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we neglect in our formula the terms, which are multiplied by x by the side of those in which this is not the case, if we put $p_o = p_{coex.}$ and if we take v_{coex} instead of v_o, which is permissible for very dilute solutions we get:

$$P = p_o - p_{coex.} = -\frac{MRT}{v_{coex.}} log\left(1-x\right)$$

which gives the well-known formula of VAN 'T HOFF when the *log* is developed and the higher powers omitted.

I wish to point out, that also a more accurate treatment yields the logarithmic form which BOLDINGH and VAN LAAR have advocated — and there could not be any doubt but it must be so — but that it also shows that VAN LAAR's statement[1]) was too absolute when he asserted that a correction term need never be applied in the numerator $v_{coex.}$ (or v_o) in connection with the size of the molecules.

In the second place I draw attention to the fact that we find the osmotic pressure exclusively expressed in what VAN DER WAALS has called thermic quantities (in opposition to caloric quantities). It appears to be unnecessary to take into consideration the heat of dilution or other quantities of heat, which VAN 'T HOFF [2]) seems to deem necessary for concentrated solutions and which EWAN [3]) has taken into consideration. Even if we had avoided all the introduced neglections, so when we had not assumed, that the vapour follows the gaslaws, nor that $v_o = v_{c_1}$ may be put in some terms, nor that the area C may be neglected compared to A, nor (the most important) that b is constant, we should evidently not have had to deal with any quantity of heat. This seems important to me, as both theoretically and experimentally the caloric quantities are much less accessible than the thermic ones.

Physics. — "*Kinetic derivation of* VAN 'T HOFF'S *law for the osmotic pressure in a dilute solution.*" By Dr. PH. KOHNSTAMM. (Communicated by Prof. VAN DER WAALS).

§ 1. When we leave out of account the more intricate theories as that of POYNTING [4]), who tries to explain the osmotic pressure from an association of solvent and dissolved substance, and that of

[1]) l. c.

[2]) K. Svenska Vet. Ak. Hand. **21.** Quoted by EWAN Zsch. phys. Ch. **14** 409 en 410.

[3]) Zsch. phys. Ch. **14,** 409 en **31,** 22.

[4]) Phil. Mag. **42,** 289.

BACKLUND [1]), who seems [2]) to require even ether waves to explain it, chiefly two theories have been developed about the nature of the osmotic pressure: the static and the kinetic theory. The first theory finds warm advocates in PUPIN [3]) and BARMWATER [4]); it seems however doubtful to me whether they have closely realised the consequences of their assertions. At least the latter brings forward as an objection to the kinetic nature of the osmotic pressure: "Ein molekulares Bombardement in einer Flüssigkeit ist mir immer etwas sonderbar vorgekommen"; notwithstanding he considers the equation of state of VAN DER WAALS by no means as a "sonderbar" instance of false ingenuity, but as an example to be followed. However this may be, he who does not want to break with all our conceptions about heterogeneous equilibrium, will not be able to explain such an equilibrium in another way than statistically i. e. as a stationary condition of a great number of moving particles. This does, of course, not detract from the fact that the question may be put what forces are required to bring about that state of equilibrium. This implies that the adherents of the static theory need not be altogether mistaken when they assert that the cause of the osmotic pressure is to be found in forces of attraction. On this point I shall add a few remarks at the end of this communication.

§ 2. Of much more importance than this static theory of the osmotic pressure is the kinetic theory. The great majority of its advocates (I shall speak presently about the few exceptions) take as their basis the equality, which has been proved experimentally and by means of thermodynamics, of the osmotic pressure and the gas pressure (the pressure which the molecules of the dissolved substance in the same space would exercise, when they were there alone and in rarefied gas state) and derives from this that they have both the same cause in this sense that the dissolved substance is present in the two cases in the same state and so acts in the same way; this is then expressed in about this way that the solvent converts the dissolved substance into the rarefied gas state. This conception seems doubly remarkable to me; first because it seems to be pretty well generally prevailing [5]), secondly because it alone seems to me to be able to

[1]) Lunds Univ. Aarsskrit **40.**

[2]) I know his paper only from an abstract in the Beibl. **29,** 375.

[3]) Diss. Berlijn 1889.

[4]) Diss. Kopenhagen 1898 and Zsch. phys. Ch. **28,** 115.

[5]) It is naturally difficult to give a proof of this opinion, therefore I shall only adduce the following citations as a confirmation.

