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ON THE SCATTERING OF THERMAL NEUTRONS BY BOUND PROTONS

BY

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INTRODUCTION

After FERMI's discovery¹⁾ of the possibility of producing slow neutrons by surrounding a source of fast neutrons by hydrogeneous substances such as paraffin wax, the problem of the mechanism of the collision between neutrons and protons has become important for the study of the properties of slow neutrons. The problem has already been treated by FERMI himself²⁾, who describes the slowing-down process in the following way. Neglecting first the fact that the protons in the paraffin are bound chemically, the fast neutrons which come from the source will make elastic collisions with the protons giving up on the average half of their kinetic energy at every collision. In this way they will soon reach thermal energies, where they will remain for a relatively long time, because now the chance that a neutron will get by a collision with a proton some of the thermal energy of the latter is about the same as that it will lose energy by the collision. The neutron will therefore diffuse round in the paraffin until it is finally captured by a proton. So long as the neutron energy is large compared with the oscillation energy of the proton it is legitimate to consider the latter as free. As the highest oscillation frequency of the proton in paraffin is of the order 3000 cm^{-1}

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1) E. FERMI, and coll., Proc. Roy. Soc. **149**, 522 (1935).

2) E. FERMI, Ric. scient. VII. II. 13 (1936). See also H. A. BETHE, Rev. of Mod. Phys., **9**, No. 2 1937.

corresponding to an energy of 0.37 volt(1) it will be correct to treat the protons as free for neutron energies down to about one volt.

Classically the total cross-section for the scattering should be the same above and below one volt, as the cross-section is classically always the geometrical area of the proton. In a quantum treatment, however, the binding of the proton has a large influence, as first pointed out by Fermi(2), who showed that one may use the Born approximation in calculating cross-sections for the slow neutrons. In this approximation the cross-section is proportional to the square of the reduced mass(3), and as this is equal to the neutron mass when the proton is bound strongly compared with the neutron energy but equal to half the neutron mass when the proton is free, it is seen that the cross-section in the first extreme case will be four times as large as in the second extreme case. For intermediate cases this chemical factor, as it is called, will lie between one and four. Fermi found by his model for the binding the value 3.3 in the case of the *C*-neutrons.

Because of this quantum effect we have therefore different stages in the slowing-down process. In the first stage, fast neutrons with energies of the order some million volts, the cross-section is experimentally found to be of the order $1-2\times 10^{-24}\,\mathrm{cm}^2$ (4) corresponding to a mean free path in paraffin of about 5 cm. Owing to the collisions the energy will soon decrease and the cross-section will therefore in-

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(1) $(\hbar\omega)_{\mathrm{volt}} = \frac{hc}{1.59\cdot 10^{-12}}\,(\tilde{\nu})_{\mathrm{cm}^{-1}} = 1.233\cdot 10^{-4}\,(\tilde{\nu})_{\mathrm{cm}^{-1}}.$

(2) Loc. cit.

(3) cf. eq. (1) p. 12.

(4) J. Chadwick, Proc. Roy. Soc. **142,** 1 (1933) and J. R. Dunning and coll., Phys. Rev. **48,** 265 (1935).

crease[1] until the energy is small compared with the energy of the excited state of the deuteron. In this second stage the cross-section will be independent of the energy and it is found[2] to be about 13×10^{-24} cm^2 corresponding to a mean free path of 1 cm for neutron energies from about 10 000 volts down to resonance energies of the order of some volts. In the third stage when the energy gets below one volt the chemical binding becomes noticeable and the cross-section increases to about 48×10^{-24} cm^2 for thermal energies[2], so that the mean free path decreases to about 0.3 cm.

For the two first stages Fermi has obtained the energy distribution of the neutrons[3] which in the second stage, where the mean free path is a constant, turns out to be proportional to $\frac{dE}{E}$. In the third stage, neutron energies below one volt, the problem of the energy distribution has neither as yet been solved theoretically, nor is it known accurately from experiments.[4]

For this last problem and for further problems connected with the slowing-down process, such as temperature effects, it is of interest to determine theoretically the effect of the chemical binding on the scattering cross-sections. Recently attempts have been made to connect such calculations with a still more extended range of problems: it has been proposed[5] to adopt for the cross-section of free protons — which is of considerable importance for the determination of the

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[1] Cf. e. g. H. A. Bethe and R. F. Bacher, Rev. of Mod. Phys., **8**, No. 2 (1936) eq. (62).

[2] M. Goldhaber and G. H. Briggs, Proc. Roy. Soc. **162**, 127 (1937) and O. R. Frisch, H. v. Halban jun. and J. Koch, Kgl. Danske Vidensk. Selsk. Skr. Mat.-fys. Med. XV, No. 10 (1938).

[3] Loc. cit.

[4] cf. later p. 9.

[5] Bethe, loc. cit.

neutron- and radiation width of excited nuclear levels[1] as well as for the theory of the deuteron and the discussion of the relation between proton-proton and proton-neutron forces[2] — instead of the direct experimental value which is not very accurate, the quotient of the thermal cross-section and a calculated chemical factor. It would, however, be much preferable for the above purposes to have a more exact experimental determination of the free proton cross-section as it is only possible to base such calculations on very rough models for the binding of the protons in paraffin and similar hydrogeneous substances. In spite of this fact it is, as we have seen, of interest to get some rough ideas about the influence of the binding, and we shall in this paper treat the problem by help of a model for the binding which we shall discuss in § 1.

§ 1. Discussion of a simplified model for the binding of the protons.

The scattering cross-section and the energy loss can be calculated exactly if the proper function for the nuclear motion in the molecules concerned is known. Theoretically it is possible from an analysis of the molecular spectra to obtain the frequencies of the vibrations and the normal coordinates which determine the form of the different normal vibrations. For the more complicated molecules, however, such as paraffin which is mostly used for the purpose of slowing down the neutrons, the resulting expressions would indeed be very complicated and unmanageable, quite apart from the fact that for these complicated molecules not all

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[1] H. A. Bethe and G. Placzek, Phys. Rev. **51**, 450 (1937).

[2] G. Breit and J. R. Stehn, Phys. Rev. **52**, 396 (1937).

the data needed are accurately known. Simpler molecules, like water for instance, have on the other hand so far only been used in the liquid state, and in this the interaction between the molecules which is of considerable importance for our problem cannot easily be treated quantitatively. We shall therefore in the present paper only discuss a very schematic model for the binding.

I. Instead of the normal vibrations we assume each proton to oscillate independently in a harmonic potential, which we shall assume to be anisotropic, since it can be deduced from molecular spectra that the protons oscillate with larger frequencies in the direction of the valency-bond than in the perpendicular directions. For the frequencies we shall take $\nu_z = 3000\ \mathrm{cm}^{-1} = 0.37$ volts, $\nu_x = \nu_y = \gamma \nu_z$ with $\gamma = 0.4$ so that $\nu_x = \nu_y = 1200\ \mathrm{cm}^{-1} = 0.148$ volts.

II. As we have already mentioned the binding has no influence classically on the scattering. This is also true if we do not consider the motion as a whole but only the separate degrees of freedom. Now we know that the nuclear motions in the molecules have also in addition to the larger frequencies which we have accounted for by the assumption I, a spectrum extending to quite small frequencies. These small frequencies we will take into consideration by assuming that the protons and their potentials can move freely like gas molecules with a MAXWELL velocity distribution, so that we substitute for the energy exchange between the neutrons and the small frequencies the exchange of kinetic energy between the neutrons and these "molecules". So long as the neutron energy can be considered large compared with the energies corresponding to these frequencies we can namely, as we have just seen, consider these separate degrees of freedom as unbound, only the fact that they are connected with the other degrees of freedom with the large frequencies must be accounted for. This we do by ascribing an effective mass to the "molecules" consisting of proton and potential, and for this effective mass we choose the value 14 times the neutron mass, which is the mass of a CH_2 group. This figure is rather arbitrary and corresponds to the conception that the energy taken up in the neutron collision by a proton is transferred to a single carbon atom in the hydrocarbon chain rather than to several of them.[1)]

Our two assumptions are of course very arbitrary and certainly not fulfilled in nature. No account is taken of interference effects, and apart from this it is known, for instance, that the frequency of the *C-C* vibrations in Æthan (C_2H_6) and other heavy carbon molecules is of the order of 1000 cm^{-1}, which is about five times the energy of thermal neutrons at room temperature[2)], so that these vibrations cannot at all be considered small. The model described is on the other hand the next simplest after that chosen by Fermi[3)], the isotropic oscillator with infinite mass, and it is certainly a better approximation than his[4)]. Taking now our model for granted, we shall first see which con-

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[1)] It must be emphasized that this model is in no way identical with a gas of CH_2 groups. Firstly, in a CH_2 group the positions of the hydrogen atoms depend on each other; this gives rise to important interference effects which we do not consider in our model; secondly, the slowing-down process by free CH_2 groups would — apart from the slowing-down by elastic collisions — take place by energy transfer to the three proper vibrations of the group and the three rotations of the group as a whole, while in our case we have two times three vibrations and no rotation.

[2)] For $T = 290°$ abs we have $kT = 0.025$ volts $= 203\ cm^{-1}$.

[3)] Loc. cit.

[4)] After the conclusion of our calculations a discussion of the effect of the anharmonic binding on somewhat similar lines has been published by Bethe, loc. cit., where, however, the influence of the thermal motions are not considered (cf. the §§ 4—6 of the present paper).

clusions regarding the influence of the binding we can draw from the model, and next we shall use the results to estimate the effect of temperature variation on the mean free path.

In order to obtain definite results regarding the last problem it is necessary to know the energy ranges of the neutrons with which we are dealing. We shall assume these to be the so-called C-neutrons, that is the neutrons which are strongly absorbed in cadmium. The range of strong absorption in *Cd* extends from 0 to about 0.3 volts.[1] Further we must know the energy distribution of the *C*-neutrons. This is not exactly known; its theoretical determination is just one of the aims of the theoretical study of the slowing-down process with which we are dealing in the present paper. Two methods of investigation have been used to determine the energy distribution of the *C*-neutrons experimentally. First the method of the mechanical velocity selector[2]. By this method it is found that at room temperature the energy distribution has a maximum for an energy of the order of kT. Second the method of absorption in Boron[3]. As the capture cross-section in Boron is assumed to follow the $\frac{1}{v}$ law[4] it is possible by absorption experiments in this element to compare the mean value of $\frac{1}{v}$ for different kinds of neutrons. If for instance the *C*-neutrons were in thermal equilibrium with the slowing-down medium this mean value and hence the Boron absorption should vary with the absolute temperature of the medium as $T^{-\frac{1}{2}}$. While between

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[1] Cf. e. g. J. G. Hoffman and H. A. Bethe, Phys. Rev. **51**, 1021, (1937).

[2] J. R. Dunning and coll. Phys. Rev. **48**, 704 (1935). Cf. also Bethe, loc. cit.

[3] For a survey of the literature cf. Frisch, Halban and Koch loc. cit.

[4] R. Frisch and G. Placzek, Nature **137**, 357 (1936). D. F. Weekes, M. S. Livingston and H. A. Bethe, Phys. Rev. **49**, 471 (1936).

