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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,

as they are often declared to be. And if the current opinion — which certainly greatly contributes to the greater popularity of the osmotic pressure compared with that of the thermodynamic potential — were really correct, that we can form a clear idea of the physical meaning of the first quantity and *not* of the second, then there could not be any doubt for him which method to prefer, if for the rest the circumstances were quite the same.

But this current opinion seems to me hardly tenable and on the other hand I believe that in many respect the thermodynamical potential is preferable to the osmotic pressure, and that therefore it will be advisable to put the question whether it would not be better to return to the older method both for scientific investigation and for instruction?

§ 2. This question has lately again been put forward by Mr. VAN LAAR in an address for the “Bataafsch Genootschap” at Rotterdam¹⁾, which was followed by an article “Over tastbare en ontastbare grootheden” (On palpable and impalpable quantities)²⁾. Though I readily admit, that these papers have induced me to consider the problem of the osmotic pressure specially, there would not be any reason for me to discuss Mr. VAN LAAR’s views here, when only his address had appeared. For I can fully subscribe to the general tendency of this paper though of course I would not be responsible for every statement, as moreover has already appeared from my preceding communications in these Proceedings — and I should therefore only have to consider what in my opinion would have to be added to his address. His second paper, however — and in this I have specially in view § § 6 and 7, pointed out as the gist of his paper by the author himself — Mr. VAN LAAR seems to me to harm rather than to promote the good cause, which he has espoused with so much ardour, and already for this reason I feel it incumbent upon me to protest against this part of his reasoning. I think that I accurately represent the gist of it as follows: It is true that we cannot form a clear idea³⁾ of the nature of the thermodynamic potential, but we cannot do so for the osmotic pressure either. Nor is this surprising, for the improved philosophical insight of the last years gives us the conviction that our natural philosophy never works with any but fictitious (though sharply defined) ideas,

¹⁾ Also published in Chem. Weekblad, 1905, N^o. 1.

²⁾ Chem. Weekblad, 1905, N^o. 9.

³⁾ Mr. VAN LAAR speaks of a “palpable conception” (tastbaar begrip). It would lead me too far if I would account for the reason why I think that I may, nay even ought to substitute the term chosen here for it.

which must not and cannot claim in the least to represent the real nature of things. It is also owing to this insight, that several voices have been raised of late in favour of the use of the thermodynamical potential.

§ 3. Now I think that I have convincingly proved the incorrectness of the second thesis in the preceding paper, and as I gladly and with full conviction range myself with the "tastbaarheidsmensen," (those who want to form a clear idea of the physical meaning of each term used), whose opinion Mr. VAN LAAR severely condemns, his reasoning would lead me to take side against the thermodynamic potential party when I could subscribe to his first and his last thesis more than to his second. This however, is by no means the case.

The last philosophical-historical thesis I can, naturally, not discuss here and I confine myself therefore to that concerning the physical meaning of the thermodynamical potential. It seems to me that we can form an idea of this quantity which need not be inferior to that of any other statistical quantity. That Mr. VAN LAAR has overlooked this fact seems chiefly owing to two circumstances of which it may appear that one can have hardly any influence, for it is simply a question of nomenclature. Following a common way of speaking, which does not seem to me the less reprehensible for the fact that it is of frequent occurrence, Mr. VAN LAAR does not give the name of "thermodynamical potential" to the quantity introduced by GIBBS into science by that name, but to one of the other functions introduced by GIBBS, the ζ -function. There are more reasons than only a feeling of deference, which make this undesirable. The real (GIBBS') potential *is* really a potential, i. e. it is constant in a space where equilibrium prevails, and its not being constant means, that there is no equilibrium. At least when there act no capillary or external forces; and in this case the resemblance of the thermodynamic potential with the potentials of other energies stands out perhaps the more clearly. For in this case we need only add to the (GIBBS') thermodynamic potential the other potentials, which exist in that space in order to get a quantity, the total potential, which now also is constant throughout the space in case of equilibrium. The ζ -function has neither the one property, nor the other, except when we have to deal with a simple substance without capillary layers, in which case it becomes identical with the thermodynamic potential.

