

The Bakerian Lecture: On Osmotic Force

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## PHILOSOPHICAL TRANSACTIONS.

VII. THE BAKERIAN LECTURE.—On Osmotic Force.

By Thomas Graham, F.R.S. &c.

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THE expression "Osmotic Force" (from ωσμος, impulsio) has reference to the endosmose and exosmose of Dutrochet.

We may succeed in covering a solution of salt occupying the lower part of a glass jar by a stratum of pure water without much intermixture of the two liquids. A force, however, is thereby brought into action which carries up the salt in a gradual manner, dispersing it and ultimately producing a uniform mixture of the salt with the whole volume of water. The molecules of salt have the liquid condition when in solution as well as those of water itself, and we have in the experiment the contact of two different liquids, which must of necessity diffuse through each other, the molecules of a liquid being self-repellent, or subject to a force the same in kind but less in degree as that which gives to gases their elasticity and diffusibility.

The force of liquid diffusibility will still act if we interpose between the two liquids a porous sheet of animal membrane or of unglazed earthenware; for the pores of such a septum are occupied by water, and we continue to have an uninterrupted liquid communication between the water on one side of the septum and the saline solution on the other side.

To impel by pressure any liquid through the pores of such a septum may be extremely difficult, from the interference of frictional resistance and the attraction of capillarity. But these last forces act on masses and not on molecules, and the ultimate particles of water and salt which alone diffuse, appear really to permeate the channels of the porous septum with little or no impediment. A comparative experiment on diffusion, with and without septa, is easily made by means of a wide-mouthed phial, which is filled completely with the saline solution and then immersed in water, in one experiment with the mouth of the phial open, and in the other experiment with the mouth covered by membrane. In a fixed time, such as seven days, a certain quan-

tity of salt leaves the phial by diffusion. This quantity was reduced to one-half when the strong and thick membrane of the ox-gullet was used to cover the mouth of the phial; and it was not affected in a sensible degree by passing through a thinner membrane, consisting of ox-bladder with the outer muscular coat removed. In the last experiment the actual diffusates were 0.631 gramme common salt in the absence of the membrane, and 0.636 gramme common salt with the membrane interposed, which may be considered as the same quantity. The diffusion of a salt appears to take place, therefore, without difficulty or loss through the substance of a thin membrane, although the mechanical flow of a liquid may be nearly stopped by such an obstacle.

It is well to bear in mind the last fact in the consideration of what is seen in an endosmotic experiment. An open glass tube, with one end expanded into a bell form and covered by tight membrane, forms a vessel which may be filled with a saline solution and immersed in a jar of pure water. The volume of liquid in this osmometer soon begins to increase and is observed to rise in the tube, while the simultaneous appearance of salt in the water of the jar may easily be verified. M. Dutrochet described the result as the movement of two unequal streams through the membrane in opposite directions, the smaller stream being that of the saline solution flowing outwards, and the larger that of pure water flowing inwards. The double current has been always puzzling, but the expression of the fact becomes more conceivable when we say (as we may do truly) that the molecules of the salt travel outwards by diffusion through the porous membrane. It is not the whole saline liquid which moves outwards, but merely the molecules of salt, their water of solution being passive. The inward current of water, on the other hand, appears to be a true sensible stream or a current carrying masses. The passage outwards of the salt is inevitable, and being fully accounted for by diffusibility, requires no further explanation. It is the water current which requires consideration, and for which a cause must be found. This flow of water through the membrane I shall speak of as osmose, and the unknown power producing it as the osmotic force. It is a force of great intensity, capable of supporting a column of water many feet in height, as shown in Dutrochet's well-known experiments, and to which naturalists are generally disposed to ascribe a wide sphere of action, both in the vegetable and animal kingdoms.

Cannot liquid diffusion itself, it may first be asked, contribute to produce osmose? Diffusion is always a double phenomenon, and while molecules of salt pass in one direction through the membrane, molecules of water no doubt pass by diffusion in the opposite direction at the same time, and replace the saline molecules in the osmometer. Water also is probably a liquid of a high degree of diffusibility, at least it appears to diffuse four times more rapidly than alcohol, and four or six times more rapidly therefore than the less diffusive salts. A possible consequence of such inequality of diffusion is, that while one grain of a certain salt diffuses out of the osmometer, four or six grains of water may diffuse into the osmometer. Liquid diffusion, I believe, generally tends to increase the volume of liquid in the osmometer, and a

portion, if not the whole, of the small osmose of chloride of sodium, sulphate of magnesia, alcohol, sugar, and many other organic substances may be due to the relatively low diffusibility of such liquefied bodies compared with the diffusibility of water. But many substances, it will immediately appear, are replaced in experiments of endosmose, not by four or six, but by several hundred times their volume of water, and manifestly some other force besides diffusion is at work in the osmometer.

An explanation of osmose has been looked for in capillarity by Poisson, Magnus, and by Dutrochet himself. Combining diffusion with this idea, we might imagine that the pure water which first occupies the pores of the septum, suffers a sudden and great loss of its capillarity-force when the salt of the osmometer enters the pores by diffusion and mixes with the water they contain. Experiments published by Dutrochet give a capillary ascension to pure water of 12 millimeters, and to a solution of common salt, of density 1·12, 6·14 millimeters, or only one-half of the former ascension. If a porous septum, occupied by such a saline solution, had the same solution in contact with one surface and pure water in contact with the other surface (the actual condition of the septum in an osmotic experiment), the pure water should enter the pores from its high capillary attraction, and, like a solid piston, force out the saline solution from them: the saline solution so displaced would go to swell the liquid within the osmometer. When the pure water, now again occupying the pores, came in time to acquire salt by diffusion, the displacement would be repeated, and a continuous osmose or flow of water inwards be in fact established.

This explanation is attended with certain physical difficulties, but it is unnecessary to discuss these, as the experimental basis of the hypothesis is unsound. The great inequality of capillarity assumed among aqueous fluids does not exist. Many saline solutions which give rise to the highest osmose are, I find, undistinguishable in capillarity from pure water itself. To obtain constant results with saline solutions, the capillary tube must be retained for some minutes in the saline solution at a boiling temperature, and afterwards be cooled without removal from the liquid, otherwise the indications are singularly irregular and most fallacious.

The near equality in capillarity of solutions of the most different composition is very apparent in my observations, which are placed together in the following series of capillary ascensions:—

## Capillary ascension of several liquids in the same glass tube.

**************************************										Millimeters.
Water, at 58° Fahr	•	•	•	. •	•	•	•	•	•	17.75
Water, at $66^{\circ}$	•	•	•	•	•		•	•		17.55
Carbonate of potash, 0.25 per cent., in	wa	ter	, at	63	3°	٠.,		•	•	17.2
Carbonate of potash, 10 per cent., in w	ate	er, a	at 6	$66^{\circ}$			•		•	17.55
Carbonate of soda, 1 per cent., at 61°			•						•	17.55
Carbonate of soda, 10 per cent., at 55°		•				•	•	•	•	16.85
Sulphate of potash, 1 per cent., at 58°					•			•	•	17.15

	limeters.
	6.3
Sulphate of soda, 1 per cent., at 55°	7.75
Sulphate of soda, 10 per cent., at 58°	6.95
Hydrochloric acid, 1 per cent., at 63°	7.5
Sulphuric acid, 0.1 per cent., at 63°	7.4
Sulphuric acid, 1 per cent., at 63°	6.35
Sulphuric acid, 5 per cent., at 63°	6.65
Sulphuric acid, 10 per cent., at 63°	6.25
Sulphuric acid, undiluted (HOSO <sub>3</sub> ), at 63°	8.1
Oxalic acid, 1 per cent., at $66^{\circ}$	7:35
Oxalic acid, 4 per cent., at 62°	7.2
Ammonia, 0·1 per cent., at 66°	6.65
Ammonia, 1 per cent., at 66°	6.12
Ammonia, 12 per cent. (0.943 sp. gr.), at 66°	5.05
Sugar, 10 per cent., at 65°	6.3
Alcohol, 0.8 per cent. (0.9985 sp. gr.), at 60°	5.5
Alcohol, 4.5 per cent. (0.992 sp. gr.), at 63°	3.2
Alcohol, 7.8 per cent. (0.987 sp. gr.), at 60°	1.05
Alcohol, 71 per cent. (0.869 sp. gr.), at 63°	6.

Alcohol falls in the greatest degree below water in capillarity, yet the former substance is one of the least remarkable for the power to occasion osmose.

The newer facts to be related also increase the difficulties of the capillary theory of osmose.

My own experiments on osmose were made with both mineral and organic septa.

I. A convenient earthenware or baked clay osmometer is easily formed by fitting a glass tube and cover to the mouth of the porous cylinder, often used as a cell in Grove's battery, as in fig. 1; the cylinder was generally 5 inches in depth by 1.7 inch in width, inside measure, and was capable of holding about six ounces of water. Gutta percha is much preferable to brass as the material for the cap or cover. The glass tube above was also comparatively wide, being 0.6 inch or 15 millimeters in diameter, and was divided into millimeters. It was not more than 6 inches in length. Each of the divisions or degrees amounted approximatively to  $\frac{1}{750}$ th part of the capacity of the clay cylinder.

In conducting an experiment, the cylinder, always previously moistened with pure water, was filled with any saline

solution to the base of the glass tube, and immediately placed in a jar of distilled water, of which the level was kept adjusted to the height of the liquid in the tube of

Fig. 1.

the osmometer throughout the whole experiment, so as to prevent inequality of hydrostatic pressure. The volume of water in the jar was comparatively large, fifty to eighty ounces. The rise or fall of the liquid in the tube was noted hourly for five hours. This rise commenced immediately, and was pretty uniform in amount for each hour during the short period of the experiment. The object aimed at was to observe the osmose of the solution before its composition was materially altered by dilution and the escape of salt by diffusion. The quantity of salt diffused from the osmometer into the water-jar during the experiment was also observed. After every experiment the osmometer was washed out by distilled water, which was allowed to permeate the porous walls of the cylinder, under the pressure of a column of water of about 30 inches in height, for eighteen hours. All the experiments were made at a temperature between 56° and 64°. The clay osmometer attained a considerable degree of uniformity in its action, when the same saline solution was diffused from it once in each of two or three successive days, with a washing between each experiment. A single observation is not much to be relied upon, as the first experiment often differs considerably from the others. One per cent. solutions were always used when the proportion of salt is not specified. Much larger proportions of salt have hitherto been generally employed, but it was early observed that the osmose absolutely greatest is obtained with small proportions of salts in solution. One part of salt to 400 water gives a higher osmose in earthenware than any other proportion for the great majority of substances. Osmose appeared, indeed, to be peculiarly the phenomenon of dilute solutions.

With the same proportion (1 per cent.) of different substances, the osmose varied from 0 to 80 degrees. Occasionally, instead of a rise of liquid in the tube, a fall was observed; the fall may be spoken of as negative osmose, to distinguish it from the rise or positive osmose.

Soluble substances of every description were tried, and find a place in the following classes:—

1. Substances of small osmotic power in porous earthenware; osmose under 20 of the millimeter degrees (ms.).

This class appears to include nearly all neutral organic substances, such as alcohol, pyroxylic spirit, sugar, glucose, mannite, salicin, amygdalin, salts of quinine and morphine, tannin, urea; also certain active chemical substances, which are not salts nor acids; chlorine water, bromine water.

The great proportion of neutral salts of the earths and metals proper also, belong to the same class, such as chloride of sodium, of which the positive osmose was greatest in a solution containing no more than 0·125 per cent., being 19 ms. with that proportion of salt, but falling off and often becoming slightly negative with 1 per cent. and higher proportions of salt in solution. Chloride of potassium is similar.

Nitrate of soda gave an osmose of 8, nitrate of silver of 18 ms.

The salts of the magnesian oxides are all low and sometimes slightly negative.

Chlorides of barium and strontium both gave 18 ms.; nitrate of strontia, 5 ms.; sulphate of magnesia, 0.5 per cent., 2 ms.; 1 per cent., 2 ms.; 2 per cent., 3 ms.; sulphate of zinc was very similar, +2 to -2 ms., from 0.5 to 2 per cent.; chloride of mercury, 1 per cent., gave 6 and 8 ms. in two experiments.

- 2. Substances of an intermediate degree of osmotic force; osmose from 20 to 35 degrees. Sulphurous acid gave 20 ms. Certain vegetable acids have a similar osmose. Tartaric acid, in solutions of 0.25, 1 and 4 per cent., gave 24, 26 and 28 ms.; citric acid, 1 per cent., 30 ms. Also monobasic acids, such as hydrochloric acid, nitric acid, acetic acid, have the same moderate osmotic action in porous earthenware.
- 3. Substances of considerable osmotic power in porous earthenware; osmose from 35 to 55 ms.

In this class are found the polybasic mineral acids: sulphuric acid, 0.5 per cent., gave even 63 ms.; 2 per cent., 54 ms., or nearly the same osmose as the smaller proportion of acid.

In another earthenware cylinder, the following observations on the osmose of sulphuric acid were successively made:—

The results exhibit much similarity of osmose through a great range (1 to 100) in the proportion of acid. So small a quantity of this acid as 1 part in 1000 water, appears to give as great an osmose as any larger proportion of acid.

Certain neutral salts, sulphate of potash, sulphate of soda, sulphate of ammonia, belong to the same class.

With sulphate of soda the osmose for the different proportions 0·125, 0·25, 1 and 4 per cent. of salt, was 46, 47, 36 and 24 ms. respectively; the osmose diminishing with the increased proportion of salt.

Of sulphate of potash, 0.25 per cent. gave 51 ms.; 1 per cent. 46 ms., and 4 per cent. 38 ms., showing no great change from one quarter to 4 per cent.; chromate of potash, 1 per cent., gave an osmose of 54 ms.

4. Substances exhibiting the highest degree of osmotic power in porous earthenware.

Salts of the alkalies, possessing either a decided acid or alkaline reaction, and certain neutral salts of potash.

Binarseniate of potash gave 66 ms.; Rochelle salt 82 ms.

With binoxalate of potash the osmose observed in an earthenware osmometer was—

Of salts having alkaline properties, phosphate of soda gave 70.5; borax, carbonate of soda and bicarbonate of soda all gave numbers which ranged above 60 ms. in various osmometers.

To the same class also belong certain strong acids, phosphoric acid giving an osmose of 62 ms., glacial phosphoric acid of 73 ms.

The caustic alkalies have probably too strong a disorganizing action upon the septum to allow osmose to proceed undisturbed. They give a positive osmose when present in a minute proportion, but very soon attain their *terme moyen*, and then become slightly negative.

Caustic soda, 0.01 per cent., gave 24 ms.; 0.02 per cent., 29 ms.; 0.05 per cent., 31 ms., which was the highest osmose observed; 0.1 per cent., 22 ms.; 0.25 per cent., 3 ms.; 1 per cent. and 2 per cent. of caustic soda gave both —10 ms.

It appears most clearly that highly osmotic substances are also chemically active substances. Both acids and alkaline substances possess the affinities which would enable them to act upon the silicates of lime and alumina, which form the basis of the earthenware septum. Lime and alumina were accordingly found in solution after osmose, and the corrosion of the septum appeared to be a necessary condition of the flow.