400° and room temperature no deviation from this $T^{-\frac{1}{2}}$ law has been found the increase of the Boron absorption between room- and liquid air temperature, and still more between liquid air and liquid hydrogen temperature, is much less than would follow from a $T^{-\frac{1}{2}}$ law. This proves that at least for temperatures of liquid air and downwards the energy distribution of the C-neutrons cannot be represented by a Maxwell distribution with the temperature of the slowing-down medium. The question how far their energy distribution can be represented by a Maxwell distribution corresponding to a higher temperature or by a mixture between a maxwellian and a non-maxwellian part shall not be discussed here. In view of these possibilities, however, it remains interesting to investigate the energy dependence of the scattering cross-section for a Maxwell beam of neutrons. We shall therefore for the purpose of the following calculations assume the C-neutrons to obey the Maxwell law throughout. A consequence of this assumption together with the assumptions made about the binding mechanism is, however, that we cannot expect a direct comparison of the results of our calculations with experiment to give a quantitative agreement.

§ 2. **General theoretical remarks.**

As first proved by Fermi[1] it is possible to find a "rectangular hole" potential V' with radius $\varrho' << \lambda$ and depth D', which substituted for the neutron-proton potential will give correct cross-sections in the Born approximation so long as the following conditions are satisfied:

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[1] Loc. cit. Cf. also Bethe, loc. cit. Part B p. 123.

I. The de Broglie wave-length, λ,[1] for the neutron relative to the proton must be large compared with the range of the neutron-proton force, ϱ:

$$\lambda >> \varrho .$$

II. The total cross-section, Q, must be small compared with the square of the wave-length:

$$Q << \lambda^2.$$

III. For I to be satisfied one can deduce[2] that the dimension of the proton wave function, a, must be large compared with the range of the neutron-proton force:

$$a >> \varrho .$$

For slow neutrons and protons bound in paraffin all these conditions are certainly satisfied, as for such neutrons λ is of the order of 10^{-9} cm or more, Q is of the order of 48×10^{-24} cm^2 and we further know that ϱ and a are respectively of the order of 10^{-13} cm and at least 10^{-9} cm.

For the differential cross-sections per unit solid angle $d\omega$, $I_{mn}(\theta, \varphi)$, where $I_{mn}(\theta, \varphi)\, d\omega$ is defined as the number of neutrons which are scattered, after having excited the proton from its m'th into its n'th state, into the solid angle $d\omega$ in the direction θ, φ per unit time and per scatterer, if there in the incident beam is one neutron crossing unit area per unit time at the place of the scatterer, we have now in the Born approximation the well known expressions[3]

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[1] This is for non-relativistic energies given by $(\lambda)_{\mathrm{cm}} = \frac{h}{(2\, m_N E_N)^{1/2}} = 2.85 \times 10^{-9}\ E_N^{-1/2}$ when $E_N = \frac{1}{2} m_N v_{rel}^2$ is measured in volts, v_{rel} being the velocity of the neutron relative to the proton.

[2] For instance by Fourier analyzing the wave function of the proton in respect to velocity.

[3] Cf. e. g. Mott and Massey, "Theory of Atomic Collisions", p. 100, eq. (21). (The equation is erroneous, the factor $\frac{k_{mn}}{k_0}$ missing). It will be seen that in this approximation I depends on θ only, not on φ.

$$
\left.\begin{aligned}
& I_{mn}(\theta) = \\
&= \frac{k_{mn}}{k_0}\left|\frac{2M_N}{4\pi\hbar^2}\int d\tau_N \int d\tau_P \exp(i\boldsymbol{k}''_{mn}\boldsymbol{r})\, V'(|\boldsymbol{r}_N-\boldsymbol{r}_P|)\,\psi_n^*(\boldsymbol{r}_P)\,\psi_m(\boldsymbol{r}_P)\right|^2 \\
& \boldsymbol{k}''_{mn} = \boldsymbol{k}_0-\boldsymbol{k}_{mn},\quad k_0^2 = \left(\frac{2\pi}{\lambda_0}\right)^2 = \frac{2M_N E_0}{\hbar^2}, \\
& k_{mn}^2 = \frac{2M_N}{\hbar^2}\left(E_0-(E_n-E_m)\right),\quad \theta = \sphericalangle(\boldsymbol{k}_0,\boldsymbol{k}_{mn})
\end{aligned}\right\}\quad (1)
$$

where ψ_m and ψ_n are the wave functions of the proton before and after the collision, $\boldsymbol{k}_o$ and $\boldsymbol{k}_{mn}$ the initial and final wave vectors [1] of the neutron, and M_N, E_o the *reduced* mass and energy of the neutron.

In this expression V' only depends on the distance between the neutron and the proton, so taking $\boldsymbol{r}_N-\boldsymbol{r}_P$ as a new variable in the $d\tau_N$ integration we can at once perform this and using that the exponential is equal to unity by this integration due to $\lambda >> \varrho'$ we get

$$I_{mn}(\theta) = q\cdot\frac{k_{mn}}{k_0}\left|\int \psi_n^*(\boldsymbol{r}_P)\exp(i\boldsymbol{k}''_{mn}\boldsymbol{r}_P)\,\psi_m(\boldsymbol{r}_P)\,d\tau_P\right|^2 \qquad (2)$$

$$q = \frac{M_N^2}{4\pi^2\hbar^4}\left|\int V'\,d\tau\right|^2 = \frac{4}{9}\,\frac{M_N^2}{\hbar^4}\,(D'\varrho'^{\,3})^2 \qquad (3)$$

Equation (3) we can write in the following way using the expression for the total cross-section for scattering between a neutron and a free proton [2] which we shall denote by Q_{free}

$$\pi q = \left(\frac{M_N}{m_N}\right)^2\cdot Q_{\text{free}}. \qquad (4)$$

We emphasize here that the expression (1) or (2) is calculated in coordinates relative to the center of gravity of the system in which the proton is bound and as this fact sometimes gives

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[1] The wave vector is just the momentum vector divided by $\hbar$.

[2] Cf. Note 1, eq. (N 5).

rise to a little confusion we shall briefly give the definitions here, the transformation formulae being derived in Note 2. In the theory for two-body collisions *three* different coordinate systems are used.[1] First the system where the one particle is at rest before the collision, which we shall call the *rest* system and denote by R.[2] (All variables denoted by capital letters). Next the system where the center of gravity of the two particles is at rest both before and after the collision, which we shall call the *center of gravity* system and denote by C. (All variables denoted by small letters with an asterisk). Finally the system which has its origin in the center of gravity of the one particle both before and after the collision, which we shall call the *relative* system and denote by r. (All variables denoted by small letters). Let the two particles have masses m_1, m_2 and coordinate vectors $\boldsymbol{R}_1$, $\boldsymbol{R}_2$, then the center of gravity, $\boldsymbol{R}_c$, is defined by

$$m_1\boldsymbol{R}_1 + m_2\boldsymbol{R}_2 = (m_1 + m_2)\boldsymbol{R}_c \tag{5}$$

The coordinates referred to the center of gravity are next defined by

$$\boldsymbol{r}_1^* = \boldsymbol{R}_1 - \boldsymbol{R}_c, \qquad \boldsymbol{r}_2^* = \boldsymbol{R}_2 - \boldsymbol{R}_c \tag{6}$$

Putting (6) into (5) we get

$$\boldsymbol{r}_1^* = -\frac{m_2}{m_1}\boldsymbol{r}_2^* \quad \text{or} \quad r_1^* = \frac{m_2}{m_1}r_2^*, \quad \theta_1^* = \pi - \theta_2^*, \quad \varphi_1^* = \varphi_2^* + \pi \tag{7}$$

if we introduce polar coordinates. Finally the relative coordinates are defined by

$$\boldsymbol{r}_2 = \boldsymbol{R}_2 - \boldsymbol{R}_1 = \boldsymbol{r}_2^* - \boldsymbol{r}_1^*, \qquad \boldsymbol{r}_1 = 0 \tag{8}$$

the particle with index one being taken as the particle initially resting in the R system. Using (5) we then have, introducing the reduced mass

$$\left.\begin{aligned}
&M = \frac{m_1 \cdot m_2}{m_1 + m_2} \\
&\boldsymbol{r}_2^* = \frac{M}{m_2}\boldsymbol{r}_2 \quad \text{or} \quad r_2^* = \frac{M}{m_2}r_2, \quad \theta_2^* = \theta_2, \quad \varphi_2^* = \varphi_2 \\
&\boldsymbol{r}_1^* = -\frac{M}{m_1}\boldsymbol{r}_2 \quad \text{or} \quad r_1^* = \frac{M}{m_1}r_2, \quad \theta_1^* = \pi - \theta_2, \quad \varphi_1^* = \varphi_2 + \pi.
\end{aligned}\right\} \tag{9}$$

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[1] The following also applies to the case where one or both of the two particles are complex, consisting of more parts. In this case the mass is the total mass and the coordinatevector is the one of the center of gravity.

[2] It should be noted that this system it not always identical with the coordinatesystem in which we make the observations, cf § 4.

We see from (9) the important fact that the angle of the colliding particle is the same in the C system and in the r system, due to

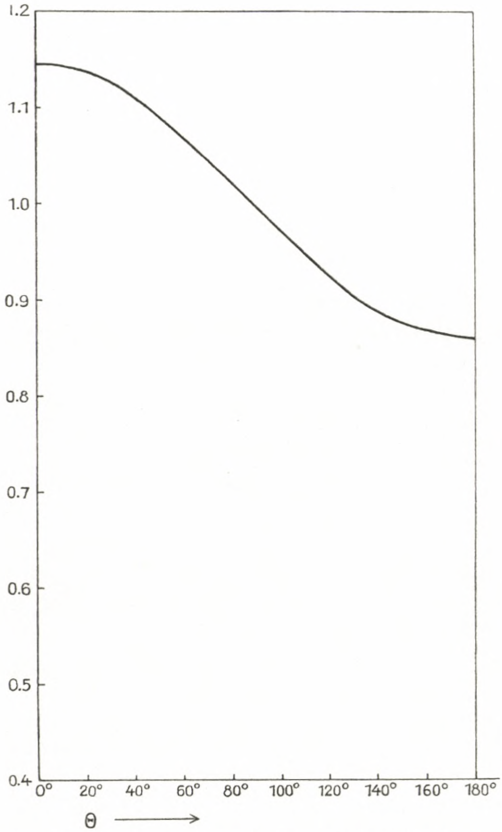

FIG. 1. *Angular distribution of scattered neutrons in the rest system corresponding to isotropic distribution in the center of gravity system, for* $m_S = 14\, m_N$.

which circumstance the formula (1) is often said to be derived in the C system in spite of the fact that it is really derived in the r system.

From the formulae (2) and (4) we can at once deduce that, as was already mentioned in the introduction, the total cross-section will be nearly four times as large as the one for a free proton when the proton is strongly bound, which means that the space in which the proper function of the proton is different from zero is very small compared with the wave-length of the neutron. We can then put the exponential equal to one, so that we get quite independent of the form of the proper function of the proton

$$I_{mn}(\theta) = q \cdot \frac{k_{mn}}{k_0} \delta_{mn} = q \cdot \delta_{mn} \tag{10}$$

which means that only elastic scattering can occur and that this is spherical symmetric in the *relative* system just as is the case for scattering by a free proton.[1] In the *rest* system, however, we will no longer get the cos Θ law[2] due to the mass of the scatterer being now larger than the neutron mass. In Fig. 1 we have plotted in units of q the curve for (10) transformed to the *rest* system[3] for the mass of the scatterer, m_S, equal to 14 m_N.

