

Physics. — *“On a Condition for the Equilibrium of a Liquid with its Vapour Given by BOLTZMANN, and the Relation between this Condition and the Thermodynamic Potential.”* By J. W. DEKKER. (Communicated by Prof. J. D. VAN DER WAALS JR.).

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§ 1. In § 60 of the 2nd part of his “Gastheorie” BOLTZMANN gives a condition for the equilibrium between liquid and vapour of a simple substance, which, in a somewhat more general way, may be expressed thus that the expression

$$v_b \cdot e^{-\frac{\epsilon_{mol}}{kT}}$$

must be the same in the two phases.

In this v_b is, per gramme molecule, the space available for a last molecule centre amidst the other molecules already present, ϵ_{mol} the potential energy of 1 molecule in relation to the others, kT the double of the mean kinetic energy per degree of freedom. As when n represents the number of molecules per gramme molecule, $n\epsilon_{mol} = 2\epsilon_{pot}$, i.e. twice the potential energy per gramme molecule, and $nkT = RT$, hence $\frac{\epsilon_{mol}}{kT} = \frac{2\epsilon_{pot}}{RT}$, according to the above condition

$$v_b \cdot e^{-\frac{2\epsilon_{pot}}{RT}}$$

hence the logarithm of this expression multiplied by $-RT$, i.e.

$$2\epsilon_{pot} - RT \log v_b$$

must have the same value in the two phases.

I shall now show that in general this expression is not quite correct, but that

$$\epsilon_{pot} - \frac{\partial \epsilon_{pot}}{\partial v} \cdot v - RT \log v_b$$

should be substituted for it.

The former expression is in conformity with this only when $\epsilon_{pot} = -\frac{a}{v}$, which expression BOLTZMANN also uses in the § mentioned.

§ 2. Let us first follow the course taken by BOLTZMANN.

When 1 gramme molecule of liquid coexists with 1 gramme molecule

of vapour, and we bring one more molecule inside the space in which the two phases are found, a volume $(v_b)_1$ is available in the liquid, a volume $(v_b)_2$ in the vapour for the centre of this molecule.

If there were no cohesion, the ratio between these available volumes would be at the same time the ratio of the chances that, with given position of the other molecules, the last molecule would be in the liquid or in the vapour.

BOLTZMANN multiplies the ratio of the available volumes on account of the prevailing attractive forces by

$$e^{-\frac{(\varepsilon_{mol})_1}{kT}} : e^{-\frac{(\varepsilon_{mol})_2}{kT}}$$

to arrive at the ratio of chance mentioned.

In this he interchanges, however, the potential energy ε_{mol} of some molecule in one of the two phases with the potential energy of the last molecule which we think admitted extra with given position of the other molecules. It is this latter energy that we must take into account for the ratio of probability, and in general this energy is not equal to ε_{mol} .

We have much sooner to do here with the increase of energy at constant volume (and constant temperature) when the number of molecules in the volume v is brought from n to $n+1$ than with the energy per molecule ¹⁾.

This increase of energy, $\left(\frac{\partial \varepsilon_{pot}}{\partial n}\right)_v$, may be expressed by the aid of $\left(\frac{\partial \varepsilon_{pot}}{\partial v}\right)_n$.

For when the number of molecules is changed from n to $\varkappa n$, and at the same time the volume from v to $\varkappa v$, the potential energy becomes $\varkappa \varepsilon_{pot}$, hence it increases by $(\varkappa-1)\varepsilon_{pot}$. For $\varkappa = 1 + d\varkappa$ this increase becomes, therefore, $d\varepsilon_{pot} = \varepsilon_{pot} d\varkappa$. Further dn is then $= n d\varkappa$ and $dv = v d\varkappa$. Now (T being constant) we have the following equation:

$$d\varepsilon_{pot} = \left(\frac{\partial \varepsilon_{pot}}{\partial n}\right)_v dn + \left(\frac{\partial \varepsilon_{pot}}{\partial v}\right)_n dv,$$

hence:

$$\varepsilon_{pot} d\varkappa = \left(\frac{\partial \varepsilon_{pot}}{\partial n}\right)_v n d\varkappa + \left(\frac{\partial \varepsilon_{pot}}{\partial v}\right)_n v d\varkappa$$

and therefore:

$$\left(\frac{\partial \varepsilon_{pot}}{\partial n}\right)_v = \frac{1}{n} \left\{ \varepsilon_{pot} - \left(\frac{\partial \varepsilon_{pot}}{\partial v}\right)_n v \right\}.$$

