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**Physics.** — “*Some remarks on Dr. PH. KOHNSTAMM's last papers.*”

By J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

1. With interest and full approval I read Dr. KOHNSTAMM's three papers on the osmotic pressure<sup>1)</sup>. From them it appeared to me that, practically, he perfectly agreed with me. Only with regard to a few points there are differences of opinion — only *in appearance*, however, as I shall show in what follows.

On pages 723—729 l. c., namely, KOHNSTAMM gives also a *thermodynamic* derivation of the osmotic pressure, which seems to lead to a somewhat different result from mine. He finds, namely, in the numerator finally the quantity  $v_x - x \frac{db}{dx}$  instead of  $v_0$ . [I use here my notation;  $v_0$  is the molecular volume of the pure solvent (KOHNSTAMM's  $v_0$ ),  $v_x$  that of the solution, in which the dissolved substance is present with a concentration  $x$  (K.'s  $v_0$ )]. But here he overlooks that according to his approximations  $v_0$  may be written for the latter. For on page 726 an integral is neglected, among others on the strength of the fact that  $v_x - b$  approaches to 0. He puts therefore  $v_x = b$ , in consequence of which  $v_x - x \frac{db}{dx} = b - x \frac{db}{dx} = b - x(b_2 - b_1) = b_1$ . This however, is the value of  $b$  or  $v$ , when  $x = 0$ , so  $v_0$ .

So KOHNSTAMM finds exactly the same thing as I found already in 1894 in a much simpler way. In my method no integral need be split into three parts, and we need not neglect anything but the compressibility of the liquid (which is of course also done by KOHNSTAMM), so that my result (the compressibility excepted) is *perfectly accurate*, which cannot be said of that of KOHNSTAMM.

2. The above mentioned method has been repeatedly published by me. [Z. f. Ph. Ch. XV, 1894; Arch. Teyler (Théorie générale), 1898; Lehrbuch der math. Chemie, 1901; Arch. Teyler (Quelques remarques sur la théorie des solutions non-diluées), 1903; and recently in the “Chemisch Weekblad”, 1905, N<sup>o</sup>. 9]. The derivation may follow here once more.

If there is namely, equilibrium between the solution with the concentration  $x$  under a pressure  $p$ , with the pure solvent with a concentration 0 under the *arbitrary* pressure  $p_0$  (e.g. that of the saturated vapour, or of the atmosphere etc.), the molecular potentials

<sup>1)</sup> These Proc. VII, 723—751.

of the solvent in the two liquid phases (separated by a semipermeable membrane only passable by the solvent) are the same. Hence:

$$\mu(0, p_0) = \mu(x, p) \dots \dots \dots (1)$$

But evidently we have the identity

$$\mu(0, p_0) = \mu(0, p) - \int_{p_0}^p \frac{\partial \mu_0}{\partial p} dp.$$

Here  $\frac{\partial \mu_0}{\partial p} = v_0$  (for meaning of  $v_0$ , see §1). So we have also:

$$\mu(0, p_0) = \mu(0, p) - \int_{p_0}^p v_0 dp.$$

If we now assume  $v_0$  to be *independent of the pressure* — which KOHNSTAMM thinks perfectly permissible — we get:

$$\mu(0, p_0) = \mu(0, p) - v_0(p - p_0).$$

Substituting this in (1), we get at once:

$$\pi = p - p_0 = \frac{1}{v_0} (\mu_0 - \mu_x)_p, \dots \dots \dots (2)$$

by which the osmotic pressure is immediately brought into connection with the difference of the molecular potentials of the pure solvent and of that in the solution, *both under the same pressure p*.

Now we can in the usual way replace  $\mu_0 - \mu_x$  by its value. We find then, as has been frequently derived:

$$- RT \log(1 - x) - \frac{\alpha x^2}{(1 + rx)^2} + RT \log \frac{v_x - b}{v_0 - b_1} \text{ etc.}$$

in which the latter terms is often neglected, and  $\alpha$  and  $r$  have the known meaning.

In this way the apparent deviation with regard to  $v_0$  has been disproved. My statement, therefore, that in the numerator for  $v_0$  no correction term need be applied (see KOHNSTAMM, p. 729), was by no means "too absolute".

3. When reading through KOHNSTAMM's paper, I was further struck by the following in my opinion inaccurate assertions.

On p. 739 it says: "It appears from the explanation convincingly, that VAN LAAR goes too far, when he states, that we cannot speak of osmotic pressure in an *isolated* solution."

I fully maintain this view. For in the kinetic explanation of

KOHNSTAMM the osmotic pressure in an isolated solution is established, *only when* he places semi-permeable walls or planes in it. But then it is of course no isolated solution any more! What I demonstrate is no more than this: Without semipermeable membrane no osmotic pressure. And to this KOHNSTAMM will certainly not have any objection, witness the cited question of PUPIN how it is possible, that e. g. a  $\text{CaCl}_2$ -solution of no less than 53 atm. could be held in a thin glass vessel without bursting it! I do not see very well, what objection KOHNSTAMM can have to my assertion. For this is the *core* of the question, with regard to which he proves to be quite of my opinion in another place (cf. p. 742).

4. What KOHNSTAMM further observes on pages 742—4 with regard to the idea “thermodynamic potential”, and what he says on “palpable conceptions” may be very well left undiscussed here. For this is only a question of words, which does not affect the real nature of the affair at all. Every one who works with the thermodynamic potential, means with it the  $\zeta$ -function of GIBBS, which perfectly determines the condition of equilibrium, as it must be *minimum* in this case.

Finally I may only be allowed to point out that Dr. KOHNSTAMM has evidently misunderstood me, where he says that he thinks the request to supply something “as a substitute” for the osmotic pressure and the kinetic conception of it less unreasonable than it seems to *me* (p. 746).

I, namely, spoke of the osmotic pressure in an *isolated* solution. And I very distinctly added: nothing can be put in the place for what *does not exist*. And I wrote further, that the *usual* (faulty) *kinetic* conception of the osmotic pressure (i. e. where there are semi-permeable membranes) must be replaced by a perfectly new kinetic explanation, in which inter alia, the process of diffusion at the membrane is put more into the foreground (Ch. Weekbl., 1905, N<sup>o</sup>. 9).

And where KOHNSTAMM himself has made a very laudable attempt in this direction (l. c. p. 729—741) to explain the osmotic pressure, I have after all reasons for satisfaction, though he has wisely abandoned the idea of drawing up an equation for non-diluted solutions in *this* way.

And as to the *thermodynamic* derivation, in this KOHNSTAMM has been less fortunate in my opinion; where he has tried to substitute for my perfectly exact, and yet so simple derivation an indirect, elaborate derivation, the result of which on account of some neglects cannot even lay claim to perfect accuracy.