It was found impossible to exhaust the whole soluble matter of the walls of the earthenware osmometer, by washing, either with water, or with a dilute acid, for the process of decomposition appeared to be interminable. After such washings the action of an osmometer was often greatly modified upon salts of moderate osmose, such as chloride of sodium; and similar changes gradually took place in the osmometers when used in ordinary experiments with saline solutions.

It is on this account that I avoid the lengthened detail of numerous experiments which were made with the earthenware osmometer, and confine myself to general statements.

Further, the potash salts were also largely kept back or absorbed by the earthenware, a phenomenon of the same class as the retention of alkalies by aluminous soils, which has been studied by Messrs. Thomson and Way.

Other septa, which were not acted upon by the salts, were found deficient in osmotic activity, although possessed of the requisite degree of porosity. Gypsum, compressed charcoal, and tanned sole-leather, gave rise to no osmose when permeated by saline solutions. White plastic clay had an osmotic power which was quite insignificant when compared with that of baked clay: now the former may be considered as an aluminous compound, upon which the decomposing action of water has been already exhausted, while the latter is in a form more liable to decomposition, in consequence of an effect of heat upon the constitution of the aluminous silicates of the

clay. A plate of Caen stone, which is an impure limestone, was greatly more active with a solution of carbonate of potash than a plate of pure white marble was. The effect of impurities in making limestone suitable for osmose did not escape the observation of Dutrochet; it was referred by him to the attraction of alumina for water. Mere capillarity, therefore, is insufficient to produce the liquid movement, while the vis motrix appears to be some form of chemical action.

For the proper appreciation of a chemical theory of the osmotic force, I would now invite attention to a purely speculative subject, namely, the molecular constitution of water and saline solutions. Allowing that water, in the state of vapour, is correctly represented as a compound of one equivalent of oxygen and one of hydrogen, it may still be true that the molecule of *liquid water* is a varying aggregate of many such molecules, or is n times HO. But if so much is conceded, a new and peculiar grouping of the atoms of oxygen and hydrogen becomes not only possible but probable. Instead of arranging them in a series of pairs of H+O, H+O in our compound molecule, we may give a binary form to that molecule in which a single atom of oxygen is the negative or chlorous member, and the whole other atoms united together form a positive or basylous radical. In this radical we have a certain multiple of HO with one H in excess, the last condition being most usual in compound radicals, such as methyl, ethyl, benzoyl, &c., which have all a single unbalanced equivalent of hydrogen;  $H_n O_n = (H_{m+1} O_m) + O$ .

Further, this new oxide should be more easily decomposed than oxide of hydrogen, HO. The basicity of the radical  $(H_{m+1} O_m)$  depends upon the disproportion of the equivalents of oxygen and hydrogen in its constitution, there being one of hydrogen in excess. Now that disproportion becomes less as we ascend, as in 3H+2O, 11H+10O, 101H+100O; and the more feeble the basyl-atom, it may be supposed to retain less forcibly its fellow oxygen-atom or other negative element with which it is combined. When water, therefore, has to undergo decomposition in a voltaic circle, it will naturally assume the molecular arrangement supposed, as being the binary form which is most easily divisible into a positive and negative element, or that in which water is most easily decomposed.

This molecular view has been brought forward at present principally for the aid which it gives in conceiving what is known as electrical endosmose.

This interesting phenomenon, first well developed by our colleague Mr. Porrett, has very lately been defined with great clearness by M. Wiedemann\*. The water which accumulates at the negative pole (or follows the hydrogen), in the electrolysis of the pure liquid, is found to be exactly proportional to the amount of circulating affinity; that is, with every equivalent of hydrogen that is discharged at the negative pole the same quantity of water arrives there, and will force its way through a porous diaphragm to reach that destination. The reason now suggested is, that the travelling basylous atom in the voltaic decomposition is not hydrogen simply, but

<sup>\*</sup> Wiedemann, Poggendorff's Annalen, vol. lxxxvii. p. 321.

the voluminous basylous molecule  $(H_{m+1}O_m)$  above described; which again breaks up at the negative pole into hydrogen and water,  $(H_{m+1}O_m)=mHO$  and H.

But even although such a representation of the circumstances of electrical endosmose may not be fully admitted, the phenomenon itself is of great service to us, as showing that in the occurrence of chemical decompositions affecting ultimate particles, sensible volumes of water may be involved and set in motion.

Further, in considering the action of chemical affinity between bodies in solution, between an acid and alkali for instance, we are apt to confine our attention to the principal actors in the combination, and to neglect entirely their associated water of hydration. Yet both the acid and base may have large trains of water attached to them by the tie of chemical union. Sulphuric acid certainly evolves heat with the fiftieth equivalent of water that is added to it, and probably in dilute solution that acid is capable of having a still greater number, indeed an indefinitely large number of equivalents of water combined with it. In fine there is reason to believe that chemical affinity passes, in its lowest degrees, into the attraction of aggregation.

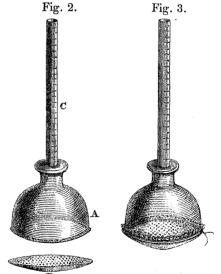
The occurrence of chemical decomposition within the substance of a porous resisting septum may be calculated to bring into view the movement and disposal of the water chemically associated in large quantities with the combining substances; as the interposition of a porous diaphragm in electrical endosmose makes sensible a translation of water in voltaic decompositions which is not otherwise observable.

II. The osmose of liquids has hitherto been principally studied in septa of animal membrane, which from their thinness, their ready permeability combined with a sufficient power of resistance to the passage of liquids under pressure, have great advantages over mineral substances.

The great proportion of the experiments of the present inquiry were also made with animal membrane.

The membrane osmometer employed, which is only a modification of the classical instrument of Dutrochet, was prepared as follows:—

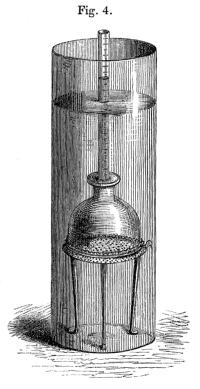
The mouth of a little glass bell-jar A (fig. 2) had first loosely applied to it a plate of perforated zinc B slightly convex, and then the membrane was tied tightly over the latter for the sake of support (fig. 3). The quantity of metal removed in the perforations of the zinc plate amounted to 49 per cent. of the weight of the zinc. This plate was always varnished or painted to impede, if not entirely prevent, the solution of the metal by acid fluids. The usual



diameter of the bulb was about 3 inches or 75 millimeters, and its capacity equal to 5 or 6 oz. of water. The tube C was usually not more than 6 inches in length, but comparatively wide, its diameter being about 7.5 millimeters, that is one-tenth MDCCCLIV.

of the diameter of the mouth of the bulb, and it was divided into millimeters. The action of an osmometer depends chiefly upon the extent of membrane-surface exposed, and very little upon the capacity of the instrument. Hence the relation of diameters (or areas) between the bulb and tube was adopted in preference to the relation in capacity, the area of a section of the tube being one-hundredth of the area of the disc of membrane, or rather it was reduced by calculation to this relation by means of a coefficient for each instrument. Hence a rise of liquid in the tube amounting to 100 millimeters, indicates the admission into the bulb of a sheet of water of 1 millimeter (one twenty-fifth part of an inch) in depth, over the whole surface of the membrane, and so in proportion for any other rise in the tube. These millimeter divisions (ms.) of the tube mark therefore degrees of osmose which have an absolute and equal value in all instruments. The bulb of the instrument filled with the solution to be operated upon was placed within a cylindrical glass jar of distilled

water, containing at least sixty ounces (fig. 4), and during the experiment inequality of hydrostatic pressure was carefully avoided by maintaining the surface of the water in the jar at the level of the liquid in the tube. The osmometer was supported upon a tripod of perforated and painted zinc, at a height of about 4 inches from the bottom of the glass cylinder. The osmose was observed hourly for five hours, during which time it advanced in general with considerable uniformity. In an experiment with fresh ox-bladder as the septum and a solution of 1 per cent, of carbonate of potash in the osmometer, the rise, in five consecutive hours, was 10, 12, 11, 14, 13 millimeter degrees, and in five hours immediately following, 13, 12, 9, 11 and 12 millimeter degrees, making sixty degrees in the first, and fiftyseven degrees in the second period of five hours. The quantity of salt which diffused outwards during the experiment of five hours was also frequently determined, usually by evaporating the liquid of the waterjar to dryness; it rarely exceeded one-tenth part of the



salt originally present in the osmometer. The membrane itself was also weighed before it was applied to the osmometer, and again when its use was discontinued, which was generally after six or eight experiments had been made with the membrane. A loss of the substance of the membrane was always observed, varying from 20 to upwards of 40 per cent. of its original weight.

The outer muscular coat of bladder soon becomes putrescent, and from changes in its consistence, and the large quantity of salts and other soluble substances which it yields by decomposition, gives occasion to much irregularity in the experiments. The great change in the amount of osmose often produced by merely turning the mem-

brane, observed by M. MATTEUCCI and others, depends often, I believe, upon the soluble matter of the muscular coat being thrown outwards or inwards, according as the membrane is applied. The muscular coat was on this account removed from the ox-bladder employed, and the serous membrane remaining found to acquire greatly increased activity, and also to act with much greater regularity in successive experiments. The membrane so prepared could be used for weeks together without the slightest putrescence of any part of it. Two of these thin membranes, or a double membrane, was often applied. The weight of a disc of single membrane,  $4\frac{1}{2}$  inches in diameter in a dry state, varied from about 0.5 to 1.2 gramme. The soundness of the membrane of an osmometer and its degree of permeability were always roughly tested before an experiment, by filling the bulb, without its tube, completely with water, hanging it up in air, and observing how frequently a drop fell from the instrument. The time between each drop varied, with suitable membranes, from one to twenty The times in which water permeated the same membranes by osmose minutes. varied between much narrower limits, perhaps from one to two.

The quantity of salt which traversed different membranes by diffusion, was also found to be in proportion to the osmotic permeability of the membranes, and not to their mechanical porosity.

To wash the membranes, they were macerated in distilled water after every experiment for not less than eighteen hours, without being ever removed from the glass bulb. A membrane also was never allowed to dry, but was kept humid as long as it was in use for experiments.

Osmose in membrane presented many points of similarity to osmose in earthenware. The membrane was constantly undergoing decomposition, soluble organic matter being found both in the fluid of the osmometer and in the water of the outer jar after every experiment; and the action of the membrane appeared to be exhaustible, although in a very slowand gradual manner. Those salts and other substances, of which a small proportion is sufficient to determine a large osmose, are, further, all of the class of chemically active substances, while the great mass of neutral organic substances and perfectly neutral monobasic salts of the metals, such as the alkaline chlorides, possess only a low degree of action.

When a solution of the proper kind is used in the osmometer, the passage of fluid proceeds with a velocity wholly unprecedented in such experiments. Take, for instance, the rise in five hours exhibited in a series of experiments upon solutions of several different proportions of carbonate of potash, made in succession with the same membrane in the order in which they are related.

With 0·1 per cent. carbonate of potash, a rise of 182 ms. With 0·1 per cent. carbonate of potash, a rise of 120 ms. With 0·1 per cent. carbonate of potash, a rise of 199 ms. With 0·5 per cent. carbonate of potash, a rise of 246 ms. With 0·5 per cent. carbonate of potash, a rise of 194 ms. With 1 per cent. carbonate of potash, a rise of 205 ms. With 1 per cent. carbonate of potash, a rise of 207 ms.

Or the rise in the same time with another membrane which had been previously exposed to a steam heat of 212° for ten minutes without impairing its activity.

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With 1 per cent. carbonate of potash at 60° Fahr., a rise of 402 ms. With 0·1 per cent. carbonate of potash at 60° Fahr., a rise of 196 ms. With 0·1 per cent. carbonate of potash at 60° Fahr., a rise of 153 ms. With 2 per cent. carbonate of potash at 60° Fahr., a rise of 511 ms. With 4 per cent. carbonate of potash at 60° Fahr., a rise of 781 ms. With 10 per cent. carbonate of potash at 60° Fahr., a rise of 863 ms.
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In the last experiment a rise of fluid in the tube of upwards of 30 inches occurs in five hours, and so much water is impelled through the membrane as would cover its whole surface to a depth of 8.6 millimeters, or one-third of an inch. Both membranes, but particularly the first, show the comparatively great activity of small proportions of salt, the average osmose of 0.1 per cent. of carbonate of potash in the first osmometer being 167 millimeter degrees, and of 1 per cent. 206 millimeter degrees.

Now the quantity of carbonate of potash which diffuses out of the osmometer into the water-jar, was determined by the alkalimetrical method in the second and third of the 0·1 per cent. observations first related, and found to be in both cases 0·018 gramme (0·28 grain); the quantity of water also which entered in return can be calculated from the known capacity of the tube of the osmometer, of which each millimeter division represented 0·060 gramme of water; and consequently 167 divisions represent 10·020 grammes (155 grains) of water. We have, in 0·1 per cent. solution,

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Mean diffusate of carbonate of potash . . . 0.018 \text{ gramme} = 1
Mean osmose (of water) . . . . . . . . 10.020 \text{ grammes} = 556
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The conclusion is, that while the membrane was traversed during the five hours of an experiment by 1 part of carbonate of potash passing outwards, it was traversed by 556 parts of water passing inwards.

In the two experiments with 1 per cent. solution of carbonate of potash in the same osmometer, the diffusates were 0·192 and 0·198 gramme of carbonate of potash, which are sensibly ten times greater than the diffusates of the 0·1 per cent. solution. But the mean osmose of the 1 per cent. solutions is greater than that of the 0·1 per cent. solutions only in the proportion of 206 to 167, or as 1 to 0·81. The ratio in question however varies greatly in different membranes. We have, consequently, in 1 per cent. solution,—

Whatever, therefore, be the nature of the chemical action occurring in the membrane which influences osmose, a minute amount of that action appears to be capable of producing a great mechanical effect.

All idea of contractility or organic structure being the foundation of the osmotic

action of membrane, was excluded by the observation that similar large effects could be obtained from a septum of pure coagulated albumen.

A convenient albumen osmometer is constructed by covering the opening of the bulb of the former instrument by ordinary thin cotton calico, which is best applied wet, and painting over the outer surface of the calico two or three times with undiluted egg albumen, an hour being allowed to elapse between each application of the albumen. The instrument is then suspended in the steam rising from boiling water for a few minutes, so as to completely coagulate the albumen. The albuminated calico may then be macerated for twenty-four hours before use, by placing the osmometer in cold water, to dissolve out the soluble salts of the albumen. It should be preserved always in a humid state. Before application to the calico, the albumen in many cases was neutralized with acetic acid and filtered, the more completely to obliterate every trace of organic structure.

The osmose in a particular instrument of this kind was, at 50°, for

- 1 per cent. carbonate of potash . . . 211 ms
- 1 per cent. carbonate of potash . . . 367 ms.
- 1 per cent. carbonate of potash . . . 387 ms.
- 0.1 per cent. carbonate of potash . . . 127 ms.
- 0.1 per cent. carbonate of potash . . . 124 ms.