For the total elastic cross-sections we get from (10)

$$Q_{nn} = 4\pi q = 4\left(\frac{M_N}{m_N}\right)^2 Q_{\text{free}} \tag{11}$$

using (4). For the case $M_N = m_N$ i. e. $m_S = \infty$ the factor of Q_{free} in (11) reduces to the factor 4 first obtained by Fermi.[4] We have in this work taken $m_S = 14\, m_N$ throughout so that

$$4\left(\frac{M_N}{m_N}\right)^2 = 4\left(\frac{14}{15}\right)^2 = 4 \cdot 0.871 = 3.48 \tag{12}$$

which makes a considerable difference.

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[1] Cf. Note 1.

[2] Cf. Note 2 eq. (N 19).

[3] Cf. Note 2 eq. (N 18).

[4] loc. cit.

§ 3. The anisotropic oscillator.

We now in (2) put the wave functions for our anisotropic oscillator and as these are products of three wave functions for a one-dimensional harmonic oscillator, the matrix element will be a product of the matrix elements of the type given by eq. (N 24) in Note 3. Using the formulae (N 32) and (N 35) in Note 3 we have at once for the 0 → 0 transition, which is the only one we shall treat here

$$\left.\begin{aligned} I_{00} &= q\cdot\exp\left(-\frac{1}{2}a_z^2\left[\frac{1}{\gamma}\left(k''^2_{00_x}+k''^2_{00_y}\right)+k''^2_{00_z}\right]\right) \\ a_z &= \left(\frac{\hbar}{M_p\,\omega_z}\right)^{1/2}, \quad \frac{1}{2}k''^2_{00}a_z^2 = \varepsilon\,\frac{E_0}{\hbar\,\omega_z}\,4\sin^2\frac{\theta}{2}, \\ \varepsilon &= \frac{M_N}{M_p}{}^{[1]}, \quad E_0 = \frac{1}{2}M_N v_{rel}^2 \end{aligned}\right\} \quad (13)$$

M_P being the reduced mass of the *proton*, $\omega_z = 2\pi\nu_z$, ν_z the frequency of the oscillation in the direction of the z-axis and θ the angle between $\mathbf{k}_0$ and $\mathbf{k}_{00}$ i. e. the scattering angle of the neutron.

Further we must take the mean value of (13) over all directions of the oscillator. This we do by taking the axes of the oscillator as coordinate system and averaging over all directions of $\mathbf{k}''_{00}$ in respect to this system, the length of $\mathbf{k}''_{00}$ being kept constant. In this way we get, denoting the mean value by $\overline{I_{00}}\big|_{osc}$[2]

$$\overline{I_{00}}\Big|_{osc} = q\cdot\exp\left(-\frac{k''^2_{00}a_z^2}{2\gamma}\right)\int_0^1\exp\left(\frac{1}{2}k''^2_{00}a_z^2\left(\frac{1}{\gamma}-1\right)t^2\right)dt \quad (14)$$

We introduce as new variable the dimensionless quantity

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[1] Cf. eq. (N 36).

[2] A mean value we shall in this paper always denote by this symbol.

$$W = \varepsilon \frac{E_0}{\hbar\,\omega_z} = \frac{E_N}{\hbar\,\omega_z} \frac{\varepsilon}{1+\frac{m_N}{m_S}}, \quad E_N = \frac{1}{2} m_N V_N^2 \qquad (15)$$

where V_N is the velocity of the neutrons in the *rest* system, and then we can write (14) in the following form, due to

$$\frac{1}{2} k''^2_{00} a_z^2 = 4\,W \sin^2\frac{\theta}{2} \quad \text{(by (13))}$$

$$\overline{I_{00}}\Big|_{\mathrm{osc}} = q \cdot \frac{\exp\left(-\frac{1}{\gamma}\,4\,W\sin^2\frac{\theta}{2}\right)}{\left(\frac{1}{\gamma}-1\right)^{1/2} 2\,W^{1/2}\sin\frac{\theta}{2}} \int_0^{\left(\frac{1}{\gamma}-1\right)^{1/2} 2\,W^{1/2}\sin\frac{\theta}{2}} \exp\left(t^2\right) dt \qquad (\gamma \leq 1). \quad (16)$$

For $\gamma = 1$ we get the cross-section for the isotropic oscillator[1]

$$I_{00}^{is} = q \cdot \exp\left(-4W\sin^2\frac{\theta}{2}\right). \qquad (17)$$

In Fig. 2 we have plotted in units of q the curve (16)[2] transformed to the *rest* system[3] for two different values of W, $W = 0.0697$ (full line) and $W = 0.0156$ (dotted line) which correspond to $\hbar w_z = 0.37$ volts, $\gamma = 0.4$, $m_S = 14\,m_N$ and E_N equal to the effective energy of neutrons at room respectively at liquid air temperature, i. e. 90° abs.[4] It is seen that even at liquid air temperature there is still a considerable deviation from the spherical symmetry which is always assumed in calculations about the diffusion of thermal neutrons.[5]

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[1] Cf. Fermi, loc. cit., and Note 3 eq. (N 34).

[2] The function $\int_0^x \exp(t^2)\,dt$ is tabulated in Jahnke-Emde "Tables of Functions", p. 106.

[3] Cf. Note 2 eq. (N 18)

[4] Cf. § 6 p. 38.

[5] Cf. Fermi and Bethe, loc. cit.

The curves in Fig. 2 can also be represented by the function

$$I_{00}^{is''} = \frac{1}{3} I_{00}^{is} + \frac{2}{3} I_{00}^{is'}, \qquad I_{00}^{is'} = I_{00}^{is}\left(\frac{1}{\gamma} W\right), \tag{18}$$

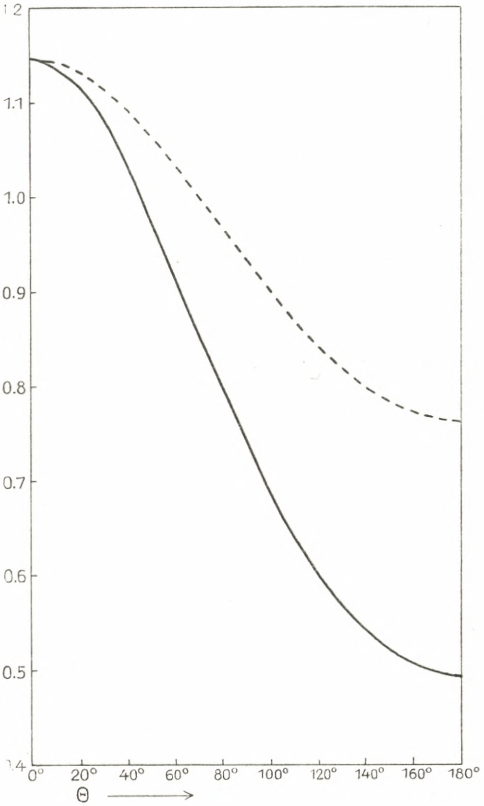

Fig. 2. *Angular distribution in the rest system of neutrons scattered by anisotropic oscillator. Full line corresponds to $W = 0.0697$, dotted line to $W = 0.0156$, W given by (15).*

where I_{00}^{is} is given by (17) and $I_{00}^{is'}$ stands for the same function with $\gamma\omega$ substituted for ω, which we can write as in (18) with W given by (15). The reason why the curves (16) and (18) are so like is easily seen analytically by expanding in powers of W. We then get

$$\left.\begin{aligned} \overline{I_{00}}\Big|_{\mathrm{osc}} &= q\cdot\exp\left(-\frac{1}{\gamma}4\,W\sin^2\frac{\theta}{2}\right)\left[1+\frac{1}{3}[\,]+\frac{1}{10}[\,]^2+\frac{1}{42}[\,]^3+\cdots\right] \\ I_{00}^{is''} &= q\cdot\exp\left(-\frac{1}{\gamma}4\,W\sin^2\frac{\theta}{2}\right)\left[1+\frac{1}{3}[\,]+\frac{1}{6}[\,]^2+\frac{1}{18}[\,]^3+\cdots\right] \\ &[\,] = \left(\frac{1}{\gamma}-1\right)4\,W\sin^2\frac{\theta}{2} \end{aligned}\right\}\quad(19)$$

so that the two curves have the same starting point and starting tangent and the difference comes first in the second power of W.

From (14) we can now by integrating over θ and φ get the mean value of the total cross-section. The result is

$$\overline{Q_{00}}\Big|_{\mathrm{osc}} = \int_0^{2\pi} d\varphi \int_0^{\pi} \overline{I_{00}}\Big|_{\mathrm{osc}} \sin\theta\, d\theta = \pi q\cdot\int_0^1 \frac{1-\exp\left(-4\,W\frac{1}{\gamma}\left[1-(1-\gamma)t^2\right]\right)}{W\frac{1}{\gamma}\left[1-(1-\gamma)t^2\right]}\,dt. \quad (20)$$

For $\gamma = 1$ we get the well-known formula for the isotropic oscillator[1]

$$Q_{00}^{is} = \pi q\cdot\frac{1-\exp(-4\,W)}{W}. \quad (21)$$

In FIG. 3 we have in the full curve plotted (20) in units of Q_{free}[2] for $\gamma = 0.4$ and $m_S = 14\,m_N$. Also we have in the same figure in the dotted curve plotted the curve analogous to (18),

$$Q_{00}^{is''} = \frac{1}{3}Q_{00}^{is} + \frac{2}{3}Q_{00}^{is'}, \qquad Q_{00}^{is'} = Q_{00}^{is}\left(\frac{1}{\gamma}W\right), \quad (22)$$

As we know from (19) the two curves have the same starting point and starting tangent. This can also be seen by direct expanding in powers of W

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[1] Cf. FERMI, loc. cit. Cf. also Note 4.

[2] Cf. eqs. (4) and (12).

