phase occurs, besides $Ba Br_2 . 2H_2O$ and $Ba(OH)_2 . 8H_2O$, the oxy-bromide:

$$Ba Br_2 . BaO . 5H_2O \quad \text{or} \quad Ba\Big\langle {Br \atop OH} . 2H_2O$$
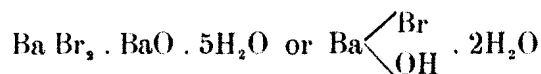
This salt has already been described previously [1]; the other oxy-bromide:

$$Ba Br(OH) . 3H_2O$$

which has also been described [1]) was not found at 25°.

The system: $Ba I_2—BaO—H_2O$.

In this system also, the isotherm of 25° has been determined; in addition to $Ba I_2 . 7H_2O$, $Ba I_2 . 2H_2O$ and $Ba(OH)_2 . 8H_2O$ the oxy-iodide:

$$Ba I_2 . BaO . 9H_2O \quad \text{or} \quad Ba\Big\langle {I \atop OH} . 4H_2O$$
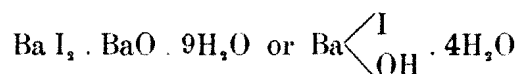
also described previously, occurs as solid phase. [2])

Besides the above systems, various other ones are now being investigated; the results of this research will be communicated later.

Physics. — *"Accidental deviations of density in mixtures"*. By Dr. L. S. ORNSTEIN (Communicated by Prof. H. A. LORENTZ).

The theory of accidental deviations of density in mixtures does not differ, as for the principles, from that of the deviations of density in systems containing only one kind of molecules. To calculate these deviations I shall apply the canonical ensembles of GIBBS [3]).

1. Let us suppose a mixture of k substances to be in a volume v, n_1 being the number of molecules of the kind 1, n_x that of the kind x, and n_k that of the kind k. Besides the coordinates and moments of the centres of gravity, a number of internal coordinates and moments can be used to characterize the state of the molecules. Let us imagine a canonical ensemble built up of those systems. We shall denote by x_{11}, y_{11}, z_{11} . . . . . z_{1n1} the coordinates of the centres of gravity for the molecules of the first kind, those of the x-molecules will be represented by $x_{x1} \ldots z_{xnx}$.

In order further to characterize the system, we shall introduce

[1]) BECKMANN, J. f. prakt. Chem. N. F, **27** 132 (1883).

[2]) BECKMANN. Ber. **14**, 2156.

   E. TASSILLY, Compt. rend. **120**, 1338.

[3]) I shall confine myself to a single phase, the coexistence of phases offering no particular difficulties. I dealt with this question in my dissertation (comp. p. 114).

the moments belonging to the coordinates (the internal ones and those of the centres of gravity) mentioned above. Now, suppose $d\lambda_i$ to represent an element of the extension in phase of the internal coordinates and moments. Consider the integral

$$\int e^{-\varepsilon'/\Theta} dx_{11} \ldots dz_{knk}\, d\lambda_i ,$$

where ε' is the total energy ε diminished by the energy of the progressive motion of the centres of gravity. The integration with respect to the coordinates of the centres of gravity must be extended over the $3(n_1 + \ldots n_x + n_k)$-dimensional space $v3\Sigma n_x$, whereas all values that are possible without dissociation of the molecules are to be ascribed to the internal coordinates and moments.

If, in the case considered, there exists a sphere of repulsion such as there is with rigid, perfectly elastic molecules, then the consequence will be that ε' takes an infinite value for certain configurations, and therefore the parts of the integral corresponding with these configurations will not contribute to it. Just as in the case of a simple substance and in that of a binary mixture[1]), one can show in this case that the integral may be put into the form

$$\{\omega\,(\mathrm{n}_1 \ldots \mathrm{n}_x \ldots \mathrm{n}_k)\,.\,v\}^{\overset{k}{\underset{}{\Sigma}}\, n_x}$$

where $\mathrm{n}_x = \dfrac{n_x}{v}$, i. e. the number of molecules of the kind $\varkappa$ pro unit of volume.

The function ω may be determined if the structure of the molecules is given; but for our purpose it is sufficient for us to know that the integral can be reduced to the form mentioned above.

2. We now imagine the volume V to be divided into a great number of equal elements of volume $V_1 \ldots V_\lambda \ldots V_l$, and we want to know the number of systems in a canonical ensemble for which the element V_λ contains respectively $n_{1\lambda} \ldots n_{x\lambda} \ldots n_{k\lambda}$ of the different molecules. We have for the numbers $n_{x\lambda}$

$$\overset{l}{\underset{1}{\Sigma}}\, n_{x\lambda} = n_x.$$

the total number of molecules of each kind being given.