If now also in §§ 6 and 7 Mr. VAN LAAR had directed his attention instead of to the ζ -function, to the real potential, as he has done in § 4, where he carries out his calculations by means of it, it would probably not have escaped his notice that he wrongly represents the

thermodynamic potential (whether it be in one sense or in the other) as the last, most fundamental quantity, which determines the internal condition of a body. As such we cannot take others than v and T (if necessary of course x , y , etc.); that this is not only a subjective "point of view" appears perhaps most clearly from the study of the theory of capillarity, as VAN DER WAALS has given it.

§ 4. From this follows naturally, that we must try to form an idea on the relation between the thermodynamic functions and these fundamental quantities, and this does not seem so very difficult to me just with regard to the thermodynamic potential. Let us only consider the following. Thermodynamics teach, that however composite the equilibrium may be, the total potential of every component must be the same in two phases which are in equilibrium; the kinetic theory, or in plain language, common sense that in all those cases equilibrium is only possible when an equal number of particles of each substance passes from the first phase into the second phase and vice versa. Now VAN DER WAALS has shown ¹⁾ that in the case of equilibrium of vapour and liquid, whether in a simple substance or a binary mixture, the two conditions are simply the same fact stated in different terms. It does not seem hazardous to me nor jumping to conclusions to conclude from this that these two conditions, which are always at the same time fulfilled or not fulfilled, also in other cases will agree in signification and that therefore the physical meaning of the thermodynamic potential ²⁾ of an homogeneous phase, on which no external forces act, is nothing but the number of particles which per second reach a wall as defined in the preceding communication § 4 under 2, if this wall is thought in the midst of that homogeneous phase.

¹⁾ Verslagen Kon. Akad. Amsterdam (4) 3, 205 and Arch. Néerl. 30, 137.

²⁾ I choose purposely the words "that the physical meaning of etc." and not "that the thermodynamic potential is equal to etc." For the equality of the two quantities would require an "absolute" scale of thermodynamic potential. For from the equality of the conditions mentioned follows only:

$$M\mu = F(N) + C. \dots \dots \dots (1)$$

where F is such a function, that $M\mu$ is a one-valued function of N and reversely N of $M\mu$. This however, is not of material influence, for formula (1) expresses only, that we begin to count the thermodynamic potential from another point than the number of particles (which agrees with the fact that our thermodynamic potentials always include an undetermined constant) and that we make use of another unity when measuring one quantity than when measuring the other. There is therefore perfect concordance of our case and that of the temperature measured e.g. according to Celsius and certainly nobody will object to the statement, also when he thinks of this temperature scale, that the physical meaning of the temperature is the mean vis viva of the centres of gravity of the molecules.

Yet this definition requires some further elucidation, because the number of molecules under consideration reaches a bounding plane of the phase, which does not exercise any attraction on those particles, whereas on the particles discussed above and whose number has been calculated by VAN DER WAALS, viz. those which pass from the one phase into the other, a force *does* work directed to the other phase. But this difference is in my opinion, only apparent. Also in the equations arrived at by VAN DER WAALS, one member refers exclusively to one phase, the other to the second phase; there are no terms in them consisting of factors, one of which refers to the first phase, another to the second. That we had to arrive at that result, may be easily understood, for the thermodynamic potentials themselves refer either to the one or to the other phase and are quite determined by the condition of that phase.

That at least in the definition of the thermodynamical potential one number may be put instead of the other, appears as follows. Let us consider a liquid in equilibrium with its vapour. The number of particles that now passes, per unit of area, through the bounding layer is that which VAN DER WAALS treats of; let us now place on this liquid a layer of a substance which does not attract the molecules; let this layer be thick with respect to the spheres of action and provided with narrow channels. The number of particles that penetrates into these channels on either side is the number, which we used in our definition. Now I assert that the introduction of this layer cannot disturb the equilibrium of the homogeneous phases¹⁾, i.e. their pressure and concentrations will not change. For if this had been the case we should have been able to construct with the aid of such a layer a so-called perpetuum mobile of the second kind, and should have come in conflict with the second law of the theory of heat. From this follows that equality of the number

¹⁾ The equilibrium in the non-homogeneous, capillary layer is disturbed by introducing such a wall. For, as VAN DER WAALS has shown (cf. the footnote p. 735) the equilibrium in a plane of such a layer is only stable in consequence of the attractive forces exercised by the surroundings. When introducing the solid layer in question the condition in the transition layers will be considerably modified, which might also be anticipated. This does not affect our reasoning, for by the word "homogeneous" we have positively excluded these transition layers in our definition. That this was necessary in any case appears already from the fact, to which we have already called attention above, that the thermodynamic potential for such layers is no longer the quantity which determines the equilibrium, but that it is replaced by the total potential. We must therefore certainly not have recourse to such layers, in order to get acquainted with the thermodynamic potential in its simplest signification.

meant by VAN DER WAALS implies equality of that used by us in the definition, and that we may therefore substitute the latter for the former in the definition of the thermodynamic potential.