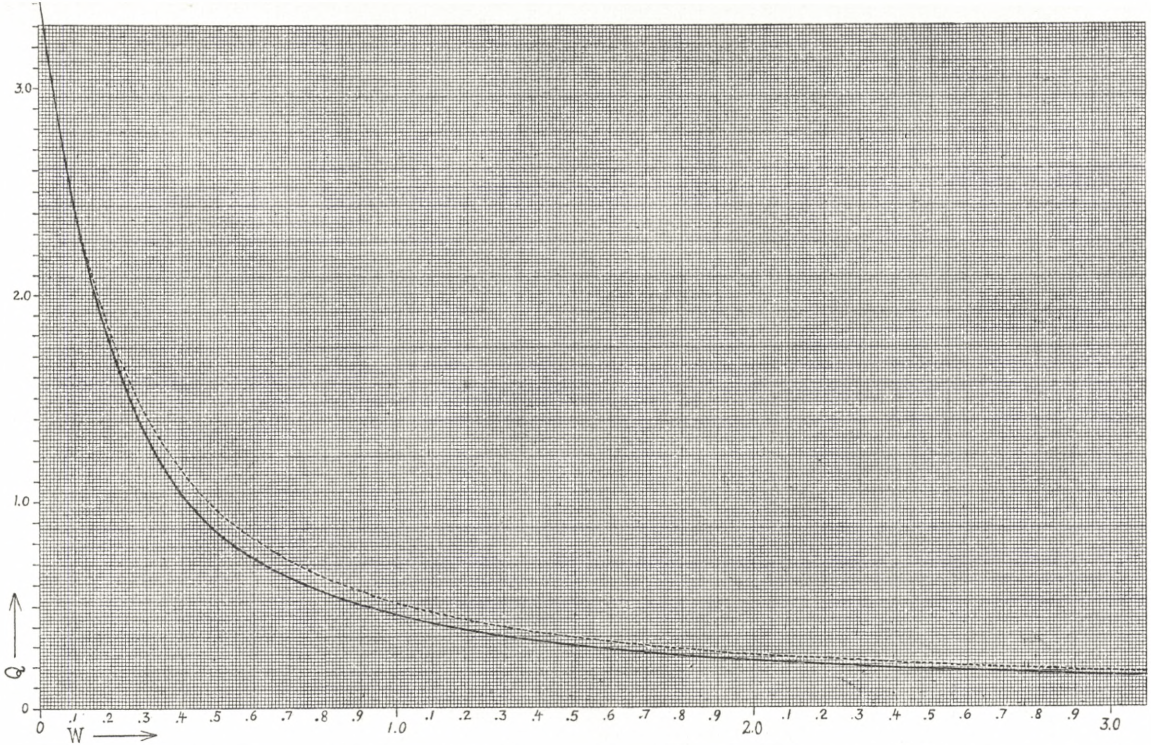

Fig. 3. *Energy dependence of total elastic scattering cross-section for anisotropic oscillator with $\gamma = 0.4$ (full line). Dotted line corresponding mean value for isotropic oscillators (see text). (The unit on the ordinate axis is Q_{free} whereas the curves are plotted in units (= 50 mm) of $\pi q = 0.871 \cdot Q_{free}$ (cf. eq. (11)) so one ordinate unit equals $50/0.871 = 57.4$ mm.)*

$$\left.\begin{aligned}
\overline{Q_{00}}\Big|_{\mathrm{osc}} &= \pi q \cdot 4 \sum_{n=0}^{\infty} \frac{\left(4\,W\frac{1}{\gamma}\right)^n}{(n+1)!}(-1)^n \sum_{s=0}^{n} \binom{n}{s} (-1)^s \frac{(1-\gamma)^s}{2s+1} = \\
&= \pi q \cdot 4 \left[1 - 2\,W \frac{1}{\gamma}\left(\frac{1}{3}\gamma + \frac{2}{3}\right) + \frac{8}{3} W^2 \frac{1}{\gamma^2}\left(\frac{1}{5}\gamma^2 + \frac{4}{15}\gamma + \frac{8}{15}\right) + \cdots\right] {}^{1)} \\
Q^{is''}_{00} &= \pi q \cdot 4 \sum_{n=0}^{\infty} \frac{\left(4\,W\frac{1}{\gamma}\right)^n}{(n+1)!}(-1)^n \left(\frac{1}{3}\gamma^n + \frac{2}{3}\right) = \\
&= \pi q \cdot 4 \left[1 - 2\,W \frac{1}{\gamma}\left(\frac{1}{3}\gamma + \frac{2}{3}\right) + \frac{8}{3} W^2 \frac{1}{\gamma^2}\left(\frac{1}{3}\gamma^2 + \frac{2}{3}\right) + \cdots\right].
\end{aligned}\right\} \quad (23)$$

Since $\gamma \leq 1 - (1-\gamma)\,t^2 \leq 1$ (due to $\gamma = 0.4 < 1$) in the integration range of t in (20) we can for large W neglect the exponential and we find then after elementary integration

$$\begin{aligned}
\overline{Q_{00}}\Big|_{\mathrm{osc}} &= \pi q \cdot \frac{\gamma}{2(1-\gamma)^{1/2}}\, ln \left(\frac{1 + (1-\gamma)^{1/2}}{1 - (1-\gamma)^{1/2}}\right) \cdot W^{-1} \\
Q^{is''}_{00} &= \pi q \cdot \left(\frac{1}{3} + \frac{2}{3}\gamma\right) \cdot W^{-1}
\end{aligned} \qquad (W >> 1) \quad (24)$$

For $\gamma = 0.4$ the two coefficients are respectively 0.531 and 0.6. That $I^{is''}_{00}$ and $Q^{is''}_{00}$ are very nearly equal to $\overline{I_{00}}\big|_{\mathrm{osc}}$ and $\overline{Q_{00}}\big|_{\mathrm{osc}}$ is also physically plausible. $I^{is''}_{00}$ and $Q^{is''}_{00}$ we can namely interprete as the average cross-sections for scattering in a substance consisting to one third of oscillators with energy $\hbar\,\omega_z$ and to two thirds of oscillators with energy $\gamma\,\hbar\,\omega_z$, while we by $\overline{I_{00}}\big|_{\mathrm{osc}}$ and $\overline{Q_{00}}\big|_{\mathrm{osc}}$ are averaging over all directions of one oscillator with one degree of freedom oscillating with an energy $\hbar\,\omega_z$ and two degrees of freedom oscillating with an energy $\gamma\,\hbar\,\omega_z$, so that one would think that the two kinds of averaging would give nearly the same result, which is

1) This series is, as is easily verified, identical with BETHE loc. cit. Part B eq (463), if we put $m_S = \infty$, as then our $\pi q \rightarrow \sigma_0$, $W \rightarrow \varepsilon_1$, $W\frac{1}{\gamma} \rightarrow \varepsilon_2$ by BETHE.

in fact found to be the case as we have just seen. Due to the expression (20) being far more complicated than the expression (22), we shall in the following use $Q_{00}^{is''}$ instead of $\overline{Q_{00}}|_{osc}$, the error being negligible especially as we shall only be interested in that part of (20) which belongs to small values of W.

§ 4. Influence of the temperature motion of the scattering centers.

We must now take the second feature of our binding model into consideration. At the same time we shall define a new scattering cross-section which can be directly measured. The cross-section is as a rule determined experimentally by measuring the absorption in varying thicknesses of paraffin.[1] If now the scatterer does not rest but moves with a velocity $\boldsymbol{v}_S$ relative to the coordinate system in which we are measuring, it is clear that another number per unit time of neutrons will be turned out of the beam and so we shall find another absorption coefficient. This number of neutrons expelled from the beam we can easily get by using the fact that the total cross-section is the same in all Galilei systems[2] and so the total number scattered per unit time and per scatterer or the probability for a scattering process is just

$$P = \varrho\, v_{\text{rel}}\, Q$$

where ϱ is the density of the neutron beam, i. e. number per unit volume, $\boldsymbol{v}_{\text{rel}}$ the velocity of the neutrons relative to the scatterer and Q the total cross-section calculated in the *relative* system. In an experiment, however, we can

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[1] Cf. e. g. E. Amaldi and E. Fermi, Phys. Rev. **50**, 899 (1936).

[2] Cf. Note 2.

only measure the velocity of the neutrons relative to our *observing* system, $\boldsymbol{v}_N$, and not the one relative to the scatterer, $\boldsymbol{v}_{\mathrm{rel}}$, and so we must define an experimental cross-section Q_{exp} by the equation

$$P = \varrho\, v_N\, Q_{\mathrm{exp}} \tag{25}$$

so that the experimental cross-section is given in terms of the usual one by

$$Q_{\mathrm{exp}} = \frac{v_{\mathrm{rel}}}{v_N}\, Q. \tag{26}$$

Now we can take our second assumption about the binding model into consideration, the velocity $\boldsymbol{v}_S$ of the scatterer not being constant, but distributed according to some probability law, $F(\boldsymbol{v}_S)$, the probability for finding the scatterer with a velocity between $\boldsymbol{v}_S$ and $\boldsymbol{v}_S + d\boldsymbol{v}_S$ being just equal to $F(\boldsymbol{v}_S)\, d\boldsymbol{v}_S$. So on the average we shall find the scattering probability, which we shall denote by $\overline{P}|_S$, equal to

$$\overline{P}|_S = \frac{\int P F(\boldsymbol{v}_S)\, d\boldsymbol{v}_S}{\int F(\boldsymbol{v}_S)\, d\boldsymbol{v}_S}$$

and so the average experimental cross-section, $\overline{Q_{\mathrm{exp}}}|_S$, will be given by

$$\overline{Q_{\mathrm{exp}}}|_S = \frac{\int \frac{v_{\mathrm{rel}}}{v_N}\, Q\, F(\boldsymbol{v}_S)\, d\boldsymbol{v}_S}{\int F(\boldsymbol{v}_S)\, d\boldsymbol{v}_S} \tag{27}$$

For $F(\boldsymbol{v}_S)\, d\boldsymbol{v}_S$ we have assumed the Maxwell distribution

$$F(\boldsymbol{v}_S)\, d\boldsymbol{v}_S = \left(\frac{\mu}{\pi}\right)^{3/2} \exp\,(-\mu\, v_S^2)\, d\boldsymbol{v}_S, \qquad \mu = \frac{m_S}{2\,k T_S} \tag{28}$$

where m_S is the mass of the scatterer (which we in this paper have chosen to be equal to 14 times the neutron mass), k is the Boltzmann constant[1], T_S is the absolute temperature, and the constant is chosen so that $\int F(\boldsymbol{v}_S)\, d\boldsymbol{v}_S = 1$.

For Q we ought to take the expression (20), but as we are not interested in temperatures much higher than room temperature, the main part of the integral in (27) will come from that part of Q which belongs to values of the energy not much higher than $\frac{3}{2} kT$ which means that our variable W[2] will be of the order 0.1 due to the value of $\hbar\omega_z$ having been chosen equal to 0.37 volts. For small values of W, however, we have seen that (20) can be approximated by $Q_{00}^{is''}$ defined in (22), so that we can safely put $Q_{00}^{is''}$ instead of the Q from (20) into (27). We have therefore first to put (21) into (27) and we get then using (15) and (28)

$$\left.\left\{\begin{aligned} \overline{Q^{is}_{\mathrm{exp}}}\Big|_S &= \pi q \cdot \frac{\left(\frac{\mu}{\pi}\right)^{3/2}}{\mu' v_N} \int \left|\boldsymbol{v}_S - \boldsymbol{v}_N\right| \left[\frac{1 - \exp\left(-4\mu' \left|\boldsymbol{v}_S - \boldsymbol{v}_N\right|^2\right)}{\left|\boldsymbol{v}_S - \boldsymbol{v}_N\right|^2}\right] \times \\ &\quad \times \exp\left(-\mu v_S^2\right) d\boldsymbol{v}_S, \qquad \mu' = \frac{1}{2}\frac{M_N \varepsilon}{\hbar\omega_z} \end{aligned}\right.\right\} \tag{29}$$

Taking $\boldsymbol{v}_S - \boldsymbol{v}_N = \boldsymbol{v}$ as new variable and choosing a polar coordinate system with $\boldsymbol{v}_N$ as polar axis the integration can be worked out and we get[3]

$$\overline{Q^{is}_{\mathrm{exp}}}\Big|_S = \pi q \cdot \mu'^{-1} v_N^{-2} \times$$

$$\times \left[\Phi\left(\mu^{1/2} v_N\right) - \exp\left(-\frac{4\mu'\mu}{4\mu'+\mu} v_N^2\right)\left(\frac{\mu}{4\mu'+\mu}\right)^{1/2} \Phi\left(\frac{\mu v_N}{(4\mu'+\mu)^{1/2}}\right)\right] \tag{30}$$

where $\Phi(x)$ is the Gauss error function defined in eq. (N 49).