This number of systems ζ, which I shall call the frequency of the systems mentioned, is represented by the formula

$$\zeta = N e^{\frac{\Psi}{\Theta}} \overset{k}{\underset{1}{\prod}} \left\{ (2\,\pi\,\Theta\,m_x)^{\frac{3}{2}n_x}\, n_x! \overset{l}{\underset{1}{\prod}} \left\{ \frac{\omega_\lambda\,(\mathrm{n}_{1\lambda} \ldots \mathrm{n}_{x\lambda} \ldots \mathrm{n}_{k\lambda})\,V_\lambda}{n_{x\lambda}!} \right\}^{n_{x\lambda}} \right\}, \quad . \;(1)$$

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[1]) Comp. my dissertation and these Comm. 1908, p. 107.

m_x denoting the mass of a molecule of the kind x. We now can ask, for which values of the numbers $n_{x\lambda}$ this frequency is a maximum. In this way we find for the k conditions to which the densities in the most frequently occurring system are submitted:

$$- log\, n_{x\lambda} + \sum_1^l (n_{x\lambda}) \frac{d\, log\, \omega_\lambda}{\partial\, n_{x\lambda}} + log\, \omega_\lambda = f_x, \quad . \quad . \quad . \quad (2)$$

x from 1 to k. These conditions can be satisfied by means of a homogeneous distribution of each of the x kinds over the volume V. Further the second variation of ζ or of $log\, \zeta$ has to be negative. If we denote by $n_{x\lambda}$ the values in the most frequently occurring system, then the frequency ζ_Δ of the system in which these numbers have the values $n_{x\lambda} + \tau_{x\lambda}$ can be represented by

$$\zeta_0 = \zeta_0\, e^{-Q} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The quantity Q is a homogeneous quadratic function of the numbers $\tau_{x\lambda}$. Taking the sum of ζ_Δ with respect to all possible values of these numbers i.e. from $-\infty$ to $+\infty$, we obtain $\sum \zeta_\Delta = N$, from which Ψ can be calculated.

Proceeding in this way we find

$$e^{-\frac{\Psi}{\Theta}} = \prod_1^k (2\pi\Theta m_x)^{\frac{3n_x}{2}} \{\omega(n_1 \ldots n_x \ldots n_k)\}^{n_x}, \quad . \quad . \quad . \quad (4)$$

In calculating Ψ, which is equivalent to the free energy, we must neglect a factor of the order of unity. However, the formula is rigorously exact, the above-mentioned being a mere verification of the equation (3). For keeping in mind the definition of GIBBS, we have for Ψ

$$e^{-\frac{\Psi}{\Theta}} = \int e^{\frac{-2\varepsilon' + m_x x_{1x}^2}{2\Theta}} m_1 d\dot{x}_{11} \ldots dx_{11}\, d\lambda_i$$

and therefore

$$e^{-\frac{\Psi}{\Theta}} = \prod_1^k (2\pi\Theta m_x)^{\frac{3}{2}n_x} \int e^{-\frac{\varepsilon'}{\Theta}} dx_{11} \ldots dz_x n_x,$$

and we see that according to the definition of the function ω, the formula given for Ψ holds exactly [1].

If we would have as a separate system of volume V_λ the $n_{1x} \ldots n_{x\lambda} \ldots n_{x\lambda}$ molecules being now in the volume V_λ, then the free energy of this system would be given by the formula

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[1]) Comp. also my dissertation p. 56, 112, 126.

$$e^{-\frac{\Psi_\lambda}{\Theta}} = \prod_1^k (2\pi\Theta m_\varkappa)^{\frac{3}{2}n_{\varkappa\lambda}} \{\omega(\mathrm{n}_{1\lambda} \ldots \mathrm{n}_{\varkappa\lambda} \ldots \mathrm{n}_{\nu\lambda}) V_\lambda\}^{n_{\varkappa\lambda}}.$$

The function Ψ_λ may be used to transform the formula for the frequence ζ. For, applying the theorem of STIRLING, we can write ζ in the form

$$\zeta = N e^{-\frac{\Psi}{\Theta}} \prod_1^k (2\pi\Theta m_\varkappa)^{\frac{3}{2}n_\varkappa} n_\varkappa^{n_\varkappa} \prod_1^l \left\{\frac{\omega_\lambda(\mathrm{n}_{1\lambda}\ldots\mathrm{n}_{k\lambda}) V_\lambda}{n_{\varkappa\lambda}}\right\}^{n_{\varkappa\lambda}}$$

and therefore, introducing Ψ_λ, we obtain for ζ

$$\zeta = N e^{-\frac{\Psi}{\Theta}} n_1^{n_1} \ldots n_\varkappa^{n_\varkappa} \ldots n_k^{n_k} \prod_1^l \left\{ e^{-\frac{\Psi_\lambda}{\Theta}} \prod_1^k \frac{1}{n_{\varkappa\lambda}^{n_{\varkappa\lambda}}} \right\}$$

