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Physics. — “On “osmotic temperatures” and the kinetic signification of the thermodynamic potential.” By Prof. PH. KOHNSTAMM. (Communicated by Prof. J. D. VAN DER WAALS).

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1. It may be presumed to be known, at least in Holland, how easily the laws of the diluted solutions are derived from the general differential equation of VAN DER WAALS for coexisting phases:

$$V_{21} dp = \frac{W_{21}}{T'} dT + (x_2 - v_1) \left(\frac{\partial^2 \zeta}{\partial x_1^2} \right)_{\rho, T'} dx_1 \dots \dots (1)$$

The law for the osmotic pressure alone does not immediately follow from the equation in the above form for the simple reason that it has been supposed in the derivation of this equation that the pressure in the two coexisting phases is equal. If we, however, return to the derivation of equation (1), we see at once the relation between this equation and the law of VAN 'T HOFF. This derivation, namely, runs as follows. As in two coexisting phases 1 and 2 the thermodynamic potential e. g. of the first substance must be equal, and also in two other coexisting phases 1' and 2', the change of this thermodynamic potential between 1 and 1', and 2 and 2' must also be the same, and so if we take 1 and 1' near each other, and represent the molecular thermodynamic potential of the first substance as usual by μ_1 , the equation:

$$[d\mu_1]_1 = [d\mu_1]_2$$

holds.

Now from:

$$\mu_1 = \zeta - v \left(\frac{\partial \zeta}{\partial x} \right)_{\rho, T'}$$

follows:

$$d\mu_1 = d\zeta - \left(\frac{\partial \zeta}{\partial x} \right)_{\rho, T'} dx - v d \left(\frac{\partial \zeta}{\partial x} \right)_{\rho, T'}$$

And as

$$d\zeta = v dp - v_1 dT + \left(\frac{\partial \zeta}{\partial x} \right)_{\rho, T'} dx$$

and

$$d \left(\frac{\partial \zeta}{\partial x} \right)_{\rho, T'} = \left(\frac{\partial^2 \zeta}{\partial x^2} \right)_{\rho, T'} dx + \left(\frac{\partial^2 \zeta}{\partial x \partial p} \right)_{T'} dp + \left(\frac{\partial^2 \zeta}{\partial x \partial T} \right)_{\rho} dT = \left(\frac{\partial^2 \zeta}{\partial x^2} \right)_{\rho, T'} dx + \left(\frac{\partial v}{\partial x} \right)_{\rho, T'} dp - \left(\frac{\partial \eta}{\partial x} \right)_{\rho, T'} dT$$

we get:

$$d\mu_1 = \left\{ v - x \left(\frac{\partial v}{\partial x} \right)_{\rho T} \right\} dp - \left\{ \eta - x \left(\frac{\partial \eta}{\partial x} \right)_{\rho T} \right\} dT - x \left(\frac{\partial^2 \zeta}{\partial x^2} \right)_{\rho T} dx. \quad (2)$$

Equating of this expression for the first and the second phase, and joining the terms with dp , dT , and dx we get equation (1). When, however, we do not perform these operations, but keep to equation (2), we immediately find the law of VAN 'T HOFF. For we now reason as follows. The compressed dilute solution is in equilibrium with the solvent under normal pressure; so the thermodynamic potential of the solvent, which can freely move through the membrane, must be the same in the solution and in the pure solvent. And so the modification in the thermodynamic potential brought about on one hand by the increase of pressure, on the other by the addition of the dissolved substance, must be equal to zero, and so, as $dT = 0$:

$$\left\{ v - x \left(\frac{\partial v}{\partial x} \right)_{\rho T} \right\} dp = x \left(\frac{\partial^2 \zeta}{\partial x^2} \right)_{\rho T} dx$$

follows from (2).

Now for an exceedingly dilute solution $x \left(\frac{\partial^2 \zeta}{\partial x^2} \right)_{\rho T} = \frac{RT}{1-x}$; in the first member of the equation we can neglect the term with x , and we need not make a difference between the v of the solution and that of the solvent, and so we get:

$$v dp = \frac{RT}{1-x} dx^1,$$

the law of VAN 'T HOFF.