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[1] $k = 1.371 \times 10^{-16}$ erg grad^{-1} $= 8.623 \times 10^{-5}$ volts grad^{-1}. For room temperature, $T = 290°$ abs, we have $kT = 0.0250$ volts.

[2] Cf. eq. (15).

[3] Cf. Note 5.

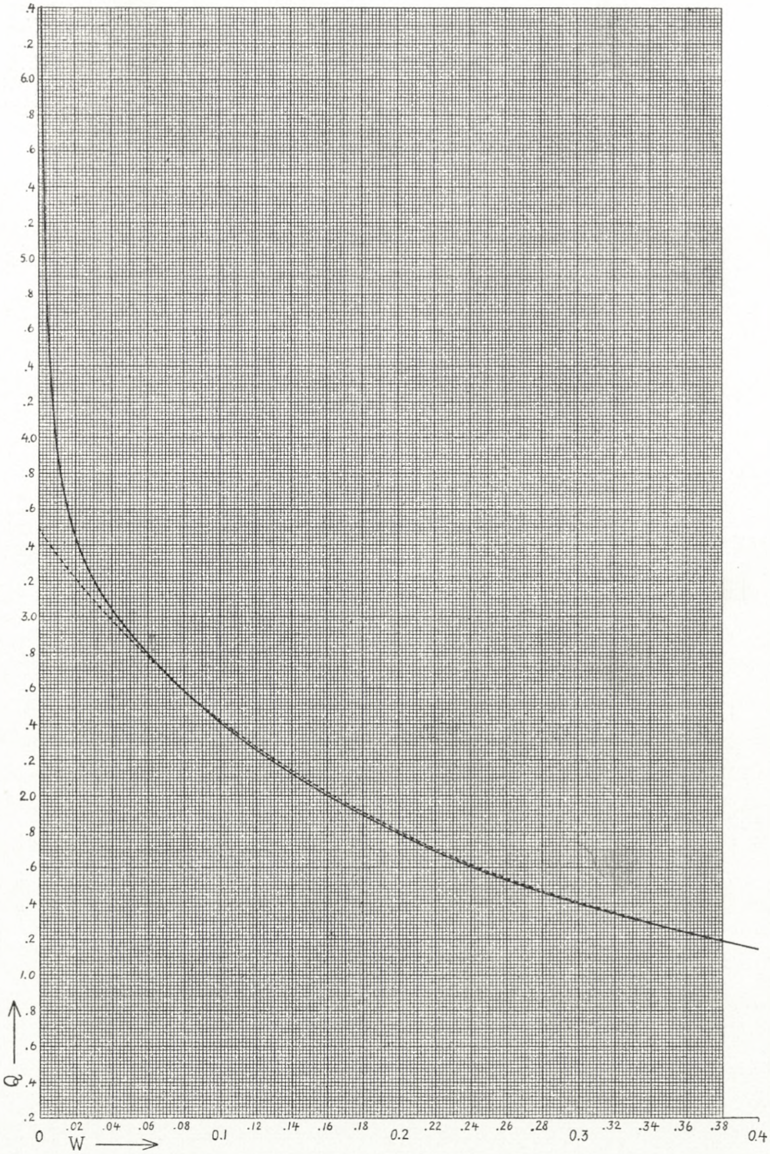

FIG. 4. *Energy dependence of scattering cross-section (in units of Q_{free}) for scattering centers at room temperature, i. e. 290° abs (full line). Dotted line corresponds to resting scattering centers.*

We introduce now the new dimensionless variables W[1] and s defined by

$$\left.\begin{aligned} W &= \mu' v_N^2 = \frac{\frac{1}{2} m_N v_N^2}{\hbar\,\omega_z} \, \frac{\varepsilon}{1+\dfrac{m_N}{m_S}}, \\ s &= \frac{\mu'}{\mu} = \frac{k T_S}{\hbar\,\omega_z} \, \frac{\varepsilon}{1+\dfrac{m_S}{m_N}}, \quad \varepsilon = \frac{M_N}{M_P} \ \text{(cf. eq. (N 36))} \end{aligned}\right\} \tag{31}$$

Putting (31) into (30) we finally find, due to $\mu v_N^2 = \frac{1}{s} W$

$$\left.\overline{Q^{is}_{\text{exp}}}\right|_S = \pi q \cdot W^{-1} \times$$

$$\times \left[\Phi\left(\left(\frac{1}{s} W\right)^{1/2}\right) - (1+4s)^{-1/2} \exp\left(-\frac{4\,W}{1+4\,s}\right) \Phi\left(\left(\frac{\frac{1}{s} W}{1+4\,s}\right)^{1/2}\right) \right]. \tag{32}$$

For $\left.\overline{Q^{is'}_{\text{exp}}}\right|_S$ we find the same formula only with $\frac{1}{\gamma} W$ and $\frac{1}{\gamma} s$ substituted for W and s. In FIG. 4 we have in the full curve plotted

$$\left.\overline{Q^{is''}_{\text{exp}}}\right|_S = \frac{1}{3} \left.\overline{Q^{is}_{\text{exp}}}\right|_S + \frac{2}{3} \left.\overline{Q^{is'}_{\text{exp}}}\right|_S \tag{33}$$

in units of Q_{free}[2] as a function of W for $m_S = 14\,m_N$, $\hbar\,\omega_z = 0.37$ volts, $\gamma = 0.4$ and $T_S = 290°$ abs which makes $s = \frac{1}{222}$. Also we have plotted the curve for $Q^{is''}$[3] and it is seen that for $W > 0.1$ the two curves are identical. The reason for this can easily be seen analytically from eq.

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[1] The W here is formally equal to W in (15) only the E_N there is now the kinetic energy in the *observation* system and not in the *rest* system as in (15). Only for $T_S = 0°$, i. e. resting scattering centers, these two systems are identical.

[2] Cf. eqs. (4) and (12).

[3] Cf. eq. (22).

(32). For x greater than 2.5 $\Phi(x) = 1$ and so we get, due to $s << 1$

$$\overline{Q^{is}_{\exp}}\Big|_S = \pi q \cdot W^{-1}\left(1 - \exp(-4W)\right) = Q^{is}, \quad \left(\frac{1}{s}W\right)^{1/2} > 2.5$$

and so under the same condition

$$\overline{Q^{is''}_{\exp}}\Big|_S = Q^{is''}.$$

This result we also get if we take the temperature of the scatterer $T_S = 0^\circ$ which means that the scatterer is resting, and we should therefore as cross-section find just $Q^{is''}$ which is in fact the case.

For neutrons of room temperature $E_{\text{kin}} = kT = 0.025$ volts we have $W = 0.063$ and we see from the curve that the corresponding $\overline{Q^{is''}_{\exp}}\big|_S$ is equal to $2.76 \cdot Q_{\text{free}}$. If we take $E_{\text{kin}} = \frac{3}{2}kT$ we get $W = 0.095$ and $\overline{Q^{is''}_{\exp}}\big|_S = 2.46 \cdot Q_{\text{free}}$.[1]

§ 5. Maxwell distribution of the incident neutrons.

From the formulae (32) and (33) we can already draw conclusions about the temperature effects. In order to be able, however, to compare the results with experiments, we must take into consideration that the beams of thermal neutrons which can be produced in praxis, e. g. by slowing down fast neutrons in paraffin, are never homogeneous but have some energy distribution. As discussed in § 1 this is not known quite exactly, but we shall here approximate it by the Maxwell distribution. If $e(E)$ is the Maxwell distribution for the *current*, that means that the

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[1] As will be seen later, the effective energy is 1.103 kT at room temperature, cf. § 6 especially p. 38. The correct value is therefore $2.69 \cdot Q_{free}$ (cf. also Table 1, $T_S = T_N = 290^\circ$).

probability for the neutron which hits the scatterer having an energy between E and $E+dE$ is $e(E)\,dE$, then the cross-section which would be measured should just be the average value of $\overline{Q_{\text{exp}}}\big|_S$

$$\frac{\int \overline{Q_{\text{exp}}}\big|_S\, e(E)\,dE}{\int e(E)\,dE}.$$

In praxis, however, this is not the value measured due to the fact that the Boron detector which is mostly used to measure the intensity of the neutron beam is not equally sensible for all neutron energies, but absorbs according to the $\frac{1}{v}$ law. If we then by $I(E)$ denote the sensibility of the detector, that means the fraction of the neutrons hitting the detector which it records, then what is really measured is obviously the following average value of the cross-section $\overline{Q_{\text{exp}}}\big|_S$ which we shall denote by $\overline{\overline{Q_{\text{exp}}}\big|_S}\Big|_N$

$$\overline{\overline{Q_{\text{exp}}}\big|_S}\Big|_N = \frac{\int \overline{Q_{\text{exp}}}\big|_S\, e(E)\,I(E)\,dE}{\int e(E)\,I(E)\,dE} \tag{34}$$

and this we shall now calculate.

The Maxwell distribution for the *current*, $e(E)$, is proportional to $v_N F(\boldsymbol{v}_N)\,d\boldsymbol{v}_N$, $F(\boldsymbol{v}_N)\,d\boldsymbol{v}_N$ being given in (28) if we substitute N for S, or transformed from velocity to energy, proportional to

$$E_N^{1/2}\cdot 2\pi^{-1/2}(kT_N)^{-3/2}E_N^{1/2}\exp\left(-\frac{E_N}{kT_N}\right)dE_N.$$

Due to the $\frac{1}{v}$ law we have further that

$$I(E) = \alpha E^{-1/2}$$

where α is some constant characteristic for the detector used. So we get that

$$e(E)\,I(E)\,dE = \alpha\,F(E)\,dE, \qquad \int F(E)\,dE = 1$$

and as the factor α drops out in (34), what we have to calculate is in fact only the mean value in regard to the MAXWELL distribution for the *density*

$$\overline{\overline{Q_{\exp}}\Big|_S}\Big|_N = \int \overline{Q_{\exp}}\Big|_S\, F(E)\,dE. \tag{35}$$

For $\overline{Q_{\exp}}\big|_S$ we have now to put $\overline{Q^{is''}_{\exp}}\big|_S$ given by (32) and (33), and we must therefore first calculate $\overline{\overline{Q^{is}_{\exp}}\big|_S}\big|_N$. If we define a new dimensionless quantity, n, by

$$n = \frac{kT_N}{\hbar\,\omega_z}\,\frac{\varepsilon}{1+\dfrac{m_N}{m_S}}, \qquad \varepsilon = \frac{M_N}{M_P} \;\text{(cf. eq. (N 36))} \tag{36}$$

we can write

$$F(E)\,dE = G(W)\,dW = 2\,\pi^{-1/2}\,n^{-3/2}\,W^{1/2}\exp\left(-\frac{1}{n}\,W\right)dW$$

and putting this and (32) into (35), we get

$$\overline{\overline{Q^{is}_{\exp}}\Big|_S}\Big|_N = \pi\,q\cdot 2\,\pi^{-1/2}\,n^{-3/2}\times$$

$$\times\int_0^\infty W^{-1}\left[\Phi\left(\left(\frac{1}{s}\,W\right)^{1/2}\right) - (1+4\,s)^{-1/2}\exp\left(-\frac{4\,W}{1+4\,s}\right)\Phi\left(\left(\frac{\frac{1}{s}\,W}{1+4\,s}\right)^{1/2}\right)\right]\times \tag{37}$$

$$\times\, W^{1/2}\exp\left(-\frac{1}{n}\,W\right)dW.$$

Both integrals are here of the same type

$$\int_0^\infty W^{-1/2}\exp\left(-\alpha^2 W\right)\Phi\left(\beta\, W^{1/2}\right)dW = 2\,\pi^{-1/2}\,\alpha^{-1}\,\text{Arctg}\,\frac{\beta}{\alpha}$$

which formula is proved in Note 6.