For the further discussion we shall not use the free energy Ψ_λ, but a function ψ_λ [1]), closely connected with it, and being defined by the equation

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[1]) We can somewhat more closely explain the introduction of the function ψ_λ (comp. also my dissertation p. 52 s.). We shall compare the free energy of the system considered above to the free energy of the same system in gaseous state and in a volume so great that it can be considered as an ideal gas. We now can easily show the free energy of the mixture in the gaseous state to be equal to the sum of free energies of the components, if each of them occupies the same volume as their mixture. Further we can suppose that the volume of each of the substances (which now occur as simple substances in k separate volumes), is changed in such a way, that the number of particles pro unit of volume which is to be taken very great, amounts to ν (arbitrarily chosen) for all k systems. The volume occupied by the $\varkappa^{th}$ component now amounts to $\dfrac{n_{\varkappa\lambda}}{\nu}$. In this state $\left(\dfrac{n_{\varkappa\lambda}}{\nu}\right)^{n_{\varkappa\lambda}}$ will be so great that $(\omega(v)n^{\varkappa\lambda})$ may be put equal to unity.

We therefore find for the free energy of each of the components, originating from the element λ

$$e^{-\frac{\Psi'_{\varkappa\lambda}}{\Theta}} = (2\pi\Theta m_\varkappa)^{\frac{3}{2}n_{\varkappa\lambda}} \left(\frac{n_{\varkappa\lambda}}{\nu}\right)^{n_{\varkappa\lambda}}.$$

And for their total free energy:

$$e^{-\frac{\Psi'_\lambda}{\Theta}} = e^{-\frac{\sum_1^k \Psi'_{\lambda\varkappa}}{\Theta}} = (2\pi\Theta m_\varkappa)^{\frac{3}{2}\sum_1^k n_{\varkappa\lambda}} \prod_1^k \left(\frac{n_{\varkappa\lambda}}{\nu}\right)^{n_{\varkappa\lambda}}$$

For the difference between the free energy in the state from which we started and that in the zero-state considered we find

$$e^{-\frac{\psi_{\lambda}}{\Theta}} = \prod_{1}^{k} \left(\frac{\omega_{\lambda} V_{\lambda}}{n_{\varkappa\lambda}}\right)^{n_{\varkappa\lambda}} = \prod_{1}^{k} \left(\frac{\omega_{\lambda}}{n_{\varkappa\lambda}}\right)^{n_{\varkappa\lambda}}.$$

Introducing the function ψ_{λ} we obtain for ζ

$$\zeta = N e^{\frac{\Psi}{\Theta}} n_{1}^{n_{1}} \ldots n_{\varkappa}^{n_{\varkappa}} \ldots n_{k}^{n_{k}} \prod_{1}^{k} (2\,\pi\,\Theta\,m_{\varkappa})^{\frac{3}{2}n_{\varkappa}} \prod_{1}^{l} e^{-\frac{\psi_{\lambda}}{\Theta}}.$$

The volume being given, the function ψ is a function of the densities $n_{\varkappa}$, for

$$-\frac{\psi}{\Theta} = \sum_{1}^{k} n_{\varkappa} \{log\,\omega\,(n_{1} \ldots n_{\varkappa} \ldots n_{k}) - log\,n_{\varkappa}\} =$$

$$V \sum_{1}^{k} \{n_{\varkappa}\,log\,\omega\,(n_{1} \ldots n_{\varkappa} \ldots n_{k}) - log\,n_{\varkappa}\}$$

3. We shall use the form now given to ζ to put the question of probability of deviations in such a form that the deviations of density appear from our formulae. We then have to examine for which values of the densities $log\,\zeta$ will be a maximum. Suppose $n_{\varkappa\lambda}$ to represent these values and $\varrho_{\varkappa\lambda}$ to represent the deviations of densities for other systems, then

$$\sum_{1}^{l} \varrho_{\varkappa\lambda} = 0.$$

For $d\,log\,\zeta$ we have

$$d\,log\,\zeta = -\frac{1}{\Theta}\left[\sum_{1}^{l}\sum_{1}^{k}\frac{\partial\psi_{\lambda}}{\partial n_{\varkappa\lambda}}\varrho_{\varkappa\lambda} + \frac{1}{2}\sum_{1}^{l}\left\{\frac{\partial^{2}\psi_{\lambda}}{\partial n_{1\lambda}^{2}}\varrho_{1\lambda}^{2} + \ldots\right.\right.$$

$$\left.\left.\ldots + 2\frac{\partial\psi_{\lambda}}{\partial n_{\varkappa\lambda}\partial n_{2\lambda}}\varrho_{1\lambda}\varrho_{2\lambda} + \ldots\right\} \ldots\right] \quad \ldots \quad (1^{a})$$