2 Now when we consider the osmotic phenomenon, the thought of introducing the idea "osmotic temperature" as analogy of the osmotic pressure, naturally suggests itself, and this has repeatedly been done²⁾. The reasoning is then as follows. The equilibrium through the semipermeable membrane is disturbed when on one side a substance is dissolved, because then the number of particles of the solvent per unit of volume decreases. So if we want to reach a state in which an equal number of particles move from the left towards the right and from the right towards the left we must either raise the pressure of the solution, in consequence of which more solvent molecules are forced out, or its temperature, so that the number of outgoing molecules will be increased by the greater velocity. Now the increase of temperature which must be given to the solution

¹⁾ Cf. Théorie Moléculaire § 18.

²⁾ Cf. c. g. VAN LAAR, These Proc. IX, p. 61.

above the solvent to bring about that an equal number of particles enter and leave through the membrane, is called the "osmotic temperature" of this solution. Now the supposition naturally suggests itself that this state is reached when the thermodynamic potential of the substance passing through the membrane has again become equal in the solution and the solvent. This thesis would undoubtedly be correct, if the considerations concerning the kinetic signification of the thermodynamic potential which I gave in These Proc. April 1905, were perfectly true. There I tried to demonstrate that the physical meaning of the thermodynamic potential of an homogeneous phase on which no external forces act is nothing but the number of molecules which per second reaches a wall, which is placed in the middle of this homogeneous phase, when the wall does not attract the molecules, and is thick with respect to their sphere of action. I expressed this definition by the formula:

$$M\mu = F(N) + C \dots \dots \dots (3)$$

in which N is the number of molecules in question, and C a constant. It is clear that what has been said above follows from this formula; for the numbers of molecules which leave solution and solvent through the membrane, are then entirely determined by the thermodynamic potential.

If now, however, on this ground, we try to determine from equation (2), what the "osmotic temperature" will be for a certain solution, we come to an absurdity. For, again neglecting the terms with α , we get for the osmotic temperature at constant pressure:

$$\eta dT = RT d\alpha \dots \dots \dots (4)$$

So this would imply that we could determine the total amount of entropy of the solvent through the experimental determination of $\frac{dT}{d\alpha}$. And this now is an absurdity. For when we reason purely thermodynamically and so define the entropy by $d\eta = \frac{dQ}{T}$ — and we have used no other definition of the entropy in deriving equation (4), — the entropy has no definite value, but an indefinite, and undefinable additive constant occurs in it; only differences of entropy have a definite value. ¹⁾

3. It is not difficult to point out the error in the reasoning which has led us to this absurdity. We have imposed the condition that

¹⁾ Only by starting from another, kinetic definition of the entropy, we can assign a definite value to the entropy in a definite system of units. Cf. These Proc. XIII p. 705, seq.

the thermodynamic potential of the substance passing through the membrane should be the same on the two sides, and we were not justified in this. For it is indeed true that in states of *equilibrium* the thermodynamic potential of a-component is the same in every phase, but here we have no state of equilibrium, because there continues to exist a difference of temperature between solution and solvent, and so a current of heat. It is just by this that the "osmotic temperature" is distinguished from the osmotic pressure, that the latter gives a state of equilibrium, though under special restricting conditions (the membrane).

Yet it is clear that it must be possible to reach a stationary state by rise of temperature in the way indicated; but the condition on which this takes place, must not be defined in this way that the thermodynamic potentials become equal. As it is self-evident that this condition will have to be that the total number of particles passing through the membrane is zero, it follows further that formula (3) cannot be maintained, and will have to be replaced by a relation of the form:

$$N = F(\mu, T). \quad (5)$$

Other quantities than the temperature (and constants) cannot occur in this relation, because the properties of the thermodynamic potential in equilibrium, i.e. at one definite temperature in all phases, require that equation (5) reduces to (3) for constant temperature. It is now necessary for both problems to define the form of equation (5) closer. It is clear that a purely thermodynamic reasoning is not adequate to do so, because the problem we want to solve, falls outside thermodynamics as relating to states of non-equilibrium. Thermodynamics can only give indications about the solution, however valuable these may be; the solution itself can only be obtained by kinetic means. One of these indications is this that the function of equation (5) will have to be of such a nature that the condition $N_1 = N_2$ does not lead to the absurd result (4). Now this absurdity already disappears when equation (5) is brought into the form:

