

acteristic of "Bishop's Ring," and distinguishable at Honolulu for two years. Apparently there has recently been a great reinforcement added to the material in the upper atmosphere, which produces the afterglows.

Is this owing to the August eruption in Alaska, which is said to have distributed ashes at a distance of 250 miles?

Prof. C. J. Lyons, in charge of tidal observations in Honolulu, reports the period of highest mean tide to have extended itself this year into November, or fourteen months later than the last similar period. The mean sea level is now over ten inches higher than it was last April. It is also somewhat higher than has been shown by any previous tide registers in Honolulu. Mr. Lyons regards this as of special importance, taken in connection with the oscillation of the earth's axis, now established by the combined observations at Berlin and Honolulu.

Honolulu, November 8.

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OSMOTIC PRESSURE.

OF the various properties which have found a common explanation in the new theory of solutions, there are none perhaps to which more interest attaches than to osmotic pressure; and although, on account of the experimental difficulties, the observations as yet accumulated on this subject are but scanty, they have so largely contributed to the novel ideas involved in the new theory, that they merit special attention.

Since accounts of osmotic pressure are finding their way into few English text-books, it may be worth while glancing at the main features which have led up to the present state of the question.

It has long been known that if an aqueous solution—say, of sugar—be separated from pure water by a piece of animal membrane, that movements of the water and of the sugar take place through the membrane. If the solution be contained in an open vessel, the base of which is composed of membrane, on partially immersing the vessel in water it is easy to see that more water enters the vessel than solution leaves it. The level of liquid within rises above that without the vessel, different pressures being thus set up on opposite sides of the membrane.

To this process wherein currents pass through a membranous septum, the terms "osmosis," "osmose," and "diosmose" have been applied. The last of these is perhaps to be preferred, as it serves to indicate that two currents are involved in the phenomena. Investigations carried out as indicated above were concerned with the measurement of what was termed the "endosmotic equivalent." That is the ratio of the amount of water passing *into* the solution to the amount of dissolved substance passing in the opposite direction. Consistent measurements of this quantity could not be obtained, however, for it was found that the nature of the membrane exercised a marked influence upon its magnitude. The kind of membrane employed, or, with the same membrane, its thickness or freshness, or even the direction in which water passed through it, was of importance. Thus in illustration of the last point, water passes more readily outwards through eel's-skin, more readily inwards through frog's-skin.

To obtain quantitative relations in this field it thus became essential to eliminate the influence of the membrane, and more recently this end seems to have been attained by the use of membranes artificially prepared.

These artificial membranes differ from those of animal origin in the remarkable particular that although they allow water to pass through, they present a barrier to the passage of certain dissolved substances. On this account they have been termed semi-permeable membranes, and by their use measurements of osmotic pressure have been made possible.

To carry out such measurements the first point to be solved was to obtain a membrane of sufficient strength.

The substance which has been found to be most satisfactory as a membrane-former is copper ferrocyanide. When aqueous solutions of potassium ferrocyanide and copper sulphate are carefully brought into contact a pellicle of copper ferrocyanide is formed where the two solutions meet. In this condition the pellicle is much too fragile to sustain even slight differences of pressure; but by the following simple device, employed first of all by W. Pfeffer, satisfactory results have been obtained.

If a cell similar to the ordinary porous pot of a voltaic battery be lowered into a solution of copper sulphate while at the same time a solution of potassium ferrocyanide be poured into its interior, the two solutions meet somewhere within the walls of the cell and deposit a film of copper ferrocyanide. Little diaphragms of membrane are thus produced stretching across the pores of the cell-wall, which furnishes the necessary support, and by taking suitable precautions a membrane may thus be obtained capable of withstanding a pressure of several atmospheres.

The behaviour of a solution when separated from pure solvent by such a semi-permeable membrane differs markedly from what takes place when an animal membrane is employed. In the latter case, at the outset water adds itself to the solution; the level of liquid and the pressure on the solution-side of the membrane thus rise until a maximum pressure-head is attained, which, roughly speaking, is greater the stronger the solution used. Seeing, however, that dissolved substance is continually escaping from the solution through the membrane, as soon as the maximum is reached the pressure-head begins to fall until eventually it vanishes, the levels of liquid on either side of the membrane being the same.

If, on the other hand, a semi-permeable membrane be employed, as before, a maximum pressure is attained; but since dissolved substance cannot leave the solution, this maximum pressure as well as the concentration of the solution remain constant.

When this constant state of things is established the excess of pressure on the solution-side of the membrane over that on the solvent-side, whatever it may mean, is termed the "osmotic pressure" of the solution. It is therefore customary to reserve the term *osmose* to phenomena relating to semi-permeable membranes; *diosmose* being used in cases where, as with animal membranes, dissolved substance as well as solvent can traverse the membrane. It is obvious that when the pressure is established as indicated above, the original concentration of the solution has been altered by the entrance of solvent, and the observed osmotic pressure refers of course to the solution having the final concentration. If, however, we imagine the vessel containing the solution to be closed at the top, a quantity of air being imprisoned over the solution, pressure may be set up by compressing this air, only a small quantity of solvent being allowed to enter. If, further, the air enclosure be tapped by a manometer, measurements of the pressure may be taken, and by making the air enclosure and the volume of the manometer small enough the quantity of solvent entering while pressure is being established may be neglected, the original concentration of the solution remaining practically unaltered. This is the principle of the method employed in measuring osmotic pressure in absolute units.

