to impacts, between the molecules of the liquid S and the molecules of the solid piston Q. We are left absolutely without theoretical guide as to the resultant force due to the impacts of S molecules and D molecules striking the other piston, P, and rebounding from it, and their attractions upon its molecules; and as to the numbers per unit volume of the S molecules on the two sides of MM, except that they are not generally equal.

No molecular theory can, for sugar or common salt or alcohol, dissolved in water, tell us what is the true osmotic pressure against a membrane permeable to water only, without taking into account laws quite unknown to us at present regarding the three sets of mutual attractions or repulsions: (1) between the molecules of the dissolved substance; (2) between the molecules of water; (3) between the molecules of the dissolved substance and the molecules of water. Hence the well-known statement, applying to solutions, Avogadro's law for gases, has manifestly no theoretical foundation at present; even though for some solutions other than mineral salts dissolved in water, it may be found somewhat approximately true, while for mineral salts dissolved in water it is wildly far from the truth. The subject is full of interest, which is increased, not diminished, by eliminating from it fallacious theoretical views. Careful consideration of how much we can really learn with certainty from theory (of which one example is the relation between osmotic pressure and vapour pressure at any one temperature) is exceedingly valuable in guiding and assisting experimental efforts for the increase of knowledge. All chemists and physicists who occupy themselves with the "theory of solutions," may well take to heart warnings, and leading views, and principles, admirably put before them by Fitzgerald in his Helmholtz Memorial Lecture (*Transactions of the Chemical Society*, 1896) of January 1896 (pages 898-909).

KELVIN.

METHOD FOR MEASURING VAPOUR PRESSURES OF LIQUIDS.¹

Apparatus for realising the proposed method is represented in the accompanying diagram. Two Woolff's bottles, each having a vertical glass tube fitted airtight into one of its necks, contain the liquids the difference of whose vapour pressures is to be measured. Second necks of the two bottles are connected by a bent metal pipe, with a vertical branch for connection with an air pump, provided with three stopcocks, as indicated in the diagram. Each bottle has a third neck, projecting downwards through its bottom, stopped by a glass stopcock which can be opened for the purpose of introducing or withdrawing liquid. The upper ends of the glass tubes are also connected by short india-rubber junctions with a bent metal pipe carrying a vertical branch for connection with an air-pump. This vertical branch is provided with a metal stopcock.

To introduce the liquids, bring open vessels containing them into such positions below the bottles that the necks project downwards into them. Close the glass stopcocks of these lower necks, open all the other six stopcocks, and produce a slight exhaustion by a few strokes of the air-pump. Then, opening the glass stopcocks very slightly, allow the desired quantities of the liquids to enter, and close them again. They will not be opened again unless there is occasion to remove the whole or some part of the liquid from either bottle; and, unless explicitly mentioned, will not be included among the stopcocks referred to in what follows. It will generally be convenient to make

the quantities of the two liquids introduced such, that they stand at as nearly as may be the same levels in the two bottles, as indicated in the drawing.

Operation No. 1.—Close the stopcock on the lower passage from the bottles to the air-pump (which, for brevity, we shall call the lower air-pump stopcock); and, with the other five stopcocks all open, work the air-pump till the liquid in one of the glass tubes rises to within a centimetre of the india-rubber collar round its top.

Operation No. 2.—Open the lower air-pump stopcock till the liquids fall down the tube, nearly down to hydrostatic equilibriums in the bottles. Close it again, and work the air-pump till the liquid in one of the glass tubes rises to within a centimetre of the india-rubber collar.

Operation No. 3.—Repeat operation No. 2 over and over again until you cannot, however long you go on pumping, get the liquid in either tube to rise within a centimetre of the india-rubber collar.

Operation No. 4.—Continue Operation No. 3 until the

¹ "On a Differential Method for Measuring Differences of Vapour Pressures of Liquids at One Temperature and at Different Temperatures." (Communicated to the Royal Society of Edinburgh, January 18.) By Lord Kelvin, G.C.V.O.I.

liquid that rises higher than the other stands steadily at a convenient marked point, when the air-pump is kept vigorously going, with the lower air-pump stopcock closed. This marked point may be perhaps a few centimetres below the india-rubber collar, so as to allow the liquid surface of it to be conveniently seen through a wide glass cylinder containing hot or cold water around it, applied to fulfil the thermal conditions referred to in Operation No. 6. In these present circumstances the vapour pressure is practically equal throughout the upper bent tube, and the portions of the glass tubes between its ends and the liquid surfaces in the two glass tubes. Hence the more volatile of the two liquids is kept cool at its surface by rapid evaporation, and the less volatile liquid is kept warm by rapid condensation of vapour into it, so that, by flow of vapour through the bent tube, the difference of temperatures required to equalise the vapour pressures is very nearly maintained.

