the shortening reflex and the paradoxal contraction. I am inclined to suppose that the latter is the pathological form of the first.

The curves I have given as physiological were those taken in a patient with a severe trigeminus-neuralgia caused by periostitis alveolaris, who is now cured. His reflexes were not altered in the least.

The curves 3 and 4 were taken from the healthy side of a hemiplegic patient and are perhaps not to be considered as purely physiological. There is some reason to suppose, that hemiplegia may cause a heightening of the shortening reflex of the healthy extremity.

Amongst the pathological forms of the reflex we might perhaps include some forms of hysterical contracture and also some cases of crampi. But I intended to consider only the physiological aspects of the reflex.

Physics. — *"On the thermodynamical functions for mixtures of reacting components."* By Dr. L. S. Ornstein. (Communicated by Prof. H. A. Lorentz).

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

In his dissertation Dr. P. J. H. Hoenen has developed a theory of the thermodynamical functions for mixtures of reacting components [1]. Considerations closely connected to those of this dissertation are obtained if the statistical method of Gibbs is applied to the study of the equilibrium in chemical systems. I will show this in the following communication, and will restrict myself to the case that only one kind of reactions is possible in the mixture, the extension to other cases being possible without any difficulty.

In the following considerations I shall use a canonical ensemble of the modulus $\Theta\left(=\dfrac{R}{N}T\right)$ (R is the constant of Avogrado for the grammolecule, N the number of molecules present in this quantity of matter. We might as well use the micro-canonical ensembles, but for the calculations then being somewhat more complicated.

The molecules participating in the reaction are indicated by $\mu_1 \cdot \cdot \mu_x \cdot \cdot \cdot \mu_k$
Then the reaction will be characterised by the stoechiometrical formula

$$\sum_1^k \nu_x \mu_x = 0 \qquad \qquad (1)$$

the numbers ν_x indicating the smallest numbers of molecules that

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[1] Dissertation Leiden 1912, comp. also these proceedings XV p. 614.

can take part in the reaction. The v's are necessarily whole numbers, some of them must be negative.

We will imagine the molecules to be built up of atoms $a_1...a_\pi...a_p$ in such a way that the chemical formula for the $\varkappa^{th}$ molecule is

$$\mu_\varkappa = y_{\varkappa 1} a_1 + \cdots y_{\varkappa \pi} a_\pi + \cdots y_{\varkappa p} a_p \quad \cdots \quad \cdots \quad (2)$$

the numbers $y_{\varkappa \pi}$ being positive whole numbers or zero.

We will first treat the case that the system has so great a volume that the mutual action of the molecules may be neglected in the expression of the energy.

The state of the system can be characterised by the coordinates of the centres of gravity of the molecules and the corresponding moments of momentum and by a certain number of internal coordinates and moments of momentum. The expression giving the energy of each molecule consists in the kinetical energy of the centrum of inertia, a quadratic expression in the moments of momentum of this centrum, the coordinates of the centrum of inertia not playing a part. Further in the energy corresponding to the internal coordinates, which I shall represent by $\varepsilon_\varkappa$. An element of the extension in phase corresponding to the internal coordinates of the $\varkappa^{th}$ molecules will be represented by $d\iota_\varkappa$. Be the mass of the molecules $m_\varkappa$.

Be the total number of systems of the ensemble N, the statistical free energy Ψ.

.₊·We now want to know the number of systems (z'') in this ensemble, for which $n_1 \ldots n_\varkappa \ldots n_k$ molecules of the different kinds are present in the volume V. That is to say those molecules produced by a completely specified combination of atoms, for which the internal coordinates and moments are situated in completely determined elements $d\lambda_1 \ldots d\lambda_\varkappa \ldots d\lambda_k$. As for the situation of the molecules within the volume V, and the moments of momentum of the centres of gravity, we will not apply any restricting conditions [1]). We find for z''

$$z'' = Ne^{\frac{\Psi}{\Theta}} \prod_1^k (2\pi m_\varkappa \Theta)^{\frac{3}{2} n_\varkappa} \left(e^{-\frac{\varepsilon_\varkappa}{\Theta}} d\lambda_\varkappa \right)^{n_\varkappa} V^{n_\varkappa} \quad \cdots \quad (3)$$

The number of systems in which no restrictions are applied not even for the internal coordinates and moments is obtained by integrating over the $d\lambda_\varkappa$'s with respect to all possible values.

