processes within the metal. Since, however, the viscosity of steel decreases in marked degree from soft to hard * one would first have to show that the viscosity in cold hard steel is greater than the viscosity in the hot tempered steel, in any comparison.

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WHILE the new school of physical chemists has been busy pushing on the theory of dilute solutions to all its available conclusions, physicists have been more concerned about the secure establishment of the premises on which all these conclusions are based. The feeling of physicists has been well voiced by FitzGerald in the last Faraday lecture at the Chemical Society of London, and Poynting's paper on "Osmotic Pressure" (Phil. Mag. 1896, October) is one attempt at securing a sound physical foundation for the theory of solutions. The present paper is another. The reasons usually assigned for the remarkable fact that the laws of the osmotic pressure of a solute in a solvent are the same as if the solvent were annihilated and the solute left as a perfect gas, are quite inadequate, because they would apply to any selected lot of the molecules of the solvent, and therefore to all the molecules, with the result that the laws of a perfect gas would have to hold for all fluids down to and in the liquid state. The essence of the whole matter lies in this:—Why should the laws of gases hold for the osmotic pressure of the solute, when the solvent is in a condition involving enormous departure from the laws of gases? The answer is to be found in a closer study of the semipermeable membrane. If we seek to picture to ourselves how a membrane allows water molecules to pass, but not sugar molecules, our simplest conception of its structure is that of a mesh, amidst the threads of which the water molecules are packed in such a manner as to give way before one another almost as in ordinary water, while the sugar molecules are held back by the mesh. Thus the mesh forms a solid or quasi-solid framework through which water can pass with high viscous resistance, while the sugar molecule is absolutely blocked. Now if the framework turns back the sugar molecules, it must take the force of their

* Barus, Phil. Mag. [5], xxvi. p. 183 (1888); cf. 'Nature,' xli. p. 309 (1890).
† Communicated by the Author.
blows and shield the water molecules from them. If then we suppose a semipermeable membrane separating water and a dilute solution of sugar in water, the sugar molecules are to be regarded as replacing some water molecules, but their collisions on the water in the membrane are rendered inoperative by the shielding action of the framework, so that the water molecules in the membrane receive more impacts on the side of the pure water than on the side of the solution, and therefore water flows through the membrane, until in the solution there is enough excess of hydrostatic pressure established to compensate for the inoperative impacts of the sugar molecules; this inequality of pressure which can be hydrostatically balanced is the osmotic pressure. Next as to its laws. Let us find the number of molecules that in a second cross unit area of a plane in a collection of molecules. We know that in the case of a gas with \( n \) molecules per unit volume and mean velocity \( v \) the number is \( nv/6 \). Next consider a number arranged in cubical order, the edge of each cube being \( d \), and each molecule oscillating through a distance \( a \) smaller than \( d \) in a fixed direction parallel to one set of edges; then a molecule crosses a plane within distance \( a \) of its central position \( v/2a \) times a second in the same direction, and a plane at greater distance than \( a \) no times a second. If then a plane is placed at random at right angles to the vibrating molecules its chance of being traversed by molecules is \( a/d \), therefore an area \( d^2 \) similarly placed at random will on the average be crossed \( (v/2a)(a/d) \) times a second; so that unit area is on the average crossed \( nv/2d^2 \) times a second by molecules, that is to say, \( nv/2 \) times. If the molecules were vibrating in all directions and we assumed that a third of them vibrated in any direction, and the remaining two thirds in directions at right angles to it, we should then have the average number of times unit plane is crossed as \( nv/6 \), the same as in the case of the perfect gas. We can easily see after these two special cases that the result is general, no matter how crowded the molecules may be, so long as the time of collision of a molecule may be neglected; because as each molecule keeps moving on with the same average velocity, if it is diverted by collision with another, then on the average the only effect of collision is to alter the actual path of each molecule, but not the average space traversed: thus in any collection of molecules moving at random, whether as compact as in a liquid or as free as in a gas, the number of times a unit plane is crossed by molecules per second is \( nv/6 \).