As conditions of equilibrium we now find

$$\frac{\partial\psi_{\lambda}}{\partial n_{\varkappa\lambda}} = f_{\varkappa} \quad \lambda \text{ from 1 to } l \quad \ldots \ldots \quad (7)$$

Further

$$\frac{1}{2}\sum_{1}^{l}\left\{\frac{\partial^{2}\psi_{\lambda}}{\partial n_{1\lambda}^{2}}\varrho_{1\lambda}^{2} + \ldots 2\frac{\partial^{2}\psi_{\lambda}}{\partial n_{1\lambda}\partial n_{2\lambda}}\varrho_{1\lambda}\varrho_{2\lambda} + \ldots\right\} > 0 \quad \ldots \quad (8)$$

$$e^{-\frac{\Psi - \sum \Psi'_{\lambda}}{\Theta}} = \prod_{1}^{k}\prod_{1}^{l}\left\{\left\{\frac{\omega(n_{1\lambda}..n_{\varkappa\lambda}..n_{\varkappa\lambda})}{n_{\varkappa\lambda}}\right\}^{n_{\varkappa\lambda}} v^{n_{\varkappa\lambda}}\right\} = e^{-\frac{\sum_{1}^{l}\psi_{\lambda}}{\Theta}} v^{\sum_{1}^{k}n_{\varkappa}}$$

the quantity v being an additive constant without any physical meaning; $\Sigma\psi_{\lambda}$, however, being connected with the difference of free energy from the zero state defined above.

The left member of this inequality consists of l terms, each of which relates to an element of volume v_λ. If we take into consideration that $\psi_\lambda = \dfrac{v_\lambda}{v} \psi = \dfrac{1}{l} \psi$, then it is seen that we have

$$\frac{\partial^2 \psi_\lambda}{\partial n_{\varkappa\lambda}^2} = \frac{1}{l} \frac{\partial^2 \psi}{\partial n_\varkappa^2}$$

and

$$\frac{\partial^2 \psi_\lambda}{\partial n_{\varkappa\lambda} \partial n_{\varkappa'\lambda}} = \frac{1}{l} \frac{\partial^2 \psi}{\partial n_\varkappa \partial n_{\varkappa'}} \qquad \cdots \cdots \quad (9)$$

The coefficients of all l forms therefore will be the same for all corresponding terms. In order to find the condition which is to be fulfilled by the coëfficients in (8), we will consider the case

$$\varrho_{1\lambda} = -\varrho_{1\lambda'} \quad , \quad \varrho_{\varkappa\lambda} = -\varrho_{\varkappa\lambda'} \quad , \quad \varrho_{k\lambda} = -\varrho_{k\lambda'}$$

all other ϱ's being 0. For this case we have for all possible values of the ϱ's

$$\frac{\partial^2 \psi}{\partial n_1^2} \varrho_{1\lambda}^2 + 2 \frac{\partial^2 \psi}{\partial n_1 \partial n_2} \varrho_1 \varrho_{2\lambda} + \cdots > 0,$$

only the index λ occurring.

The conditions, necessary for this to be true, are that 1. the discriminant Δ

$$\Delta = \begin{vmatrix} \dfrac{\partial^2 \psi}{\partial n_1 k} & \dfrac{\partial^2 \psi}{\partial n_1 \partial n_k} & \dfrac{\partial^2 \psi}{\partial n_1 d n_k} \\[2mm] \dfrac{\partial^2 \psi}{\partial n_1 \partial n_\varkappa} & \dfrac{\partial^2 \psi}{d n_\varkappa^2} & \dfrac{\partial^2 \psi}{\partial n_\varkappa \partial n_k} \\[2mm] \dfrac{\partial^2 \psi}{\partial n_1 \partial n_k} & \dfrac{\partial^2 \psi}{\partial n_k \partial n_k} & \dfrac{\partial^2 \psi}{\partial n_k^2} \end{vmatrix} > 0 \quad \cdots \quad (10)$$

whereas the same must be true for the determinants originating from the discriminant if we successively omit the right-hand column and the last row. The conditions under which the system is really a maximum and therefore stable, agree with the well-known thermodynamical conditions of stability.