$$N = C \frac{\mu}{RT} \quad (6)$$

in which the factor R is required by the consideration that N is a number of molecules that reaches a certain surface in the unit of time. As μ is of the dimension of an energy, also the denominator will have to be of this dimension, the factor C being in a certain relation with the unit of time and surface. If we draw up the condition of equilibrium by the aid of (6), it runs of course as follows:

$$\left(\frac{\partial \frac{\mu}{RT}}{\partial x} \right)_{\nu, T} dx + \left(\frac{\partial \frac{\mu}{RT}}{\partial T} \right)_{\nu, x} dT = 0$$

or

$$\frac{x \left(\frac{\partial^2 \zeta}{\partial x^2} \right)_{\nu, T} dx}{RT} = \frac{T \left(\frac{\partial \mu}{\partial T} \right)_{\nu, x} - \mu}{RT^2} dT$$

or

$$\frac{dx}{1-x} = \frac{-T\eta + xT \left(\frac{\partial \eta}{\partial x} \right)_{\nu, T} - \varepsilon + T\eta - pv + x \left(\frac{\partial \varepsilon}{\partial x} \right)_{\nu, T} - xT \left(\frac{\partial \eta}{\partial x} \right)_{\nu, T} + px \left(\frac{\partial v}{\partial x} \right)_{\nu, T}}{RT^2} dT$$

in which it is just the terms with η that are cancelled. Now it appears, however, that also this expression is still too simple, for now ε is found in the result, in which also an indefinite constant occurs in consequence of the potential energy. So instead (6) we must have an expression of the form:

$$N = C \frac{\mu - f(T)}{RT} \dots \dots \dots (7)$$

in which $f(T)$ is either a constant, or a function of T which is still further to be determined. But let us now still put the condition that N becomes equal to zero for very great volumes, and always remains positive in other cases. Then we see that (7) cannot satisfy this, because for very great volume the entropy becomes infinite and so the thermodynamic potential becomes negative infinite. This consideration requires a dependence of the form:

$$N = C e^{\frac{\mu - f(T)}{RT}} \dots \dots \dots (8)$$

in which it does not make any difference whether we take C as a constant, or as a function of T , as long as $f(T)$ remains quite arbitrary.

4. Further than equation (8) thermodynamic theory cannot go. So we must now try if we cannot confirm the up to now only plausible result in a kinetic way, and get a further insight into the nature of $f(T)$. By the way indicated by VAN DER WAALS SR. in his communication on the kinetic meaning of the thermodynamic potential¹⁾ this is easily obtained. We need only modify the train of reasoning in so far, that we do not direct our attention to the equality of the number of molecules that passes from the liquid into

¹⁾ Verslagen Kon. Akademie III, 205—219.

the gas phase, and vice versa, but independent of the second phase determine the number of particles which may detach themselves from the surrounding homogeneous phase, i.e. which are able entirely to overcome the power of attraction of the phase in which they are found, and so can reach a space where if no external forces are active the potential energy is maximum and the kinetic pressure may therefore be put zero.¹⁾

However, a few objections may be advanced to the method followed i. e., particularly with respect to the way in which the loss of energy is calculated when a molecule leaves the homogeneous phase. I am indebted to Prof. VAN DER WAALS JR. for the following proof, in which these difficulties are evaded.

Let N' be the number of molecules of one gram molecule, $\frac{a}{v}$ its potential energy, then the potential energy which one molecule loses when it is removed from the phase to a place where the potential is zero, is $\frac{2a}{N'v}$. The influence of the collisions which one molecule meets with from another, can be reduced to a pressure on the distance sphere, as this is frequently done in the derivation of the equation of state by the virial method. This pressure, which we shall call P , is equal to $p + \frac{a}{v^2}$ or $\frac{MRT}{v-b}$.

If we want to determine the chance that a molecule escapes from the phase through the capillary layer, we shall have to take this pressure into account. For it is not constant through the capillary layer, but will gradually decrease if we traverse the capillary layer from the liquid in the direction towards the vapour.