Putting in the correct values for α and β we get after an elementary calculation

$$\left.\begin{aligned} \overline{\overline{Q^{is}_{\exp}\Big|_S}\Big|_N} &= \pi q \cdot 4\pi^{-1} n^{-1} \times \\ \times \Bigg[\operatorname{Arctg}\left(\frac{n}{s}\right)^{1/2} &- (1+4(n+s))^{-1/2} \operatorname{Arctg}\left(\frac{1}{1+4(n+s)}\cdot\frac{n}{s}\right)^{1/2}\Bigg] \\ s = \frac{kT_S}{\hbar\,\omega_z}\,\frac{\varepsilon}{1+\frac{m_S}{m_N}}, &\quad n = \frac{kT_N}{\hbar\,\omega_z}\,\frac{\varepsilon}{1+\frac{m_N}{m_S}}, \\ \frac{n}{s} = \frac{T_N}{T_S}\frac{m_S}{m_N}, &\quad \varepsilon = \frac{M_N}{M_p} = \frac{m_S^2}{m_S^2 - m_N^2} \quad \text{(cf. eq. (N 36))} \end{aligned}\right\} \quad (38)$$

For $T_S = 0°$ we have found[1] that $\overline{Q^{is}_{\exp}\Big|_S} = Q^{is}$ so that we can obtain $\overline{Q^{is}}\Big|_N$ by putting $s = 0$ in (38)

$$\overline{Q^{is}}\Big|_N = \lim_{s\to 0} \overline{\overline{Q^{is}_{\exp}\Big|_S}\Big|_N} = \pi q \cdot 2 n^{-1}\left(1-(1+4n)^{-1/2}\right)$$

due to $\operatorname{Arctg}\infty = \frac{\pi}{2}$.

For $\overline{\overline{Q^{is'}_{\exp}\Big|_S}\Big|_N}$ we get the same formula with $\frac{1}{\gamma}s$ and $\frac{1}{\gamma}n$ substituted for s and n respectively, and so finally

$$\overline{\overline{Q^{is''}_{\exp}\Big|_S}\Big|_N} = \frac{1}{3}\,\overline{\overline{Q^{is}_{\exp}\Big|_S}\Big|_N} + \frac{2}{3}\,\overline{\overline{Q^{is'}_{\exp}\Big|_S}\Big|_N} \cong \overline{\overline{Q_{\exp}\Big|_S}\Big|_N}. \quad (39)$$

In Fig. 5 we have plotted the curve (39) in units of Q_{free}[2] as a function of T_N for various values of T_S with $m_S = 14\,m_N$, $\hbar\,\omega_z = 0.37$ volts, and $\gamma = 0.4$. The values are also given in Table 1. We see that for $T_S = T_N = 290°$ the cross-section is 2.7 times larger than the free cross-section. Amaldi and Fermi[3] find experimentally for the ratio of the two cross-sections the value 3.7. The experi-

[1] Cf. p. 27.

[2] Cf. eqs. (4) and (12).

[3] loc. cit.

mental value for the free proton cross-section measured with resonance neutrons is, however, very inaccurate, as already mentioned in § 1.

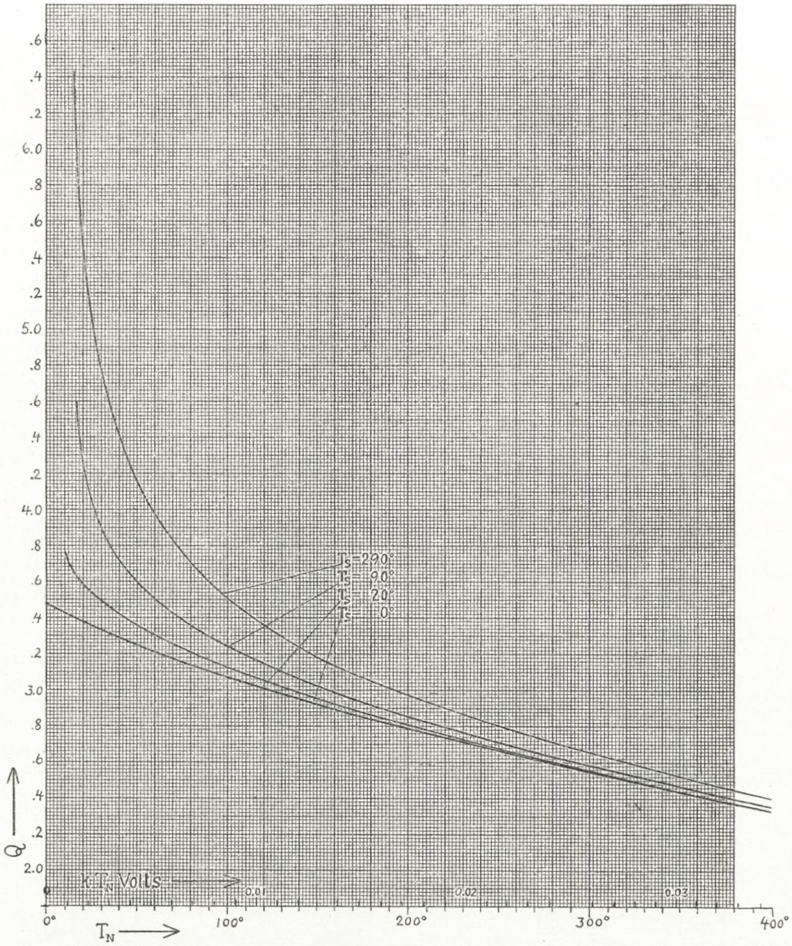

Fig. 5. *Scattering cross-sections (in units of Q_{free}) for neutron beams with Maxwell distribution as function of neutron temperature for different values of the temperature of the scattering centers.*

We see further that for liquid air temperature the cross-section is 34 % higher than for room temperature, the scat-

Table 1. *The total elastic scattering cross-section in units of Q_{free} as a function of T_S and T_N given by eq. (39) with $m_S = 14\, m_N$ i. e. $\pi q = 0.871 \cdot Q_{free}$ (cf. p. 15).*

T_N T_S	20°	90°	290°	kT volts	
0°	3.39	3.11	2.58	0	
20°	3.59	3.17	2.58	0.00172	liquid hydrogen temperature
90°	4.26	3.30	2.61	0.00776	liquid air —
290°	5.49	3.61	2.69	0.0250	room —

terer being kept at room temperature. The agreement with the experimental value of 26 % found by Fink[1] is even better than can be expected in view of the rough assumptions of our model[2]. The values for liquid hydrogen temperature (20° abs) are only given for the sake of illustration, as for temperatures as low as these our model loses every justification. In this case, infinite effective mass would be the more appropriate approximation.

In order to see how much of the variation in our curves comes from the special form of the cross-section of the anisotropic oscillator and how much from the motion of the scattering centers $\left(\text{the factor } \frac{v_{\text{rel}}}{v_N} \text{ in (26)}\right)$ we have to compare the curves with the curve for $T_S = 0$, as the latter contains only the first influence. We see that the difference is negligible for room temperature but gets important for liquid air temperature. Another way of studying the influence of the motion of the scattering centers consists in calculating $\overline{\overline{Q_{\text{exp}}}\Big|_S}\Big|_N$ for Q equal to a constant. Putting this into (27) we find, proceeding exactly as in the

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[1] G. A. Fink, Phys. Rev. **50**, 738 (1936). A similar value was found by Frisch, Halban and Koch, loc. cit.

[2] Cf. § 1.

calculation of $\overline{Q^{is}_{\text{exp}}}\Big|_S$, the only new formula needed being given in Note 7,

$$\overline{Q^{\text{const}}_{\text{exp}}}\Big|_S = Q\cdot\frac{s}{2\,W}\left[\Phi\left(\left(\frac{W}{s}\right)^{1/2}\right)\left(1+\frac{2\,W}{s}\right)+\frac{2}{\pi^{1/2}}\left(\frac{W}{s}\right)^{1/2}\exp\left(-\frac{W}{s}\right)\right] \quad (40)$$

where W and s are given by eqs. (31). It is seen that (40) is only a function of $\frac{W}{s}$ as it must be, since $\hbar\,\omega_z$ does not enter into the problem considered here. Also it is seen that, due to $\Phi(\infty) = 1$, we get for $s = 0$ or for $\left(\frac{W}{s}\right)^{1/2} >> 1$ that, as is physically obvious,

$$\overline{Q^{\text{const}}_{\text{exp}}}\Big|_S = Q.$$

Putting further (40) into (35) we get, after elementary calculations, the only new integral needed being given in Note 8,

$$\overline{\overline{Q^{\text{const}}_{\text{exp}}}\Big|_S}\Big|_N = Q\cdot 2\,\pi^{-1}\,n^{-1}\left[(ns)^{1/2}+(n+s)\ \text{Arctg}\left(\frac{n}{s}\right)^{1/2}\right] \quad (41)$$

n being given by (36). Also here $\hbar\,\omega_z$ drops out, as it must, since (41) only depends on $\frac{n}{s}$. Further we get for $T_S = 0°$

$$\lim_{s\to 0}\ \overline{\overline{Q^{\text{const}}_{\text{exp}}}\Big|_S}\Big|_N = Q$$

as we must get, since $\lim\limits_{s\to 0}\ \overline{Q^{\text{const}}_{\text{exp}}}\Big|_S = \text{const}$, and $\overline{\text{const}}\big| =$ const. In FIG. 6 we have plotted the curves (41) as function of the two temperatures for $m_S = 14\,m_N$ and Q being taken equal to $\overline{\overline{Q^{is''}_{\text{exp}}}\Big|_S}\Big|_N$ for $T_S = 0°$ and $T_N = 290°$, that is $Q = 2.58\cdot Q_{\text{free}}$[1], so that we can directly compare these

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[1] Cf. TABLE 1.

curves with the curves in FIG. 5. It is seen that the general character of the curves is the same, coming from the common integrations, but that the curves in FIG. 5 have another asymptote coming from the special function chosen for Q in (27).

