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the solid condition at least double molecules occur The difference between α- and β-cinnamic acid might then have its origin in the manner in which the single molecules are placed in the double molecule.

The difference between these two assumptions consists in this that the first admits of a difference in the solid condition only, whereas the second renders possible a difference for the solution also.

A further investigation will have to decide which representation is in harmony with the facts. I hope to revert to this in detail, shortly.

Physics. — "*Some Remarks on the Osmotic Pressure*". By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of May 29, 1915).

With much interest I read Prof. EHRENFEST's paper [in the Proceedings of this Academy (April 1915)] on the kinetic interpretation of the osmotic pressure.

However, I can concur neither with the deeper ground of his interesting considerations, nor with the "Remarks" that are added to them, which in some respect may be considered as resulting from the foregoing considerations.

Prof. EHRENFEST knows that I feel a special interest in the osmotic pressure and its correct interpretation, so that he will no doubt excuse me if I once more return to it.

I will therefore briefly summarize my objections, already set forth in different papers[1]), in a number of Theses.

THESIS I. The results of a kinetic theory must necessarily be in accordance with the established results of Thermodynamics.

If the results of the kinetic theory differ from those of Thermodynamics, the kinetic theory in question is not valid.

THESIS II. Through the equating of the molecular thermodynamic potentials of the water in the solution and of the pure water outside it [there exists namely only thermodynamic equilibrium between the "*water*" on either side of the membrane, as this is supposed to be permeable only to water] the thermodynamic theory leads to[2])

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[1]) See particularly: Sechs Vorträge (1906), p. 17—36, and These Proc. of June 1906, p. 53 et seq. Also Zeitschr. f. physik. Ch. **64**, p. 629 et seq. (1908).

[2]) I gave this simple derivation already in 1894 (Zeitschr. f. physik. Ch. **15**, p, 463 et seq).

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

when $\mu(x, p)$ is the molecular potential of the water in the solution (in which x is the molecular concentration of the dissolved substance, p the pressure of equilibrium), and $\mu(0, p_0)$ that of the pure water (in which the concentration of the dissolved substance is 0, the pressure of equilibrium p_0).

Now:

$$\left.\begin{aligned} \mu(x, p) &= f(T) + pv_x + \alpha x^2 + RT \log(1-x) \\ \mu(o, p_0) &= f(T) + p_0 v_0 \end{aligned}\right\},$$

and hence — as in dilute solutions v_x (the molecular volume of the water in the solution) can be equated to v_0 [1] (the molecular volume of the pure water):

$$(p-p_0)v_0 = -RT \log(1-x) + \alpha x^2,$$

or

$$\underline{\pi = p - p_0 = \frac{RT}{v_0}[-\log(1-x) + \alpha x^2)}, \quad . \quad . \quad . \quad . \quad (1)$$

when π represents the "osmotic" pressure. In this α is the so-called "influencing" coefficient in consequence of the *interaction* of the molecules of the solvent and those of the dissolved substance. It is known that α is represented by the expression [2]:

$$\alpha = \frac{a_1 b_2{}^2 + a_2 b_1{}^2 - 2a_{12} b_1 b_2}{b_1 b^2},$$

in which the numerator passes into $(b_2\sqrt{a_1} - b_1\sqrt{a_2})^2$, when $a_{12} = \sqrt{a_1 a_2}$ can be put.

THESIS III. All kinetic theories, therefore, which for *non-diluted* solutions lead to expressions which remind directly of the equation of state of gases and liquids (e.g. with $v-b$ etc., and *without logarithmic* member) must be rejected. (Therefore the theories of WIND, STERN and others).

THESIS IV. For very diluted solutions (I) passes into

$$\pi = \frac{RT}{v_0} x,$$

VAN 'T HOFF's well-known equation. Yet it is easy to see that the deviations for non-diluted solutions are much slighter than those for

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[1] v_x and v_0 only differing in a quantity of the order x^2, the difference can always be thought included in the term αx^2.

[2] See among others Z f. ph. Ch. **63** (1908), p. 227—228 (Die Schmelz- und Erstarrungskurven etc.).

the corresponding non-ideal gas state. (Cf. Sechs Vorträge p. 29—30, and the cited paper in These Proc., p. 57 et seq).

Already from this we are led to surmise that the so-called osmotic pressure has an *entirely different ground* from what the analogy of the behaviour of the dissolved substance to that of the same substance in the corresponding gas state would lead us to suspect, and that there is here no close *relation*, only *analogy*. Particularly the occurrence of the term $-\log(1-x)$ (which only passes into x at $x=0$) in the expression (1) for the osmotic pressure should have admonished to caution. This term continues to exist in the most dilute solutions.