If we choose the Z -axis normal to the capillary layer and if we think σ (the radius of the distance sphere) so small compared with the thickness of the capillary layer that over the distance 2σ we may consider the pressure P as a linear function of z , the force with which a molecule is pressed outside by the pressure P will be equal to $-\frac{4}{3}\pi\sigma^3\frac{dP}{dz}$. So the total work which is exerted by P on

¹⁾ Prof. VAN DER WAALS JR. points out to me that these conditions need not always be satisfied in the neighbourhood of a wall as was mentioned in my previous paper, which is easily seen if we think of liquid phases in the neighbourhood of their critical temperature. So if we want in general to define the thermodynamic potential kinetically in a definite case only by means of properties of this phase itself, and not of coexisting phases — and this seems desirable to me in many respects — we must replace the definition by means of a non-attracting wall by the purely mathematic one given in the text.

an outgoing molecule is:

$$-\frac{4\pi}{3} v^3 \int \frac{dP}{dz} dz = \frac{4}{3} \pi v^3 (P_l - P_g) = \frac{2b_0}{N} (P_l - P_g)$$

So when a molecule penetrates into the capillary layer in the direction from the liquid to the gas, it can traverse it entirely only when the z -component (u) of the velocity is so great that:

$$\frac{1}{2} m u^2 > \left(\frac{2a}{Nv} \right)_l - \left(\frac{2a}{Nv} \right)_g - \frac{2b_0}{N} (P_l - P_g).$$

Let us call the smallest value of u which satisfies this u_m , we then find the number of particles which escapes from the liquid per second as follows: Let n be the number of particles per cm^3 , so $n = \frac{N'}{v}$ ($v =$ the volume of 1 gram molecule), then the number that has a velocity component u in the z -direction is $\frac{n}{\sqrt{\pi}} e^{-\frac{u^2}{v^2}} d\frac{u}{v}$, and the number which passes through an area of 1 cm^2 with that velocity:

$$\frac{n}{\sqrt{\pi}} u e^{-\frac{u^2}{v^2}} d\frac{u}{v}$$

So the number that passes from liquid to vapour is:

$$\frac{n\alpha}{\sqrt{\pi}} \int_{u=u_m}^{u=\infty} \frac{u}{v} e^{-\frac{u^2}{v^2}} d\frac{u}{v} = \frac{n\alpha}{2\sqrt{\pi}} e^{-\frac{u_m^2}{v^2}}$$

If we have to deal not with a simple substance, but with a mixture of $(1-x)$ molecules 1st kind and x molecules 2nd kind, and if we want to ascertain the equilibrium for molecules 1st kind, we get, as is easy to see, the same expression, in which, however,

$$n = \frac{N'(1-x)}{v} \quad (v = \text{the volume of 1 gram molecule of the mixture})$$

and:

$$\frac{1}{2} m_1 u_m^2 = \left[\frac{2 \{ (1-x) a_1 + x a_{12} \}}{N'v} \right]_l - \left[\frac{2 \{ (1-x) a_1 + x a_{12} \}}{N'v} \right]_g - \frac{2RT}{N'} \left(\left[\frac{b_1(1-x) + b_{12}x}{v-b} \right]_l - \left[\frac{b_1(1-x) + b_{12}x}{v-b} \right]_g \right)$$

The expressions $\frac{(1-x)RT}{v-b}$ and $\frac{xRT}{v-b}$ here represent the partial pressures exerted resp. by molecules of the 1st and of the 2nd kind on the distance spheres round those of the 1st kind. The available spaces

being different for the molecules of different kinds, the denominators $v-b$ should strictly speaking also have different values. As it is here, however, only our purpose to examine what function μ is of N , we may disregard these differences.