§ 5. In this way we have obtained a clear idea of the nature of the thermodynamic potential, which so far as I can see is in no respect second to that of temperature, external pressure, kinetic pressure, number of collisions, mean length of path etc. That for all this it is not always easy to derive in a special case the value of the thermodynamic potential from this kinetic meaning is self-evident, as well as that it will possibly always be more desirable to derive the thermodynamic potential by means of thermodynamic functions than from direct kinetic considerations. It is true that we do not avoid the latter in this way either, but we make use of the result of these considerations, as it is given in the equation of state. In these two respects, however, the thermodynamic potential is in no way inferior to the osmotic pressure, as appears from my two preceding communications, specially from § 8 of the second.

§ 6. Mr. VAN LAAR informs us, that in connection with his address he had been asked "to supply something as a substitute" for the osmotic pressure and the kinetic conception of it, something that "conveys some meaning".¹⁾ This request seems by no means so unreasonable to me as it seemed to Mr. VAN LAAR and I think that I have complied with it in the preceding pages. Now I may be allowed to prove that this "something else" is at the same time "something better".

First of all it seems not very appropriate to me to give a quantity of pressure such a prominent place in the theory of mixtures. As soon as we deal with this theory in general, i. e., include also external forces and capillary phenomena (which are very often of great importance, I need only mention critical points) it appears, that the pressure is a quantity we may only handle with great caution and which may certainly not be treated as fundamental variable.²⁾ In a much higher degree this objection holds for the osmotic pressure. For this is, as we have seen, not a quantity which is characteristic for the state in which the solution is; the peculiar laws of the osmotic pressure are not due to the fact that matter in dilute solution is in a particular, peculiar condition, they originate — in their generality — only from our arbitrariness, which by means of fictitious ideas, calls peculiar conditions into existence on paper, which never exist in reality. For let us not close our eyes to this

¹⁾ Chem. Weekblad 1905 No. 9, § 3. The inverted commas are Mr. VAN LAAR'S.

²⁾ Cf. the footnote on p. 735.

undeniable fact — and least of all should they do so who are so averse to “hypotheses” — that though all those semipermeable walls may be realised in a few cases, yet we have on the other hand thousands and thousands of cases, where we have not the slightest foundation for belief in their existence. What reason can there be for assuming, that there will ever be found a wall permeable to toluol, but not to benzol, and another wall, permeable to benzol and not to toluol, and what else is it but a fiction to speak of a wall, permeable to cane-sugar and not to water. (For also this is necessary, see VAN 'T HOFF, Vorlesungen II, 24). And let us even put the most favourable case: that such walls existed really, does it not remain perfect fiction then to try and treat the theory of concentrated solutions with them? We need only bear in mind that steel, our strongest material, however thick it is taken, can hardly bear pressures above 5000 atms, what to think then of a semipermeable wall for which such a pressure is but a trifle. And now I do not in the least object to such fictitious ideas when they are quite unavoidable — this is sufficiently proved by what precedes — but what is the use of using them, when we have another quantity of simple signification, which *is* characteristic of the condition in which the mixture is, which can be defined solely from the properties of the substance with which we have to deal?

To this comes another difficulty. He who works with the osmotic pressure — history teaches it — is but too apt to consider a mixture not as an individual, which must be examined in itself and must be known from itself, but as another substance (solvent), more or less modified by the presence of the “dissolved substance”. In this way we lose quite sight of the fact, that the two components in a mixture are present in exactly the same condition (the singular theory of the “gaslike nature” of the dissolved substance proves it): we begin to overlook, that “dissolved substance” and “solvent” are perfectly arbitrary names, which have only a right to existence when we confine ourselves to one of the two extreme cases; we are led to try and explain the properties of a substance from those of another, which is often in quite different circumstances; we begin to apply all kinds of hazardous approximations and compromises; we get to the most extraordinary association and dissociation theories. How fruitful on the contrary the opposite method is, the whole work of VAN DER WAALS, the experimental and theoretic material (inter alia on the behaviour of mixtures with respect to the law of corresponding states) gathered specially at Leiden may prove.