"If we look a little more closely into the matter, we find that in the case of dilute solutions, at least, there is far more likelihood of the dissolved substance

explain, why the theory of the osmotic pressure has become so quickly popular, whereas GIBBS' method for the solution of the same problems was scarcely noticed. In fact the view mentioned possesses all qualities required for great popularity: it seems to give a very simple, clearly illustrating explanation for the striking law discovered by VAN 'T HOFF; it is allied to the universally known gaslaws; it seems to make us acquainted in the osmotic pressure with a quantity, which is as characteristic for the dissolved state as the well-known external pressure for a gas. On the other hand it does not seem to carry weight that this "explanation" is, properly speaking, no more than an explanation of words, which leaves undecided exactly that which had to be explained, viz. how it is, that the solvent acts on the dissolved substance in this way. It is, however, worse that this explanation clashes with everything we know of liquids and gases, and therefore is to be rejected. We need only think of the well-known experiment with a bell jar, closed at the bottom by a membrane, filled with a solution of cane sugar and placed in a vessel with pure water, which forces its way in till equilibrium has been established. If now the pressure P, exerted on the membrane, was a consequence of the fact, that the dissolved substance in the bell jar was in a state which more or less resembles the gasstate, then those molecules of the dissolved substance would have to exert the same pressure also on the glass wall of the bell jar, in other words, the water molecules would exert the same pressure

being in a condition comparable with that of a gas." (WALKER, Introduction to Physical Chemistry, 148).

"Ich glaube dargethan zu haben — *im Gegensatz zu der zur Zeit allgemeinen Auffassung* — dass es nicht notwendig ist eine freie Bewegung der gelösten Moleküle wie für die Gase anzunehmen. Wenn ein fester Körper in einer Flüssigkeit gelöst, oder eine Flüssigkeit mit einer anderen gemengt wird, so wird eine neue Flüssigkeit erhalten, von deren Molekülen es nicht gestattet ist, andere Beweglichkeit anzunehmen, als diejenige, die Flüssigkeiten charakterisiert." (BARMWATER l. c. pag. 143). "Aus den klassischen Arbeiten von VAN 'T HOFF und ARRHENIUS geht nun hervor, dass die Körper bei Gegenwart von Lösungsmittel thatsächlich mehr oder minder dem Gaszustand näher gerückt werden," and a little before: "Andererseits konnte ich mir .... nicht verhehlen, dass gerade diese Gegenwart und Einwirkung des Lösungsmittels doch die notwendige Vorbedingung für den Eintritt des gasähnlichen Zustandes sei: .... daher ist aber ein gasähnlicher (also kinetischer) Zustand nur unter dieser Einwirkung vorhanden und hört sofort auf, sobald diese Einwirkung beseitigt ist. *Es sei betont, dass diese Auffassung durchaus nichts Neues bietet, dass sie vielmehr wohl einem Jeden eigen ist, der den Begriff des osmotischen Druckes kennen gelernt hat.*" BREDIG. l.c. p. 445 and 114). The italics are mine, the spacing the cited authors'.

Finally cf. VAN LAAR's address in the "Bataafsch Genootschap", p. 2 and 3 and the example cited there.

on that wall from the inside and from the outside (of 1 atm.). This now is a perfectly unacceptable result, as immediately appears from what follows. Let us imagine the same solution as in the bell jar inclosed in a cylinder with a piston under the pressure of its saturated vapour $p - \Delta p$, where Δp is the decrease of vapourpressure. The cane sugar molecules contribute nothing to that pressure or hardly anything [1]), as appears from the fact that they cannot pass into the vapour (at least not in a measurable degree); all the pressure is furnished by the water molecules. Now we compress the liquid, till it has got a pressure $P + p$, it is now in perfectly the same condition as the liquid in the bell jar, when we except the immediate neighbourhood of the membrane. On the supposition made just now the water molecules would exert a pressure p against the piston, the sugar molecules a pressure P, i. e. the pressure of the latter would have increased by an amount about 1000 times that of the former, whereas their initial pressure was at least a hundred thousand times smaller. And the result would be that the, let us say 2, sugar molecules, which are found to every 1000 water molecules would exert a pressure twice as great as the 1000 particles together. It is beyond doubt that the pressure $P + p$ on the piston or the glass wall of the bell jar is exclusively exerted by the watermolecules, and if he meant this, LOTHAR MEYER was certainly right when he asserted [2]), that the osmotic pressure was a result of the collisions of the solvent.