So if we take into consideration that $\frac{1}{2}m_1N'v^2 = MRT$, the number of particles which passes from the liquid to a space where the potential energy is maximum and the kinetic pressure $= 0$, amounts to:

$$N = \frac{N'(1-x)\alpha}{v\sqrt{2\pi}} e^{-2 \left\{ \frac{(1-x)a_1 + xa_{12}}{v} \right\} + 2RT \left\{ \frac{b_1(1-x) + b_{12}x}{v-b} \right\}} \frac{RT}{RT}$$

or

$$N = C \sqrt{T} e^{-2 \left\{ \frac{(1-x)a_1 + a_{12}x}{v} \right\} + 2RT \left\{ \frac{b_1(1-x) + b_{12}x}{v-b} \right\} + RT l \frac{1-x}{v}} \frac{RT}{RT} \quad (9)$$

where $C = \sqrt{\frac{RN'}{2\pi m}}$.

5. It remains to show that the expression in the exponent agrees with $\mu = f(T)$ of equation (8).

Now, if we leave the pure functions of the temperature out of consideration, the thermodynamic potential becomes:

$$pv = RT l(v-b) - \frac{a_1}{v} - x \left\{ \frac{RT \frac{db}{dx}}{v-b_1} - \frac{da}{v} \right\} + RT l(1-x) \quad (10)$$

if b may be considered as a constant. This is, of course not the case in the liquid state, and accordingly we can only expect to obtain agreement between (9) and (10), when we neglect terms with higher powers of $\frac{b}{v}$.

If we write $pv = RT \frac{v}{v-b} - \frac{a}{v}$, the terms with a from equation (10) become:

$$-\frac{2a - x \frac{da}{dx}}{v} = -\frac{2a_1(1-x) + 2a_{12}x}{v}$$

and so these terms perfectly agree with those of (9).

With neglect of the higher powers of $\frac{b}{v}$, the terms with b from

equation (10) can be reduced as follows:

$$\begin{aligned}
 -l(v-b) - \frac{x \frac{db}{dx}}{v-b} + \frac{v}{v-b} &= -l(v) - l\left(1 - \frac{b}{v}\right) - \frac{x \frac{db}{dx}}{v-b} + \frac{v}{v-b} = \\
 &= -l(v) + \frac{b}{v} - \frac{x}{v} \frac{db}{dx} \left(1 + \frac{b}{v}\right) + 1 + \frac{b}{v} = -l(v) + 1 + \frac{2b - x \frac{db}{dx}}{v} = \\
 &= 1 - l(v) + \frac{2b_1(1-x) + 2b_2x}{v}.
 \end{aligned}$$

So these terms too perfectly agree with those of equation (9), provided the higher powers of $\frac{b}{v}$ are neglected. So the $f(T)$ of equation (8) should be chosen so that the functions only dependent on temperature disappear from the thermodynamic potential, and the whole expression is multiplied by \sqrt{T} . So the two methods, the kinetic and the thermodynamic method supplement each other. Thermodynamically it can be shown that the quantity which occurs in the exponent of equation (8), must necessarily be the thermodynamic potential, at least as regards its dependence on v and x ; but concerning its pure functions of the temperature thermodynamics cannot give a decision. On the other hand the kinetic theory is adequate to show, that we must get an equation of the form of equation (8) for N , and it can determine the $f(T)$. It can, however, show with only a very rough approximation — until a proper expansion into series for b is known — that the occurring function of the volume and the concentration is the same as that which occurs in the thermodynamic potential. If these two methods are combined, we may, in my opinion, conclude with certainty, that the number of particles under investigation is really represented by the formula:

$$N = C \sqrt{T} e^{\frac{\mu'}{RT}} \dots \dots \dots (11)$$

in which μ' represents the thermodynamic potential without its functions only dependent on the temperature.

6. Now it is easy to draw up the equation for the "osmotic temperature" by means of formula (11). A stationary state will, namely, set in when the number of molecules going to pass through the membrane on one side of it has increased by rise of temperature as much as it has decreased by the addition of the dissolved substance, or in other words, when:

$$\left(\frac{\partial N}{\partial x}\right)_{\rho, T} dx + \left(\frac{\partial N}{\partial T}\right)_{\rho, x} dT = 0 \dots \dots (12)$$

If we write $\mu' = \mu + F(T)$, in which now :

$$F(T) = - \int_0^T c_{v\infty} dT - E + T \int_1^T \frac{c_{v\infty}}{T} dT + TH$$

and in which μ is the ordinary thermodynamic potential, then

$$- \left(\frac{\partial \mu}{\partial x}\right)_{\rho, T} dx = \frac{dT}{T} \left\{ T \left(\frac{\partial \mu}{\partial T}\right)_{\rho, x} + TF'(T) - \mu - F(T) + \frac{RT}{2} \right\}.$$

follows immediately from equation 11 and 12, when the differentiations have been carried out.