The correct rate is rarely obtained in the first observation, as seen above, in osmometers of albumen as well as of other materials.

The albumen plate has generally a greater thickness than prepared membrane, which appears to diminish proportionally the quantity of salt which escapes by diffusion.

The diffusate in the three experiments above of 1 per cent. carbonate of potash was 0.024, 0.038 and 0.042 gramme of the salt. The largest proportion of carbonate of potash (0.042 gramme) which was obtained in the last of the three experiments was replaced by 23.220 grammes of water, or 552 times the weight of the salt.

An obvious and essential condition of osmose is difference of composition in the two fluids in contact with the opposite sides of the porous septum. With the same solution, or with pure water, in contact with both surfaces of a membrane there may be chemical action, but it will be equal on both sides, and although probably attended with movements of the fluids, yet nothing will be indicated, as the movements, being equal and in opposite directions, must neutralize each other. Difference of composition in the two fluids is necessary in order that there may be inequality of action upon the two sides of the membrane. It is difficult however, with respect to the chemical action, to ascertain either its true sphere or its exact nature. No substance appears to be permanently deposited in the membrane during osmose, even by easily decomposed metallic salts, such as salts of lead and mercury. The action upon the membrane is probably of a solvent nature, and its seat may possibly be ascertainable

when two membranes are used together. Some observations made on the comparative loss of weight of the outer and inner membrane have not, however, shown any remarkable difference. But this again may arise from the great proportion of the loss in both membranes being due to the ordinary solvent action of water alone, and the operative solvent action of the osmotic salt being comparatively minute in amount; or it may depend, and I am most inclined at present to take this view, upon the chemical actions being of a different kind on the two sides of the membrane, and not upon the inequality simply of one kind of action. Such a supposition was suggested by the fact, which will immediately appear, that osmotic activity and easy decomposition are properties often found together in binary compounds. The basic and acid agents then developed are both capable of acting upon albuminous septa. We may imagine, for instance, in the osmotic action of a neutral salt, the formation within the thickness of the septum of a polar circle, one segment of which (composed of the binary molecules of the salt) presents a basic molecule to the albumen at the inner surface of the septum, and an acid molecule to the albumen at the outer surface, the circle being completed through the substance of the septum which forms the second segment. Both surfaces of the septum would be acted upon, but at one side we should have combination of the albumen with an alkali, on the other side with an This however must be taken as a purely ideal representation of the condition of the septum in osmose. I have not discovered such a polar condition of the septum, and I doubt whether the galvanometer could be properly applied to exhibit it, as the placing of the poles of that instrument in the dissimilar fluids existing on opposite sides of the septum would alone be sufficient to give rise to voltaic polarization. present I must confine myself to the enunciation of certain general empirical conclusions respecting the operation of chemical affinity in osmotic experiments.

With animal septa, frequent examples of the outward flow of liquid from the osmometer present themselves, causing the liquid column to fall instead of rise in the tube. This phenomenon (exosmose) I have spoken of as negative osmose. The observation of Dutrochet, that oxalic acid in the osmometer, and also tartaric acid at a certain point of concentration, give rise to negative osmose, I have been able to generalise in so far as acids have universally either a negative osmose, or lie at the very bottom of the positive class.

Oxalic acid gave in membrane, for 1 per cent. acid, -148 ms. and -141 ms.; and for 0·1 per cent., -10 and -27 ms. In another membrane, 1 per cent. of the same acid alone gave -136 ms.; with the addition of 0·1 per cent. hydrochloric acid, -181 and -168 ms. By the addition of 0·1 per cent. of chloride of sodium, a salt which in small proportions is nearly neutral to osmose, the negative osmose of 1 per cent. oxalic acid fell in the same membrane to -45 ms., and with the addition of 0·25 per cent. of chloride of sodium the osmose was +6 ms., or became slightly positive. The negative osmose of 1 per cent. of oxalic acid, in a membrane where it amounted to -56 and -57 ms. in two experiments, became, with the addition of 0·1 per cent.

of albumen -46 ms.; of 0.25 per cent. of albumen -20 ms.; of 0.25 per cent. of gelatin -59 ms., and of 0.25 per cent. of sugar -53 ms.

In albuminated calico, the osmose of 1 per cent. of oxalic acid was also negative, namely -13, -16 and -20 ms. in three successive observations. With the addition to the oxalic acid of 0·1 per cent. hydrochloric acid, the osmose became -46 and -58 ms.; and with the addition of 0·1 per cent. of sulphurous acid, the osmose became -62 and -58 ms.

Of hydrochloric acid introduced into the membrane-osmometer in the small proportion of 0·1 per cent., the negative osmose was -92, -37 and -27 ms. in three successive experiments. The negative osmose of hydrochloric acid was still more powerfully counteracted than that of oxalic acid, by the association of a minute proportion of chloride of sodium with the acid. The negative osmose of this acid appears to be extremely precarious. It is reversed by a great variety of neutral soluble substances, and on that account can rarely be observed at all with bladder undivested of its muscular coat.

In a certain prepared membrane, *sulphuric acid*, 0·1 per cent., gave an osmose of -4, +8 and +7 ms.

Nitric acid, 0.1 per cent., gave an osmose, at 58°, of +8 and +23 ms.

Tribasic phosphoric acid, 1 per cent., gave -6 and -7 ms., at 61° and 63°. The diffusates of phosphoric acid, in the same experiments, amounted to 0·143 and 0·130 gramme.

The glacial or monobasic phosphoric acid, 1 per cent., gave +137 and +131 ms., at 55°, which is a considerable positive osmose, an interesting circumstance when taken in connexion with the deficient acid character of that modification of phosphoric acid. The same acid, 0·1 per cent., gave a positive osmose in the last membrane of 28 and 23 ms.

Citric acid, 1 per cent., gave 39 and 36 ms.; 31 and 31 ms., at 62°; the first in membrane and the second in albumen.

The same acid, 1 per cent., after being fused by heat, gave, at  $63^{\circ}$ , -38 and -35 ms. in membrane; 0 m. and -2 ms. in albumen.

A small proportion of fused citric acid, 0.1 per cent., gave on the other hand a slight positive osmose, namely 15 ms. and 2 ms. in the previous membrane and albumen osmometers respectively.

Tartaric acid, 1 per cent., gave 18 and 19 ms. in membrane, at 68°; with 20 ms. in albumen, at 62°.

The same acid, after being fused by heat, gave -68 and -61 ms. in membrane, at  $57^{\circ}$ , showing a molecular change from fusion, as in citric acid.

The diffusate in the last two experiments was 0.123 grm. and 0.132 grm. of acid.

In albumen the osmose of fused tartaric acid remained slightly positive, being 5 and 2 ms. for 1 per cent., at 60°, and 5 and 3 ms. for 0·1 per cent., at the same temperature.

Racemic acid, 1 per cent., gave 4, 11 and 7 ms. in three experiments, at 55°, in the last used membrane; with 15 and 22 ms. at the same temperature in albumen; or was always slightly positive like tartaric acid.

Acetic acid, in the proportions of 0·1, 0·5 and 1 per cent., gave sensibly the same small positive osmose, 25 to 28 ms., at 57° to 62°, in membrane.

A saturated solution of *carbonic acid* in water gave 25 and 26 ms. in membrane, with 20 and 22 ms. in albumen, both at 65°.

The last solution, diluted with an equal bulk of water, gave an osmose of 15 and 18 ms. in membrane, and 16 ms. twice in albumen, both at 63°.

Terchloride of gold is negative in its osmose like the stronger acids, giving -49 and -54 ms. in membrane, at  $64^{\circ}$ , with much reduction of metallic gold in the substance of the membrane.

Bichloride of platinum, made as neutral as possible by evaporation, gave for the 1 per cent. solution -32 and -30 ms. in membrane, at  $61^{\circ}$ . For the 0·1 per cent. solution, a positive osmose of 27, 14 and 5 ms. in three successive experiments made with the last membrane, at  $64^{\circ}$ ,  $65^{\circ}$  and  $62^{\circ}$ . The same 1 per cent. solution gave in albumen, at  $61^{\circ}$ , a positive osmose of 54 and 50 ms.; the 0·1 per cent. solution also, at  $64^{\circ}$ , gave 43 ms. Albumen appears thus to be less adapted for bringing out the negative osmose of various substances than membrane is.

In membrane, bichloride of tin, 0·1 per cent., gave -24 ms., at 61°; 1 per cent. -46 and -71 ms., at 59°. The addition to the last of 0·5 per cent. of sulphuric acid gave -63 ms., or did not alter the character of the osmose. But partial neutralization of the 1 per cent. tin solution, by ammonia, on the other hand, gave 0 m., or destroyed all osmose. One per cent. of bichloride of tin gave only a small negative osmose in albumen, namely 5 ms. twice, at 59°.

Oxalic acid carries the highly negative character of its osmose into the binoxalate of potash, of which 1 per cent. of anhydrous salt gave in membrane -112 and -99 ms., at 62°; 0·1 per cent., -30 ms., at 60°. One per cent. of the same salt in albuminated calico gave -20 ms., at 60°. A saturated solution of binoxalate of potash, containing 2·5 per cent. of salt, gave -15 ms. in the last osmometer.

Bisulphate of potash, 1 per cent., gave 4 and 7 ms. in membrane, at 56°; in albumen, 7, 3 and 6 ms., at 56°.

A solution of bitartrate of potash, saturated in the cold, also gave a small positive osmose, namely 4 and 2 ms. in membrane, and 20 and 17 ms. in albumen, both at 56°. Other supersalts tried gave also a small positive osmose, such as binarseniate of potash and bichromate of potash. It becomes doubtful therefore whether any of the supersalts of potash are negative, except the acid oxalates of that base.

Neutral organic substances dissolved in water appear to be generally deficient in the power to give rise in membrane to that osmose which depends upon a small quantity of the soluble substance, such as I per cent., or a still less proportion. The osmose obtained in ox-bladder employed without removing the muscular coat, was, in 1 per cent. solutions of the substances, salicin 5 ms., tannin 3 ms., urea 4 ms., gelatin 9 ms., amygdalin 6 ms., lactine 7 ms., glucose 7 ms., gum-arabic 18 ms., and hydrochlorate of morphine 4 ms.

The relations to osmose of alcohol and sugar were more fully examined. With these and other chemically inactive substances, the osmose, although small for 1 per cent., increases progressively with larger proportions of the substance, and also bears a close relation to the proportion of substance diffused outwards, circumstances which give a mechanical character to the osmose. It is with such substances that the influence of diffusibility upon osmose is most likely to betray itself. They have a peculiar interest in the study of the phenomenon, as they present a certain small but remarkably uniform amount of osmose without the known intervention of any strong chemical affinities.

Alcohol.—In describing an experiment I shall endeavour to put forward all the circumstances which can be supposed to influence in any way the result.

In the table which follows, Column I. contains the proportion of absolute alcohol, by weight, which is dissolved in the water of the osmometer.

A 10 per cent. solution is prepared by weighing 10 grammes of the substance, and then adding water to it so as to make up the liquid to the volume of 100 grammes of water. It is necessary to make up in this way solutions used in experiments of diffusion and osmose, in order to preserve a true relation in solutions containing the different proportions of substance, for it is a fixed volume (not weight) of these solutions which must be used in the osmometer. We come thus to have with a 20 per cent. solution of alcohol exactly twice as much alcohol in the osmometer as with a 10 per cent. solution of alcohol, and so of other proportions.

The membrane of the osmometer is always to be considered as fresh, or as used for the first time in the first experiment narrated, and the observations to be made successively as they stand in the table. The length of maceration in cold water to which the membrane has been exposed previous to the osmotic experiment, as before described, is given in Column V. By the most frequent time of one day is to be understood the space of eighteen hours, which intervened between experiments on successive days.

The hydrostatic resistance of the membrane given in Column VI. is the length of time, in minutes, observed to elapse between the fall of two drops from the bulb of the osmometer filled with distilled water, and hung up in air as already described. The temperature of the water in the glass cylinder during the experiment is noted in Column VII.; the rise of fluid in the tube of the osmometer or osmose, in millimeter divisions of the tube, appears in Column II., and the absolute amount of the same osmose is expressed in Column III. in grammes, or more strictly in gramme measures of water. Lastly, the weight of diffusate found in the water of the glass cylinder appears in Column IV. These last two data, the osmose and diffusate, both in grammes, afford the means of comparing the weight of substance which has MDCCCLIV.

escaped from the osmometer with the weight of water which has entered the osmometer in the same time. It is necessary however to recollect, that the apparent osmose or rise observed, is only the excess in volume of the liquid which has entered over the volume of the liquid which has left the osmometer. To obtain the full volume of water which has entered (the true osmose), it is therefore necessary to add the bulk of the substance diffused to the osmose observed.

I.	II.	III.	IV.	v.	VI.	VII.
Alcohol in solution.	Rise or osmose in millimeter degrees.	Rise or osmose in grammes of water.	Diffusate of alcohol in grammes.	Previous maceration of membrane.	Hydrostatic resistance of membrane.	Temperature, FAHR.
per cent.				days.	min.	0
0.25	12			$1\frac{1}{2}$	8	$6\mathring{3}$
0.25	7			1	8	63
1	10			1	6.	66
1	15			1	6	66
2	20		•••	1	6	67
2	22			1	6	69
5	45	1.984	0.521	2	6	72
5	45	1.984	0.452	1	8	70
10	70	3.072		1	8	67
10	76	3.328	••••	1	8	67
20	107	4.672		1	8	67
20	109	4.800		1	8	67

TABLE I.—Alcohol in Osmometer A of double membrane during five hours.

A second series of observations was made simultaneously, in another membrane osmometer, in order to ascertain the degree of concordance to be expected in such experiments.

I.	II.	III.	IV.	v.	VI.	VII.
Alcohol in solution.	Rise or osmose in millimeter degrees.	Rise or osmose in grammes of water.	Diffusate of alcohol in grammes.	Previous maceration of membrane.	Hydrostatic resistance of membrane.	Temperature, FAHR.
per cent.				days.	min.	
1	14			$2\frac{1}{2}$	12	$6\mathring{3}$
1	14		•••••	1	12	63
2	19		•••••	1	8	66
2	19			1	8	66
5	46			1	8	67
5	54	2.432	0.579	1	8	69
10	90	4.028	1.505	2	6	72
10	96	4.332		1	8	70
20	120	5.396		1	8	67
20	123	5.472	•••••	1	4	67
20	137	6.156	••••	-1	4	67
20	142	6.384		. 1	4	67

Table II.—Alcohol in Osmometer B of double membrane for five hours.

It will be observed that the osmose increases with the proportion of alcohol, but not in so rapid a ratio; the osmose of the 20 per cent. solution being about only ten

times greater than that of the 1 per cent. solution in both series. The hydrostatic resistance of the membrane B falls off in a remarkable manner in the later experiments, indicating an increased facility of permeation, which may influence the increased osmose in the last two observations of this series. The results otherwise of the two series exhibit a fair amount of correspondence, both in the degree of osmose and the amount of diffusate for the same proportions of alcohol in the two osmometers. It should be added, that in several instances the water in the jars was changed after the third hour of the experiment, with the higher proportions of 10 and 20 per cent. The alcohol was determined, after it had been concentrated by two distillations, by means of Drinkwater's table of densities.