Also in this respect the theory of the gaslike character of the dissolved substance falls short, as it leaves perfectly unexplained why in an isolated solution, e.g. a cane sugar solution, which in a glass vessel stands under atmospheric pressure, nothing is perceived of the gaslike character of the dissolved substance. For that in this case solvent and dissolved substance are less closely in contact than in the osmotic experiment, cannot seriously be asserted.

§ 3. If therefore we must not seek the explanation of the laws of the osmotic pressure in a particular condition of matter, characteristic of dilute solutions, then the remarkable fact formulated by VAN 'T HOFF calls the more peremptorarily for an explanation.

Nobody less than LORENTZ and BOLTZMANN have made attemps to do this [2]), but even their endeavours do not seem to me to have solved the problem entirely. In saying this I agree with Prof. LORENTZ's own opinion, at the beginning of his paper he terms it a "freilich nur zum Teil gelungene Untersuchung". As to the reasons of this partial failure, however, I shall most likely differ in opinion with Prof. LORENTZ.

[1]) Perhaps the pressure of these molecules would even prove to be negative.

[2]) Zsch. Phys. Ch. 5, 23.

For what is the case? The behaviour of liquids is entirely dominated by the occurrence of the quantities a and b in the equation of state. Only matter in dilute solution seems to emancipate itself from it, according to the law of VAN 'T HOFF, where neither the a nor the b occurs. This fact calls for an explanation. Now it is not difficult to understand, why the a can disappear here; the membrane is bounded on one side by the solution, on the other side by the pure solvent. If we now think it thin compared to the extent of the sphere of action, then it is clear that at the membrane the force $\frac{a_x}{v_0^2}$ which works towards the solution, is in first approximation neutralized by the force $\frac{a}{v_g^2}$ towards the other side. It is more difficult to see why also the b vanishes, i. e. why the molecules of the dissolved substance seem to move as through a vacuum, instead of through a space, which is occupied for a very great part by the molecules of the solvent.

Just on this most important point Prof. LORENTZ's paper leaves us in the dark, for so far as I have been able to see. And it seems to me beyond doubt, that in the first place this is due to an inaccurate interpretation of the term "kinetic pressure". According to Prof. LORENTZ it is always equal to $^2/_3$ of the kinetic energy of the centres of gravity of the molecules which are found in the unity of volume. It is therefore independent of the volume of those molecules. Now this would only be a question of nomenclature, if not that kinetic pressure was also defined as the quantity of motion, carried through the unity of surface in the unity of time by the motion of the molecules; and that this quantity is dependent on the number of collisions and so on the volume of the molecules does not seem open to doubt to me after KORTEWEG's proof [3]). In agreement with this the kinetic pressure is represented in the equation of state by $MRT/v-b$. In consequence of his definition LORENTZ replaces this

[1]) Zsch. phys. Ch. **7**, 37 and Arch. Néerl. **25**, 107.

[2]) Zsch. phys. Ch. **6**, 474 and **7**, 88.

[3]) Verslagen Kon. Ak. Amst. (2) **10**, 363 and Arch. Néerl. **12**, 254. Compare also the simpler, perhaps even more convincing proof for one dimension in Nature **44**, 152. As the attentive reader will notice Prof. LORENTZ's proof (l. c. 39) does not take into account the collisions and the fact ensuing from them, that a quantity of motion skips a distance or moves with infinite velocity for a moment. And the admission of the validity of KORTEWEG's reasoning appears, as it seems to me, already from the fact, that Prof. LORENTZ has to assume for the solid bodies introduced by him, that they are immovable (l. c. 40) or of infinite mass (l. c. 42) which comes to the same thing in this case.

quantity by MRT/v, and so his paper cannot give any elucidation on the point which requires it most. But that notwithstanding we owe to LORENTZ's labour a considerable widening of our views, will as I hope, appear from the continuation of this communication.

Also BOLTZMANN's paper leaves us in the dark as to the question why the quantity b, which in other cases plays such an important part for liquids, seems to have no influence on the value of the osmotic pressure. In the equations, which he draws up, he never takes the size of the molecules into account [1]) and it does not appear why he does not do so. Further he stops at the result, that the osmotic pressure is equal to the sum of the pressures exercised by the two kinds of molecules, without discussing the part played by the different kinds. For these reasons I cannot see a satisfactory solution of our problem in BOLTZMANN's paper either.