And with the values for $\left(\frac{\partial \mu}{\partial x}\right)_{\rho, T}$ and $\left(\frac{\partial \mu}{\partial T}\right)_{\rho, x}$ from equation (2)

$$v \left(\frac{\partial^2 \zeta}{\partial x^2}\right)_{\rho, T} dx = \frac{dT}{T} \left\{ TF'(T) - \varepsilon - pv - F(T) + \frac{RT}{2} \right\} \dots (13)$$

when we may consider the terms with x as small.

Then with $\varepsilon = - \frac{a}{v} + \int_0^T c_{v\infty} dT + E$ and the above-mentioned value

of $H(T)$ the righthand member becomes :

$$\frac{dT}{T} \left\{ \frac{a}{v} - pv + \frac{RT}{2} \right\}$$

Now at low temperature pv may be neglected by the side of $\frac{a}{v}$, and for the latter expression we may write $\frac{RTv}{v-b}$. On the supposition already introduced by us that v is small, $\left(\frac{\partial^2 \zeta}{\partial x^2}\right)_{\rho, T}$ passes into $\frac{RT}{v(1-x)}$, so that finally the differential equation of the "osmotic temperature" becomes :

$$\frac{dx}{1-x} = \frac{dT}{T} \left\{ \frac{v}{v-b} + \frac{1}{2} \right\} \dots \dots \dots (14)$$

It is evident that the second member is positive, and this result was, of course, already certain beforehand.

7. In connection with this result a single remark may be allowed me. We might think that the experimental determination of the "osmotic temperature" would give a new means for the determination of the quantity b in the liquid state; this is, however, not the case. This

appears when we do not wait till (13) to introduce the simplification that ρv may be neglected by the side of $\frac{a}{v}$, but introduce it immediately in (11). If we write this equation in the form :

$$l(N) = lC + \frac{1}{2} lT + \frac{\mu'}{RT}$$

we find as condition for the stationary state :

$$\left(\frac{\partial \frac{\mu'}{RT}}{\partial x} \right)_{\rho, T} dx = \frac{dT}{2T} + \left(\frac{\partial \frac{\mu'}{RT}}{\partial T} \right)_{\rho, x} dT \quad \dots \quad (15)$$

Now on the mentioned supposition, and neglecting again the terms with x , we have :

$$\frac{\mu'}{RT} = \frac{-\frac{a}{v}}{RT} - l(v-b) + l(1-v) = -\frac{v}{v-b} - l(v-b) + l(1-v)$$

and so :

$$\left(\frac{\partial \frac{\mu'}{RT}}{\partial x} \right)_{\rho, T} = -\frac{dv}{1-x}, \quad \left(\frac{\partial \frac{\mu'}{RT}}{\partial T} \right)_{\rho, x} = \frac{2b-v}{(v-b)^2} \left(\frac{\partial v}{\partial T} \right)_{\rho=0} \quad (16)$$

$\left(\frac{\partial v}{\partial T} \right)_{\rho=0}$ we find from the equation :

$$\frac{a}{v^2} = \frac{RT}{v-b}$$

by differentiation ; the result becomes after some reduction :

$$\left(\frac{\partial v}{\partial T} \right)_{\rho=0} = \frac{v(v-b)}{T(2b-v)} \quad \dots \quad (17)$$

If we substitute this result and that of (16) into (15), we get again (14). So we see now that (14) does not give an independent determination of $\frac{v}{v-b}$, but that we can just as well determine this quantity from (17). And as the quantities occurring in (17) can undoubtedly be determined experimentally with much greater accuracy than the "osmotic temperature", there is no reason to expect that equation (14) will be able to give us any new information about the b in the liquid state. And in my opinion this obviates every reason, at least for the present, to try and conquer the undoubtedly very considerable difficulties which will confront us in an experimental investigation of "osmotic temperatures".