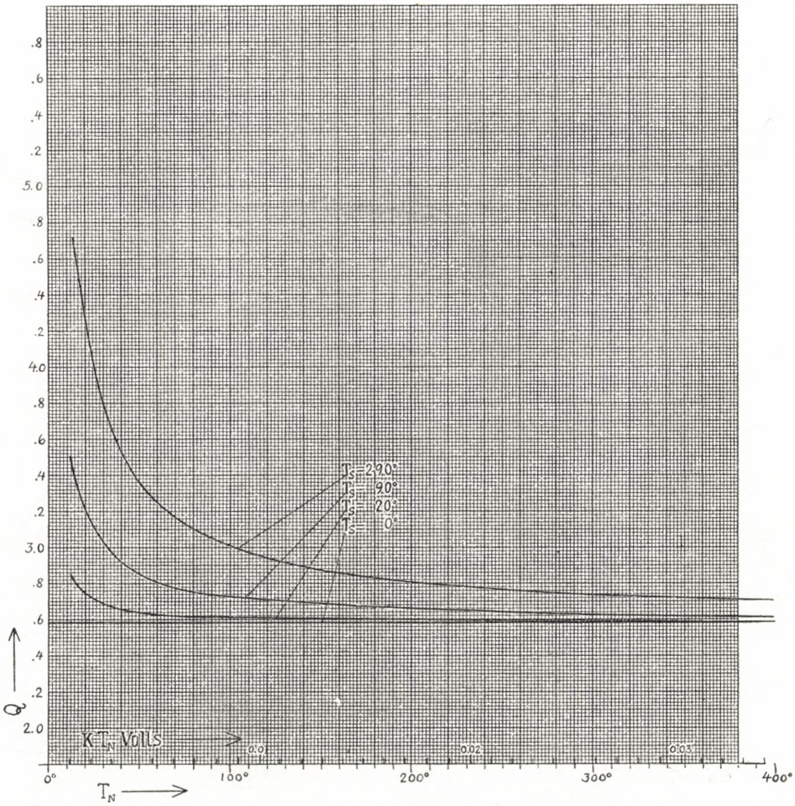

FIG. 6. *Same as FIG. 5 for a scattering cross-section which does not depend on neutron energy in the center of gravity system.*

§ 6. **Effective neutron energy.**

With the help of the curves in FIG. 4 and FIG. 5 we can now treat the problem of the effective neutron energy. By this we mean that energy, $\bar{E}$, which a homogeneous beam of neutrons must have in order that the *scattering* cross-section shall be equal to that of a MAXWELL beam of temperature T_N. For $\bar{E}$ we therefore have the equation

$$\overline{Q_{\exp}}\Big|_S\,(\bar{E}) = \overline{\overline{Q_{\exp}}\Big|_S}\Big|_N\,(kT_N). \tag{42}$$

Now our expressions for the Q's are not given directly as functions of the energies but of the variables W, n and s. We have, however,[1]

$$\left.\begin{aligned} &W = \alpha E, \qquad n = \alpha E_N, \qquad s = \beta E_S \\ &\alpha = \frac{1}{\hbar\omega_z}\frac{\varepsilon}{1+\frac{m_N}{m_S}} = 2.52 \text{ volts}^{-1}, \quad \beta = \frac{1}{\hbar\omega_z}\frac{\varepsilon}{1+\frac{m_S}{m_N}} = 0.180 \text{ volts}^{-1} \end{aligned}\right\} \tag{43}$$

for

$$\hbar\omega_z = 0.37 \text{ volts} \quad \text{and} \quad m_S = 14\, m_N$$

where E is the energy of the homogeneous neutron beam in the coordinate system of the *observer* and E_N, E_S are equal to kT_N and kT_S respectively. So we can solve the equation (42) in terms of W, n and s. This can, however, only be done analytically in a few special cases.

$$\text{I. case:} \quad \left(\frac{n}{s}\right)^{1/2} << 1.$$

As the highest temperature we are interested in is less than say 1000° = 0.0862 volts, we see that both n and s are small compared to unity and so we can in this case expand everything in (38) with the result that

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[1] Cf. eqs. (31) and (36).

$$\overline{\overline{Q^{is''}_{\exp}}\Big|_S}\Big|_N = \pi q \cdot \frac{16}{\pi}\left(\frac{s}{n}\right)^{1/2}. \tag{44}$$

From this formula we see that Q is large for $\left(\frac{n}{s}\right)^{1/2} << 1$ and from the curve for $\overline{Q^{is''}_{\exp}}\Big|_S$ we can conclude that the corresponding value of $\left(\frac{W}{s}\right)^{1/2}$ is also small. By expanding in eq. (32) we then find

$$\overline{Q^{is''}_{\exp}}\Big|_S = \pi q \cdot \frac{8}{\pi^{1/2}}\left(\frac{s}{W}\right)^{1/2}. \tag{45}$$

Putting (44) and (45) into (42) we readily find that the effective energy is given by

$$\overline{E} = \frac{\pi}{4} kT_N \qquad \left(\text{for } \left(\frac{n}{s}\right)^{1/2} << 1,\ n << 1,\ s << 1\right) \tag{46}$$

independent of the temperature of the scattering centers. This value is also the effective energy of a Maxwell beam in regard to *absorption* in Boron[1] (while we define the effective energy in regard to *scattering*) because the cross-sections in both cases vary as $\frac{1}{v}$ (cf. eq. (45)).

If we take also higher powers in the expansions into consideration, we are able to get information about the starting tangent of the curve $\frac{\overline{E}}{kT_N} = f(kT_N)$. The calculations are however lengthy and we shall therefore only give the result found, namely that for small values of E

$$\frac{\overline{E}}{kT_N} = \frac{\pi}{4}\left(1 - \varkappa^2 kT_N\right) \tag{47}$$

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[1] Cf. e. g. H. H. Goldsmith and F. Raseti, Phys. Rev. **50**, 328 (1936). Cf. also Bethe, loc. cit. Part B p. 136.

$\varkappa$ being a numerical constant depending on T_S, so that the curve is seen to decrease at the beginning when kT_N is increased.

$$\text{II. case:} \quad \left(\frac{n}{s}\right)^{1/2} >> 1.$$

This we cannot fulfil for all values of s if we still want both s and n to be small compared to unity. If, however, all three conditions are fulfilled, we can put Φ and Arctg equal to 1 and $\frac{\pi}{2}$ respectively and we get then from (32) and (38)

$$\overline{Q^{is}_{\mathrm{exp}}\Big|_S} = \pi q \cdot 4(1-2W), \quad \overline{\overline{Q^{is}_{\mathrm{exp}}\Big|_S}\Big|_N} = \pi q \cdot 4(1-3n). \quad (48)$$

For $Q^{is'}_{\mathrm{exp}}$ we get the same expressions with $\frac{1}{\gamma} W$ and $\frac{1}{\gamma} n$ substituted for W and n respectively. From (42) we then easily obtain

$$\bar{E} = \frac{3}{2} kT_N \quad \left(\text{for } \left(\frac{n}{s}\right)^{1/2} >> 1,\ n << 1,\ s << 1\right). \quad (49)$$

This is the classical relation that the mean energy of a Maxwell beam is equal to $\frac{3}{2} kT$, which result we would also expect to turn out under the conditions stated above.

$$\text{III. case:} \quad \left(\frac{n}{s}\right)^{1/2} >> 1,\ n >> 1.$$

In this extreme case we would find independently of s

$$\overline{Q^{is}_{\mathrm{exp}}\Big|_S} = \pi q \cdot W^{-1}, \quad \overline{\overline{Q^{is}_{\mathrm{exp}}\Big|_S}\Big|_N} = \pi q \cdot 2n^{-1} \quad (50)$$

and so from (42)

$$\bar{E} = \frac{1}{2} kT_N \quad \left(\text{for } \left(\frac{n}{s}\right)^{1/2} >> 1,\ n >> 1\right). \quad (51)$$

This case is, however, not of much physical importance, as we cannot neglect the inelastic scattering for energies which make $n >> 1$.

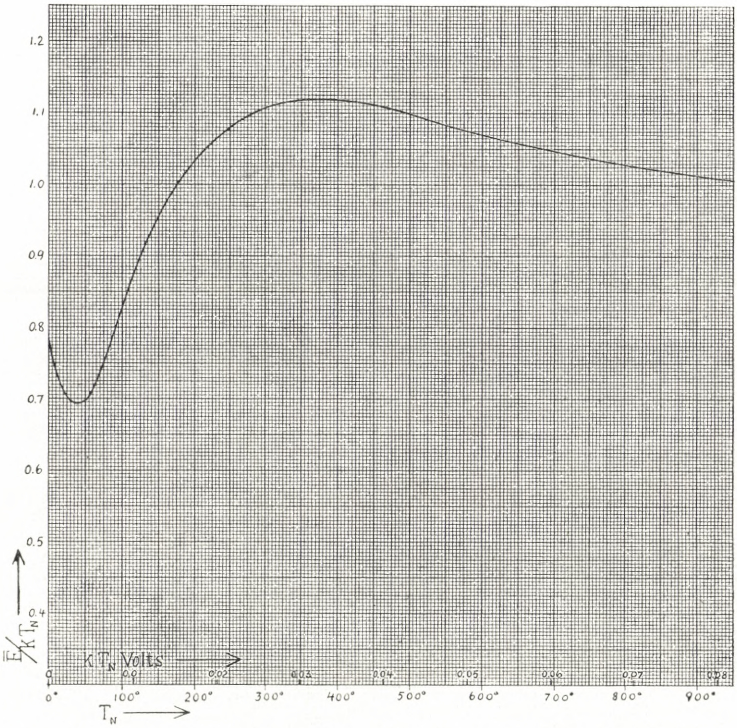

Fig. 7. *Effective neutron energy as function of neutron temperature.*

In Fig. 7 we give the curve for $\frac{\overline{E}}{kT_N}$ as a function of kT_N for $T_S = 290°$ found numerically from the curves in Figs. 4 and 5. This "pipe" like curve we have already used in § 2[1] to obtain that the effective neutron energy at room and at liquid air temperature is equal to $1.103\, kT_N$ and $0.795\, kT_N$ respectively.

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[1] Cf. p. 17.

Note 1.

For our potential V' we have assumed $\lambda \gg \varrho'$[1], so we know that all the phases will be negligible except the first one, this being given by[2]

$$\eta_0 = \operatorname{arctg}\left(\frac{k_0}{k'}\operatorname{tg} k'\varrho'\right) - k_0\varrho'. \tag{N 1}$$

Further[3]

$$I(\theta, \varphi) = \left|\frac{1}{2ik_0}\left(\exp(2i\eta_0) - 1\right)\right|^2 = \frac{\eta_0^2}{k_0^2} \tag{N 2}$$

since $\eta_0 \ll 1$. As in our case $k'\varrho'$ and $k_0\varrho'$ are both small, we can expand the tg and arctg in (N 1) with the result

$$\eta_0 = \frac{1}{3}k_0\varrho'^3(k'^2 - k_0^2) = \frac{1}{3}k_0\varrho'^3\cdot\frac{m_N D'}{\hbar^2}. \tag{N 3}$$

Putting (N 3) into (N 2) we find

$$I = \frac{1}{9}\frac{m_N^2}{\hbar^4}(D'\varrho'^3)^2 \tag{N 4}$$

which shows that I is independent of both the angle and the velocity of the neutrons so that the scattering is spherically symmetric.[4]

Since $Q = \int I\,d\omega$ we finally get for the total cross-section for scattering of slow neutrons by free protons, that this is a constant given by

$$Q = \frac{4\pi}{9}\frac{m_N^2}{\hbar^4}(D'\varrho'^3)^2. \tag{N 5}$$

Note 2.

As the transformation formulae between different coordinate systems are often used but seldom given in full, we shall here compile them for reference. Firstly let us consider two coordinate systems K and K^* so that K^* has axes parallel to the axes of K and further moves along the positive x-axis of K with constant velo-

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[1] Cf. p. 10.

[2] Cf. e. g. Mott and Massey, "Theory of atomic collisions" eq. (30), p. 29. $\left(\text{The mass there is equal to the reduced mass, } \frac{m_N}{2}\right)$.

[3] Mott and Massey, loc. cit. eq. (17), p. 24.