§ 4. To arrive at a solution it seems in the first place necessary to give three definitions.

1st. Given a fluid. Placed in it a body of perfect elastic impermeable substance, which does not exert any attraction on the molecules of the fluid. The thickness of this body (or this surface) be infinitely small; let us suppose it to have an area of 1 cm². The "kinetic pressure" in that fluid is then the quantity of motion in unity of time transferred by the molecules of the fluid to this body (or obtained in the elastic collisions from this body).

2nd. In the second place I imagine a body [2]), which is distinguished

[1]) See specially l. c. 475 equation (4), which is evidently incorrect, when part of the cylindre is not open to the centres of the molecules, because it is occupied by distance spheres of other molecules.

[2]) That I assume that the body does not attract the molecules of the fluid, is for simplicity's sake, but it is not essential. If we imagine a wall, which *does* attract the fluid, more molecules will reach its surface (cf. the footnote p. 739) and hence will impart a greater quantity of motion to the wall. But on the other hand the particles of the surface will now be drawn into the fluid with an equally greater force. The elastic displacement of the particles of the surface of the solid wall, and with it (with sufficient elasticity) that of the layers lying under it, in other words the pressure which propagates in the solid body, and which would be measured with a manometer of any kind, will be perfectly the same in the two cases. If we wish to take also negative external pressures into account, we shall even have to give the definition by means of an attracting body, because in this case a non-attracting body would not even be reached by the molecules of the fluid. (Cf. the well-known fact that for the observation of the negative pressure strongly adhering walls are required). In this case the impulse of the attraction of the molecules is simply greater than the quantity of motion which they impart to the wall (and which may still be very great). the elastic displacement is therefore not from the fluid, but towards it.

Also in the case that we wish to take capillary layers into account, our definition

from the just mentioned body only by its being very thick compared to the sphere of action of the molecules. The quantity of motion transferred by this body per unity of time to the molecules, is called the "external pressure" in that fluid.

3nd. In the third place I place in the fluid (which I now suppose to be a mixture) a body, which is distinguished from that mentioned under 2 only by the fact that the molecules of one component (solvent) pass through it without any change in their velocity. I shall leave undiscussed here whether such a body can actually occur. The pressure to which this body is now subjected, and which might be measured e. g. by the elastic displacement of the particles of its surface, I call the "osmotic" pressure in that solution.

From these definitions it is already clear that in dilute solutions the osmotic pressure defined here must be of the order of the kinetic pressure exerted by the dissolved substance, and not of that of the external pressure. For these two differ, in that $\frac{a}{v^2}$ has disappeared for the kinetic pressure, and this will also be the case for the osmotic pressure defined here, as appears from the reasoning given above (§ 3). I shall further show, that in dilute solutions this osmotic pressure has the value indicated by the law of VAN 'T HOFF, and that in any case it is as great as the well known experimentally introduced and measurable osmotic pressure, i. e. the difference in external pressure of solution and pure solvent under the pressure of its own vapour in equilibrium through a semipermeable wall.

calls for fuller discussion. First of all this applies to what we have just now said, for just as for negative pressures so also in the capillary layer, as VAN DER WAALS has shown in his theory of capillarity, the attraction of the surrounding layers is a necessary condition for stable equilibrium. But further, as HULSHOFF has shown (These Proc. 8, 432 and Diss. Amsterdam 1900), the above defined quantity does not obey the law of PASCAL any more, because measured in the direction of the layer and perpendicular to it, it has a different value. In this case we might perhaps speak of a total external pressure, which might be split into an external fluid pressure and an external elastic pressure. The consideration of capillary layers round a free floating sphere, teaches us further, that the "external" in the name "external pressure" must not be understood in such a way, as might easily be done, viz. that the reactive force of this pressure, as it prevails in a certain point, would act in points outside the system in question, which would always be more or less arbitrary, as we may choose the limits of our system arbitrarily. The assertion: the external pressure is in a point of the fluid so great, comes simply to this, that *when I should place a strange body at that place, without altering the condition more than necessary* for this, this body would experience a pressure of such a value, and would suffer an elastic modification in form which corresponds to it, so differing in the capillary layer in different directions.

§ 5. For this proof I must refer to a formula of CLAUSIUS used by me already before [1]). Imagine a point which can freely move in a space W. CLAUSIUS [2]) shows — which is already plausible beforehand — that the number of collisions of this point per second against a wall of area S is proportional to S/W (the factor of proportion depends only on the velocity of the point).