4. We are now able to determine the mean values of the squares of deviations $\varrho^2_{\varkappa\lambda}$ and of the products $\varrho_{\varkappa\lambda} \varrho_{\varkappa'\lambda}$ [1]).

As is easily seen we have

$$\overline{\varrho^2_{\varkappa\lambda}} = \overline{\varrho^2_{\varkappa\lambda'}} \qquad \cdots \cdots \cdots \quad (11)$$

and

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[1]) Mathematically speaking, our problem is one of correlate probability, my formulae agreeing with formulae Prof. J. C. KAPTEIJN communicated to me after I had solved this problem.

$$\overline{\varrho'_{x\lambda}\,\varrho_{x'\lambda}} = \overline{\varrho_{x\lambda}'\,\varrho_{x'\lambda'}} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (11a)$$

To define $\varrho^2{}_{11}$ e. g., we have

$$\overline{\varrho^2{}_{11}} =$$

$$= \frac{\displaystyle \int\limits_{-\infty}^{+\infty}\!\!\cdot\cdot\!\!\int\limits_{-\infty}^{+\infty} \partial^2{}_{11}\, e^{-\frac{1}{2\Theta l}\sum\limits_{1}^{l}\left\{\frac{\partial^2\psi}{\partial n_1{}^2}\varrho^2{}_{1\lambda} + \cdot\cdot\, 2\frac{\partial^2\psi}{\partial n_1 \partial n_2}\varrho_{1\lambda}\,\varrho_{2\lambda}\cdot\cdot\right\}}\,d\varrho_{11}\cdot\cdot\,d\varrho_{kl}}{\displaystyle \int\limits_{-\infty}^{+\infty}\!\!\cdot\cdot\!\!\int\limits_{-\infty}^{+\infty} e^{-\frac{1}{2\Theta l}\sum\limits_{1}^{l}\left\{\frac{\partial^2\psi}{\partial n_1{}^2}\varrho^2{}_{1\lambda} + \cdot\cdot\, 2\frac{\partial^2\psi_2}{\partial n_1 \partial n_2}\varrho_{1\lambda}\,\varrho_{2\lambda}\right\}}\,d\varrho_{11}\cdot\cdot\,,\,d\varrho_{kl}}\cdot$$

Now, $\Sigma\,\varrho_{1\lambda} = 0$, etc. In order to take this into account in determining $\varrho^2{}_{11}$, we introduce new variables instead of $\varrho_{1_2}\cdot\cdot\,\varrho_{1\lambda}\cdot\cdot\,\varrho_{1l}$:

$$\varrho_{1\lambda} = \varrho'_{1\lambda} - \frac{1}{l-1}\varrho_{11} \quad \lambda \text{ from } 2 \text{ to } l.$$

Then we have

$$\sum\limits_{\lambda\,2}^{l}\varrho'_{1\lambda} = 0.$$

We also introduce for $\varrho_{1\varkappa}\cdot\cdot\,\varrho_{\varkappa l}$ new variables in a similar way. The exponents of the integral then can be expressed by

$$\frac{1}{2l\Theta}\left\{\varrho^2{}_{11}\frac{\partial^2\psi}{\partial n_1{}^2}\left(1 + \frac{1}{l-1}\right) + \right.$$

$$\left. + 2\,\varrho_{11}\,\varrho_{21}\frac{\partial^2\psi}{\partial n_1 \partial n_2}\left(1 + \frac{1}{l-1}\right)\cdot\cdot\,\varrho^2{}_{k1}\frac{\partial^2\psi}{\partial n^2{}_k}\left(1 + \frac{1}{l-1}\right) + C\right\},$$

where C is a quadratic function in the $\varrho'_{1\lambda}\,\varrho'_{2\lambda}$ ($\lambda\, 2$ to l).

Now, taking into account the conditions $\Sigma\varrho'_{1\lambda} = 0$, we can integrate with respect to the variables $\varrho'_{\varkappa\lambda}$ i.e. with respect to the elements $2\cdot\cdot\,\lambda\cdot\cdot\,l$; the result in the numerator being cancelled by that in the denominator. In this way we find