If then our unit area is taken on the surface of the semi-
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permeable membrane in contact with the dilute sugar solution, each molecule of sugar in being turned back receives momentum $2mv$, so that the whole pressure taken by unit area of the meshes of the membrane is $nmv^2/3$, where $n$ is the number of molecules of sugar per unit volume. Thus for the osmotic pressure we have arrived at exactly the same expression as for the gas pressure of the sugar molecules if the water were annihilated and the sugar remained as a perfect gas. By the nature of the argument, we are not involved in any difficulties in the way of its leading us to assert Boyle's law as holding down to and in the liquid state. We assert that what holds down to and in the liquid state for any fluid is that the number of times a unit plane is crossed in the same direction by molecules per second is $nv/6$, and as the result of this and of the property of semipermeability the identity of the laws of osmotic pressure with those of perfect gases comes to pass, notwithstanding that the complete equation for the pressure of the pure water of the dilute sugar solution involves all the complications of collisions and powerful attractions with absolute departure from Boyle's law and Charles' law.

The reason why we cannot assert that a liquid having $n$ molecules to unit volume exerts a pressure $nmv^2/3$ on the solid wall containing it because of collisions, is that a unit area of the wall cannot be regarded as a random unit area, but a very special one with the special condition that no molecule can pass it. Now the meshes of our semipermeable membrane in turning back the molecules of sugar give the unit plane containing them a special property, but when the solution is dilute and the numerous water molecules pass freely, the meshes cause what is only a slight derangement from the conditions of a random plane, and in our first approximation we have neglected this derangement on account of its slightness. Molecules of sugar can be turned back by molecules of water which project beyond the plane of the mesh by any fraction of their diameter.

As the surface of a solid wall bounding liquid cannot be treated as an average plane we have to take a special method of calculating the total collisional pressure on it, as for instance that in "The Kinetic Theory of Solids" (Phil. Mag. [5] xxxii.). The essential distinction then between a semipermeable membrane and a solid wall in relation to a dilute solution is that while the membrane has special relation to only the few dissolved molecules, the solid wall has a special relation to all the solvent as well as the dissolved molecules.

A derivative result of some importance from our argument is the identity of the mean kinetic energy of the molecules of
liquids and gases at the same temperature; for it is involved in
the result that the equation for the osmotic pressure of the
dissolved sugar molecules comes out as if they were in the
gaseous state: many lines of investigation have already made
this identity tolerably certain, but none so simply and clearly
as van't Hoff's discovery of the identity of the osmotic
pressure laws with those of perfect gases.

Van't Hoff has shown how, given semi-permeability, it is
possible by thermodynamics to deduce the laws of dilute
solutions in a simple manner; the difficulty has been to get a
conception on molecular grounds of the rationale of osmotic
pressure and the simple laws of dilute solutions. But with a
direct molecular explanation for osmotic pressure we can then
adopt van't Hoff's thermodynamical extensions and treat the
whole matter as placed on a molecular basis; but for the sake
of the illustration we will essay a direct molecular explanation
of another typical simple law of dilute solutions, namely, that
of the lowering of vapour-tension.