We now put

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1) Comp. for the case that one should want to specify for these quantities also, my diss. p. 39, where the case of non-reacting molecules is treated.

$$(2\pi m, \Theta)^{\tfrac{3}{2}} V \int e^{-\tfrac{\varepsilon,}{\Theta}} d\lambda, = I, \quad \ldots \ldots \quad (4)$$

in which the integration must be extended over the above mentioned space. Now the number of the systems considered z' may be represented by

$$z' = N e^{-\tfrac{\Psi}{\Theta}} \prod_{1}^{k} I_{,'}^{n} . \quad \ldots \ldots \quad (5)$$

Now we have to determine the number of systems in which the atoms are combined so as to give $n,$ molecules of the xth kind, etc. We must bear in mind that the total number of atoms of each kind is fixed; so that when x_π is the number of atoms of the πth kind, we have p equations of the form

$$n_1 y_{1\pi} + \ldots n, y, \pi + \ldots n_k y_{k\pi} = x_\pi \quad \ldots \ldots \quad (6)$$

Now, in order to get the number of combinations possible, we must in the first place consider that x_π atoms are to be combined into groups of $n_1 y_{1\pi} \ldots$ particles in

$$\frac{x_\pi!}{(n_1 y_{1\pi})! \ldots (n, y, \pi)! \ldots (n_k y_{k\pi})!} \quad \ldots \ldots \quad (7)$$

different ways.

Further, that the number of different ways, in which $n_1 y_{1\pi}$ particles are to be combined into n_1 groups of $y_{1\pi}$ particles, is given by

$$\frac{(n_1 y_{1\pi})!}{(y_{1\pi})_{n_1} n_1! (y_{1\pi}-1)!} \quad \ldots \ldots \quad (8)$$

In order finally to obtain the total number of cases possible, we still ought to consider in how many ways the n_1 groups of $y_{11} \ldots y_{1\pi} \ldots y_{1p}$ particles may be combined into molecules $a_1 y_{11} + \ldots a, y_{1\pi} \ldots + a_p y_{1p}$. Suppose β_1 of the quantities $y_{1\pi}$ to differ from zero, then the wanted number of the combinations in question will be

$$(n_1!)^{\beta_1 - 1} \quad \ldots \ldots \ldots \quad (9)$$

For the total number of combinations we find, bearing in mind that $(n_1!)^{\beta_1}$ etc. occurs in the denominator

$$\frac{x_1! \ldots x_\pi! \ldots x_p!}{n_1! \ldots n,! \ldots n,! (y_{11} \ldots y_{1\pi} \ldots y_{1p})^{n_1} \ldots (y_{k1} \cdot y_{k\pi} y_{k\pi})^{n_k} (y_{11}-1)! \ldots (y_{kp}-1)!} \quad (10)$$

By uniting into a constant C the quantities not depending on $n,$ we get for the total number of systems, in which $n, \ldots,$ molecules x are present (z)

$$z = C \prod_1^k \frac{I_{,}^{n_{,}}}{n_{,}! \, (y_{,1} \ldots y_{,\tau} \ldots y_{,\mu})^{v_{,}}} \quad \ldots \quad (11)$$

(in which only those $y_{,\pi}$'s are to be taken into account that differ from zero). I will represent the factor $(y_{,1} \ldots y_{,\tau} \ldots y_{,\mu})$ by $s_{,}$.

Now in order to examine which of all systems is the most frequently occurring in the ensemble, which therefore is the system in equilibrium, we have to consider for which values of the $n_{,}$, z or $\log z$, i. e.

$$\sum_1^k n_{,} \, (\log I_{,} - \log n_{,} + 1 - \log s_{,}) \quad \ldots \ldots \quad (12)$$

is a maximum, ($n!$ being developed here according to the formula of STIRLING). The variations to which the numbers $n_{,}$ are submitted are ar_{π}, in which a is a positive or negative whole number. The condition of equilibrium that is reached in this way is

$$\sum_1^k v_{,} \, (\log \varGamma_{,} - \log n_{,} - \log s_{,}) = 0 \quad \ldots \ldots \quad (12')$$