With this value for the potential energy of the last molecule it is

¹⁾ I do not assign much cogency to the reasoning given in this §. I only give it to show, where and how BOLTZMANN's derivation must be modified to arrive at the correct result. More cogent proofs follow in § 3 and § 4.

found that the chances that this molecule is in one phase or in the other, are to each other as the values of the expression

$$\frac{\varepsilon_{pot} - \frac{\partial \varepsilon_{pot}}{\partial v} v}{v_b \cdot e^{-\frac{\varepsilon_{pot} - \frac{\partial \varepsilon_{pot}}{\partial v} v}{n k T}}}.$$

The number of molecules in liquid and vapour being to each other in the same ratio as these chances, and these numbers having the same value (for we took a gramme molecule of both), the latter expression, hence also

$$\varepsilon_{pot} - \frac{\partial \varepsilon_{pot}}{\partial v} \cdot v - RT \log v_b$$

must be equal in the two phases.

§ 3. In a stricter way than in the preceding § we can arrive at the same result by the aid of GIBBS's statistical method, as it has been applied by ORNSTEIN to molecular problems.

Starting from the question as to which is the most frequent system divided into two homogeneous phases, from a canonical ensemble with modulus θ , ORNSTEIN finds as one of the conditions for this system, that the first derivative $f'(n)$ of a certain function $f(n)$ of the number of molecules n per cm^3 must have the same value in the two phases. This function is :

$$f(n) = n \log \frac{\omega}{n} + \frac{an^2}{2\theta}.$$

In this ω is in relation to our v_b in a way to be specified later; $-\frac{an^2}{2}$ has been simply substituted for the potential energy per cm^3 , hence the more general form of the function is:

$$f(n) = n \log \frac{\omega}{n} - \frac{\varepsilon_{pot}}{v\theta}.$$

It follows from this that:

$$f'(n) = \frac{d(n \log \omega)}{dn} - \log n - 1 - \frac{1}{v\theta} \cdot \frac{\partial \varepsilon_{pot}}{\partial n}.$$

Now, however, ω is in relation with v_b according to the equation:

$$\frac{d(n \log \omega)}{dn} = \log \frac{v_b}{v}.$$

while:

$$\frac{\partial \varepsilon_{pot}}{\partial n} = \frac{\partial \varepsilon_{pot}}{\partial n} \cdot \frac{n}{n} = \frac{\partial \varepsilon_{pot}}{\partial n} \cdot v = \frac{v}{n} \left(\varepsilon_{pot} - \frac{\partial \varepsilon_{pot}}{\partial v} \cdot v \right)$$

1) Appl. de la mécanique statistique de GIBBS. Arch. Néerl. S. III A, t. 4 (1918), p. 262 et seq.

2) Cf. loc. cit. p. 230.

and as $-\log v - \log n = -\log n$ is the same in both cases, and $n\theta = RT$, our condition becomes that

$$\log v_b - \frac{1}{RT} \left(\varepsilon_{pot} - \frac{\partial \varepsilon_{pot}}{\partial v} \cdot v \right),$$

hence also

$$\varepsilon_{pot} - \frac{\partial \varepsilon_{pot}}{\partial v} \cdot v - RT \log v_b$$

must have the same value in the two phases.