Let us now consider a wall as defined under 2, and draw a plane parallel to that wall at a distance $^1/_2\ \sigma$ (σ is the diameter of the molecules, which we think spherical); this plane we call plane of impact, because the centre of a molecule, which strikes against the wall, lies in this plane. Now we apply CLAUSIUS' formula to this wall. In this we must allow for the fact that the centre of a molecule cannot move freely throughout the volume of the fluid; for within the distance spheres (spheres drawn round the centre of every molecule with a radius σ) it cannot come; instead of v we have therefore to put $v-2b$, when $2b$ [3]) is the volume of the distance spheres. Now the whole plane of impact, however, is not accessible to collisions either, part of it also falls within the distance spheres. In order to fix this part we draw two planes at distances h and $h+dh$ parallel to the plane of impact. We determine how many centres of molecules are found between them and what part of the plane of impact is within their distance sphere. In order to find what part of the plane of impact falls at all within distance spheres, we must integrate with respect to h between 0 and $^1/_2\ \sigma$. It appears then, that instead of S we must put $S(1-b/v)$ in the formula for the number of collisions against the wall, so that the pressure becomes proportional to

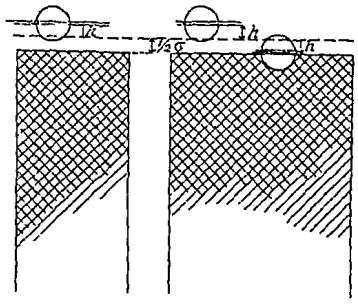

Fig. 1.

$$\frac{S\left(1-\frac{b}{v}\right)}{v-2b}$$

or in first approximation

[1]) These Proc. VI. 791.

[2]) Kinetische Theorie der Gase, 60.

[3]) For simplicity I confine myself to the first term, even if we have to deal with liquids; this is permissible here, because the other terms have no more influence on *our* question (the derivation of the law of VAN 'T HOFF) than the first.

$$\frac{S}{v-b}$$ [1])

§ 6. Now we apply the reasoning of the preceding paragraph to the collisions of the dissolved substance on a wall defined as under 3. We assume the solution to be so diluted, that the volume of the molecules of the dissolved substance may be neglected compared with the whole volume. For simplicity — though it is not essential to the proof — we assume now also that the molecules are spheres. Then here too the available space must again be put equal to $v-2b$; but the part of the plane of impact, accessible to collisions, is now different. For as the molecules of the solvent pass through the wall, their centres may now just as well be on the other side of the plane of impact. We have therefore not to integrate with respect to h from 0 to $^1/_2\,\sigma$, but from $-\,^1/_2\,\sigma$ to $+\,^1/_2\,\sigma$, which evidently yields the double value. The pressure on the wall becomes therefore proportional to

$$\frac{S(1-2b/v)}{v-2b} = \frac{S}{v}$$ [2])

so that the influence of the molecules of the solvent vanishes and VAN 'T HOFF's formula is proved for the quantity defined by us.

§ 7. That this quantity has further always the same value as the quantity which may be measured experimentally, is proved as follows. Let us think the action of the membrane in such a way that it suffers the molecules of the solvent to pass through freely, but repels those of the dissolved substance perfectly elastically. Something similar would take place when the membrane worked as a "molecule sieve", i.e. when the pores were such as to allow the molecules of the solvent (thought smaller) to pass, the others not. According to the definition the latter will then exert a pressure on the membrane equal to our osmotic pressure. The other molecules passing through the wall unmolested, there is no mutual action with the wall, and so they do not exert any force on it.

[1]) If one should object to the train of reasoning followed here, one can find in BOLTZMANN's "Gastheorie" a proof for this formula which intrinsically agrees perfectly with that given in this paper, but will appear stricter to some. There one will also find the above given integration carried out.

[2]) It is clear that we shall get the same result, when we do not take $2b$, but $f\,(b/v.)$ for the volume of the distance spheres. For as the place of the plane of impact with respect to the molecules of the solvent is quite arbitrary in our present case, the part of the plane of impact, which lies within the distance spheres will stand to the whole area in the same proportion as the volume of the distance spheres to the whole volume.

The experimentally measurable difference in pressure on either side of the membrane must therefore have the same value as the quantity defined by us.