Several experiments were made to determine the proportion of the diffusate of alcohol from 5 and 20 per cent. solutions respectively of that substance, in membrane osmometers. The mean proportion was as 1 to 3.02, which is mentioned here, as I was led at first to a different conclusion by earlier and imperfect experiments.

Sugar.—The osmose of sugar in membrane was examined very fully, in the hope that the simple effect of diffusion would be exhibited without being modified by any chemical action, in a substance so entirely neutral.

Crystallized cane-sugar was made use of.

I.	II.	III.	IV.	v.	VI.	VII.
Sugar in solution.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate of sugar in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, FAHR.
per cent.				days.	min.	0
1	21	1.027		1	4	64
1	8	0.395	0.150	9	$2\frac{1}{2}$	63
1	19	0.948	0.140	1	$3\frac{1}{2}$	63
2	19	0.948	0.178	1	$2\frac{1}{2}$	66
	19	0.948	0.182	1	$egin{array}{cccccccccccccccccccccccccccccccccccc$	66
2 5	39	1.900	0.438	1	$2\frac{1}{2}$	67
5	49	2.370	0.480	1	$2\frac{1}{2}$	69
10	66	3.239	1.110	2	$2\frac{1}{2}$	72
10	79	3.871	0.853	1	$2\frac{1}{2}$	70
10	76	3.713	0.840	1	3 *	67
20	121	5.975	1.376	1	3	67
20	117	5.688	1.485	1	3	67

TABLE III.—Sugar in Osmometer D of double membrane for five hours.

It was very desirable to find whether the deviations from a regular progression seen in the numbers for the osmose and diffusate in the preceding results are essential, or accidental and peculiar to the present membrane. It was also desirable to find whether a membrane would stand the repetition of such a series of experiments and continue to give similar results. A double series of experiments were accordingly made with new membrane.

I.	II.	III.	IV.	v.	VI.	VII.
Sugar in solution.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate of sugar in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, FAHR.
per cent.				days.	min.	
0.25	5	0.240		2	10	63
0.25	9	0.420	0.050	1	10	63
1	12	0.531	0.110	1	8	66
1	11	0.472	0.106	1	10	66
2	24	1.060	0.205	1	8	67
2 2 5	31	1.357	0.208	. 1	8	69
5	65	2.891	0.600	2	8	72
5	63	2.773	0.555	1	8	70
10	89	3.953	1.073	1	10	67
10	104	4.602	0.967	1	10	67
10	96	4.248		1	10	67
20	133	5.900	1.457	1	10	67
20	106	4.720	1.643	10	10	64
20	118	5.251	1.656	1	6	64
1	19	0.826	0.105	1	6	68
1	19	0.826		1	6	65
2	24	1.062	0.153	1	6	65
2 2 5	25	1.121	0.162	1	6	64
5	37	1.652	0.435	2	8	66
5	33	1.425	0.470	2	8	67
10	69	3.068	0.757	2	8	67
10	76	3.363		1	8	69
20	110	4.807		1	8 3	70
20	112	4.956	1.540	2	3	70

TABLE IV.—Sugar in Osmometer E of double membrane for five hours.

The diffusates of sugar (Column IV.) were obtained by evaporating the fluid of the water-jar to dryness, at 212°, and therefore contain organic matter dissolved out of the membrane; the weight of each of the diffusates is increased by this addition a few thousandths, but not in such a quantity as to affect the result to an extent that is at all material, except in the first diffusate recorded, that from the 0.25 per cent. solution.

Although the results exhibit several irregularities, yet starting from the 1 per cent. observation, in the first series of Table IV., the amount both of osmose and diffusate appears compatible with an arithmetical progression in the observations from 1 to 10 per cent. Thus the average rise in the 1 per cent. solution is 11.5 millimeter degrees, and in the 10 per cent. solution 96.3 ms.; the average diffusate in the 1 per cent. solution is 0.108 gramme, and in the 10 per cent. solution 1.020 gramme.

But with the 20 per cent. solution both osmose and diffusate fall off greatly, and the osmose more than the diffusate. The osmose of the 20 per cent. solution may be taken as 125 ms.,—the mean of the first and third observations, 133 and 118, the intermediate observation 106 being obviously exceptional, possibly from the unusually long maceration of the membrane immediately preceding that experiment. Hence the osmose only rises from 96·3 ms. to 125 ms., while the proportion of sugar in the osmometer was increased from 10 to 20 per cent.

The mean diffusate of sugar also increases with the same change only from 1.020 gramme to 1.585 gramme.

In the second series of observations with the same membrane, given in the lower part of the same Table, both the osmose and diffusate fall off, to an extent which is perhaps pretty fairly represented by the 10 per cent. solution, which gives a mean osmose of 72.5 ms. against 96.3 ms. in the former series, and a diffusate of 0.757 gramme against 1.020 gramme in the former series. A rough proportionality between the two series of observations is sufficiently indicated.

Two observations are recorded in the last series which must not be allowed to mislead. These are the comparatively high osmose of 19 ms. for the 1 per cent. solution, which is accidental, and arises from the 1 per cent. experiments having been immediately preceded by the high proportion of 20 per cent. The other observation referred to is the high diffusate of the last 20 per cent. solution at the bottom of the table, which has no doubt been occasioned by the sudden diminution in the hydrostatic resistance of the membrane from 8 to 3 in that which is the last experiment of the series. The membrane, indeed, appears to be giving way after its long use, for the osmometer had been exposed to the action of water for thirty-five days without intermission.

The reason why the diffusion and osmose are smaller in the second series of experiments than in the first series (nearly as 3 to 4), is (I believe), that the membrane softens and swells somewhat by the protracted action of water; a change in the structure of the membrane which impedes diffusion by increasing the length of the channels through which the salt has to travel.

It may now be interesting to discover the proportion between the water which enters and the sugar which leaves the osmometer in these experiments. That proportion appears not to vary greatly in the range from the 1 to the 10 per cent. solution. For a mean result, the sum of the eight diffusates between 1 and 10 per cent. inclusive, in the first series of observations of Table IV., may be taken, and the osmose belonging to the same experiments. There is so obtained 3.824 grammes of sugar diffused against an osmose of 17.639 grammes of water. But this, the apparent osmose, has to be increased by the bulk of the sugar diffused, which may be estimated at ten-seventeenths of its weight of water, or 2.25 grammes. Adding the last quantity to 17.639 grammes, we obtain—

Hence the sugar appears to be replaced in osmose by rather more than five times its weight of water. The less complete experiments with alcohol, previously described, indicate a nearly similar relation to its replacing water.

Calculating, in like manner, the observations made upon each of the five proportions of sugar in Table III., we obtain numbers for the replacing water which oscil-

late about the general result first stated; the mean diffusates of sugar and amounts of replacing water were in the different solutions:—

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In 1 per cent. solution, 0·145 grm. sugar to 0·756 grm. water . . . 1 to 5·21 In 2 per cent. solution, 0·180 grm. sugar to 1·054 grm. water . . . 1 to 5·85 In 5 per cent. solution, 0·459 grm. sugar to 2·405 grm. water . . . 1 to 5·22 In 10 per cent. solution, 0·934 grm. sugar to 4·158 grm. water . . . 1 to 4·43 In 20 per cent. solution, 1·430 grm. sugar to 6·672 grm. water . . . 1 to 4·66
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The mean of the various solutions is 1 part of sugar replaced by 5.07 water.

The phenomenon of the osmose of sugar partakes very much of a physical character, and may possibly prove to be nothing more than the exchange of sugar for water by the purely mechanical operation of diffusion.

A third series of observations on sugar were made in an osmometer of albuminated calico. The results, it will be seen, are quite in accordance with those of the membrane osmometers.

I.	II.	III.	IV.	v.	VI.	VII.
Sugar in solution.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate of sugar in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, FAHR.
per cent.			-	day.	min.	
1	16	0.684	0.124	ľ	2	59
1	22	0.912	0.156	1	10	60
4	31	1.311	0.476	1	1	61
4	42	1.767	0.505	1	1	63
4	34	1.425	0.542	1	1	63
10	92	3.876	1.283	1	0.50	63
10	106	4.389	1.179	1	0.66	64
10	90	3.762	1.193	1	1	63

Table V.—Sugar in Osmometer F of Albuminated Calico for five hours.

This osmometer is remarkable for the variable but generally very small amount of its hydrostatic resistance, a condition of the septum which is apt to increase the diffusate, owing to the expulsion of a portion of the solution by the pressure of the dense solution. The diffusates of sugar (Column IV.) may be considered as nearly proportional to the per-centage of sugar in the osmometer. The osmose of the 4 and 10 per cent. solutions are also nearly proportional, the means being 36 and 96 ms.; but the osmose of the 1 per cent. solution is sensibly in excess. A slight excess in the early experiments with an albumen osmometer is, it may be remarked, not unusual, and appears to be due to the considerable quantity of soluble matter, with an alkaline reaction, which the fresh albumen affords to the water in the osmometer, this soluble matter then acting as an osmotic body.

Sulphate of Magnesia.—This salt was selected to illustrate the osmose of neutral salts. The sulphate of magnesia is neutral to test-paper. It appears, further, to be

incapable of passing into the condition of a stable supersulphate or subsulphate by combining with an excess of either acid or base, and is not decomposed in diffusion. Such properties secure to a salt a remarkable indifference, or absence of chemical activity, and recommend sulphate of magnesia for our present purpose.

In a fresh double membrane, 1 per cent. of sulphate of magnesia (anhydrous) gave the small osmose of 13 and 14 ms., at 63°, in two experiments.

A full series of observations was made by means of the osmometer F, used above with sugar, but with the osmotic septum of course changed.

I.	II.	III.	1V.	v.	VI.	VII.
Sulphate of magnesia (anhydrous).	Rise in millimeter degrees.	Same in grammes of water.	Diffusate of salt in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, FAHR.
per cent.				days.	min.	0
2	30	1.254		2	10	72
2	33	1.368	0.265	1	10	70
2 5	73	3.078	0.540	1	10	67
5	76	3.192	0.553	1	10	67
10	152	6.384	1.020	1	10	67
10	134	5.529	0.962	1	10	67
20	238	9.918	1.623	10	15	64
20	283	11.836	1.687	1	3.5	64
1	23	0.969	0.119	1	5	68
1	20	0.855	0.120	1	5	65
2	30	1.254	0.227	1	5	65
2	29	1.197	0.233	1	5	64
2 5	69	2.907	0.490	2	6	66
5	68	2.850	0.485	1	6	67
10	132	5.529	0.959	2	6	67
10	140	5.871	0.845	1	6	69
20	277	11.628		1	6	70
20	291	12.198	2.012	2	6	70

Table VI.—Sulphate of Magnesia in Osmometer F of double membrane for five hours.

The diffusate increases in a somewhat less ratio than the proportion of salt in the osmometer in both of the two series of observations contained in the preceding Table. But a similar falling off in the amount of diffusate from the higher proportions of salt takes place in the diffusion of the same salt, from open phials, as appeared in former experiments on the diffusion of sulphate of magnesia\*.

The different solutions then operated upon, and the ratio between the diffusates they gave, were as follows:—

Solutions of sulphate of magnesia diffused . 2 4 8 16 24 per cent. Ratio of diffusate of these solutions . . . 2 3.671 6.701 11.785 15.678

<sup>\*</sup> Philosophical Transactions, 1850, p. 822.

The proportions of sulphate used in the present osmotic experiments were different, but ratios may be found for them by interpolation, and are given below. We are thus enabled to make the following comparison of the diffusion from different proportions of sulphate of magnesia: (1) in the absence of membrane; (2) in the first series of osmotic experiments given in the preceding Table; (3) in the second series of observations of the same Table:—

(3) Ratio of diffusates with membrane . . . 2 4.24 7.82 17.34

If the last number (17.34) given for the 20 per cent. solution of the later osmotic series be excluded, and it is manifestly in considerable excess from some accidental cause, the three sets of ratios must be allowed to exhibit considerable agreement.

The membrane appears to have a slight effect in reducing the diffusates of the higher proportions of salt; and this reduction is greater in the early experiments (2) than in the late experiments (3), made with the same osmometer. The comparative diffusion of different proportions of sulphate of magnesia appears, therefore, not to be much deranged by the intervention of membrane.

The average osmose of sulphate of magnesia likewise exhibits a pretty uniform progression. In the first series of experiments of Table VI., we find for the different proportions of salt in solution an osmose of 31.5, 74.5, 143 and 260.5 ms.; numbers which are in the ratio given below:—

In the later experiments of the same Table, the different proportions of salt (omitting the first and last proportions) give an average osmose of 29.5, 68.5 and 136 ms., of which the ratios may be stated as follows:—

The osmose appears here to follow more closely in its value the proportion of salt in solution than the diffusate can be said to do, either in open vessels or through membrane; so far, therefore, the osmose and diffusate do not preserve a constant proportion to each other with this salt.

No correction need be applied to the observed osmose of sulphate of magnesia, as this salt does not sensibly increase the bulk of the water in which it is dissolved. The weight of diffusate in Column IV. may, therefore, be immediately compared with the weights of water in Column III. It then appears that in the first series of the osmotic observations in the Table—

In 2 per cent. solution, 1 sulphate of magnesia is replaced by 5:16 water.

In 5 per cent. solution, 1 sulphate of magnesia is replaced by 5.74 water.

In 10 per cent. solution, 1 sulphate of magnesia is replaced by 6.01 water.

In 20 per cent. solution, 1 sulphate of magnesia is replaced by 6.57 water.

According to the average of the whole proportions, sulphate of magnesia is replaced by 5.87 times its weight of water.

While in the later observations of the same Table—

In 2 per cent. solution, 1 sulphate of magnesia is replaced by 5:33 water.

In 5 per cent. solution, 1 sulphate of magnesia is replaced by 5.9 water.

In 10 per cent. solution, 1 sulphate of magnesia is replaced by 6.32 water.

According to the average of the whole proportions of salt in these later observations, sulphate of magnesia is replaced by 5.85 times its weight of water.

The want of uniformity exhibited above in the relation between the quantities of water and salt goes some way to prove that the osmose of sulphate of magnesia in membrane is not pure diffusion, for the ratio between the exchanging water and salt (the diffusion-volumes) should then remain constant.

On the other hand, the approximation to uniformity favours the idea of the existence of a numerical relation between the osmose and diffusate. So also may the circumstance be considered, that sugar and sulphate of magnesia, which approximate as seen above in their osmose, were found before to have a similar degree of diffusibility\*. The facts appear to afford a strong presumption, but no demonstrative proof, of the intervention of diffusion in governing the results of osmose in such neutral substances. The influence of diffusion becomes more difficult to trace in the osmose of three other neutral salts, which I shall now introduce. What has been represented as the chemical agency now begins to interfere more sensibly, although not to govern the results entirely as it appears to do in less strictly neutral salts.