§ 7. Now one may object to this, that all these are theoretical

objections of more or less value, but that they are outweighed by the practical advantage that calculations with the osmotic pressure are so much simpler than with the thermodynamic potential, but this objection lacks all foundation. For kinetic calculation cannot be meant in this, and for the thermodynamic calculation it holds on the contrary, that when making use of the thermodynamic potential we need not take one step, which we are not obliged to take in exactly the same way when making use of the osmotic pressure. In order to prove this, I should like to reprint and follow step by step the proof given by VAN 'T HOFF in his Vorlesungen, but as this proof — carefully selected by VAN 'T HOFF from considerations partly from himself, partly from Lord RAYLEIGH, partly from Dr. DONNAN, so undoubtedly the finest and simplest to be found — covers two pages in print, I shall only indicate the principal operations and put in juxtaposition the operations, which are required for the thermodynamic potential with the same neglects.

1. Remove from a solution of osmotic pressure P a quantity of solvent, occupying a volume v . The substance yields an amount of work \underline{Pv} .

2. Neglect the change in vapour tension and the contraction of the solution. (This is not expressly stated, but is evidently necessary for the proof).

3. Let the quantity of dissolved substance, dissolved in v , evaporate osmotically; let its volume be V , the work done is:

$$\underline{pV}$$

(when we neglect v by the side of V).

1. The thermodynamic potential is:

$$M\mu = pv + \int_{v_0}^v p dv + MRT \ln(1-x) + F(T) + \int_{v_0}^v \left(\frac{\partial p}{\partial r} \right)_{vT} dv$$

pv becomes here $\underline{p_0 v_0}$.

2. Neglect the variability of p with x and the compressibility of the liquid, then

$$\int_{v_0}^v \left(\frac{\partial p}{\partial x} \right) dv = 0 \quad \text{en} \quad \int_{v_0}^{v_{c_1}} p dv = 0.$$

3.

$$\int_{v_{c_1}}^{v_{c_2}} p dv = \underline{p_c (v_{c_2} - v_{c_1})}$$

4. Let the vapour expand to infinite volume, the work done is:

$$\int_V^\infty p dv = \underline{MRTl \frac{V_\infty}{V}}$$

4.

$$\int_{v_{c_2}}^i p dv = \underline{MRTl \frac{\gamma}{v_{c_2}}}$$

5. Now press the vapour again into the solution, then a work is done by the substance:

$$-\int_V^\infty p dv = -\underline{MRTl \frac{V_\infty}{V}}$$

5. The thermodynamic potential of pure water is:

$$M\mu = pv + \int_{v_g}^i p dv + F(T)$$

$$\int_{v_g}^{\gamma} p dv = \underline{MRTl \frac{\gamma}{v_{c_2}}}; \quad pv = \underline{p_c v_{c_2}}$$

6. The total quantity of work must be zero, so:

$$Pv = pV$$

which in spite of the different notation is the same, when $\log(1-x)$ is replaced by $-x$.

6. The two potentials are the same, so:

$$(p_0 - p_c) v_{c_1} = -MRTl(1-x)$$

So it is seen that to every integration on the right corresponds an operation on the left of exactly the same nature, though it does not always refer to the same substance. The only difference is that on the right the integration is carried out directly and that on the left pistons and membranes are worked with. Now I do not think that any one can easily set greater store by a clear physical meaning of operations than I do, but that we should not be able to carry out an integration along an isotherm without bringing in two pistons and three membranes, seems rather too much of a good thing.

§ 8. And now we have considered the most favourable case: dilute solutions; how is it with more concentrated ones? It will certainly be possible to devise also for them cycles so that the calculations introduced in my first paper may be carried out without mentioning the name: "thermodynamic potential", but it will not be found possible by a thermodynamic method to draw up a formula for the osmotic pressure without determining the integrals occurring in it.