$$\overline{\varrho^2{}_{11}} = \frac{\displaystyle \int\limits_{-\infty}^{+\infty}\!\!\cdot\cdot\!\!\int\limits_{-\infty}^{+\infty} \varrho^2{}_{11}\, e^{-\frac{1}{2(l-1)\Theta}\left\{\varrho^2{}_{11}\frac{\partial^2\psi}{\partial n_1{}^2} + \cdot\cdot\, 2\,\varrho_{11}\,\varrho_{21}\frac{\partial^2\psi}{\partial n_1 \partial n_2}\right\}}\,d\varrho_{11}\cdot\cdot\,d\varrho_{k1}}{\displaystyle \int\limits_{-\infty}^{+\infty}\!\!\cdot\cdot\!\!\int\limits_{-\infty}^{+\infty} e^{-\frac{1}{2(l-1)\Theta}\left\{\varrho^2{}_{11}\frac{\partial^2\psi}{\partial n_1{}^2} + \cdot\cdot\, 2\,\varrho_{11}\,\varrho_{21}\frac{\partial^2\psi}{\partial n_1 \partial n_2}\right\}}\,d\varrho_{11}\cdot\cdot\,d\varrho_{k1}}\cdot$$

According to a well-known theorem (comp. GIBBS El. Pr. in Stat. Mech. p. 205) we have

$$\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} e^{-\dfrac{1}{2\,\Theta\,(l-1)}\left\{\dfrac{\partial^2\psi}{\partial n_1^2}\varrho^2_{11}+..2\dfrac{\partial^2\psi}{\partial n_1\partial n_2}\varrho_{11}\,\varrho_{21}..\right\}}\,d\varrho_{11}\,\partial\varrho_{x_1}..d\varrho_{k_1}=$$

$$(2\,\pi\,(l-1)\,\Theta)^{\frac{k}{2}}\,\frac{1}{\Delta^{1/2}},\ .\quad .\quad .\quad .\quad .\quad . \tag{13}.$$

where Δ is the determinant defined by (10). Differentiating the logarithm of (13) with respect to $\dfrac{\partial^2\psi}{\partial n_1^2}$, we find

$$\overline{\varrho^2_{11}}=(l-1)\,\Theta\,\frac{\Delta_{11}}{\Delta}$$

and in general

$$\overline{\varrho^2_{x\lambda}}=(l-1)\,\Theta\,\frac{\Delta_{xx}}{\Delta}\quad .\quad .\quad .\quad .\quad .\quad .\quad . \tag{14}$$

whereas at the same time we find

$$\overline{\varrho_{x\lambda}\,\varrho_{x'\lambda}}=(l-1)\,\Theta\,\frac{\Delta_{xx'}}{\Delta}\quad .\quad .\quad .\quad .\quad .\quad . \tag{14a}$$

The quantities Δ_{xx} and $\Delta_{xx'}$ represent in the usual way the minor determinants in Δ.

If l is great with respect to 1, then we can replace $l-1$ by l, and this quantity by $\dfrac{V}{V_\lambda}$, and keeping in mind that $\Theta=\dfrac{RT}{N}$, we have

$$\overline{\varrho_x^2}=\frac{RT}{N}\,\frac{V}{V_\lambda}\,\frac{\Delta_{xx}}{\Delta}\quad .\quad .\quad .\quad .\quad .\quad .\quad . \tag{15}$$

$$\overline{\varrho_x\,\varrho_{x'}}=\frac{RT}{N}\,\frac{V}{V_\lambda}\,\frac{\Delta_{xx'}}{\Delta}\quad .\quad .\quad .\quad .\quad .\quad . \tag{15a}$$

where ϱ_x and $\varrho_{x'}$ are used to denote $\varrho_{\lambda x}$ and $\varrho_{\lambda x'}$.

We can still modify these equations by introducing the free energy for the unit of volume filled with the given density. As $\psi=V\overline{\psi}$, we obtain $\Delta=V^k\,\overline{\Delta}$ ($\overline{\Delta}$ then relating to the determinant (10) for $\overline{\psi}$). $\Delta_{xx}=V^{k-1}\,\overline{\Delta}_{xx}$ etc. and we find

$$\overline{\varrho^2_x}=\frac{1}{V_\lambda}\,\frac{RT}{N}\,\frac{\overline{\Delta}_{xx}}{\overline{\Delta}},$$

and

$$\overline{\varrho_x\,\varrho_{x'}}=\frac{1}{V_\lambda}\,\frac{RT}{N}\,\frac{\overline{\Delta}_{xx'}}{\overline{\Delta}}.$$

Taking into account that $\tau_{x\lambda}$, being the deviation from $n_{x\lambda}$, amounts to $V_\lambda\varrho_{x\lambda}$, we find

$$\overline{\tau_{\varkappa\lambda}{}^2} = V_\lambda \frac{RT}{N} \frac{\overline{\Delta_{\varkappa\varkappa}}}{\overline{\Delta}} .$$

