.

Duration, Hours.	$BaCl_2$—Increase, Mm.	H_2O—Decrease, Mm.	Total Difference, Mm.
16	1.8	2.5	4.3
42	2.0	3.5	5.5
62	2.0	4.0	6.0
80	2.0	4.5	6.5
Days.			
8	2.0	5.0	7.0

Now Clogging the Capillaries by Precipitation.

System B: $BaCl_2$ (saturated), *vs.* $0.1N$ H_2SO_4. $d = 4$ cm.

Hours.	Mm.	Mm.	Mm.
16	1.8	2.8	4.6
42	2.5	3.5	6.0
90	2.5	4.5	7.0

Days.			
5	3.0	5.0	8.0
7	3.0	5.2	8.2

In *Table VIII* and *Fig. 10* are shown the results of an experiment (*System B*), in which the capillary spaces are diminished in size by precipitation of $BaSO_4$ within them; water placed against the saturated $BaCl_2$ solution in *System A* is substituted by tenth-normal sulphuric acid.

The narrowing of the capillary tubes is seen to result in the increase of our Effect.

8. Experiments with Other Substances.—The experiments described thus far were carried out with $FeCl_3$ and $BaCl_2$ *vs.* water. Without presenting numerical values, we see from *Figs. 11* and *12* that the effect is obtained also with *KCl* (univalence) and with $AlCl_3$ (trivalence), and with non-electrolytes such as *Cane sugar.*

Experiments we carried out with *Urea* will be described in *Section 10.*[1]

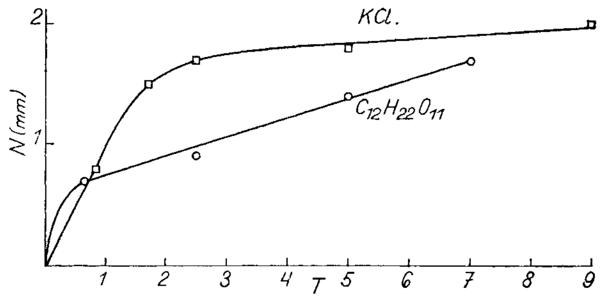

Fig. 11.—N, Increase of level in mm.; T, Time in days; Paper dry at start.

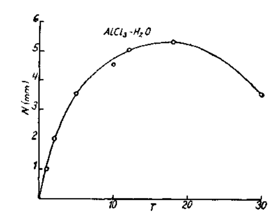

Fig. 12.—N, Increase of level in mm.; T, Time in days; Paper wet at start.

It might appear strange that cane sugar gives but a relatively small Effect as compared with that of the salts. However, when comparing the curves in *Fig. 11*, we see that only the *beginning* of the curve of the sugar has been measured, while the KCl curve, after about 8 days, runs practically horizontal, the curve for the sugar, during the same time, shows a decided, almost linear rise. The thought suggests itself to hold the high molecular weight of the sugar, and the high viscosity of its solutions responsible for the smaller velocity displayed in producing the Effect. In addition, this experiment with cane sugar was conducted at the time when the importance of preliminary wetting had not yet been recognized.

9. Quantities of Liquids Retained by the Filter Paper.—In the first part of this paper, attention was called to the relatively large quantities of liquid held by the filter paper. These quantities vary, not only according to the kind of filter paper used (cf. *Section 6*), but also according to the nature of the solution.

(*End of First Instalment.*)

[1] Alcohols used in the experimental apparatus herein described, showed *peculiar movements,* concerning which we shall report in a later communication.