Introducing

$$I_{,} = (2\pi m_{,} \varTheta)^{\frac{3}{2}} V \chi$$

for I_k. we get

$$\prod_1^l n_{,}^{v_{,}} = V^{\sum_1^k v_{,}} T^{\frac{3}{2} \sum_1^l v_{,}} \prod_1^k \left(\frac{2\pi m_{,} R}{N} \right)^{3/_2 v_{,}} \chi^{v_{,}} s_{,}^{-v_{,}} \ldots \quad (13)$$

As χ contains still terms that depend on T, this formula cannot yet be compared to that of Dr. HOENEN, however, in many regards it is already analogous to it. Now, applying the theorem that $\frac{R}{N} \log w$, (in which w is the probability of a state) is identical with the entropy, we find the entropy η of an arbitrarily chosen state to be given by

$$\eta = \frac{R}{N} \sum_1^k n_{,} \{ \log I_{,} - \log n_{,} + 1 - \log s_{,} \} \quad \ldots \ldots \quad (14)$$

This quantity therefore must agree with the entropy of a non-equilibrium state as defined by Dr. HOENEN. As appears from what is mentioned above, it possesses the quality of being a maximum in the state of equilibrium.

Now I will first use the result we obtained to calculate $\varPsi$ and through means of it the equation of state. Developing z with respect to a and summing up. we find for $\varPsi$

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$$e^{-\frac{\Psi}{\Theta}} = C' \prod_1^k \frac{I_{\nu}^{n_{\nu}}}{n_{\nu}'(y_{\nu 1} \ldots y_{\nu p})^{n_{\nu}} e^{-n_{\nu}}} \quad \ldots \ldots \quad (15)$$

C' is obtained from C, by dividing the total number of systems; n_{ν} denotes the value in the state of equilibrium.

Applying the relation

$$p = -\frac{\partial \Psi}{\partial V}$$

we find for the pressure

$$p = \frac{\Theta}{V} \sum_1^k n_{\nu} + + \Theta \sum_1^k (log\, I_{\nu} - log\, n_{\nu} - log\, s_{\nu}) \frac{(n_{\nu} - n_{\nu}')}{dV},$$

where n_{ν} relates to the state of equilibrium of the volume V, n_{ν}' to that of the volume $V + dV$. These numbers always differ av_{ν}, and so, taking into account the condition of equilibrium, we find

$$p = \frac{R\,T}{N\,V} \sum_1^k n_{\nu} \quad \ldots \ldots \ldots \quad (16)$$

In order to calculate the average energy we can apply the relation

$$\bar{\varepsilon} = \Psi - \Theta \frac{\partial \Psi}{\partial \Theta}$$

which gives, when the condition of equilibrium is taken into account

$$\bar{\varepsilon} = \sum_1^l n_{\nu} \left\{ \frac{3}{2} \frac{R}{N} T + \Theta^2 \frac{\partial\, log\, \chi_{\nu}}{\partial \Theta} \right\}.$$

Now, in many cases χ_{ν} inasmuch as it depends on Θ, may be represented by $\Theta^{\nu} q$, (q independent of Θ) or in other cases by a complicate function of Θ. So, in the first case,

$$\bar{\varepsilon} = \frac{R}{N} T \sum_1^k n_{\nu} \left(\frac{3}{2} + \gamma_{\kappa} \right)$$

Putting the energy that is supplied when the numbers n_{ν} change with ν_{ν}, $c = \frac{R}{N} \sum \nu_{\nu} \left(\frac{3}{2} + \gamma_{\nu} \right)$, then we find that the condition of equilibrium (13) changes for this case into

$$\prod_1^k n_{\nu}^{\nu_{\nu}} = V^{\sum_1^k \nu_{\nu}} T^{\frac{N}{R}c} \prod_1^k \left\{ \left(\frac{2\pi\, m_{\nu}\, R}{N} \right)^{3/2} q_{\nu}\, s_{\nu} \right\}^{\nu_{\nu}} \quad . \quad . \quad (13^a)$$

When we represent the energy of the molecules ε_{ν} by a constant a_{ν} plus a function of the internal coordinates, then in the formula (13^a) the factor

$$-\sum_{1}^{k} e^{\frac{a, v, N}{TR}}$$

still must be added. The formula obtained in this way agrees with that of p. 12 and 13 of the cited dissertation.