THESIS V. If actually the osmotic pressure was caused by the pressure of the *dissolved substance* (the old theory revived!), as EHRENFEST also assumes again, the pressure of the "sugar" molecules against the semi-permeable membrane would cause the *reverse* of what is actually observed. Then there would namely no water pass from the side of the pure solvent through the membrane into the solution, and give rise to the hydrostatic counterpressure $=\pi$ in the ascension tube of the osmometer — but this water would on the contrary be checked, since the pressure in the *solution* would be greater from the outset than in the pure water!

THESIS VI. In reality the osmotic pressure is caused by the water, penetrating through the semi-permeable membrane *into* the sugar solution, which gives rise to a hydrostatic pressure, which prevents the *further intrusion* of the water. *This* excess of pressure $\pi = p - p_0$ is the so-called "osmotic pressure" of the solution.

THESIS VII. Every theory, which would try to interpret the occurrence of the osmotic pressure *kinetically*, should be based on the *diffusion* of the water molecules on both sides of the membrane. Quite generally one can assume then two solutions of different concentration x_1 and x_2 on both sides of the membrane. If one confines oneself to a solution of the concentration x and pure water, one has what follows: In the unity of time there diffuse a certain number of water molecules of the pure water towards the solution, and another number from the solution towards the water. But on account of the solution containing less water than the pure water, there will go — parallel with the prevailing diffusion pressure — more particles of the water to the solution than the reverse.

In ordinary circumstances the dissolved substance (sugar) would also diffuse, but this diffusion is now arrested by the semi-permeable membrane, so that the diffusion is only brought about by the water.

Thesis VIII. Apart from what actually takes place on or in the semi-permeable membrane — hence when simply an imaginary membrane is taken, which does allow one sort of molecules to pass through, but not the other kind — it is easy to determine the just mentioned numbers of diffusing molecules according to Boltzmann's method (in agreement with the kinetic interpretation of the thermodynamic potential). (See among others Sechs Vorträge p. 20—21). Then the *required logarithmic member* arises of its own accord.

Thesis IX. If there is *interaction* between the two kinds of molecules, another term ax^2 simply arises *by the side* of $-log(1-x)$. If however $\alpha = 0$, as is the case for so-called ideal solutions (this is also the "imaginary" case to which E. alludes in his Remarks) *all the above remarks continue to be valid* unimpaired — which is in contradiction with E.'s view in his Remarks. The diffusion, the *intrusion* of the water till the required excess of pressure has been reached — everything remains the same.

E.'s opinion that the rise of the water in the osmometer can only take place through the three factors named by him, of which the interaction of the two kinds of molecules is one, must therefore be rejected with the greatest decision.

To what absurdities this conception would lead appears from this that when as dissolved substance a substance is taken with a very high critical temperature, and when this substance yet forms an "ideal" solution with water, *without interaction* ($\alpha = 0$), as is the case with many organic substances (also sugar), the partial vapour pressure of that dissolved substance (e. g. sugar) is vanishingly small with respect to that of water. So there does not take place any "evaporation" at all. According to E. the vapour pressure of the sugar would become equal to the osmotic pressure — which for a normal solution amounts to no less than 24 atmospheres! In reality the partial pressure of the dissolved sugar will perhaps amount to a billionth m.m. in the imaginary case mentioned by E. (sugar is about in that case).

Thesis X. It appears in my opinion sufficiently from the above that the kinetic interpretation of the osmotic pressure — which is always reappearing again in new forms — is moving and has moved in a wrong direction, and should again be founded on the simple *diffusion phenomenon,* as was indicated by me already more than 20 years ago, and was further worked out by me ten years ago (Sechs Vorträge l. c.).

OBSERVATIONS. Though I wish a long otium cum dignitate to all incorrect kinetic theories, I would by no means be considered a personal foe to the osmotic pressure — the significance of which for the theory of the dilute solutions was set forth by VAN 'T HOFF in the ingenious way characteristic of him.

My earlier and later opposition was only directed against two later introduced abuses (with which Prof. EHRENFEST of course entirely agrees), namely:

1. Against the extension of the idea (*thought as reality*) to *isolated homogeneous* solutions (i. e. when no semipermeable membrane is thought to exist), in which of course no real pressure of 24 atms. for every dissolved gr. mol. occurs.

2. Against the *practical application* of the idea to *non-diluted* solutions, which application I thought undesirable in view of the inaccuracies which then occur and which are not to be ascertained — which can give rise to very erroneous conclusions (and have indeed done so!). Then the general theory of the thermodynamic potential (or free energy) is the obvious and sure way.

The *existence* of the osmotic pressure has never been called in question by me. One does not give calculations and interpretations of something that does not exist! But it exists only in a solution that is *separated* by a *semi permeable membrane* from the pure solvent (or from a solution of slighter concentration) — and manifests itself then through a *diffusion pressure from* the pure solvent *towards* the solution (so just the *reverse* of what the kinetic interpreters imagine).