Chloride of Sodium.—The osmose of chloride of sodium possesses a certain interest independently of such theoretical considerations.

\* Philosophical Transactions, 1850, p. 10.

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Table VII.—Chloride of Sodium in	Osmometer C of double membrane
for five	hours.

I.	II.	III.	IV.	v.	VI.	VII.
Chloride of sodium.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate of salt in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature,
per cent.				days.	min.	. 0
0.25	12	0.552		2	16	$6\mathring{3}$
0.25	8	0.368	0.068	1	16	63
1	3	0.138	0.230	1	6	66
1	13	0.598	0.242	1	8	66
2	11	0.506	0.506	1	6	67
2	16	0.736	0.511	1	3	69
5	46	2.34	1.513	2	3	72
5	51	2.30	1.468	1	2	70
10	78	3.496	2.994	1	15	67
10	82	3.60	2.648	1	2	67
20	165	7.36	6.645	1	2	67
20	167	7.452	6.190	1	2	67

Chloride of sodium is known to diffuse with nearly double the rapidity of sulphate of magnesia in the smaller proportions of salt, and with a still higher velocity in the larger proportions of salt; accordingly the diffusates in the last Table exceed those of sulphate of magnesia in a corresponding ratio. The osmose appears pretty uniform, but with a tendency to fall below the average rate of the salt in the low proportions, such as 1 and 2 per cent., and to exceed the same rate in the higher proportions of salt. In a septum of single membrane, the osmose of a 10 per cent. solution was observed to rise to a high amount.

Table VIII.—Chloride of Sodium in Osmometer H of single membrane for five hours.

I.	II.	III.	IV.	v.	VI.	VII.
Salt in solution.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate of salt in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, FAHR.
per cent. 2 2 10 10	21 24 272 311	1.04 1.20 13.28 15.68	0.917 0.955 6.502 7.850	day. 1 1 1 1	min. 16 16 16 12	66 68 68 68

An observation was made on the osmose of a high proportion of salt with another single membrane, differing from the last in offering considerably less hydrostatic resistance.

TABLE IX.—Chloride of Sodium in Osmometer I of single membrane for five hours.

I.	II.	III.	IV.	v.	VI.	VII.
Salt in solution.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate of salt in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, FAHR.
per cent. 10 10	198 194	8·692 8·528	3·968 5·297	days. 3	min. 2•5 2•5	68 68

To these I add a series of observations of the osmose of the same salt in albumen, with the view of exhibiting the phenomenon in septa of that material. The well-preserved proportionality of the diffusate is remarkable.

Table X.—Chloride of Sodium in Osmometer K of albuminated calico for five hours.

I.	II.	III.	IV.	v.	VI.	VII.
Salt in solution.	Rise in millimeter degrees.	Same in grammes.	Diffusate in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature,
per cent.				days.	min.	0
1	16		0.141	4	8	$6\mathring{5}$
1	27	••••	0.219	1	8	62
4	39	• • • • • • • • • • • • • • • • • • • •		1	2	60
4	34		0.625	3	2	56
10	43		1.580	. 1	3	59
10	61		1.615	1	3	60
10	72		1.597	1	3	61
1	27	•••••	0.153	1	2.5	63
1	22	••••	0.141	2	4	63
0.1	27		0.016	1	2.5	63
0.1	29	•••••	0.018	1	4	64

Chloride of Barium.—Chloride of barium in its rate of diffusion from open vessels much resembles the chloride of sodium. Considerable analogy between the same salts is also observed in osmotic experiments.

TABLE XI.—Chloride of	Barium in	Osmometer Lot	f double membrane	for five hours.
IMBER III. CHICKE	LOGITUIL III		i adabid indinidianc	

Salt in solution.         Rise in millimeter degrees.         Same in grammes of water.         Diffusate in grammes.         Previous maceration.           per cent.         2         35         1.476	Hydrostatic resistance.  min. 10 10 8 6	72 70 67
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	10 10 8 6	70 67
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	10 8 6	70 67
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	8 6	70 67
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	6	67
5 111 4.674 1.640 1	1	67
9336 3000	1 10	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	10	67
10 154 6.478 4.491 1	10	67
10   133   5.576   3.395   10	16	64
10   136   5.74   2.929   1	4	64
20 267 11.214 6.860 1	8	68
20 283 11.79 7.030 1	8	65
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	8	65
1 74 3.116 0.230 1	8	64
5   $74$   $3.116$   $0.602$   $2$	8	66
5 74 3.116 1.587 1	8	67
10   152   6.396   3.795   2	8	67
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	8	69
20 337 14.186 1	8	70
20   320   13.448   8.130   1	8	70

Chloride of Calcium.—The diffusion of chloride of calcium in open vessels has been observed to fall below that of chloride of barium as 7.5 to 6.5\*. But in membrane, judging from the following observations, the diffusion of chloride of calcium is the more rapid of the two. The osmose has also a tendency to rise, particularly in the larger proportions of chloride of calcium. The replacing water often exceeds twice the weight of the salt diffused.

Table XII.—Chloride of Calcium in Osmometer M of double membrane for five hours.

I.	II.	ш.	IV.	v.	VI.	VII.
Salt in solution.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature,
per cent.				days.	min.	
2	6	0.258		2	8	7 <b>2</b>
2	6	0.258	0.795	1	8	70
2 5	45	1.935	2.29	1	8	67
5	60	2.64	1.83	1	3	67
5	51	2.24	2.636	1	8	67
10	228	9.92	4.256	1	8	67
10	188	8.24	3.607	10	12	64
10	176	7.76	3.11	1	6	64
20	389	17.2	6.075	1	3	68
20	398	17.6		1	3	65
2	24	1.04	0.668	1	4	65
2 2 5	27	1.2	0.625	1	4	64
5	81	3.6	1.512	2	5	66
5	83	3.68	1.467	1	5	67
10	185	8.16	3.158	2	5	67
10	181	8	3.317	1	5	69
20	406	18	6.695	1	5	70
20	416	18.4	6.992	1	5	70

<sup>\*</sup> Philosophical Transactions, 1850, pages 817 and 819.

These three chlorides, possessing about double the diffusibility of sugar and sulphate of magnesia, should be replaced by half as much water as the latter substances. Some approach to this ratio may be perceived amid much irregularity in the observed osmose of the chlorides.

Proceeding now to the salts in which the osmose appearing to depend upon chemical properties preponderates greatly over osmose from diffusion, I may introduce these substances under the metals which they contain for the sake of their relations in composition.

## Potassium and Sodium.

Hydrate of Potash.—A highly intense osmose appears to be determined by caustic alkali, but it is necessary to apply the smallest proportions of alkali to avoid the rapid dissolution of the membrane. In double membrane 0.01 per cent. of hydrate of potash, or 1 alkali in 10,000 water, gave an osmose of 81 and 58 ms. By four times as much alkali, or 0.025 per cent., an osmose of 49 and 67 ms. was produced. These are the greatest effects.

On increasing the proportion of hydrate of potash to 0.5 per cent. the osmose sunk to 22 and 26 ms.; with 1 per cent. of hydrate of potash to 13 ms. The permeability to hydrostatic pressure was always very great, being never less than one drop in a minute.

By the action of the alkali in the last experiment the permeability was increased from three to nine drops, and the membrane entirely ruined.

A similar experiment with hydrate of potash was made in albuminated calico with similar osmotic results. In the 0.01 per cent. solution an osmose of 76 and 58 ms. was observed; in 0.025 per cent. solution 87 and 126 ms.; in 0.5 per cent. solution 15 and 12 ms., and in 1 per cent. solution -10 ms., or a small negative osmose. The permeability both before and after the last experiment was represented by one drop in one minute; in both the half per cent. experiments the permeability was one drop in three minutes; in the preceding 0.025 per cent. solutions one drop in  $2\frac{1}{2}$  minutes, and at the beginning one drop in ten and five minutes with the 0.01 per cent. solutions. The alkali first became sensible to the test-paper in the water-jar, in the diffusion of the 0.025 per cent. solutions. During both series of experiments the temperature ranged from  $58^{\circ}$  to  $62^{\circ}$ .

Carbonate of Potash.—The high osmose of this salt has already been often referred to in illustration of the influence of alkaline salts. The following experiments may be compared with those upon the neutral substances lately discussed, particularly in regard to their diffusates. They show also the comparative influence of membrane applied single and double to an osmometer.

per cent.

2

2

10

10

635

695

892

900

28.576

31.236

40.128

40.508

		fo.	r five hou	rs.		
I.	II.	III.	IV.	v.	VI.	VII.
Proportion of salt.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, FAHR.

0.514

0.548

2.897

3.045

day.

1

1

1

1

min.

20

20

16

16

66

68

68

68

TABLE XIII.—Carbonate of Potash in Osmometer B of single membrane for five hours.

The fluid was removed from the water-jar at the expiration of the third hour, and replaced by distilled water to prevent the reaction of that portion of the salt which had already reached the jar upon the progress of diffusion from the osmometer, both in the preceding and the following series of experiments.

Table XIV.—Carbonate of Potash in Osmometer D of double membrane for five hours.

Proportion of salt.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, FAHR.
per cent. 2 2 10 10	449 484 619 595	21·883 23·621 30·178 28·993	0·324 0·400 2·764 3·150	day. 1 1 1 1	min. 16 16 16 12	66 68 68 68

In the double membrane, the average osmose of the 2 per cent. solution is reduced to 466 ms., from 665 ms. in the single membrane. The change is similar in the 10 per cent. solution, namely a reduction to 607 from 896 ms.; a reduction of nearly one-third of the osmose in the double membrane for both proportions of salt.

The difference of the diffusates is much less marked; for they may be said to be the same for the 10 per cent. solutions, namely 2.966 grammes in the single, and 2.957 grammes in the double membrane; and for the 2 per cent. solution 0.531 gramme in the single, and 0.326 gramme in the double membrane. The diffusion of carbonate of potash, as seen here in membrane, will be found to correspond well with that of chloride of sodium (Table VII.), as the diffusion of the same two salts in open vessels is known to present a near approach to equality. The great osmose or current of fluid inwards might be supposed to diminish the outward movement of the salt under diffusion by washing back the salt into the osmometer. But the diffusates of the 10 per cent. solutions appear to have suffered no remarkable reduction from that or any other cause. The diffusate of carbonate of potash, which usually passes through membrane, appears, however, to be low. In the 1 per cent. solution, formerly referred to (page 188), it was 0.195 gramme. In the series of observations, likewise already

referred to (page 187), the diffusate of carbonate was also low but remarkably uniform, namely 0.018 gramme for 0.1 per cent. solution, 0.092 gramme for 0.5 per cent. solution, and 0.196 gramme for the 1 per cent. solution.

But these determinations were all made by the alkalimetrical method, and when in subsequent observations the potash was also determined by weighing it as sulphate, the proportion of diffusate was found sensibly increased. It hence appears that carbonate of potash acts chemically upon the membrane, and that a portion of the alkali diffuses out in a neutralized state. Thus in five successive experiments with the 1 per cent. solution, in fresh double membrane, the diffusates by the alkalimetrical method were 0.208, 0.254, 0.264, 0.215 and 0.189 gramme carbonate of potash; while the actual quantity of alkali found by direct analysis corresponded in the last four observations to 0.318, 0.353, 0.287, and 0.242 gramme. The quantity of carbonate of potash which has suffered change in passing through the membrane is 0.064, 0.089, 0.072 and 0.053 gramme in these four experiments respectively.

The diffusates of carbonate of potash, increased by those quantities, approach too closely to those of chloride of sodium to warrant the supposition of any peculiar repression by membrane of the diffusion of carbonate of potash, which otherwise appeared probable.

The observations last commented upon belong to a number undertaken with the view of ascertaining three points of interest, which may excuse a fuller statement of the experiments. These points were, first, the influence upon osmose of the air dissolved in solutions of carbonate of potash, which might be supposed to take a part in the chemical action of the membrane; secondly, the effect of frequent repetition of the experiment in exhausting the osmotic activity of membrane; and, thirdly, the relation in osmose of an alkaline carbonate and phosphate.

Table XV.—Solutions in Osmometer L of double membrane for five hours.

Salt in osmometer.	Rise in millimeter degrees.	Temperature, FAHR.
Carbonate of potash, 1 per cent.  Same, deprived of air by boiling.  Same, deprived of air by boiling.  Same solution, unboiled.  Phosphate of soda (2NaO HO PO <sub>5</sub> ) 1 per cent.  Same  Same, 0·1 per cent.  Same, 0·1 per cent.  Carbonate of potash, 0·1 per cent.  Same, 0·1 per cent.  Same, 1 per cent.	439 376 353 325 268 176 194 196 190 176 227 298 335 312	63 64 65 63 56 55 58 56 58 57 65 58 64 62

It will be remarked that the highest osmose (439 ms.) is obtained in the first expe-

riment, and that the osmose falls off pretty regularly to the fifth experiment (268 ms.). The change in the aëration of the solution in the second and third experiments cannot be said to interfere with this progression. The influence of free oxygen on the membrane is not therefore indicated as a cause of osmose. It may be added, that the converse experiment of depriving the fluid of the water-jar of air by boiling, led also to a negative result. It will be remembered, further, that the osmose of oxalic acid was not interfered with by an addition of sulphurous acid, which was likely to counteract the action of oxygen, if such an action existed in osmose.

When phosphate of soda is substituted for carbonate of potash, both 1 per cent., the osmose declines from 268 to 176 ms. The phosphate of soda being repeated, the osmose rises a little, namely to 194 ms. The one-tenth per cent. solution of the same salt which follows, maintains here the considerable osmose of 196 and 190 ms. On returning again to the application of carbonate of potash in the instrument, the osmose gradually rises and regains 335 ms. for the 1 per cent. solution of that salt.

From these repetitions of osmose it may be inferred, that whatever be the nature of the chemical action on membrane which prompts osmose, that action is by no means of a rapidly exhaustible character.

It may be added, with regard to the osmotic action of extremely dilute solutions of carbonate of potash, that the osmose is lowered rapidly in proportions below one-tenth of a per cent. of that salt. The osmose of 0.01 per cent. of carbonate of potash, in double membrane, amounted only to 19, 23 and 17 ms. in three successive experiments. The osmotic action of carbonate of potash must, therefore, be inferior to that of hydrate of potash in the extreme degrees of dilution.

In the experiments of the preceding series, the influence of a salt often appears not to terminate with its presence in the osmometer, but to extend to following experiments made with other salts, or made with different proportions of the original salt. If this arises from portions of the first salt remaining in the membrane, they must be portions which are not easily washed out. The substance of membrane may possibly have an attraction for highly osmotic salts, capable of withdrawing small quantities from solution. When the membrane, however, is removed from the osmometer, after such experiments as are referred to, slightly washed and then incinerated, only minute traces of the salt last used are commonly discovered; if indeed the salt has not entirely disappeared.

Phosphate and Carbonate of Soda.—The osmose of the carbonate of soda appears to be quite similar to that of carbonate of potash. A considerable amount of information respecting the two soda salts named is conveyed in the following series of experiments, which includes also observations on the serum of ox-blood.

