PHYSICS IN PHARMACY.

BY JOHN URI LLOYD, WOLFGANG OSTWALD AND HANS ERBRING.

(Concluded from page 331, April issue.)

II. The *Second Divisional Effect* (cf. *Fig. 16, II*) is characterized, first, by a striking constancy of the height of rise, resp., the difference of level. The system is apparently in hydrostatic equilibrium. Nevertheless, considerable changes are taking place in it, as shown in *B*, *C* and *D*. The hydrostatically repressed salt solution moves upward again, as is seen by the migration of the zone of diffusion. (Cf. *B* and *C*.) Simultaneously with this return motion an increasing difference of weight must arise again (cf. *Fig. 16, II-B*).

No doubt *diffusion* is responsible for this movement of the salt in opposite direction, which becomes apparent to the eye by the formation of a gradient of concentration. The zone between colored salt solution and water is no longer relatively sharp, but spreads out. The transition becomes the more gradual the longer the duration of this divisional effect.

Now the fact is very striking that difference of level is not noticeably changed, in spite of the diffusion and in spite of the increase of weight of the salt liquid as a consequence of this diffusion. If hydrostatics alone were responsible, this fact would be incomprehensible. Hence we must look for forces which eventually act independently in opposite direction to hydrostatics, and which therefore may be able to compensate the hydrostatic pressure in the second divisional effect.

In this connection we may think first of *kinetic* factors. As stated before, the equalization of hydrostatic pressure in filter paper consumes much time. We may imagine that in the 2nd divisional effect the process of diffusion takes place faster than the hydrostatic equalization. Retardation of the hydrodynamic velocity of water by the capillary spaces of the filter paper is probably much greater (in conformity with Hagen-Poiseuille's law) than the retardation of diffusion by capillary walls. Therefore the constancy of the difference of level, notwithstanding the formation of a new hydrostatic disequilibrium by diffusion, could be explained by the great differences in diffusion velocity, and hydrodynamic velocity of the water. In this sense, the constancy of the difference of level would be merely a phenomenon of retardation, as it were, a "hydrostatic supersaturation."

However, the part played by osmotic water attraction discussed before, cannot be neglected. If the diffusing molecules in a capillary system are able to attract solvent in the manner described, they must also carry this osmotically bound water along with them in diffusion. Such carrying of osmotically attracted water would indeed be able to counteract the hydrostatic equalization of level. The water carried osmotically from left to right would therefore be approximately equal to the water which would be carried hydrostatically from right to left through increase of weight of the salt tube. We have two opposite water movements: Osmotic carriage of water from left to right, and hydrostatic movement of water from right to left, which about compensate each other in the second divisional effect; the water is thus virtually "immobilized." An osmotic carriage of water would then furnish the theoretically required pressure opposite the hydrostatic pressure, and at the

same time would explain the constancy of the difference of level during the 2nd divisional effect notwithstanding diffusion progressing.

III. The *Third Divisional Effect* is characterized by slow disappearance of the difference of level, *i. e.*, by a *reversion* of the direction of liquid movement, while the zone of diffusion migrates into the left tube and there is simultaneous decrease of the difference of weights of the two liquid cylinders in the siphon tubes (cf. *Fig. 5-III*). In this part of the process, diffusion is the sole driving force. Through diffusion the salt is transferred into the water vessel, diminishing thereby, visibly, more and more the differences of weight, resp., the hydrostatic difference of pressure which still existed in the 2nd part of the process.

With progressive diffusion a moment will be reached where the difference of weights between the 2 liquid cylinders in the siphon is zero, and then will attain a negative value. The longer water cylinder, containing but little salt, will become heavier than the short salt cylinder, which, however, is richer in salt. Thus a decrease of the difference of level and gradual equalization can take place hydrostatically.

However, it is very striking to note how exceedingly slowly and gradually this hydrostatic equalization takes place. Even after weeks of experimentation, in the course of which large quantities of dissolved salt could be demonstrated in the water vessel, complete equalization of level had never been reached. This retardation again may be caused by either kinetic factors (hydrostatics in arrear toward diffusion), or the capillary-osmotic fixation of water in the strip of filter paper; the function of this fixation we were able to recognize very distinctly in the 2nd divisional effect. When hydrostatic current and diffusion have motions in the same direction, in this case also will water be retained or osmotically immobilized in the filter paper in conformity with the ideas developed before. Similarly, water contained in salt-free filter paper shows, as is well known, depression of freezing point, compared with water in bulk.

REVIEW.

The theory of the Effect may be briefly outlined in the following summary: We accept three kinds of forces to share in the phenomenon: Primary hydrostatic forces, secondary hydrostatic forces in consequence of diffusion, and capillary-osmotic forces, which may act in opposition to hydrostatic forces. The first main rise is principally a hydrostatic effect (Capillary siphon). The hydrostatic and osmotic effects of diffusion have only a secondary share (Diffusion siphon effect and capillary osmosis).

The Second Division, characterized by the constancy of the difference of level in spite of pronounced diffusion, leads us to assume a manifestation of capillary osmosis. The hydrostatic excess pressure caused by diffusion, is not visibly balanced because the salt molecules contained in the capillary spaces osmotically attract and immobilize water molecules. In the Second Division, this capillary-osmotic attraction of water compensates the hydrostatic excess pressure caused by diffusion.

In the Third Division, salt gradually passes over into the (longer) water tube of the siphon, rendering this liquid heavier until the sign of the hydrostatic difference of pressure reverses, and the difference of level again begins to disappear. The exceeding slowness with which this equalization takes place, notwithstanding a

strong passage of salt into the water tube, is again ascribed to capillary-osmotic immobilization of water in the filter paper.