That the above described osmotic diffusion pressure for exceedingly diluted solutions has a value *as if* the sugar molecules in the sugar solution in the corresponding ideal gas state exert this pressure, is a mere coincidence, only owing to the term $-\log(1-x)$ of the so-called GIBBS' paradox; which term, as we know, is kinetically in connection with the diffusion tendency of the components of the mixture.

Only a kinetic theory of the osmotic pressure which starts from the diffusion phenomenon, arrives at the term in question (Sechs Vorträge, S. 20—21); all other theories, which imagine the pressure *in* the sugar solution, only come to *non-logarithmical* expressions with simply x (resp. c, $^1/_v$, $^1/_{v-b}$, etc.), which owing to their derivation of course remind of the ordinary gas pressure, (law of BOYLE, or for non-diluted solutions the formula of VAN DER WAALS), but which are to be called inaccurate in the most absolute sense.

Fontanivent sur Clarens, April, 1915.

Appendix during the correction.

In a correspondence on this subject with Prof. EHRENFEST (Prof. LORENTZ was namely so kind as to send him my article) it has become still clearer to me to what E.'s result, which in my opinion is erroneous, is to be ascribed.

In his considerations he namely assumes (this had not appeared to me from his paper) that the molecules of the substances do not exert any action on each other, i.e. that all the forces and actions, also those in the *collisions,* are neglected. (that the attractive forces are neglected, does not affect the correctness or incorrectness of the calculations). Prof. E. expresses this by saying: The water is quite unaffected by the sugar present, and vice versa.

This is the very core of the problem. When the water is not affected by the sugar present, then $\mu(x) = \mu(0)$, and no longer $\mu(x) = \mu(0) + RT \log (1-x)$. In other words: E. works with substances for which GIBBS's paradox has disappeared, and which have therefore become entirely free from thermodynamics. Hence he could not possibly find the expression $-\log (1-x)$ corresponding to it.

Such extra-stellary, thermodynamic-free substances have of course lost all diffusion tendency – which just causes the phenomenon of the osmotic pressure. For if the water is quite unaffected by the sugar present, there exists no impetus any longer for the water to be displaced, so that the disturbed equilibrium (between concentrations x and 0, or x_1 and x_2) is reestablished.

As so many before him, Prof. E. has in my opinion allowed himself be carried away (see e.g. p. 1241 of his paper) by the striking *analogy,* which was already mentioned in Thesis IV above. That we can only speak of analogy here, is no doubt clear after all that was remarked above. The analogy pressure of E. and others acts namely precisely in the *opposite sense* from the real osmotic pressure. In the limiting case it is not x that is found instead of $-\log (1-x)$, but $-x$! This mistaken opposite pressure is of course the consequence of the perfect freedom of the sugar molecules assumed by E. and others, which molecules now begin to exert a pressure of 24 atms. per gr. mol. on the semi-permeable wall — a pressure which of course is not exerted for ordinary solutions as we know them on earth. And where E. speaks in his paper of the kinetic interpretation of *the* osmotic pressure, it seems to me that he too should work with substances as they exist on earth, and not with such where Thermodynamics is eliminated.

For through the elimination of the actions between the molecules just the "according-to-probability unordered kinetic" element (the kinetic equivalent of Thermodynamics), which is brought about by the mutual collisions has been done away with, and only the "roughly kinetic" element remains, which then, moreover, leads to to the opposite result.

In conclusion I can adduce no better evidence of the validity of my considerations than the following.

For a *gas mixture* (even if necessary of ideal gases) of e.g. O_2 in N_2 — separated from pure N_2 by a semi-permeable membrane, which does not let through O_2 — the osmotic pressure would just as for liquid mixtures, be represented by the above equation (1). Here too the *gas mixture* would rise in an ascension tube (in consequence of the diffusion tendency of the pure nitrogen) till the necessary *counter pressure* had been reached, which then prevented the further intrusion of the nitrogen. But here too "the osmotic pressure" starts from the pure nitrogen outside the mixture, and not from the O_2 *in* the mixture. That there is here no question of a separate excess of pressure of the O_2, appears from this that at the beginning of the experiment the gas pressures on the two sides of the membrane are perfectly the same, (both $=1$ atm.), the sum of the partial pressures of the $O_2 +$ that of the N_2 of course being precisely equal to the pressure of the N_2 on the other side of the membrane. The *excess of pressure* does not make its appearance until *after* the appearance of the *diffusion* — and arises, as has been said, from the *pure nitrogen*.

These observations, which in my opinion are conclusive for this problem, have already been made and elaborated in my Lehrbuch der Mathematischen Chemie (1901), p. 30—31.

4 May. 1915.