In a gas the average velocity and the average distance
apart of the molecules are such that, although molecules are
continually approaching quite close to one another, they
seldom do so under conditions which would cause a pair to
remain within finite orbits relatively to one another; even
when two molecules collide, the relative path after the
collision is generally part of a curve extending to infinity,
just as the paths of comets are sometimes hyperbolas; the
parabola is a possible orbit for a comet, and marks the tran-
sition from the infinite hyperbola to the finite ellipse of
certain comets and the planets. So in the case of a gas
which has molecular velocity lowered by cooling to the
critical temperature, and mean distance apart reduced by
compression up to the critical pressure, the relative orbits of
colliding molecules become restricted to a finite range, one
pair of molecules that have a hold on one another entangles
another similar pair, and so on; the conditions are those of
incipient liquefaction. When the temperature is lowered,
liquefaction becomes decided, because of the more decided
entanglement, and gravitation separates out the entangled
portions into a continuous mass with horizontal surface, leaving
more space to those which had high enough velocities to
escape entanglement, and therefore still further increasing
their chances of freedom, which they enjoy as vapour in
contact with the liquid. Solidification occurs when each
molecule is imprisoned by its neighbours, or if on the surface,
is so strongly attracted that it cannot escape. But suppose a
liquid surrounding a solid, then if the molecular attraction
between solid and liquid is such that the potential energy
becomes less when a molecule of the solid is surrounded by those of the liquid than by its own sort, the conditions are favourable for the escape of the surface-molecules of solid, that is to say, the solid dissolves in the liquid and its molecules share the relative freedom of those of the liquid. Now the vapour-pressure of most solids at ordinary temperature is so low that it has not been measured, that is to say, that the molecular attraction between their molecules is so great that very few can retain their freedom; for instance, if common salt were vaporized by heat and then suddenly cooled to ordinary temperature, the molecules would capture one another so thoroughly that almost a vacuum would be created by the precipitation of the solid salt from the space filled with vapour. If, then, we try to picture what occurs at the surface of a solution where the solvent is free to evaporate into a region that ultimately becomes saturated, we must imagine the molecules of solute to be behaving practically as kinetic substitutes for those of the solvent which they displace, and participating with them in chances favourable to escape at the surface. Now, in the vapour the molecules of solvent that approach one another have speed enough also to escape from one another, whereas the strongly attracting molecules of solute freely capture one another (or possibly sometimes the molecules of solvent) with immediate entanglement and prompt return to the liquid mass, so that the region of evaporation and condensation of the solute is a very limited one near the free surface. If there are \( n \) molecules of solute to \( N \) of solvent, then the difference between a surface of the pure solvent and one of the solution is that for every \( n + N \) molecules of solvent liberated at the pure surface, there are \( N \) of solvent and \( n \) of solute set free at the surface of the solution; the latter capture one another very promptly, just as they would do if present alone, and return to the solution, while the \( N \) solvent molecules pass on to the region of vapour. Thus equilibrium at the two surfaces will be maintained in the same manner, namely, when for every \( N + n \) molecules that leave either, \( N + n \) return; but in the case of the pure solvent the vapour has to return \( N + n \) molecules for every \( N \) returned by the vapour above the solution, that is to say, the vapour-pressure over the solution is to be less than that over the pure solvent in the ratio of \( N \) to \( N + n \), which of course is the fundamental experimental law whereby molecular masses are determined from lowering of vapour-pressure*.

[* An essentially similar explanation of the effect of dissolved substances in lowering the vapour-pressure of solvents was given by Mr. F. G. Donnan in this Magazine, vol. xxxiv. pp. 411-414 (1894).—Ed., Phil. Mag.]
Thus a direct molecular explanation of the molecular lowering of vapour-pressure in solutions is available, and might be made the starting-point of the molecular theory of solutions.

It may be urged against the theory here outlined that it makes no provision for the facts of the "dissociation" of salts in watery solution, so beautifully discovered by Arrhenius, and worked out so consistently by Ostwald and the other enthusiasts of the new Physical Chemistry; but it is easy to provide for the facts of dissociation by stipulating that the word molecule is to include any mass whose translational kinetic energy is on the average that of a molecule of a gas at the same temperature. The electrically charged ion, if it is really a separate kinetic entity, must, according to the kinetic theory, be a molecule under the above stipulation; and thus the requirements of the dissociation theory of watery solutions of salts are met. Of course we should expect such dissociated ions as Cl and Na to be very mobile, and to escape with ease from the surface of a solution of NaCl; but as soon as they get free from the liquid water which is the cause of their dissociation, they will combine with avidity to form NaCl, which then returns at once to the solution in the manner described above. Thus dissociation presents no difficulty in this connexion. Evidently the very marked dissociating power of water is associated with its generally exceptional character; if water were not exceptional, it ought to be a somewhat difficultly liquefiable gas, whereas its high molecular force constrains it to liquefy and so produce a dense aggregation of swiftly moving molecules; that these should tear apart the atoms of salts with their known electrical contrast is a strange but fruitful discovery in physical chemistry. Whatever the actual cause of the dissociating power of water may be, its existence has been established almost beyond cavil, and offers no difficulty in osmotic theory, as here presented.

Such interesting cases of association as those investigated by Prof. S. Pickering would, according to the theory above outlined, need to be treated, each on its own merits, as belonging to those exceptions which, accepted grudgingly at first, are ultimately found to afford the best opening into new regions of law.

Melbourne, Sept. 1897.