Table XVI.—Solutions in Osmometer F of double membrane for five hours.

Salt in osmometer.	Rise in millimeter degrees.	Temperature, FAHR.
Phosphate of soda, 1 per cent. Same, 1 per cent. Same, 0·1 per cent. Same, 0·1 per cent. Carbonate of soda, 0·1 per cent. Same, 0·1 per cent. Same, 0·01 per cent. Same, 0·01 per cent. Same, 1 per cent. Serum of soda, 1 per cent. Serum of ox-blood, undiluted Same Same, diluted with equal vol. of water.	311 205 218 294 254 50 39 306 337 193 186	63 56 55 58 56 58 57 65 58 64 62 61 59 61

The phosphate and carbonate of soda, when alternated in the same osmometer, show considerable steadiness in their respective rates of osmose.

The inferior osmotic quality of serum is remarkable, considering the alkalinity of that fluid. The loss of osmose in serum is due, I believe, to the presence of chloride of sodium. The latter substance possesses an extraordinary power of reducing the osmose of alkaline salts, which was observed in a variety of circumstances, but which it will be sufficient to illustrate by the following series of experiments in an albumen osmometer.

Table XVII.—Solutions in Osmometer N of albuminated calico for five hours.

Salt in osmometer.	Rise in millimeter degrees.	Diffusate in grammes by analysis.	Same, by alkalimetry.	Previous maceration.	Hydrostatic resistance.	Tempera- ture, FAHR.
				days.	min.	
Carbonate of soda, 1 per cent	139	0.157	0.092	i	3	57
Same, 1 per cent.	150	0.156	0.106	1.	6	59
Same, 2 per cent.	141		0.242	1	6	65
Same, 4 per cent.	143	0.570		1	8	62
Same, 10 per cent	204	1.562	1.450	1	12	60
Same, 10 per cent	163	1.432	1.340	3	6	56
Same, 1 per cent.	138	0.216	0.147	1	6	59
Same, 1 per cent.	136	0.198	0.156	1	3	60
Same, 0.1 per cent	188		0.005	1	10	61
Same, 0·1 per cent	179			1	6	63
Carbonate of soda 0.1 per cent. + } chloride of soda 1 per cent }	32		•••••	2	6	63
Same+same	36			1	6	63
Chloride of sodium, 1 per cent	25	0.384		1	6	64
Same, 1 per cent	18	0.325		1	3	65
Carbonate of soda 1 per cent. + chloride of soda 1 per cent	69			1	5	63
Same+same	56			3	8	56
Carbonate of soda, 1 per cent		0.190	0.164	1	6	55
Same, 1 per cent	163	0.212	0.185	1	4	58
Same, 0·1 per cent	152			1	20	56
Same, 0·1 per cent.	152			1	20	58

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The osmose of the 0·1 per cent. solution of carbonate of soda is lowered by the addition of 1 per cent. chloride of sodium, from 179 ms. to 32 ms. The osmose of 1 per cent. carbonate of soda, with the addition of an equal proportion of chloride of sodium, is 56 ms., and of 1 per cent. carbonate of soda alone, immediately following, 157 ms. The osmose of these mixtures appears to be assimilated to that of chloride of sodium itself, which comes out as 18 and 25 ms. in the same series of observations.

The rise of an alkaline liquid in the osmometer appears to be equally repressed by chloride of sodium, placed outside or dissolved in the fluid of the water-jar.

In illustration of this statement, I may adduce a short series of observations made with fresh ox-bladder, having its thickness unreduced, which further show that the repressing power that appears in the chloride of sodium does not extend to two other substances, alcohol and sugar.

Salt in osmometer.	Rise in millimeter degrees.
Carbonate of potash, 0.25 per cent.  Same, 0.25 per cent.  Carbonate of potash, 1 per cent., against alcohol, 1 per cent., in jar.  Same, 1 per cent., against sugar, 1 per cent., in jar  Same, 1 per cent., against chloride of sodium, 1 per cent., in jar  Same, 1 per cent., against pure water in jar.  Same, 1 per cent., against chloride of sodium, 1 per cent., in jar  Carbonate of potash, 1 per cent. + chloride of sodium, 1 per cent., against water in jar  Carbonate of potash, 1 per cent., alone, against pure water in jar.  Same repeated	96 108 104 18 114 18 64

TABLE XVIII.—Solutions in Osmometer P of ox-bladder for five hours.

Now another neutral salt, sulphate of potash, will be found to have the reverse effect upon the osmose of an alkaline carbonate, supporting and promoting the latter. Such results show how far we still are from a clear comprehension of the agencies at work in membranous osmose. Another property of chloride of sodium, equally singular, is, that the association of this salt (by itself so indifferent) with small proportions of hydrochloric acid, such as one-tenth per cent., determines a positive osmose in membrane, which is sometimes very considerable.

The osmotic action of the albuminated calico of Table XVII. is moderate in amount, but remarkably uniform. The small tenth per cent. solution assumes a preeminence in activity which is very curious. It was often observed in the inquiry, that the small proportions of active salts were more favoured in albuminated calico than in membrane; may it not thence be inferred that it is in the albumen plate that the chemical agency operates to most advantage?

Taking the mean diffusates of chloride of sodium and carbonate of soda from the lower part of the same Table, we have 0.354 chloride of sodium against 0.201 carbonate of soda, or 1 of the former to 0.568 of the latter. The diffusates of the

same two salts, in open vessels, were more nearly in the proportion of 1 to 0.7. The comparative diffusion of carbonate of soda appears to be rather repressed than promoted by the septum.

The neutralization of a portion of the alkaline salt during the osmotic process is again indicated. The portion of carbonate of soda thus lost in the 1 per cent. solution appears to diminish on repetition of the experiment. At the head of the table, the loss in two experiments is 0.065 and 0.050 gramme; lower down, 0.069 and 0.042 gramme; and near the bottom of the table, 0.026 and 0.027 gramme. The loss with the 10 per cent. solution is 0.110 and 0.092 gramme, or not more than double the loss in the preceding 1 per cent. solutions of carbonate of soda.

Sulphates of Potash and Soda.—The sulphate of potash was made the subject of frequent experiment, with the view of obtaining light on the nature of osmose, at the commencement of the inquiry. But it is not well fitted for such a purpose, its action in the osmometer proving at first of a most perplexing character. With thick oxbladder, sulphate of potash dissolved in the proportion of 1 per cent., usually exhibited considerable osmose, that is, about one-half of the osmose of carbonate of potash in similar circumstances. The osmose of the sulphate had, however, a peculiar disposition to increase in successive repetitions of the experiment with the same membrane. The osmose of this salt might also be doubled by allowing bladder in substance to macerate for some time in the solution before the osmotic experiment; soluble matter from the membrane manifestly influenced the result considerably in all experiments with sulphate of potash.

When the removal was effected of the muscular coat of bladder, the chief source of its soluble matter, the osmose of the salt in question fell greatly in amount instead of rising, like that of the carbonate of potash.

In the prepared membrane sulphate of potash presented a small moderate osmose, like chloride of sodium. But the salt must be exactly neutral to test-paper, and the membrane also free from foreign saline matter, otherwise very different results are obtained. In a double membrane, 1 per cent. of the neutral sulphate gave 21 and 20 ms.; but the same solution, made alkaline by the addition of no more than one ten-thousandth part (0.01 per cent.) of carbonate of potash, started up to 101 and 167 ms., a much greater osmose than the proportion of carbonate of potash present gave afterwards by itself in the same membrane, namely 19, 23, and 17 ms. The influence of the alkali is so persistent, that the membrane, macerated in water for a night after the last experiments, still gave 65 ms. with 1 per cent. of pure sulphate of potash.

The osmotic activity of sulphate of soda is equally excited by a trace of alkali, and both sulphates exhibit the same character in albumen as well as in membrane. This remarkable result of the combined action of the two salts is so likely to elucidate the chemical actions prevailing in osmose, that a fuller series of illustrative experiments may be recorded. The septum was of double calico, well albuminated, and presented a good resistance to hydrostatic pressure.

Salt in osmometer.	Rise in millimeter degrees.	Temperature,
Sulphate of potash, 1 per cent	18 21	53 57
Sulphate of potash, 1 per cent.+ carbonate of potash, 0.01 per cent Same+same	139	57 62 56
Same + same Same + carbonate of potash, 0·1 per cent.	73	61 61

Same+same .....

Carbonate of potash, 0.1 per cent., alone......

Carbonate of potash, 0.1 per cent., alone.....

Sulphate of soda, 1 per cent. + carbonate of potash, 0.1 per cent. ..........

Same+same .....

Same + carbonate of soda, 0.1 per cent. .....

Carbonate of soda, 0.1 per cent., alone......

Same ......

263

92 95

257

237

299

90

127

59

57

57

62

54

54

57

TABLE XIX.—Solutions in Osmometer Q of albuminated calico for five hours.

The influence of the two alkaline carbonates in giving a high osmose to the sulphates, appears to be pretty nearly equal. The primary source of the great osmose may prove to be the action on membrane of the alkaline carbonates, which is promoted in some way by the presence of sulphate of potash, as it is retarded by the presence of chloride of sodium.

On the other hand, the moderate amount of osmose which appears to be proper to these sulphates is completely negatived by the most minute addition of a strong acid. Thus, 1 per cent. of sulphate of potash, with the addition of one ten-thousandth part (0.01 per cent.) of hydrochloric acid, had its osmose reduced, in the first experiment to 8 ms., and in the second experiment to -5 ms., the osmose becoming actually negative.

On one occasion, a specimen of well-crystallized sulphate of potash gave, when dissolved, a still more sensible negative osmose, namely -28 ms. On applying litmus to the solution, it was found to possess an acid reaction. But the addition of 0.01 per cent. carbonate of potash was sufficient to change the acid into an alkaline reaction, and to give rise to a positive osmose, amounting to 54 ms.

It occurred to me to macerate a fresh membrane in water, containing one-thousandth part (0·1 per cent.) of hydrochloric acid, for two days, before applying the membrane to the osmometer, and then to wash the membrane with distilled water till all acid reaction disappeared. With 1 per cent. of neutral sulphate of potash, this membrane gave in succession 17, 42, 35 and 62 ms.; with sulphate of soda, 1 per cent., following, 39, 25 and 25 ms.; and with sulphate of zinc (anhydrous), 1 per cent., after the last salt, 14 and 21 ms. These last results show a certain degree of unsteadiness in the osmose of the alkaline sulphates, probably arising from the osmose of these salts depending so much upon adventitious circumstances. The diffusates were carefully weighed, first when fully dried, at 212°, and again when ignited. The difference in

the weighings arose from the presence of organic matter dissolved out of the membrane, of which it gives the quantity probably somewhat exaggerated.

First diffusate, 0.328 grm. sulphate of potash.

Second diffusate, 0.362 grm. sulphate of potash, 0.019 grm. organic matter.

Third diffusate, 0.351 grm. sulphate of potash, 0.031 grm. organic matter.

Fourth diffusate, 0.366 grm. sulphate of potash, 0.025 grm. organic matter.

Fifth diffusate, 0.356 grm. sulphate of soda, 0.011 grm. organic matter.

Sixth diffusate, 0.339 grm. sulphate of soda, 0.019 grm. organic matter.

Seventh diffusate, 0.334 grm. sulphate of soda, 0.009 grm. organic matter.

Eighth diffusate, 0.239 grm. sulphate of zinc.

Ninth diffusate, 0.260 grm. sulphate of zinc.

The diffusates of the two alkaline sulphates are remarkably uniform, the diffusate of sulphate of soda falling a little under that of sulphate of potash, but not so much as in open vessels. The diffusate of sulphate of zinc is still smaller but relatively too high, as it should not much exceed one-half of that of sulphate of potash, judging from the diffusion of these salts in the absence of membrane. The organic matter accompanying the salt falls off in quantity in successive experiments, but continued to exist to the last, although it was not determined in the experiments with sulphate of zinc. The diameter of the disc of membrane was 123 millimeters, and its original weight, air-dried, 0.559 gramme.

Oxalate of Potash, Chromate and Bichromate of Potash.—The only property of sulphate of potash which seems to be connected with the positive osmose of that salt, is its bibasicity as a sulphate. The alkaline character promotes positive osmose, and this character appears to be a distinction of polybasic salts. The common tribasic phosphate of soda is strongly alkaline to test-paper, and the bibasic pyrophosphate of soda enjoys the same property in a still higher degree. The sulphates of potash and soda are certainly neutral to test-paper, but they may be looked upon as potentially alkaline from the easy severation of the second equivalent of fixed base and its replacement by water, witnessed in all bibasic salts. In monobasic salts, on the contrary, a proclivity to the acid character may be suspected. Thus although the chloride of potassium and nitrate of potash appear as neutral to test-paper as the sulphate of potash is, yet the chlorides and nitrates of the magnesian bases are more decidedly acid than their sulphates. It is just possible then on this view, that the osmotic inferiority of chloride of sodium, and the power of that salt to counteract the positive osmose of carbonate of potash, may be exhibitions of acid character belonging to the former salt. The observations of the rise in the osmometer of chloride of sodium, and also of the chlorides of barium and calcium, previously described, also have the appearance of being the effect of diffusion, modified by a slight chemical osmose of a negative character proper to these salts.

The polybasic constitution of oxalate of potash is well marked, and its positive

osmose will be found below to be considerable, although the specimen of salt employed was strictly neutral to test-paper.

This salt also, like sulphate of potash, is shown not to counteract the high positive osmose of an alkaline carbonate.

The chromate of potash, although carefully purified by crystallization, retained a slight alkaline reaction. On this account small additions were made to it of bichromate of potash in some experiments, but without materially diminishing the very sensible positive osmose of the former salt. A neutral chromate has of course the same bibasic character as a sulphate.

Table XX.—Oxalate and Chromate of Potash in Osmometer F of double membrane for five hours.

Solution of salt.	Rise in millimeter degrees.	Diffusate in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, FAHR.
1 per cent. oxalate of potash	164 153 92 90 262 337 322 273 294 246 24		days. 1 1 2 8 1 1 1 2 1 2 1 2 1 2	min. 11 10 5 6 5 3 3 3 1 1 1	65 65 63 61 56 62 68 62 55 54 56 62 58
Same	79	0.281	1	1	60

The average rise for the 1 per cent. solution of each of the salts placed in the osmometer in a pure state is, bichromate of potash 21.5 ms., chromate of potash 107.5 ms., and oxalate of potash 158.5 ms. The average diffusate for the chromate of potash is 0.3165 gramme, and for the bichromate of potash 0.2855 gramme.

Like solutions were submitted to osmose at the same time in a septum of albumen for the sake of comparison with the preceding membrane osmometer.

TABLE XXI.—Oxalate and Chromates of Potash in Osmometer K of albuminated calico.