In this way it would seem as if the two methods were essentially the same; it is not so, the osmotic pressure method has drawbacks, of which the other is free. For what is it that we really wish to learn by the two different methods? Not the osmotic pressure itself, and the properties of the solutions under that pressure, that is for concentrated solutions: in sensibly compressed state. What we

aim at are the properties of solutions under the pressure of their saturated vapour: lowering of the freezing point and the vapour tension, rise of the boiling point and coefficient of division or more accurately (cf § 6 above) freezing point, boiling point, vapour tension of the mixture and the concentration of coexisting phases. And this does not only apply to physicists and chemists, who rarely if ever work with membranes, but also to biologists, to whom they are of the greatest importance. For differences in pressure of about ten atmospheres will probably hardly ever occur in biologic experiments and a fortiori not in the living organism either. The equilibrium between two solutions will therefore never be established by difference in *pressure*, but by the difference in *concentration* required to make the pressure equal. So we have not to deal here either with compressed solutions. ¹⁾

For the calculation this implies that when making use of the thermodynamic potential we need extend the integration along the isotherm only to the pressure p_c and the thermodynamic potential may then be determined with sufficient approximation from the well-known formula for the vapour pressure:

$$-\log \frac{p_c}{p_k} = f \left(\frac{T_k}{T} - 1 \right)$$

though it be with the factor 7 determined experimentally instead of the value 4 found theoretically. But if the osmotic pressure is used we can naturally not do without the integration up to p_0 (in the term $\int \frac{\partial p}{\partial x} dv$) and it is exactly this part of the isotherm which is known the least, where e. g. the variability of b is felt strongest, even the only term, on which it has influence when the just mentioned formula for the vapour pressure is used. Quite unnecessarily therefore the result is made less reliable by the introduction of the osmotic pressure.

And supposed even that we had found the desired expression, of what use could it be to us? It is true that the quantities, which we really wish to know and which I mentioned before, are con-

¹⁾ For this reason hardly anything would be lost when in the discussion of really osmotic questions it was made a rule to treat them without "osmotic pressure" and simply to introduce the concentrations on either side of the wall; whereas in this way there would be a great gain in lucidity of expression, witness the example cited by Mr. VAN LAAR (l.c. § 5). For the interpretation given there may be correct or incorrect, it can hardly be denied that the cited phrases may be easily misunderstood in the sense of the well-known question of PURIN, which has so repeatedly been seriously discussed, how e. g. a CaCl_2 solution of no less than 53 atms. osmotic pressure could be kept in a thin glass vessel without making it burst asunder!

nected in a simple way with the osmotic pressure in dilute solutions, but we have not a single reason to assume this also for concentrated solutions, or rather we may state with almost perfect certainty that this will not be the case. How on the other hand those quantities may be determined with the aid of the thermodynamic potential, VAN DER WAALS taught us already fifteen years ago.

§ 9. And let us finally not forget that though solutions of non-volatile substances at low temperatures *do* play an important part in nature, yet they are not the *only* substances which exist, nor the only ones which deserve scientific consideration. And yet, the theory of the osmotic pressure must necessarily be confined to them. One is so accustomed to derive the laws of the rise of the boiling point and the decrease of the vapour tension from the osmotic pressure, but it is generally forgotten, that many mixtures have on the contrary lowering of the boiling point and rise of the vapour tension ¹⁾, and that at any rate if the dissolved substance is but in the least volatile, the changes in boiling point and vapour tension cannot be derived any more from the osmotic pressure. And it is obvious why. It is inherent in every definition of the osmotic pressure, that it can only be applied to those cases, in which one component may be separated from the mixture in pure condition, as NERNST has clearly stated for the first time. Hence this does not only exclude the whole region of higher temperatures, at which all substances become more or less volatile, but also all cases of not perfect separation in the liquid or solid state. Also the lowering of the freezing point is touched by this objection. It is true that the lowering of the freezing point may be computed from the osmotic pressure, but only when, as in water and sugar, the solid substance, which deposits, is not of variable composition. Solid solutions and mixed crystals, which attract at present so much attention in chemistry, cannot be treated in this way.

Physical chemistry in its present state reminds us strongly with regard to its quantitative part, of the navigation of a people, which does not yet know the compass. The coasting-trade is carried on with great vigour, the same limited region is traversed again and again; but they do not dare to venture on the main sea far from the coast, and with reason, for great is the danger of ruin in the towering waves of random hypotheses. This can only be remedied by a trustworthy compass. Physical chemistry may obtain it if it will abandon the method of the osmotic pressure and adopt that of the thermodynamic potential in connection with a well-grounded equation of state.

¹⁾ Cf. Théorie Moléculaire § 17.