§ 4. BOLTZMANN shows loc. cit. that, when $\varepsilon_{pot} = -\frac{a}{v}$ and $v_b = v \left(1 - 2\frac{b}{v} + \frac{17}{16}\frac{b^2}{v^2} \right)$ is put, and for the pressure the value corresponding to these values is assumed, i.e. $p = \frac{RT}{v} \left(1 + \frac{b}{v} + \frac{5}{8}\frac{b^2}{v^2} \right) - \frac{a}{v^2}$, the condition of equilibrium derived by him, after development of the logarithm to the term $\frac{b^2}{v^2}$ inclusive, assumes the same form as the so-

called rule of MAXWELL: $p(v_2 - v_1) = \int_{v_1}^{v_2} p dv$.

In this case the expression $2\varepsilon_{pot} - RT \log v_b$ yields the same value as the thermodynamic potential $pv - \int p dv$, provided no pure temperature term is introduced into the second expression.

I will now show that when the potential energy is left undetermined, and also the development according to $\frac{b}{v}$, which is questionable for the liquid phase, is omitted, the thermodynamic potential is accurately equal, with the exception of a temperature term, to the expression which I substituted for that of BOLTZMANN.

It is known that:

$$pv - \int p dv = \varepsilon - T\eta - \frac{\partial(\varepsilon - T\eta)}{\partial v} \cdot v$$

When the kinetic energy is omitted as a pure function of the temperature, this becomes:

$$\varepsilon_{pot} - \frac{\partial \varepsilon_{pot}}{\partial v} \cdot v - T \left(\eta - \frac{\partial \eta}{\partial v} \cdot v \right).$$

For the calculation of η we can follow the way indicated by BOLTZMANN in § 61. Hence we put:

$$\eta = Rm \log W.$$

m is the mass of a molecule (in connection with the notation adopted by us to be expressed in gramme molecules), W , the "probability of the state", consists of a temperature factor, which we may leave out of consideration here, and further of a factor indicating the number of the possibilities of distributing our n molecules over the space v , and which is put equal to the product of the volumes which the n molecules, brought each separately into the space, have at their disposal at the moment that they have been brought into it.

Hence if we represent by $2 \nu m b_\nu$, the space occupied by the distance spheres of these molecules, which have a joint mass νm , when already ν molecules have been brought into the volume v , then, disregarding the temperature factor:

$$W = \prod_{\nu=0}^{n-1} (v - 2 \nu m b_\nu)$$

and therefore, disregarding a temperature term:

$$\eta = R m \sum_{\nu=0}^{n-1} \log (v - 2 \nu m b_\nu).$$

From this formula follows:

$$\left(\frac{\partial \eta}{\partial n} \right)_v = R m \log (v - 2 n m b_n)$$

or more simply:

$$\left(\frac{\partial \eta}{\partial n} \right)_v = R m \log v_b.$$

In an analogous way as in § 2 for the energy a relation is now derived between $\left(\frac{\partial \eta}{\partial n} \right)_v$ and $\left(\frac{\partial \eta}{\partial v} \right)_n$. It is then found that:

$$\left(\frac{\partial \eta}{\partial v} \right)_n = R + \eta - \left(\frac{\partial \eta}{\partial n} \right)_v. \quad n.^1)$$

Hence:

$$\left(\frac{\partial \eta}{\partial v} \right)_n = R + \eta - R m n \log v_b = R + \eta - R \log v_b$$

and therefore, with omission of temperature terms:

$$T \left(\eta - \frac{\partial \eta}{\partial v} \cdot v \right) = RT \log v_b$$

and finally:

$$pv - \int p dv = \varepsilon_{pot} - \frac{\partial \varepsilon_{pot}}{\partial v} \cdot v - RT \log v_b.$$

¹⁾ The term R appears in consequence of the fact that the entropy defined in the above way is not simply multiplied by x when the volume and the number of molecules are made x times greater. Then the entropy becomes $\eta(x) = x \cdot \eta + R x \log x$. With increase of x from 1 to $1 + dx$ we then get $d\eta = (R + \eta) dx$.