Just as in this dissertation p. 16, we can by comparing $dQ = d\varepsilon + pdv$ and $d\eta$ show that

$$d y > \frac{dQ}{T} \qquad \qquad \qquad (17)$$

if we have to do with the changing into a state of non-equilibrium.

I will now consider what will become of our condition of equilibrium in the case we apply the theory of energy-quanta. Let us suppose we have the case of the molecules possessing 3 degrees of freedom of rotation, and l, vibratory degrees of freedom of the frequency τ ,.

The value of y, can be given then. On account of the 3 rotations it contains a factor $\Theta^{1/2}$, further the integral is equal to a product of l, integrals of the form

$$\int e^{-\frac{\varepsilon_{l//}}{\Theta}} d\lambda_{l//}$$

relating to each of the vibrations. This integral has the value

$$\frac{h\tau_{//}}{\left(1 - e^{-\frac{h\tau_{//}}{\Theta}}\right)} \quad {}^{1})$$

Introducing for each molecule the energy α, for the zero state and a constant originating from the integration with respect to the angular coordinates of the rotations, then the condition of equilibrium takes the form

$$\prod_{1}^{k} n_{//}' = V^{\sum_{1}^{l} r_{/}} \cdot T^{3\sum_{1}^{k} v_{/}} \cdot \prod_{1}^{k} e^{-\frac{a, v_{/}}{T}} S_{/}' \cdot \prod_{1}^{l} \left(\frac{h\tau_{//}}{1 - e^{-\frac{h\tau_{//}}{\Theta}}}\right)^{v_{/}} . \quad (18)$$

in which all constants relating to the molecules $\varkappa$ are contained in $S_{/}$. If the theory of quanta must be applied to some of the rotatory energies, then the exponent of T will be smaller.

As appears from the calculations of Dr. SCHEFFER [2]) the experi-

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[1]) The complications arising when equal frequencies occur are easily to be overcome Comp these proceedings 8 March 1912 p. 1103 and 1117.

[2]) These proceedings XIV. p. 743.

ments can more sufficiently be represented by applying the formula not of EINSTEIN, but of NERNST-LINDEMANN for the specifie heat; the equation (18) leads for the specific heat to the formula of EINSTEIN. For solid matter BORN and VAN KARMAN have given a theory leading to a formula which seems to represent the experiments on s. h. as well as the formula of NERNST-LINDEMAN. They start from the conception that there cannot be attributed one definite frequency to the atoms of solid matter, but that, because of the coupling a great number of frequencies occur, which accumulate infinitely at one or more definite frequencies. The fact that the formula of NERNST is the more appropriate also for gases, makes it acceptable that also in gases, through the mutual influence of molecules, there cannot be spoken of a finite number of definite frequencies.

I may still observe, that for the given consideration the way in which the system at length comes into the most frequently occurring state, is of no importance. That it will get into it, may be regarded to be sure, as well from the point of view of statistical mechanics as from that of the theory of energy-quanta.

I will still consider now in what way we can, in liquid states, come to the condition of equilibrium. We must for a moment return to equation (3), then. There we could divide into parts relating to each of the molecules, the general integral which, according to the definition of GIBBS, denotes the number of systems of given state. However, in the case now considered we cannot proceed likewise, because of the mutual influence of the molecules. The number of systems of specified state is in general given by

$$N\, e^{\frac{\Psi - \varepsilon}{\Theta}}\ d x_{11} \ldots d x_{n'}\, m_1\, d\dot{x} \ldots m_{\prime}\, d\dot{x}_{n'}\, d\lambda$$

where $x_{11} \ldots x_{n'}$ represent the coordinates of the centres of gravity, n_{11} the velocities, and where $d\lambda$ relates to the internal coordinates and moments of all molecules. Now considering a system with $n_{\prime}$ molecules $\varkappa$, built up of specified atoms, and allowing all values for the coordinates of the centres of gravity, the total number of systems obtained in this way z'' may be represented by

$$N \prod_{1}^{k} (2\pi\, m_{\prime}\, \Theta)^{\frac{3}{2} \sum_{1}^{k} n_{\prime}} \int e^{-\frac{\varepsilon'}{\Theta}}\ d x_1 \ldots d\lambda.$$