For the frequency ζ_Δ of a deviating system we have

$$\zeta_\Delta = \zeta_0 e^{-\frac{1}{2\theta l}\sum\limits_1^l \left\{ \frac{\partial^2\psi}{\partial n_1{}^2}\varrho_{1\lambda}{}^2 + ..2\frac{\partial^2\psi}{\partial n_1\partial n_2}\varrho_{1\lambda}\varrho_{2\lambda} ... \right\}} .$$

The probability of a system is proportional to ζ_Δ, and the logarithm of thus defined probability is, as I formerly showed, equivalent to the entropy [1]. The difference of entropy of the stationary and the deviating state therefore amounts to

$$-\frac{R}{2N\theta l}\sum\limits_1^l \left\{ \frac{\partial^2\psi}{\partial n_1{}^2}\varrho_{1\lambda}{}^2 + .. \right\}$$

or

$$-\frac{1}{2Tl}\sum\limits_1^l \left\{ \frac{\partial^2\psi}{\partial n_1{}^2}\varrho_{1\lambda}{}^2 + ..2\frac{\partial^2\psi}{\partial n_1\partial n_2}\varrho_{1\lambda}\varrho_{2\lambda} \right\}$$

The energy taken by the transition can therefore be expressed by

$$-\frac{1}{2l}\sum\limits_1^l \left\{ \frac{\partial^2\psi}{\partial n_1{}^2}\varrho_{1\lambda}{}^2 + . \ 2\frac{\partial^2\psi}{\partial n_1\partial n_2}\varrho_{1\lambda}\varrho_{2\lambda} .. \right\}$$

The mean value of this energy is

$$-\frac{RT}{2N}l.$$

the absolute value being

$$\frac{1}{2}\sum \left\{ \varrho_1{}^2\frac{\partial^2\psi}{\partial n_1{}^2} + 2\varrho_1\varrho_2\frac{\partial^2\psi}{\partial n_1\partial n_2} .. \right\} =$$

$$\frac{RT}{2N}\frac{l}{\Delta}\sum \left\{ \Delta_{11}\frac{\partial^2\psi}{\partial n_1{}^2} + .2\Delta_{12}\frac{\partial^2\psi}{\partial n_1\partial n_2} .. \right\} =$$

$$\frac{RT}{2N}l$$

This result agrees with that found on p. 852 of the quoted communication.

5. If χ is some observable quantity depending on the densities $n_{1\lambda}..n_{\varkappa\lambda}..n_{\varkappa\lambda}$ in the elements V_λ, then with the help of the given formula we can easily calculate the probability of a set of values $\chi_1..\chi_\lambda..\chi_l$, and the mean squares of deviations. For χ_Δ we have (limiting ourselves for a moment to a single element and therefore omitting the index)

$$\chi_\Delta - \chi_0 = \frac{\partial\chi}{\partial n_1}\varrho_1 + \frac{\partial\chi}{\partial n_\varkappa}\varrho_\varkappa + \frac{\partial\chi}{\partial n_k}\varrho_k$$

and so we have

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[1] Comp. Entropy and probability, Proceedings 1912 p. 840.

$$\overline{(\chi_\Delta - \chi_0)^2} = \overline{\xi^2} = \left(\frac{\partial\chi}{\partial n_1}\right)^2 \overline{\varrho_1^2} + 2\frac{\partial\chi}{\partial n_1}\frac{\partial\chi}{\partial n_2}\overline{\varrho_1\varrho_2} + \cdots$$

From which it appears, that

$$\overline{(\chi_\Delta - \chi_0)^2} = \overline{\xi^2} = \frac{V}{V_\lambda}\frac{RT}{N}\frac{1}{\Delta}\left\{\left(\frac{\partial\chi}{\partial n_1}\right)^2 \Delta_{11} + \cdots 2\frac{\partial\chi}{\partial n_1}\frac{\partial\chi}{\partial n_2}\Delta_{12}\cdots\right\}$$

which may also be written

$$\overline{\xi^2} = -\frac{1}{\Delta}\frac{RT}{N}\frac{V}{V_\lambda}D. \qquad \ldots \ldots \quad (16)$$