The question now arises, "Are these measurements really independent of the nature of the membrane? Has the difficulty which beset the older experiments been overcome?" To this question an immediate answer is for the coming, for, as pointed out by Prof. Ostwald, it follows from theoretical considerations that if the membrane employed is really semi-permeable, the observed osmotic pressure of a given solution must be the same, no matter of what material the membrane is com-

posed. For suppose we have a quantity of solution enclosed in a tube, one end of the tube being closed by a membrane A, the other by a membrane B, and suppose it possible that a pressure P can be developed on the membrane A when it separates the solution from pure water, which is higher than the pressure p similarly developed when B separates the solution from pure water. On immersing the tube in water, the latter will begin to pass through both membranes into the solution. When the pressure p is attained passage through B will stop, but that through A will continue; but as soon as the pressure on the solution rises above p , water will be forced out through B. The pressure P will thus never be attained, water will continuously enter through A, and pass out at B. We will thus have a machine capable of doing an infinite amount of work, which is impossible. Similar reasoning shows that p cannot be greater than P; it follows therefore that the pressure developed on each membrane is the same, that the osmotic pressure must be independent of the nature of a truly semi-permeable membrane.

Actual observations are on record in which the osmotic pressure did appear to vary with the membrane employed. A sugar solution, for example, exhibited a much lower osmotic pressure with a membrane of Prussian blue or calcium phosphate than with copper ferrocyanide. From the preceding argument it is concluded, however, that these membranes giving the lower values were not quite firm or not quite impermeable to the dissolved substance; the highest value is thus taken as the measure of the osmotic pressure which is nearest the truth.

On glancing at the results which have been obtained, the first point which strikes one is the extraordinary magnitude of the pressures thus set up. In the case of a 1 per cent. aqueous solution of nitre the pressure attains the value of $2\frac{1}{2}$ atmospheres. This value increases with the strength of the solution till at 3.3 per cent. it is no less than 6 atmospheres, this pressure being the highest which any membrane yet prepared has been able to withstand. With substances like sugar, other things being the same, the pressure is not so great, but in all cases, in order to keep it within workable limits, the solutions employed have to be dilute.

Striking as the results are themselves, their explanation is not less remarkable. The original measurements of osmotic pressure were made with the purpose of elucidating the movement of liquids in plant cells, and naturally the substances examined were such as occur in the vegetable organism—aqueous solutions of sugar, gum, dextrin, and the nitrate, sulphate, and tartrate of potassium. For some years after these observations were made, they lay comparatively unnoticed, until Prof. van't Hoff, of Amsterdam, turned them to a use undreamt of by their discoverer. From a study of the properties of dilute solutions van't Hoff came to the conclusion that the osmotic pressure was due to the bombardment of the molecules of the *dissolved substance* on the semi-permeable membrane. For when the osmotic pressure is established and equilibrium exists between solvent and solution, in the same time, equal amounts of solvent, must pass in either direction through the membrane and the impacts of the solvent molecules on the membrane will then be equal and opposed on either side, and therefore negligible. On this reasoning the pressure recorded on the manometer is taken to be that exerted by the substance in solution.

On examining the magnitude of the pressure thus attributed to the dissolved substance, in the case of a solution of sugar van't Hoff next showed that it bore the closest resemblance to the pressure of a gas. Indeed, if we calculate the pressure of a gas which at the same temperature contains as many molecules per unit volume as there are molecules of sugar per unit volume of solution, then the pressure of the gas and the osmotic pres-

sure are the same. Moreover, on thermodynamical grounds it was established that on the above hypothesis as to the nature of osmotic pressure its magnitude should be quantitatively connected with measurements of other physical properties of solutions, more especially those on the lowering of the vapour-pressure, and of the freezing point of a solvent produced by the presence of dissolved material. In this way a mass of evidence was collected, a general survey of which led to the foundation of the new theory of solutions. On this theory the dissolved substance, if the solution be dilute, is supposed to behave as if it were gaseous, the pressure it exerts—the osmotic pressure—being equal to the pressure which it would exert if it were gasified, and occupying, at the same temperature, a volume equal to the volume of the solution.

Unfortunately measurements of osmotic pressure have only been made on few substances, and only for solutions in water, but on turning to all the available observations to see how they support this novel conclusion, the most superficial examination serves to show that an agreement does not exist. Unless in the case of sugar, for no substance of known formula which has yet been investigated does the osmotic pressure agree with the corresponding gaseous pressure. These substances consist of salt solutions, and they invariably give higher osmotic pressures than theory demands. Similar disturbing influences have been observed when other physical properties of these solutions were measured, and to account for the facts an additional hypothesis has been put forward by Dr. Svante Arrhenius.