Operation No. 5.—Close the upper three stopcocks, both air-pump stopcocks being already closed, and the two lowest metal stopcocks open. Leave the apparatus to itself until the temperatures become equalised. The difference of levels of the liquids in the two glass tubes, with proper corrections for their densities and for the difference, if any, of levels of the liquid surfaces in the two bottles, measures accurately the difference of vapour pressure over them, at the temperature to which they become equalised.

Operation No. 6.—Open the upper air-pump stopcock, work the air-pump and open the stopcock over the top of one of the two liquids for a minute or two and close it again. Do the same for the other liquid. Allow temperatures to be equalised to what they were at the end of Op. 5. If any air or other foreign volatile substance¹ has escaped from either liquid along with its proper vapour, its level will be seen higher than it was at the end of Op. 5. The present operation (No. 6) must be continued long enough to distil out of either, or both liquids, any such foreign ingredients if, when originally introduced, any such impurity was contained.

Operation No. 7.—By proper thermal appliances, indicated by the dotted lines in the diagram, and the lamp under the upper bent metal tube (inserted merely as an indication that somehow the metal tube is to be always slightly warmer than the warmer of the two liquid surfaces, in order that there may be no condensation of vapour in it), bring the upper surfaces of the liquids to any other temperature, or to two different temperatures. The difference of levels of the liquids in the two tubes, with proper correction for the densities of the two liquids at their actual temperatures in different parts of their columns, gives the difference of vapour pressures for the actual temperatures of the two liquids at their upper surfaces.

Operation No. 8.—To facilitate and approximately determine the hydrostatic correction for specific gravities at the actual temperatures of the two liquids, open wide the stopcocks above the tops of the two glass tubes, and let a little air run back from the air-pump, by very cautiously and slightly opening our upper air-pump stopcock, and closing it again before the lower of the two liquid surfaces reaches the lower end of its glass tube. After that, by cautiously opening and closing our lower air-pump stopcock, let in a little air to the bottles until the mean level of the liquids in the two columns rises to nearly the same level as it had in the measured positions of Op. 5 or Op. 6. In the present circumstances, air in the upper bent metal tube resists diffusion of vapour through it sufficiently to prevent any important difference of temperatures from being produced by evaporation and condensation at the two liquid surfaces, and there is

practically perfect hydrostatic equilibrium of equal liquid pressures at the tops of the two columns.

The vapour pressure of water is accurately known through a very wide range of temperature from Regnault's experiments; hence, if pure water be taken for one of our two liquids, the mode of experiment described above determines the vapour pressure of the other liquid.

The apparatus may be kept day after day with the same liquids in it (all the stopcocks to be closed, except when it is not in use for observations); and thus, the observations for difference of vapour pressures may be repeated day after day; or a long series of observations may very easily be made to determine vapour pressures at different temperatures. Always before commencing observations, Operation 6 must be repeated to remove air or other impurity, if any air has leaked in, or if air or other foreign volatile impurity has escaped from dissolution in either liquid into the vapour space above it. KELVIN.

RELATIVE TEMPERATURES IN GEISSLER TUBES.

IN the Physical Institute of the Berlin University, Mr. R. W. Wood has been making a series of experiments, most interesting to students of astrophysics, with the object of investigating the relative temperatures at different parts of the discharge in a Geissler tube, with special reference to the stratification phenomena. Wiedemann and Hittorf, and also the theoretical calculations of Warburg, have shown that the temperature of the gas in the positive part of the discharge lies far below red heat, while that of the negative light, according to Hittorf, is at least below the melting-point of platinum. These observations are for the most part corroborated by the experiments of Mr. Wood, who has investigated in this case a fixed part of the discharge in an atmosphere of nitrogen under varying pressures and currents of different strengths. The results obtained by employing hydrogen instead of nitrogen established the fact that, under similar conditions of pressure and strength of current, the heating was only about 11 per cent. of that found in the former case. It was found difficult, however, to keep a steady current with this gas.

Perhaps more interesting are the results which he has been able to procure by determining the relative temperatures of the different parts of the space between the anode and cathode. For this he has designed a neat and very simple means, by which the positions of the bolometer inside the vacuum tube might be varied at will without impairing in the least degree the vacuum. The description of this apparatus will be found in the article in which the results of his observations have been published (*Physical Review*, November-December 1896, xxi.). We may, however, mention that the bolometer wire—that is, the wire which was placed in the different positions between the two poles of the Geissler tube to indicate the varying temperatures of the different parts of the discharge—was here composed of platino-iridium, and bent in the form of a loop. Its exact position could at any moment be read off from a vertical scale. It was thus found possible to make a complete map of the temperature changes inside the vacuum tube.

In the *unstratified* anode light the temperature was sometimes constant for the greater part of the column, rising to a maximum near the middle, and falling off as the dark space was approached. The maximum was always found when the light was on the point of stratifying, and sometimes at higher pressures. The exact conditions, however, could not be determined; but the extent of the anode light played an important part.

¹ See Ostwald, "Physico-Chemical Measurements," translated by Walker (Macmillan, 1892), last paragraph, page 112.