In the formula D represents the determinant

$$D = \begin{vmatrix} 0 & \dfrac{\partial\chi}{\partial n_1} & \dfrac{\partial\chi}{\partial n_\varkappa} & \dfrac{\partial\chi}{\partial n_k} \\[2ex] \dfrac{\partial\chi}{\partial n_1} & \dfrac{\partial^2\psi}{\partial n_1^2} & \dfrac{\partial^2\psi}{\partial n_1\partial n_\varkappa} & \dfrac{\partial^2\psi}{\partial n_1\partial n_k} \\[2ex] \dfrac{\partial\chi}{\partial n_\varkappa} & \dfrac{\partial^2\psi}{\partial n_1\partial n_\varkappa} & \dfrac{\partial^2\psi}{\partial n^2_\varkappa} & \dfrac{\partial^2\varphi}{\partial n_\varkappa\partial n_k} \\[2ex] \dfrac{\partial\chi}{\partial n_k} & \dfrac{\partial^2\psi}{\partial n_1\partial n_k} & \dfrac{\partial^2\varphi}{\partial n_\varkappa\partial n_k} & \dfrac{\partial^2\psi}{\partial n_k^2} \end{vmatrix}.$$

With the help of the given values of ζ, and of transformations which to some degree answer to those already performed, we can show that the probability of a system in which the deviations of $\chi, \xi_1 \cdots \xi_\varkappa \cdots \xi_l$, are between ξ_λ and $\xi_\lambda + d\xi_\lambda$, amounts to

$$W_\xi^{\xi+d\xi} = W_0\, e^{+\frac{\Delta}{2l\Theta D}(\xi_1^2 + \xi_\varkappa^2 + \xi_l^2)}\, d\xi_1 \cdots d\xi_\lambda \cdots d\xi_l.$$

For $\Theta\, log\, \dfrac{W_\xi}{W_0}$ we therefore have

$$\frac{\Delta}{2lD}(\xi_1^2 + \cdots \xi_\varkappa^2 + \cdots \xi_l^2).$$

The mean value of this quantity is

$$\Theta\, log\, \frac{W_\xi}{W_0} = \frac{R}{N}\, T\, log\, \frac{W}{W_0} = +\frac{\Delta}{2lD}\, l\overline{\xi^2} = -\frac{lRT}{2N}.$$

It appears from this, that $\Theta\, log\, \dfrac{W_\xi}{W_{\xi_0}} = \Theta\, log\, \dfrac{W_\rho}{W_{\rho_0}}$. The probability of a state defined with the help of the quantity χ therefore also agrees with the entropy, at least as far as the mean values which generally are only of importance, are concerned. Instead of the k partial densities also the function χ of them can serve therefore to define the entropy of deviating systems. In the quoted communication

on entropy and probability this has been shown for arbitrary observable parameters. The mean energy of deviation did not depend on the nature of the parameters, but on their number only; and also in the case considered it is not the partial density in the elements but only the number of elements discernible for observation which plays a part.

Groningen, April 1912.

Mathematics. — *"Calculus rationum."* (2nd Part). By Dr. G. DE VRIES. (Communicated by Prof. JAN DE VRIES.)

(Communicated in the meeting of March 30, 1912).

§ 16. If in the following remarkable root

$$\frac{^{n}(u)}{^{n}(v)}\ \Big|\ \frac{u}{v} = \overset{n}{\underset{1}{\varPi}}\ [^{n-}\!\!\not\!p(u),\ ^{\not\!p-1}(v)]$$

we put $v = u$, the left member assumes the form 1^{∞} apparently indefinite; the right member becomes $^{n-1}(u)^{n}$. Introducing the sign R for the ratio of two values of a variable lying infinitely close together, we can write:

$$Ry\ |\ Rx = {}^{n-1}(x)^{n}\ \text{for}\ y = {}^{n}(x).$$

This is a mutual root of two ratios lying infinitely close to unity. If it is now even obvious to introduce in agreement to the preceding a *rational radix* as measure for the field of ratio, then the significance of a mutual root of exponential numbers is strengthened by the fact that of the following forms

$$\lim_{\infty}\frac{a^{x}}{b^{x}}\ ;\quad \lim_{\infty} a^{x}\,|\,b^{x};$$

the latter has no sense, the former has.

If for the comparison of two variables a third is introduced as independent variable and if we then put

$$x = e^{f(z)}\ ;\quad y = e^{F(z)};$$

then from this can be deduced:

$$e^{f'(z)} = \lim \overset{\Delta z}{V}\left(1 + \frac{\Delta x}{x}\right)\ ;\quad e^{F'(z)} = \lim \overset{\Delta z}{V}\left(1 + \frac{\Delta y}{y}\right).$$

When joining these we find that Δz disappears when one of the mutual roots is calculated.

$$e^{F'(z)\,:\,f'(z)} = \lim\left(1 + \frac{\Delta y}{y}\right)\Big|\left(1 + \frac{\Delta x}{x}\right) = \lim \overset{\Delta Lx}{V}\frac{y + \Delta y}{y}.$$

Introducing for the rational radix the sign $V\!\!\!\!\!\!\swarrow R$