The value of the integral can always be represented by

$$V^{\sum_{1}^{k} n_{\prime}}\ f(V\, n_1\, n_{\prime} \ldots n_k\, \Theta)$$

For a gas the function f takes the form of the function considered above. We will not consider the form more closely now. This being observed, it will be. easy to point out the changes which (11), the formula that gives the number of systems, will undergo. We find

$$z = C f(V, n_1 \ldots n_r \ldots n_k, \Theta) \prod_1^k \frac{(2 \pi \Theta m_r)^{\frac{3}{2} n_r} V^{n_r}}{n_r! (s_r)^{n_r}}. \quad . \quad (19)$$

Asking again which · is the most frequently occurring state, we find for the condition of equilibrium

$$\Sigma v_r \left(-- \log n_r + \frac{3}{2} \log (2\pi \Theta m_r) + \log V - \log s_r + \frac{\partial \log f}{\partial n_r} \right) = 0. \quad . \quad (20)$$

For the statistical free energy we find

$$e^{-\frac{\Psi}{\Theta}} = \frac{C f(V n_1 \ldots n_r \ldots n_k, \Theta) V^{\sum_1^k n_r} T^{\frac{3}{2} \sum_1^k n_r}}{n_1^{n_1} e^{-n_1} \ldots n_r^{n_r} e^{-n_r} s_1^{n_1} . s_r^{n_r}},$$

the numbers $n_1 \ldots n_r$ relating here to the maximal system.

Calculating the pressure from Ψ we find

$$p = \frac{RT}{NV} \sum_1^k n_r + \frac{RT}{N} \frac{\partial \log f}{\partial V}$$

where the terms again are zero on account of the condition of equilibrium. Like Prof. H. A. LORENTZ in his "Abhandlungen" also Dr. HOENEN uses the equation of state

$$p = \frac{R}{N} \frac{T}{V} \sum_1^k n_r - q$$

(1 put it in molecular form), the term q then denotes the deviation from the gas-laws, the q there used therefore agrees with our

$$q = \frac{RT}{N} \frac{\partial \log f}{\partial V} \qquad .$$

$\log f$ may be given the form

$$\log f = -\frac{N}{RT} \int_V^\infty q \, dv + \vartheta$$

where ϑ is a function of temperature depending on the n_r also. Introducing this into (20) then

$$\sum_1^k v_r \log n_r = \sum_1^k v_k \left(\frac{3}{2} \log (2\pi \Theta m_r) + \log V - \log s_r + \frac{\partial \vartheta}{\partial n} \right) - \frac{N}{RT} \sum_1^k \int_{}^\infty \frac{\partial q}{\partial n_r} r_r dV.$$

Now if q is a function of the numbers n, the variation of q, if a varies with da, is because of dn, then being $r_/da$,

$$dq = \sum_{1}^{k} \frac{\partial q}{\partial n_/} r_/da.$$

So that this sum may be represented by $\frac{\partial q}{\partial a} da$.

The condition of equilibrium thus changes into

$$\sum_{1}^{l} r_/ \log n_/ = \sum_{1}^{k} \left\{ \left(\frac{3}{2} \log 2\pi \Theta m_/ \right) + \log V - \log s_/ + \frac{\partial \vartheta}{\partial n_/} \right\} r_/ - \frac{N}{RT} \int_{V}^{\infty} \frac{\partial q}{\partial a} dv.$$

Putting the zero-energy a, and introducing 3 vibrational freedoms then, when the remaining part of ϑ is represented by t, we get

$$\sum_{1}^{k} r_/ \log n_/ = \sum_{1}^{k} \left\{ 3 \log T + \log V - \frac{a_/N}{RT} - \log s_/ + \frac{\partial t}{\partial n_/} \right\} r_/$$

$$- \frac{N}{RT} \int_{v}^{\infty} \frac{\partial q}{\partial a} dv$$

the constant $s_/$ containing all quantities that do not depend on V and T. The quantity $\sum_{1}^{k} r_/ \log s_/$ may also be substituted by a single constant.

Also in the case considered the quantity $\frac{R}{N} \log w$ can be defined for each state as entropy, and likewise we have for the supply of heat $\frac{dQ}{T} < d\eta$ for states of non-equilibrium and $= d\eta$ for states of equilibrium.

It may be regarded as an advantage of the statistical method, that it contains at the same time the thermodynamical consideration of Dr. HOENEN, and the kinetic result — the law of GULDBERG and WAAGE — that he is bound to introduce besides his thermodynamic considerations.

Groningen, November 1912.