Reviewing again the experimental details recorded in the second part of this work, from the point of view of the theory stated, we find them in agreement with theory. The greater length of the capillary connecting tube favors the siphon effect (on account of the longer, heavier cylinder of salt solution). In addition, the capillary-osmotic forces have a more telling effect in a longer horizontal connecting tube. The influence of the nature of the filter paper, especially its content of capillary spaces upon tangential "irrigation" of the paper, seems to argue with especial force in favor of not only hydrostatic but also capillary-osmotic forces in producing the Effect. For aside from the velocity of flow, a change in the cross section of a purely hydrostatic siphon does not change in the least a purely hydrostatic effect. Our experiments with filter paper whose pores are clogged by formation of precipitates, we interpret in the same sense, also in reference to the researches of F. E. Bartell, E. Manegold and others, on the Osmosis of "permeable cells." The fact that electrolytes as well as non-electrolytes show the Effect which becomes the more pronounced the higher the concentration of the salt solution agrees with all proposed divisional explanations.

The insignificant positive influence of temperature is somewhat surprising. It is true that the densities of salt solution and water are influenced in the same direction by increase of temperature, while hydrostatically only the *difference* in density becomes active. On the other hand, both fluidity of water and the solution, as well as diffusion velocity, are materially increased with rising temperature; not so, however, the osmotic pressure which, as we know, increases by only 1/273 per degree.

Simple as the Effect appears to be, its dynamics is very involved, as the preceding Analysis demonstrates. For the further investigation of these peculiar liquid movements in capillary systems, such experimental arrangements particularly suggest themselves, in which the hydrostatic effects are eliminated as much as possible. For example, a horizontally placed and linearly extended capillary system of the same order might be such an arrangement. Although such an experiment seems very simple, it is by no means carried out as easily, as experiments of our own in this respect have already shown. Influences of gravity are very difficult to eliminate, even with horizontal arrangement, and an exact leveling in the case before us is not simple. We shall report on experiments of this kind in a later communication.

SUMMARY.

1. When two cylinders which are filled, resp., with concentrated salt solution and water, are connected by a strip of filter paper and the liquid is protected against evaporation, there will be a transfer of water into the salt solution. This experiment described by the senior author about 35 years ago, was again studied in detail, also quantitatively.

2. The Effect was easily reproduced. There are increases of level, *e. g.*, up to about 12 mm., and total differences of level to about 28 mm. It is further noted that within long periods of time (8 days or more), a maximum effect is reached; thereafter, the difference of level again decreases.

3. From a great number of numerical data, the following are presented:

(*a*) The Effect strongly increases with increasing length of the capillary connecting piece, *viz.*, the strip of paper.

(*b*) Previously wetting the paper with the solution likewise causes a strong increase of the Effect.

(*c*) It is not the transversal fineness of the pores of the paper, but rather the longitudinal capillary, *i. e.*, highly developed fibrillary structure of the paper which gives the maximum effects; soft, absorbent paper acts better than hardened, dense paper. Improvement is also attained by reducing the diameters of the capillary tubes by partially filling the spaces with highly dispersed precipitates, *e. g.*, $BaSO_4$.

(*d*) The Effect is obtained not only with electrolytes ($FeCl_3$, $AlCl_3$, $BaCl_2$, KCl), but also with non-electrolytes (Sugar, Urea).

(*e*) The Effect increases parallel with concentration; initially it increases with good approximation linearly with concentration. In the case of Urea, the concentration curves of increases of level are curved faintly convex toward the concentration axis, which is in accord with the concentration curves of osmotic pressure of concentrated molecularly dispersed and colloidal solutions.

(*f*) The Effect has a small positive temperature coefficient.

4. The problem as to the nature of the driving forces in the observed phenomenon is investigated.

It is shown that there are at least three sources of energy sharing in the production of the effect:

(1) Hydrostatic forces in capillaries; *Capillary siphon effect.*

(2) Diffusion in capillaries: *Diffusion-siphon effect.*

(3) Osmotic attraction of liquids in capillary systems: *Capillary Osmosis.*

All three forces come into play:

At the beginning of the phenomenon, the *hydrostatic effect* is dominant, then appear *diffusion* and *capillary osmosis*, and toward the end, again *hydrostatics* terminates the process.

5. Brief reference is made to the significance of the Effect in geological movements of liquids (subterranean water courses), the theory of swelling, and in biological movements of liquids.

ABSTRACT OF A PAPER BEFORE SCIENTIFIC SECTION, A. PH. A.

"Chemical Examination of Some Urographic Preparations," by George W. Collins.

Several years ago, Rowntree and his associates demonstrated that following the injection of sodium iodide solution introduced through the ureter, radiographic visualization of the pelvis of the kidney, the ureter and the bladder, pyelograms could be made. Subsequently, many iodine compounds, both simple and complex have been prepared and tested for their roentgenologic usefulness. The author reports the findings of chemical examinations of two different specimens of Iopax, also the examination of a third specimen of the product by a disinterested consulting laboratory. Several points of interest are brought forth in the investigation, including petrographic data confirming the chemical findings. A report is made of an examination of another urographic preparation known as Skiodan. Chemically, these products differ markedly. Iopax is the sodium salt of an acid derivative of an iodized oxo-aminopyridine, containing 42 per cent iodine in organic combination; while Skiodan is the sodium salt of mono-iodomethane sulphonic acid and contains 52 per cent organically combined iodine. The evaluation is made of tests and standards for the identity, purity and assay of these two preparations. In addition, there is a résumé of three other iodized products recently introduced and used in pyelography.