Solution of salt.	Rise in millimeter degrees.	Diffusate in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, FAHR.
			days.	min.	0
1 per cent. oxalate of potash			1	15	6 <b>š</b>
Same	173		1	15	65
0.1 per cent. oxalate of potash	91		1	15	63
Same	100		2	20	60
1 per cent. oxalate of potash + 0·1 per cent. carbonate of potash	161	•••••	8	15	56
Same + same	211		1	15	60
0.1 per cent. carbonate of potash	109		1	15	62
Same	120		1	15	68
1 per cent. oxalate of potash +0·1 per cent. carbonate of potash	195	,	1	15	62
Same + same	188		2	15	55
1 per cent. bichromate of potash	36	0.244	1	15	54
Same	34		2	10	56
1 per cent. chromate of potash	129	0.253	1	10	62
Same	123	0.242	1	10	58
1 per cent. chromate of potash +0·1 per cent. bichromate of potash	95	0.251	2	10	57
Same	102	0.320	1	10	60

The average rise for the 1 per cent. solution of each of the salts is, for bichromate of potash 35 ms., for chromate of potash 126 ms., and for oxalate of potash 184 ms., all a little higher than in the previous membrane osmometer. The diffusate is lower than before, probably owing to the less permeability of the albuminous septum, the weight of chromate of potash diffused being 0.2475 gramme, and of bichromate of potash 0.244 gramme.

The two chromates have been found to possess nearly equal diffusibility in open vessels, and to correspond closely in that property with sulphate of potash. The oxalate of potash exhibits a considerable osmose when present in the small proportion of one-thousandth part (0·1 per cent.), namely 91 ms. in membrane and 95·5 ms. in albumen. This is the surest indication of considerable osmotic capacity. Binoxalate of potash and free oxalic acid are both remarkable for high negative osmose.

Barium, Strontium, Calcium, Magnesium.—The salts of these metals never appear capable of producing strong positive osmose when dissolved in a proportion of less than 1 per cent. On the contrary, some of the salts of this class, particularly the nitrates, exhibit a tendency to negative osmose.

Hydrate of Baryta gave a small positive osmose for minute proportions of salt, which disappeared as the proportion of salt was increased, exhibiting an analogy in this respect to hydrate of potash. The results for hydrate of baryta in double membrane were 6, 4, 1 and 1 degrees of osmose for the 0.1, 0.25 and 0.5 per cent. solutions. In albumen the same solutions gave 0, -8, -23 and -17 ms.; and the 1 per cent. solution gave -25 ms.

Hydrate of Lime exhibited similar characters to the last base. Undiluted limewater gave in double membrane -20 ms. and -1 m.; while the same, diluted with four volumes of water, gave a positive osmose of 31 and 18 ms. In albumen the undiluted lime-water gave -48 and -30 ms.; the same, diluted with four volumes of water, gave 0 m. and 1 m.

Chloride of Strontium, 1 per cent., gave in double membrane 19, 27 and 26 ms., following chloride of barium in the same membrane, 13 and 21 ms. Nitrate of baryta, in the same membrane, gave 12, 24 and 29 ms.; nitrate of strontia, following the latter, 27 and 31 ms.

Nitrate of Lime in membrane twice gave 19 ms., following chloride of calcium with 12 and 20 ms.; in albumen nitrate of lime gave 2 and 2 ms.

The two per cent. solution of the same salt in membrane gave only 6 and 6 ms. in two experiments.

Chloride of Magnesium gave in membrane -2 ms. and in albumen 6 ms., both experiments being made with the one per cent. solution, which is always to be understood when no particular per-centage is stated.

Nitrate of Magnesia gave in membrane -24 and -20 ms. Both of these magnesian salts were prepared by saturating the acid with excess of magnesia. The tendency of monobasic salts of the magnesian class to chemical osmose of a negative character appears to be small in the salts of barium and strontium, to rise in those of calcium, and to culminate in the salts of magnesium itself.

Aluminium.—Nothing is more remarkable than the high positive osmose of certain salts of alumina. These salts emulate the alkaline carbonates in this respect. The property too appears to be characteristic of the sesquioxide type, and distinguishes the salts of sesquioxide of iron, sesquioxide of chromium and the higher oxide of uranium, as well as alumina.

Sulphate of Alumina.—The sulphates of this type do not exhibit a high degree of osmose, although they are probably more osmotic than the magnesian sulphates as a class. Sulphate of alumina, 1 per cent., gave in membrane 57 and 67 ms., and for 0.1 per cent. 24 and 31 ms.

The diffusate was small, amounting in the second observation of the 1 per cent. solution to 0.033 gramme of tersulphate of alumina, together with an excess of 0.005 grm. of sulphuric acid, according to analysis.

Chloride of Aluminium, prepared by treating hydrochloric acid with an excess of hydrated alumina, was found by analysis to approach very nearly to the proportions of the definite compound Al<sub>2</sub> Cl<sub>3</sub>. The following results with that salt were successively obtained in an osmometer of single membrane:—

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With 1 per cent., rise of 540 ms. at 50° Fahr. With 1 per cent., rise of 570 ms. at 49°, With 1 per cent., rise of 450 ms. at 47°, With 1 per cent., rise of 635 ms. at 49°,
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With 0·1 per cent., rise of 510 ms. at 54° FAHR. With 0·1 per cent., rise of 285 ms. at 48°, With 0·1 per cent., rise of 410 ms. at 56°.
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The numbers, which are all high, vary considerably among themselves, as often happens when osmose is intense and is observed in a single membrane. The temperatures of the water jar are added in these and most other observations recorded, although it was difficult to draw any positive conclusion respecting the influence of heat upon the osmose of small proportions of salt. With large proportions of neutral salts, where diffusibility prevails, the osmose appeared to increase with the temperature, as does the proportion of salt diffused. With respect to the condition of the membrane used above, the first experiment was conducted in the membrane freshly dissected and previous to any maceration or washing whatever, with a similar osmotic result, it will be observed, as in the later experiments made with the membrane after being repeatedly macerated.

In experiments of diffusing chloride of aluminium in open vessels, decomposition of that salt was observed with escape of free hydrochloric acid. The decomposition appeared however to affect much less of the chloride of aluminium than it does of the acetate of alumina.

In an albumen osmometer, chloride of aluminium gave an osmose of 245, 233 and 229 ms., at 57°, 58° and 60°, with diffusates of 0.085, 0.123 and 0.095 gramme of salt, calculated from the quantity of chlorine found in the diffusate.

In the last experiment the solution was coloured with litmus, apparently without affecting the amount of osmose.

Acetate of Alumina was prepared by precipitating pure sulphate of alumina by means of the acetate of lead. Mr. Crum has shown that in this reaction one equivalent of acetic acid becomes free, and that the acetate of alumina produced has the form  $Al_2 O_3 + 2C_4 H_3 O_3$ . A specimen of the pure binacetate, prepared by Mr. Crum, exhibited an equally high osmose as the salt mixed with free acid obtained by precipitation, which is used below.

TABLE XXII.—Acetate of Alumina in Osmometer G of double membrane for five hours.

Proportion of salt.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, FAHR.
per cent.  1  1  0·1  0·1  0·1  0·1	232 264 195 130 159 146	9·728 11·096 8·208 5·472 6·688 6·152	0.036 0.051 0.045	days. 2 1 1 2 1 2 1	min. 3.5 3.5 3.5 3.3	65 65 64 66 67 67

MDCCCLIV.

In the second and third experiments of the Table, the solutions were coloured distinctly blue, by means of the ordinary sulphate of indigo, without interfering much apparently with the osmose.

The diffusates, when given, are as binacetate of alumina, and were calculated from the alumina found in the water-jar.

In the last three observations of the one-tenth per cent. solution, the diffusate of salt is in proportion to the replacing water as 1 to 152, 131 and 137.

In osmometer F of single membrane, acetate of alumina gave a diffusate not exceeding one-third or one-fourth of the diffusate from sulphate of potash in similar circumstances. Thus, in three observations of the aluminous salt, the osmose was 356, 393 and 397 ms., with the corresponding diffusates of 0·102, 0·114 and 0·080 gramme of binacetate of alumina; while two experiments on sulphate of potash, which were intercalated between the second and third of the preceding observations, gave diffusates of 0·325 and 0·425 gramme of sulphate of potash.

The osmose of acetate of alumina does not appear to be sensibly affected by previous experiments made in the same membrane with sulphuric acid, but to fall greatly when an equal proportion of sulphate of potash is diffused along with the acetate of alumina. Of the following numbers, -4, 8, 7, 237, 7 and 18, the first three and the fifth, which are small, are the osmose of 0·1 per cent. sulphuric acid alone; the fourth, which is large, that of 1 per cent. of acetate of alumina, and the sixth that of 1 per cent. of acetate of alumina mixed with 1 per cent. of sulphate of potash, all in the same membrane. The diffusate of the pure acetate of alumina was 0·087 gramme, which is low for a 1 per cent. solution, as compared with the diffusates from the one-tenth per cent. solutions of sulphuric acid, which were 0·039, 0·042, 0·046 and 0·044 gramme of sulphuric acid.

The addition of an equal weight of chloride of sodium to the one per cent. solution of acetate of alumina, lowered the osmose of the latter salt, in osmometer F, from 397 to 267 ms. This is a small amount of interference compared with that exercised by the sulphate of potash in the same membrane.

Pure binacetate of alumina was found to be largely decomposed when diffused in open vessels, the acetic acid escaping and leaving behind the allotropic soluble alumina of Mr. Crum. This last substance is remarkable for its low diffusibility, but this subject will require further discussion on a future occasion.

Iron.—Protosulphate of Iron. This salt appeared, like sulphate of magnesia, to exhibit only the exchange by diffusion of one part of salt for five or six parts of water; the rise of fluid in the osmometer also increasing pretty uniformly with the proportion of salt. Thus, in double membrane of good resistance, 1 per cent. of this salt (always supposed anhydrous) gave 21 and 30 ms.; 4 per cent. 60 and 84 ms.; at a temperature between 61° and 64° FAHR.

Protochloride of Iron.—This salt separates itself from some other magnesian chlorides, and gives rise to a positive chemical osmose, which is considerable in amount.

To learn whether this arose from the passage of iron into the higher oxide or not, sulphurous acid and hydrosulphuric acid were mixed with the protochloride of iron, but, as will be seen below, without lessening the osmose.

Table XXIII.—One per cent. Solutions of several Magnesian Chlorides in Osmometer F of double membrane for five hours.

Salt in osmometer.	Rise in millimeter degrees.	Hydrostatic resistance.	Temperature, FAHR.
Chloride of magnesium. Chloride of zinc. Same Chloride of manganese Same Protochloride of iron. Same Protochloride of iron + 0·1 per cent. sulphurous acid Protochloride of iron saturated with SH Protochloride of iron, alone	48 54 24 34 160 197 435 404 332	min. 2 2 2 1·75 1·5 1 4 4 4	59 61 62 62 63 61 64 65 62 64 61

The osmose of protochloride of iron is large, but singularly unsteady in amount, rising from 160 to 435 ms., and falling again to 155 ms.

In another double membrane, of rather small resistance (1 min.), the osmose of the same salt was only 94, 91 and 97 ms. Between the first and second of these experiments the membrane was washed with alcohol and ether, but without changing the character of the osmose. In experiments made with this last membrane, the 2 per cent. solution of protochloride of iron gave 151 and 157 ms.; and the 5 per cent. solution 189 ms., or the osmose did not rise in proportion to the quantity of salt in solution.

Nitrate of Sesquioxide of Iron, formed by saturating dilute nitric acid by hydrated sesquioxide of iron, gave, in single membrane, the high osmose of 322 and 359 ms. for one per cent. of salt; and 153, followed by 107 ms., for 0.1 per cent. of salt. The acetate of the same oxide gave, when of a deep red colour, 207 ms., and when it had become nearly colourless, from the spontaneous precipitation of a portion of its oxide, 194 ms., or sensibly the same osmose.

Manganese.—Sulphate of manganese appeared to have no decided chemical osmose, giving in double membrane of moderate resistance (2 min.), for 1 per cent. of salt, 34, 51 and 50 ms.; for 4 per cent. of salt, 53 and 51 ms., and for 10 per cent. of salt, 57 and 59 ms. The low osmose of the larger proportions of this salt is exceptional and would require confirmation.

The chloride of manganese has already been shown to be of low osmose in membrane (24 and 34 ms. Table XXIII.); in albumen the same salt gave 13 and 14 ms.

Cobalt.—The chloride of this metal appeared to possess no decided chemical

osmose, 1 per cent. giving in double membrane 21 and 27 ms.; 0·1 per cent. 20 and 23 ms., and 1 per cent. again 44 ms.

Nickel.—The sulphate of oxide of nickel resembled that of magnesia and protoxide of iron. In double membrane 1 per cent. gave 12 and 10 ms.; 4 per cent. 38 and 38 ms.; 10 per cent. 72 and 106 ms.

The chloride of nickel, however, appeared to have a tendency to chemical osmose, like the protochloride of iron, and gave in double membrane 52, 89 and 95 ms.

Zinc.—None of the salts of this metal can be said to exhibit decided chemical osmose; sulphate of zinc giving 34 and 29 ms., nitrate of zinc 18 and 32 ms., and chloride of zinc 48 and 54 ms., all in double membrane.

Cadmium.—The nitrate of cadmium appeared to affect chemical osmose; the one per cent. solution of this salt giving, in double membrane, 90, 124 and 137 ms.

Copper.—Copper appears to possess the capacity for chemical osmose in its salts generally, with the exception of the sulphate. But no sulphate appears to be remarkable for osmotic activity. The comparative osmose of four salts of copper in the same membrane is given below.

Table XXIV.—Solutions of 1 per cent. of Salts of Copper in Osmometer E of double membrane for five hours.

Salt in solution.	Rise in millimeter degrees.	Hydrostatic resistance.	Temperature, FAHR.
Chloride of copper	154 204	min.  1 10 10 12 10 10 10 10 10	60 59 60 62 62 63 61

The rate of osmose is generally a little deranged on passing from one salt to another in the same membrane, and in consequence the second or third experiment is always to be preferred to the first made with the same salt. The preferable numbers for the osmose of the preceding salts would therefore be, sulphate of copper 48 ms., acetate 102, nitrate 204, and chloride 351. The number for the sulphate, however, is probably too high, being raised by the previous chloride.

The salts of several of the magnesian metals exhibit a much lower osmose in albumen than in membrane. In an osmometer of the first description nitrate of copper gave only 22 and 27 ms.; acetate of copper 22 and 25 ms., or no more osmose than is obtained from the corresponding salts of lime and magnesia.

Lead.—The salts of this metal are probably equally osmotic with those of copper. The nitrate and acetate of lead only were examined. The osmose of these two salts obtained in the same membrane was as follows:—

TABLE XXV.—Solutions of 1 per cent. of Salts of Lead in Osmometer M of double membrane for five hours.

Salt in solution,	Rise in millimeter degrees.	Hydrostatic resistance.	Temperature, FAHR.
Nitrate of lead	211 197 100	min. 2 2 2 2 2 2	6 <sup>4</sup> 65 62 64 61

The numbers which these results appear to authorize, were for acetate of lead 97 ms., and for nitrate of lead 204 ms. (mean of 211 and 197 ms.). The acetate exhibits, as usual, a considerably inferior osmose to the nitrate of the same base.