LORENTZ [1]), however, has shown that the assumption made here concerning the membrane is by no means necessary. On the contrary; if we assume that the membrane is thick compared with the sphere of action, that its substance fills a volume large compared with the apertures present and that it feebly attracts the molecules of the dissolved substance, whereas these are strongly attracted by the solvent — none of which are improbable assumptions — we arrive at the result, that none of the dissolved particles reaches the membrane, much less exerts a pressure on it; the membrane is then quite surrounded by the pure solvent. And that this case is really the usual one in nature is made probable by the fact, that it is by no means always the smaller molecules which pass the membrane, as we assumed above. The membrane seems therefore not to work as a molecule-sieve. We are then easily led to suppose that the membrane does not exert a positive repulsion at all on the non-passing substance, but that it only attracts those particles much less strongly than the solvent, so that the dissolved particles do not pass through the membrane, because they occur but extremely rarely in its neighbourhood. This view is supported by the fact, that only those substances seem to be non-passing which are not easily converted to vapour, and so cannot reach the limits of the liquid in virtue of their own thermal motion alone.

However this be, also in this case our conclusion holds good. For when the molecules of the dissolved substance do not (or only in an infinitely small number) reach the membrane, two planes will be found not far from the membrane, A where the molecules of the dissolved substance still have their normal density, B where this density has diminished to zero. Between B and the membrane we find then pure solvent. If we wished to discuss such a layer fully, we should, of course, have to give a theory, as VAN DER WAALS has given for the transition liquid vapour [2]), extented to a mixture in the way VAN ELDIK [3]) has done. But for our purpose this is fortunately not necessary. We need only observe, that the layer AB as a whole has now exactly the same influence on the condition of motion of the dissolved molecules as the mathematical upper surface of the membrane had just now. The layer AB as a whole will now,

[1]) l. c.

[2]) Verh. dezer Ak. (2) **1**; Arch. Néerl. **28**, 121 and Zsch. phys. Ch. **13**, 657.

[3]) Diss. Leiden 1898.

just as the membrane just now, be pressed downward with a force equal to the osmotic pressure defined by us, and transfer this force to the underlying layer of the pure solvent, which is pressed outward with this force. But this pressing force is evidently equal to the difference in pressure which may be measured experimentally [1]).

§ 8. Thus it seems to me that VAN 'T HOFF's law for dilute solutions is kinetically explained in the same way as the law of BOYLE-GAY LUSSAC-AVOGADRO for dilute gases and that of VAN DER WAALS for liquids and gases, i.e. we have obtained an kinetic insight how these laws result from the condition of motion in the homogeneous mass, while we have left out of account what happens in the eventually (probably always) present unhomogeneous bounding layers.

It appears from the explanation convincingly, that VAN LAAR goes too far, when he states [2]), that we cannot speak of osmotic pressure in an isolated solution. Here too this notion has a clear physical signification, and the laws which govern it, are to be derived.

[1]) This hydrostatic proof may easily be replaced by a purely kinetic one, though the latter is somewhat more elaborate. The layer *AB*, which (in consequence of course of the neighbourhood of the membrane) behaves as a layer of water, through which the dissolved substance cannot penetrate (Cf. NERNST's well-known osmotic experiment) imparts to the molecules of the dissolved substance per second a quantity of motion equal to the osmotic pressure defined by us, and receives itself an equally large quantity in opposite sense, which it transfers to the underlying layers, as the kinetic theory teaches. (See e. g. BOLTZMANN, Zsch. phys. Ch. **6**, 480). Now the whole mass of water, which is in the neighbourhood of the membrane, (on either side, reckoned on one side from *B*, on the other from a plane, so far from the membrane that the latter does not act on it any more), does not move downward, so it must receive an equally strong but opposed impulse, which, of course, cannot issue from anything but the membrane. Of what nature the forces acting here are is quite unknown. It cannot be the ordinary molecular attraction, for then the denser liquid found above the membrane would probably be drawn more strongly downward than that found under it upward. We might think of friction in the pores, but it would then have to be different in one direction from that in the other; in short I dare not venture on any conjecture about this. This alone is certain, such forces must exist, at least if the case put by us ever actually occurs. This appears already from the fact that the pure solvent above the membrane is subjected to a higher pressure, so has a greater density than under it. Such an equilibrium occurs for all kinds of kinetic questions (liquid vapour, gas under the influence of gravity), but the necessary condition is always a force, which at a cursory examination seems to have the result, that the *velocity* of the molecules in one part (so the temperature) would be higher than in the other, but in reality only proves to have influence on the *density*. The membrane, which furnishes this impulse, receives an equally strong one back from the reaction, and so here too, though indirectly, we see a force equal to the osmotic pressure defined by us, exercised on the membrane from the inside to the outside.

