DEDUCTION OF THE MAGNITUDE OF THE OSMOTIC PRESSURE IN DILUTE SOLUTIONS ACCORDING TO THE KINETIC THEORY

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If the kinetic energy of the moving molecules of the dissolved substance is practically the only factor which determines the magnitude of the osmotic pressure in dilute solutions, and if besides it is known from experience that this pressure is equal to the gas pressure of a number of molecules equal to that of the dissolved substance and occupying at the same temperature a volume equal to that of the solution, it would appear that the theoretical deduction of the magnitude of the osmotic pressure should be a rather simple problem. I mean a deduction which is not based on thermodynamical reasoning,¹ but on the consideration of, to use the words of Nernst, the molecular forces and the molecular motion² involved. And yet the attempts made in this direction do not appear to have been successful. Nernst³ discusses those of Boltzmann,⁴ Riecke,⁵ and Lorentz,⁶ and considers them as rather provisional (*vorläufig*). Any way they seem to lack simplicity and persuasiveness.

In the following the present writer attempts a very simple theoretical deduction of the magnitude of the osmotic pressure in dilute solutions by a consideration of the individual factors and particular conditions concerned.

The magnitude of the osmotic pressure in dilute solutions being determined by the kinetic energy of the solute, our problem

¹ van't Hoff gave us a thermodynamical deduction (*Zeit. phys. Chem.* 1, 488) which, after the manner of such demonstrations, does not enter upon the nature of the osmotic pressure.

² *Theoretische Chemie*, Second Edition, 1898, p. 240.

³ *loc. cit.*

⁴ *Zeit. phys. Chem.* 6, 474 (1890); 7, 88 (1891).

⁵ *Ibid.* 6, 564.

⁶ *Ibid.* 7, 36.

would be solved if we were able to ascertain the mean kinetic energy of the molecules of the solute and the number of impacts which they produce in unit of time on unit of area of the semi-permeable wall.

The first question then is: How great is the molecular kinetic energy of the solute at a given temperature? Obviously it will depend on three things: 1st, on the molecular kinetic energy of the solvent; 2d, on the mutual attraction between the molecules of the solvent and the solute; and 3d, on the temperature. As to the first, after equilibrium is established between the solvent and solute, the molecules of either will give as much as take and, therefore, have the same kinetic energy. But how great will this common kinetic energy be? Let us consider what the molecular kinetic energy of the solvent would be if it were alone. In that case it would, we may safely assume, depend on the temperature and the mutual attractions of its molecules. It is easy to see that these mutual attractions cannot influence the velocity of the molecules. For each molecule of a liquid, except in the surface, while constantly tossed about, is in all its positions equally attracted in all directions by the surrounding molecules; and, therefore, the total effect of these attractions on its motion is the same as if there were none. Hence the molecular kinetic energy of a liquid will depend only on its temperature, just as in the case of gases, and be, we must conclude, equal to that of gases at the same temperature.¹

Thus the molecular kinetic energy of the solvent, before the addition of the solute, will have been equal to that of a gas at the same temperature.

As to the dissolved substance we cannot but assume that it will tend to develop a molecular kinetic energy also equal to that of a gas at the same temperature.

It follows that the solvent and the solute have to be considered as contributing to the solution equal molecular kinetic

¹ This conclusion is in entire harmony with the interpretation of the liquid state as deduced, on the hand of van der Waals's equation, from the fact of the mutual interconvertibility of the gaseous and liquid states.

energy. Moreover, this kinetic energy cannot be affected, for reasons similar to those given above, by the mutual attractions of the solvent and solute. Consequently the molecular kinetic energy of the dissolved substance is equal to that of a gas at the same temperature.¹

The second question is: How great is the number of impacts produced by the molecules of the solute in unit of time per unit of area of the semipermeable wall? At the first thought one is inclined to conclude that the number of impacts, owing to the presence of the solvent which retards the forward progress of the molecules of the solute, causing them to less frequently traverse the volume of the solution, will be less than that produced by an equal number of molecules moving with the same velocity in the absence of the solvent. But on reflection it is easy to see that this conclusion is erroneous. For if a given number of molecules are uniformly distributed in a given space — which in cases under consideration they always must be — and if they move with a given velocity, then the number of molecules passing a unit of time through unit of area of a mathematical plane within that space, will be the same regardless of the circumstance whether a liquid is present which retards their forward progress or not. The consequence of the presence of the liquid can merely be this that the molecules of the solvent will linger and be tossed about for a longer time in one and the same region.

Thus liquid or no liquid, the number of molecules passing through unit of area in unit of time and hence the number of impacts on unit of area of a wall within the containing vessel depends only on the number of molecules present and their velocity.

Having proved thus that the kinetic energy of the molecules of a solute in dilute solution is equal to that of a gas at the same temperature and that the number of impacts with the same kinetic energy depends only on concentration, regardless of the presence of the solvent, we have also proved that the os-

¹A conclusion shared by a number of authors.

motie pressure of a substance in dilute solution is equal to the corresponding gas pressure of that substance.¹

Appendix

Molecular kinetic energy of a liquid

By reversing the order of reasoning given above and starting with the magnitude of the osmotic pressure, as found by experiment, a new and perhaps more rigorous proof than those hitherto advanced, can be obtained that the kinetic energy of the molecules of a liquid is equal to that of a gas at the same temperature.

The osmotic pressure in dilute solution is, as the experiment shows, equal to the corresponding gas pressure. The osmotic pressure, like the gas pressure, is a product of the mean molecular kinetic energy and the number of molecular impacts in unit of time per unit of area. Since one of the factors — the number of impacts produced by a given number of molecules of the solute — is, as shown in the foregoing, independent of the presence of the solvent and is the same for the solute in solution as it would be for it in the gaseous state, then the other factor — the kinetic energy of the molecules of the solute in solution must also be equal to that of a gas at the same temperature.

Now the molecular kinetic energy of the solute is bound to be the same as that of the solvent. Hence the molecular kinetic energy of the solvent must also have been equal to that of a gas at the same temperature. This means that, in general, the kinetic energy of the molecules of a liquid is equal to that of gas molecules at the same temperature.²

¹ In the above deduction we had in mind only substances which do not dissociate in solution.

² Of the two factors of the known osmotic pressure one — the number of impacts — is known, whence the other factor — the molecular kinetic energy — becomes known. This deduction of the molecular kinetic energy of the solute is more than merely speculative. This feature renders my reasoning in this appendix essentially different from a speculation of Ostwald (*Allgem. Chemie*, 2d Edition, Vol. I., 699) to which it is similar in form and conclusion.