Salt solutions are electrolytes, they conduct the electric current, and undergo simultaneous chemical decomposition into their constituent ions. Experiment shows that such electrolytic solutions give high osmotic pressures, more particles appear to bombard the semi-permeable membrane than if the dissolved substance behaved as a gas. The new hypothesis states that this is really the case, the additional number of particles being produced from the breaking up of the dissolved substance. It states that in a solution which can be electrolyzed a portion at least of the dissolved substance exists already decomposed or dissociated into its ions, and that although these ions cannot be separated by diffusion they are so far independent that each can exercise an effect on the semi-permeable membrane.

The extent of this electrolytic dissociation is supposed to vary with the chemical nature of the dissolved substance, and to increase with the dilution. In very dilute solutions it may be complete, the whole of the dissolved substance being supposed to exist in the state of ions.

The second hypothesis gives, therefore, some explanation why the osmotic pressure of a salt solution is greater than that of a non-electrolytic solution of sugar; it further fixes the limits between which the osmotic pressure ought to vary in the case of an electrolyte, for the lower limit should be that of undissociated gas, the higher should be that of completely dissociated gas, each original molecule having decomposed into as many sub-molecules as there are ions in each molecule of salt.

So far as these limiting conditions go, the facts support the hypothesis. In all cases the observed osmotic pressure is either equal to one or other of the limits, or lies between them. A closer scrutiny leads, nevertheless, to apparent discrepancy. It is evident that a measure of the amount of dissociation can be obtained from osmotic pressure observations. For if we divide the observed osmotic pressure by the corresponding pressure of undissociated gas we have obviously, if the preceding hypotheses are valid, the ratio of the actual number of bombarding molecules to the theoretical number had no dissociation occurred. The ratio of these two numbers is denoted by the letter " i ," a factor first used by van't Hoff. Now, on the new theory, the value of " i " can be

obtained by measurements of other properties of salt solutions, the electric conductivity, the depression of the freezing point, &c., and the theory is compared with practice by seeing if the values of " z ," as determined, say, from freezing-point observations, agree with those deduced from the osmotic pressure. The comparison shows that in some cases, some half-a-dozen in all, the two sets of values correspond; in others, and in by far the majority, no such correspondences exist. In these latter instances it is argued, and with a certain amount of experimental evidence, that the salts were not without action on the membrane employed, and that, therefore, diosmose really took place, the membrane was not truly semi-permeable. In this way the discordant observations have been put out of court.

It is thus apparent that the leading hypotheses of the new theory do not receive confirmation of the weightiest kind from observations on osmotic pressure. Indeed, were they supported by such measurements alone, they would hardly be entertained. Their mainstay, however, lies in the mass of experimental work on many other properties—evidence which it is much easier to obtain than the difficult measurements on osmotic pressure—which has been correlated and explained by their use.

been put forward in favour of the gaseous analogy. Several physicists, starting from entirely different points of view, have arrived at the result that in a dilute solution the dissolved substance should obey laws similar to those which hold for gases. At present the attitude of the prominent upholders of the new theory is one of indifference as to the exact mechanism of osmotic pressure. The numerical agreement between the measurements on solutions and those on gases is regarded as ample justification for considering dissolved substances to be in a *pseudo-gaseous* condition.

Whatever the ultimate explanation of the facts may be, there can be no doubt that the existing speculations on the nature of osmotic pressure and allied phenomena have infused new life into the study of solutions. Indeed, as instigators to fresh inquiry these hypotheses must take rank as the most fruitful of recent times.

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A SANITARIAN'S TRAVELS.

MR. ROBERT BOYLE has travelled round the world no fewer than four times for the purpose of studying sanitary science and preparing the way for the intro-



GREAT RECUMBENT FIGURE OF BUDDHA, PEGU, BURMAH.

It is only fair to add that both hypotheses, from physical as well as chemical standpoints, have met with a measure of adverse criticism. The rôle played by the membrane has also been questioned. It has been suggested that it is not really semi-permeable, allowing solvent only to pass, but just as a porous plug behaves towards a mixture of gases, it allows molecules with different momenta to traverse it at different rates. Or, again, its action has been likened to that of a palladium film towards hydrogen, compounds being formed with the membrane substance on one side, these becoming diffused and dissociated on the other. If either of these views be correct the pressures exerted by dissolved substances have probably never been measured.

On the other hand, important theoretical support has

duction of the ventilating and sanitary appliances he has invented. An interesting account of his fourth journey is given in a little book entitled "A Sanitary Crusade through the East and Australasia," consisting of a series of papers reprinted from the *Building News*. In the course of this "crusade" Mr. Boyle visited Burmah, the Malay native states, Sumatra, Siam, Borneo, Java, Australia, New Zealand, Samoa, the Sandwich Islands, and America. Of all the facts noted by him as a sanitarian the most remarkable are those relating to leprosy, a disease which he believes to be spreading to an alarming extent all over the world. He was particularly struck by the gigantic proportions the evil has assumed in Burmah. The steps of the great Shwedagon pagoda at Rangoon, the Mecca of the Indo-Chinese Buddhists, he found to be