It appeared desirable to ascertain the osmose of higher proportions of a salt, which, like the nitrate of lead, exhibits decided osmose in the 1 per cent. solution. The first results appearing low, the membrane was washed with ether after the third experiment, a treatment of the membrane which in this instance sensibly improved its osmotic power.

Table XXVI.—Solutions of Nitrate of Lead in Osmometer K of double membrane for five hours.

Proportion of salt in solution.	Rise in millimeter degrees.	Same in grammes of water.	Diffusate in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, FAHR.
per cent.					mın.	: 0
1	91	••••		0	2	6î
1	127			1	1	64
1	125			1	. 1	63
1	157	•••••		3	8	63
1	157	••••		9	12	63
2	184	••••	2.5565	1	12	63
2	195	••••		1	12	66
5	209	••••		- 1	12	66
5	229	••••		1	12	67
10	213	••••	l	ì	12	69
10	250	10.56	3.283	2	16	72

These experiments lead to the estimation of the osmose of nitrate of lead as follows:—in the 1 per cent. solution an osmose of 157 ms., in the 2 per cent. solution 195 ms., in the 5 per cent. solution 229 ms., and in the 10 per cent. solution 250 ms. This, it is to be observed, is but a small increase for the higher proportions of salt. The diffusate for the 10 per cent. solution of this salt may be considered of an average proportional amount. The replacing water then exceeds the salt diffused only about three and a half times.

It is curious that the hydrostatic resistance of the membrane increases so decidedly as the experiments advance, in the osmose of this and several other metallic salts,

particularly nitrates. It is not to be supposed, however, that this change has any material influence upon the osmose.

Uranium.—The nitrate of uranium presented a high degree of osmose. This result scarcely affects the question of the constitution of the metallic oxide present in that salt, as a high osmose is exhibited, both by the salts containing an oxide of the type  $R_2$   $O_3$ , and by a portion at least of the class of protoxides. Viewed as an aluminous salt the nitrate of uranium has a basic composition (Ur<sub>2</sub>  $O_3$  NO<sub>5</sub>), a circumstance which suggested the addition of free nitric acid to that salt in some experiments. The small proportion of one-tenth per cent. of nitric acid will be seen to have a moderate influence, and 1 per cent. of nitric acid to have an overpowering influence in reducing the extraordinary osmose of this salt.

TABLE XXVII.—Solutions of Nitrate of Uranium in Osmometer M of double membrane for five hours.

Proportion of salt in solution.	Rise in millimeter degrees.	Diffusate in grammes.	Previous maceration.	Hydrostatic resistance.	Temperature, FAHR.
1 per cent. nitrate of uranium 1 per cent. nitrate of uranium Same + 1 per cent. nitric acid Same + same Same + 0·1 per cent. nitric acid Same + same	458 44 70 304	0·078 0·102 0·205 0·136 0·078 0·108	days. 1 3 1 1 1	min. 1 1 1 3 3 3	60 61 63 66 62 61

The inferior osmose of the first observation in the Table arose from the osmose of the early hours of the experiment being less than those of the later hours, the osmose for the five hours in succession being 36, 46, 67, 77 and 63 ms.

This progression, combined with the additional circumstance to be observed, that the diffusate is below the average in the same experiment, suggests the idea of an absorbing or retaining power in the membrane for the salt, which must first be satisfied before the osmose and diffusion can proceed in a regular manner.

The diffusate is throughout small, like that of an aluminous salt.

In an albumen osmometer the osmose of the same salt was inconsiderable, namely 49 and 53 ms.; but that osmose was not further reduced by the addition of nitric acid.

Tin.—The protochloride of tin exhibits a high degree of osmose, like so many other metallic protochlorides. The one per cent. solution gave, in double membrane, an osmose of 235, 253, 289 and 275 ms. The bichloride of tin following immediately in the same membrane gave only 27 ms. But the osmose of the bichloride of this metal is essentially negative, even when the salt is made as neutral in composition as possible. It has been already described (page 192).

Antimony.—The double tartrate of potash and antimony proved rather remarkable for low osmose.

In the first experiment with a double membrane the osmose of the salt in question was 38 ms., but the osmose fell in the second and third repetitions to 12 and 17 ms. The 4 per cent. solution of the same salt gave no more than 23 and 7 ms.

Mercury.—The osmose of the salts of both oxides of this metal is always positive and generally considerable. The osmose appeared to be of least amount in the chloride (corrosive sublimate), to increase in the protonitrate, and to assume its greatest magnitude in the pernitrate. The first salt has a stability in solution which the latter two salts do not enjoy.

Extraordinary osmose is here, therefore, associated with facility of decomposition, as in so many other instances.

The influence of the presence of acids and of chloride of sodium upon the osmose of chloride of mercury was tried in the search for facts which might throw light on the osmotic process.

An acid in small proportion appears to favour, rather than otherwise, the osmose of chloride of mercury. Chloride of sodium, on the other hand, exerts its usual repressing influence upon the process.

Table XXVIII.—Solutions of Mercury in Osmometer C of double membrane for five hours.

Proportion of salt in solution.	Rise in millimeter degrees.	Previous maceration.	Hydrostatic resistance.	Temperature, FAHR.
1 per cent. of chloride of mercury	121	days. 4 3	min. 4 4	60 61
0·1 per cent. of chloride of mercury      Same	62 49	1	4 5	63 66
1 per cent. of chloride of mercury +0·1 per cent. of hydrochloric acid	163	1	5	62
Same + same	132	1	4	61
Same + 0.1 per cent. of nitric acid	152	3	5	60
Same + same		1	2	59
Same + 0.5 per cent. of chloride of sodium		1	2	61
Same + same		1	1	62

Adopting the second experiments as the most trustworthy, we have for 1 per cent. of chloride of mercury an osmose of 121 ms., and for the same, associated with half its weight of chloride of sodium, 60 ms.

The osmose of chloride of mercury in albumen was very trifling, being only 5 and 9 ms.; chloride of mercury diffused in sensible quantity, however, through both the albumen and membrane.

Protonitrate of mercury gave, in double membrane, an osmose of 232, 346 and 350 ms.; in albumen, much less, namely 47, 63 and 61 ms.

Pernitrate of mercury gave, in double membrane, 425 and 476 ms. for the one per cent. solution, and 296 ms. for the one-tenth per cent. solution, results which indicate osmotic power of the highest intensity.

The membrane preserved a considerable action after the last experiments, although macerated in water for a night, and imparted thereafter to a salt nearly neutral to osmose (nitrate of silver), a rise of 222 and 166 ms.

In albumen, pernitrate of mercury again was low, giving 32 and 54 ms. for one per cent. of the salt, and 34 and 46 ms. for the one-tenth per cent. solution.

Silver.—It is interesting to observe how this metal separates itself from mercury and the magnesian elements, and takes its place with the alkaline metals in the property of osmose, as in other chemical characters. Nitrate of silver appeared to possess a moderate positive osmose, like a salt of potash or soda. For the sake of comparison, the silver salt was followed by nitrate of soda in the experiments below.

TABLE XXIX.—Solutions in Osmometer G of double membrane for five hours.

Salt in osmometer.	Rise in millimeter degrees.	Previous maceration.	Hydrostatic resistance.	Temperature, FAHR.
1 per cent. of nitrate of silver Same	34 27 22	days.  1  1  1  2  1	min. 2 2 2 2 2 2	64 65 62 64 61 64

The experiments of the Table indicate an average osmose of 35 ms. for 1 per cent. of nitrate of silver, and of 4.5 ms. for the same proportion of nitrate of soda. A considerable diffusate of silver appeared in all the experiments with the salt of that metal.

Gold and Platinum.—The chlorides of these metals have already been shown to possess a decided negative osmose, and in that respect to rank with acids.

In concluding this paper, I may place together a series of numerical results which exhibit the osmose of substances of all classes. Some of these numbers have not been previously reported.

Osmose in membrane of 1 per cent. solutions expressed in millimeter degrees.

Chloride of zinc 45
Chloride of nickel 88
Nitrate of lead 204
Nitrate of cadmium 137
Nitrate of uranium 458
Nitrate of copper 204
Chloride of copper 351
Protochloride of tin 289
Protochloride of iron 435
Chloride of mercury 121
Protonitrate of mercury 350
Pernitrate of mercury 476
Acetate of sesquioxide of iron 194
Acetate of alumina 393
Chloride of aluminium 540
Phosphate of soda 311
Carbonate of potash 439

It will be observed that acid and alkaline salts are found at opposite ends of the series, or, while the acids possess negative osmose, the alkaline salts exhibit positive osmose in the highest degree. The remark will suggest itself, that in osmose water always appears to pass to the alkaline side of the membrane; as water also follows hydrogen and the alkali in electrical endosmose.

The chemical action must be different on the substance of the membrane at its inner and outer surfaces to induce osmose; and according to the hypothetical view, which accords best with the phenomena, the action on the two sides is not unequal in degree only, but also different in kind. It appears as an alkaline action on the albuminous substance of the membrane at the inner surface, and as an acid action on the same substance at the outer surface. The most general empirical conclusion that can be drawn is, that the water always accumulates on the alkaline or basic side of the membrane.

The analogy does not fail even when the osmometer is charged with an acid solution and the osmose is negative. The stream is then outwards to the water, which is a basic body compared with the acid within the membrane.

The high positive osmose of the salts of the alumina type is exceedingly remarkable. The property is common to salts of alumina, sesquioxide of iron, sesquioxide of chromium, and the corresponding oxide of uranium. Now the property in these salts is small where the salt is stable, as in the sulphates, but becomes great where the affinity between the acid and base is comparatively weak, as in the chlorides, nitrates and acetates of these bases, salts which can be shown to be largely decomposed in the

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experiment by the action of diffusion. When pernitrate of iron, a salt of this class, is placed in the osmometer, a rapid decomposition of the salt occurs in the membrane; the nitric acid escaping, from its high diffusibility, into the water of the jar, and leaving a basic salt on the inner surface of the membrane. Here then, as with the preceding class of osmotic bodies, the osmose of the water is towards the basic side of the membrane.

But the most curious circumstance, with reference to this empirical generalization, is observed in the magnesian class of salts. The barytic subdivision of this class, including all the soluble salts of baryta, strontia and lime, appear to be entirely unosmotic, or they oscillate between a small positive and small negative osmose. Such salts are neutral in their reaction, and further, have no disposition whatever to form subsalts. The salts of the earth, magnesia itself, offer the same characters. But in the salts of certain other oxides of the magnesian group an intensely osmotic character is developed, particularly in the salts of copper, protoxide of lead and protoxide of tin, with the exception of the soluble sulphates of these bases. Now those named are the members of the magnesian class most apt to break up into free acid and a basic salt. Like the aluminous salts, therefore, they are capable of investing the inner surface of the membrane with basicity, the necessary condition of positive osmose. Nitrate of uranium does not require to form a subsalt, as it is already constitutionally basic. The osmotic peculiarity of metaphosphoric acid, formerly referred to, also harmonizes with the same view.

Neutral monobasic salts of the alkaline metals, such as the chlorides of potassium and sodium and the nitrates of potash, soda and silver, which possess a strict and unalterable neutrality, appear to have little or no true osmotic action. The salts named, together with the neutral magnesian sulphates and certain neutral organic substances, such as alcohol and sugar, give occasion, it is true, to an increase in the fluid of the osmometer, but only to the moderate extent which the exchange of diffusion-volumes might be supposed to produce. The comparative diffusibility of all these substances is well known, with the exception, unfortunately, of that of water itself, which I could only deduce by an indirect method in my previous inquiries respecting liquid diffusion. As salts generally appeared to diffuse in water four times more rapidly than they did in alcohol, the diffusibility of water was then assumed as probably four times greater than that of alcohol, and consequently five or six times greater than that of sugar or sulphate of magnesia. Diffusion is thus made to account for the substances last named being replaced in the osmometer by five or six times their weight of water. This "diffusion-osmose" appears to follow in its amount the proportion of salt in solution, with a certain degree of regularity. "chemical osmose" of substances, on the other hand, is found of high intensity with small quantities of the substance, such as 1 per cent. or even 0.1 per cent., and to augment very slowly with increased proportions of the substance in solution.

A small proportion of common salt accompanying carbonate of potash has been

seen to possess a singular influence in diminishing the positive osmose of the lastnamed alkaline salt; while a mixture of small proportions of common salt and hydrochloric acid exhibits, with the membrane in certain conditions, an intense positive osmose which neither of these substances possess individually.

The bibasic salts of potash again, such as the sulphate and oxalate, although strictly neutral in reaction, begin to exhibit a positive osmotic power, in consequence, it may be supposed, of their resolvability into an acid salt and free alkaline base.

The sulphate of potash, when strictly neutral, has in different membranes a variable but always moderate positive osmose, an osmose which the slightest trace of a strong acid may cause to disappear entirely, or even convert into a small negative osmose.

On the other hand, a minute addition of an alkaline carbonate to the sulphate of potash appears to give that salt a positive osmose of a high order. It was seen that the mixed salts produce much more osmose than the sum of the osmose of the two salts used apart from each other.

This property of sulphate of potash must wait for its explanation, with many other facts of the subject, till fuller information is obtained than I can at present offer respecting the nature of the obscure chemical changes which occur in the membrane during osmose, and of the mode in which masses of water come to participate in these changes. The conclusion which has been drawn, that the osmose or movement of water through membrane is always towards the side of the base, is no theory or explanation of the phenomenon, but a general description, which appears to apply with sufficient accuracy to all the observations.

It may appear to some that the chemical character which has been assigned to osmose takes away from the physiological interest of the subject, in so far as the decomposition of the membrane may appear to be incompatible with vital conditions, and osmotic movement confined therefore to dead matter. But such apprehensions are, it is believed, groundless, or at all events premature. All parts of living structures are allowed to be in a state of incessant change,—of decomposition and renewal. The decomposition occurring in a living membrane, while effecting osmotic propulsion, may possibly therefore be of a reparable kind. In other respects chemical osmose appears to be an agency particularly well adapted to take part in the animal economy. It is seen that osmose is peculiarly excited by dilute saline solutions, such as the animal juices really are, and that the alkaline or acid property which these fluids always possess is another most favourable condition for their action on membrane. The natural excitation of osmose in the substance of the membranes or cell-walls dividing such fluids seems therefore almost inevitable.

In osmose there is, further, a remarkably direct substitution of one of the great forces of nature by its equivalent in another force—the conversion, as it may be said, of chemical affinity into mechanical power. Now, what is more wanted in the theory of animal functions than a mechanism for obtaining motive power from chemical decomposition as it occurs in the tissues? In minute microscopic cells the osmotic

movements should attain the highest velocity, being entirely dependent upon extent of surface. May it not be hoped, therefore, to find in the osmotic injection of fluids the deficient link which intervenes between chemical decomposition and muscular movement?

The intervention of the osmotic force is also to be looked for in the ascent of the sap of plants. The osmometer of albuminated calico appears to typify the vegetable cell; the ligneous matter of the latter being the support of a film or septum of albuminous matter, in which the active properties of the cell reside. With a vegetable salt, like oxalate of potash above, and pure water below such a septum, an upward movement of the lower fluid would necessarily ensue.