[2]) Chem. Weekblad 1905, N⁰. 9, § 3. Voordracht Bat. Gen. 3.

Whether this renders it desirable for us to give it a prominent place in the theory of solutions and make all the rest proceed from it, is a question to which I wish to revert in a separate paper.

First I must add this observation. The insight obtained in the nature of the osmotic pressure enables us to examine what quantities must occur in the formula for more concentrated solutions. In the first place it will no longer be true for concentrated solutions, that the term a/v^2 vanishes, both because on the two sides of the membrane the density v differs, and because the concentration and so the a will differ. Further — as appears from our proof — for higher concentrations the volume of the molecules will assert its influence, and not only that of the dissolved substance, but also of the solvent. For as on the two sides of the membrane the density differs, the part of the plane of impact that falls within the distance spheres of these molecules, will no longer be represented by the above given value. As finally the molecules are of different size, when the terms b_1 and b_2 occur, the term b_{12} is sure to appear. The formula found in this way will certainly not agree with the one found in the preceding communication by a thermodynamic method, for the latter is derived from the equation of state with constant b, whereas the kinetic considerations exclude all doubt that b is a function of the volume. If there should be a real diminishing of the size of molecules when passing beyond the membrane, then this fact is also to be taken into account.

Far be it from me to make an attempt to draw up such an equation. To achieve this, it would be required, as appears from what precedes, that one should be able to surmount at least all the obstacles which stand in the way of an accurate equation of state. And if this might be done — the preceding paper proves it — the final formula could be found in a way, which would not expose us again to the danger of making errors. I shall therefore not enter into the question either, in what way the formula derived in a kinetic way can satisfy the first requirement that may be put to every formula for concentrated solutions: that it yields the value ∞ for the case that the substance passing the membrane has perfectly vanished from the solution.

§ 9. I shall just add a single remark on the question whether our kinetic view implies that the so-called static theory of the osmotic pressure, which ascribes the cause of the phenomenon to attractive forces, is entirely wrong? It seems to me that from what LORENTZ has proved it appears that we must answer this question in the negative. It is true that we have seen that the attraction of solvent

and dissolved substance begins to play a part only in sensibly concentrated solutions, and that we have to explain the osmotic pressure by a "moleculares Bombardement". But the case treated by LORENTZ shows that the whole osmotic phenomenon might possibly exclusively be the consequence, not so much of the presence of attractive forces, but just of the reverse, of the want of attraction between the molecules of most solid substances and certain other solid substances which form membranes. If the adherents of the static theory mean no more than this with their assertion: that the osmotic pressure must be explained from forces of attraction, then they seem to me for the present secured against every attack.

Physics. — *"Osmotic pressure or thermodynamic potential"*. By Dr. PH. KOHNSTAMM. (Communicated by Prof. J. D. VAN DER WAALS).

§ 1. The theory of thermodynamic functions, through which GIBBS has enabled us to derive from the equation of state of a system in homogeneous condition, what heterogeneous equilibria will occur, has attracted attention only in a very limited circle during a series of years. However great the region opened for investigation by GIBBS was, the methods indicated by him seemed so abstract, that only very few dared to grapple with them. At a stroke this was changed, when in 1885 VAN 'T HOFF succeeded in replacing these methods in appearance so abstract, by another, that of the osmotic pressure, which strongly appeals to the imagination. The theory of solutions, which up to that time had only existed for a few, rapidly became one of the most frequently treated and discussed subjects of physics and chemistry; since then it has continued to enjoy undivided attention.

It stands to reason, that the attention, which now for twenty years has been so lavishly granted to the questions of heterogeneous equilibrium, have also been conducive to making GIBBS' methods for the solution of such questions known in a wider circle. But though GIBBS' name may be counted among the most famous and widely known names in the sciences of physics and chemistry, yet even now his methods cannot be said to have been universally accepted.

The adherent of a mechanical (or, if one prefers, statistical) natural philosophy has by no means reason exclusively to regret this course of affairs, for he sees in it a clear indication, that the views whose truth he advocates, are by no means so antiquated, nay even dead,