[4] It should be remarked that this means that in the *rest* system the differential cross-section is proportional to $\cos\Theta$ cf. Note 2, eq. (N 19).

city u. A particle is moving with velocity $\boldsymbol{v}^*$ in the system K^* forming an angle θ^* with the x^*-axis. In the non-relativistic case which we are here considering, $u << c$, we have then that in the K system the particle moves with velocity $\boldsymbol{v} = \boldsymbol{u} + \boldsymbol{v}^*$, the angle θ between $\boldsymbol{v}$ and the x-axis being determined by

$$\left.\begin{aligned} \operatorname{tg}\theta = \frac{b}{a} = \frac{\sin\theta^*}{\cos\theta^* + \frac{u}{v^*}}, \quad \cos\theta = \frac{a}{v} = \frac{\cos\theta^* + \frac{u}{v^*}}{\left(1 + \frac{u^2}{v^{*2}} + 2\frac{u}{v^*}\cos\theta^*\right)^{1/2}}, \\ \sin\theta = \frac{b}{v} = \frac{\sin\theta^*}{\left(1 + \frac{u^2}{v^{*2}} + 2\frac{u}{v^*}\cos\theta^*\right)^{1/2}} \end{aligned}\right\} \quad \text{(N 6)}$$

which formulae are at once deduced from Fig. 8.

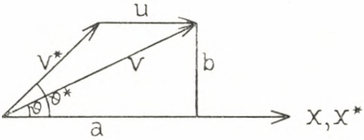

Fig. 8.

For the K- and K^*-system we now take the R and C systems[1] and shall obtain the transformation formulae (N 6) for this case, when the particle with mass m_2 moves with constant velocity V_2 along the x-axis before the collision. From (5) we find, due to $V_1 = 0$

$$\boldsymbol{u} = V_2 \cdot \frac{m_2}{m_1 + m_2} \qquad \text{(N 7)}$$

and as we assume that no outer forces are acting, this velocity is the same before and after the collision. To obtain $v_1'^*$ and $v_2'^*$ (the dashes referring to the state after the collision) and so the transformation formulae for the two scattering angles, θ_1^* and θ_2^*, we only need to use the conservation law for the energy

$$\frac{1}{2}m_1 v_1^{*2} + \frac{1}{2}m_2 v_2^{*2} - (E_n - E_m) = \frac{1}{2}m_1 v_1'^{*2} + \frac{1}{2}m_2 v_2'^{*2} \qquad \text{(N 8)}$$

where $E_n - E_m$ is the excitation energy given up by the particle 2 in order to excite the particle 1 from its m'th to its n'th state

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[1] Cf. p. 13.

during the collision. This energy can be positive or negative; for $m = 0$ it is positive for all n. Using (7) and $\boldsymbol{v}_1^* = -\boldsymbol{u}$, $\boldsymbol{v}_2^* = \boldsymbol{V}_2 - \boldsymbol{u}$, we get from (N 8) due to (N 7)

$$v_2'^{*2} = V_2^2\left(\frac{m_1}{m_1+m_2}\right)^2 - 2\,\frac{m_1}{m_2}\,\frac{(E_n - E_m)}{(m_1+m_2)} \tag{N 9}$$

(N 6) is now fully determined by (N 7) and (N 9), but only in the case of elastic scattering, $E_n - E_m = 0$, we get simple analytic expressions. In this case we get, using (7)

$$v_2'^* = \frac{m_1}{m_1+m_2}\cdot V_2, \qquad v_1'^* = \frac{m_2}{m_1}\,v_2'^* = u \tag{N 10}$$

so that (N 6) becomes, independently of V_2, using (9)

$$\left.\begin{aligned}
&\operatorname{tg}\Theta_2 = \frac{\sin\theta_2}{\cos\theta_2 + \dfrac{m_2}{m_1}}, \qquad \cos\Theta_2 = \frac{\cos\theta_2 + \dfrac{m_2}{m_1}}{\left(1 + \dfrac{m_2^2}{m_1^2} + 2\,\dfrac{m_2}{m_1}\cos\theta_2\right)^{1/2}},\\
&\sin\Theta_2 = \frac{\sin\theta_2}{\left(1 + \dfrac{m_2^2}{m_1^2} + 2\,\dfrac{m_2}{m_1}\cos\theta_2\right)^{1/2}}\\
&\Theta_1 = \frac{1}{2}(\pi - \theta_2), \quad \Phi_1 = \varphi_2 + \pi, \quad \Phi_2 = \varphi_2
\end{aligned}\right\} \tag{N 11}$$

so $0 \leqq \Theta_2 \leqq \pi$ when $m_1 \neq m_2$, but $0 \leqq \Theta_2 \leqq \frac{\pi}{2}$ when $m_1 = m_2$ because we then simply get

$$\Theta_2 = \frac{1}{2}\,\theta_2$$

which, combined with (N 11), gives the well-known relation

$$\Theta_1 + \Theta_2 = \frac{\pi}{2}.$$

Solving (N 11) for θ_2 we find

$$\sin(\theta_2 - \Theta_2) = \frac{m_2}{m_1}\sin\Theta_2 \tag{N 12}$$

which for $m_1 >> m_2$ reduces to

$$\theta_2 = \Theta_2 + \frac{m_2}{m_1}\sin\Theta_2.$$

Further we can, using the conservation laws, deduce the formulae for the energies before and after the collision in the *rest* system:

$$\left.\begin{aligned} E_2 &= \frac{1}{2}\, m_2 V_2^2, \quad E_1 = 0 \\ E_2' &= E_2 \left(1 - \frac{4\, m_1 m_2}{(m_1 + m_2)^2} \cos^2 \Theta_1\right), \\ E_1' &= E_2 \frac{4\, m_1 m_2}{(m_1 + m_2)^2} \cos^2 \Theta_1 \end{aligned}\right\} \qquad (\mathrm{N}\ 13)$$

By definition we have for the cross-sections that

$$I_{mn}(\Theta, \Phi)\, d\Omega = I_{mn}(\theta^*, \varphi^*)\, d\omega^* = I_{mn}(\theta, \varphi)\, d\omega \qquad (\mathrm{N}\ 14)$$

(dropping the index 2) which we can write, due to $\Phi = \varphi^* = \varphi$

$$I_{mn}(\Theta, \Phi) = I_{mn}(\theta, \varphi) \frac{\sin \theta}{\sin \Theta} \frac{d\theta}{d\Theta}\,. \qquad (\mathrm{N}\ 15)$$

For the special case of elastic scattering, $m = n$, we get from (N 11)

$$\frac{\sin \theta}{\sin \Theta} = \left(1 + \frac{m_2^2}{m_1^2} + 2\frac{m_2}{m_1} \cos \theta\right)^{1/2} \qquad (\mathrm{N}\ 16)$$

$$\frac{d\Theta}{\cos^2 \Theta} = \frac{1 + \frac{m_2}{m_1} \cos \theta}{\left(\cos \theta + \frac{m_2}{m_1}\right)^2}\, d\theta. \qquad (\mathrm{N}\ 17)$$

Putting (N 16) and (N 17) into (N 15) we finally get using (N 11)

$$\left.\begin{aligned} I_{nn}(\Theta, \Phi) = I_{nn}(\theta, \varphi) \frac{\left(1 + \frac{m_2^2}{m_1^2} + 2\frac{m_2}{m_1} \cos \theta\right)^{3/2}}{\left(1 + \frac{m_2}{m_1} \cos \theta\right)} = I_{nn}(\theta, \varphi) \cdot g(\theta) \\ \left(1 - \frac{m_2}{m_1}\right)^2 \leq g(\theta) \leq \left(1 + \frac{m_2}{m_1}\right)^2. \end{aligned}\right\} \qquad (\mathrm{N}\ 18)$$

For $m_1 >> m_2$ we get

$$g(\theta) = 1 + 2\frac{m_2}{m_1} \cos \theta = 1 + 2\frac{m_2}{m_1} \cos \Theta.$$

In the special case $m_1 = m_2$ we find the well-known formula

$$g(\theta) = 4 \cos \frac{\theta}{2} = 4 \cos \Theta. \qquad (\mathrm{N}\ 19)$$

The function $g(\theta)$ we can transform to Θ by (N 11) and we find then

$$g(\theta) = \frac{\left(\frac{m_2}{m_1}\cos\Theta + \left(1 - \frac{m_2^2}{m_1^2}\sin^2\Theta\right)^{1/2}\right)^2}{\left(1 - \frac{m_2^2}{m_1^2}\sin^2\Theta\right)^{1/2}} \qquad \text{(N 20)}$$

which for $m_1 >> m_2$ just reduces to $1 + 2\frac{m_2}{m_1}\cos\Theta$.

From (N 14) we can at once deduce that the *total* cross-sections in the two coordinate systems are identical. This is, however, only a special case of the more general theorem that the *total* cross-section is the same in all GALILEI systems.1) This is readily seen from the definition. Calling the probability for the scattering process P, that is the number per unit time and per scatterer scattered out of the beam, the cross-section Q is defined as the ratio between P and the number in the incident beam crossing unit area per unit time *at the place of the scatterer*, so that we have

$$Q = \frac{P}{\varrho\, v_{\mathrm{rel}}} \qquad \text{(N 21)}$$

where ϱ is the density of the beam, that is the number of particles per unit volume, and v_{rel} is the velocity of the beam relative to the scatterer. Since P, ϱ and v_{rel} are the same in all GALILEI systems, Q is at once seen to be invariant.2)

From (N 14) we can also deduce the transformation formulae for the differential cross-sections from one GALILEI system K to another K^*. The formulae for the angles are, when $\boldsymbol{u}$ is the velocity of the system K^*, measured in K

$$\left.\begin{aligned}
\cos\Theta &= \frac{\cos\Theta^* + \frac{u}{v_2^*}\cos\theta_1^* + \frac{u}{v_1^*}\cos\theta_2^* + \frac{u^2}{v_1^*\, v_2^*}}{\left(1 + \frac{u^2}{v_1^{*2}} + 2\frac{u}{v_1^*}\cos\theta_1^*\right)^{1/2}\left(1 + \frac{u^2}{v_2^{*2}} + 2\frac{u}{v_2^*}\cos\theta_2^*\right)^{1/2}}\\
\sin\Phi &= \frac{\sin(\varphi_1^* - \varphi_2^*)\sin\theta_2^*}{(1 - \cos^2\Theta)^{1/2}\left(1 + \frac{u^2}{v_2^{*2}} + 2\frac{u}{v_2^*}\cos\theta_2^*\right)^{1/2}}
\end{aligned}\right\} \text{(N 22)}$$

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1) By a GALILEI system is understood a coordinate system which moves with constant velocity along a straight line.

2) We have only considered the non-relativistic case. In the relativistic case Q is also invariant so long as the coordinate systems move in the direction of the current.

(with the expression for $\cos \Theta$ inserted from the above formula)

$$\begin{aligned} \theta_{1,2}^* &= \sphericalangle\, (\boldsymbol{v}_{1,2}^*, \boldsymbol{u}), & \varphi_1^* - \varphi_2^* &= \sphericalangle\, ([\boldsymbol{v}_1^* \times \boldsymbol{u}], [\boldsymbol{v}_2^* \times \boldsymbol{u}]) \\ \Theta^* &= \sphericalangle\, (\boldsymbol{v}_1^*, \boldsymbol{v}_2^*), & \Phi^* &= \sphericalangle\, ([\boldsymbol{v}_1^* \times \boldsymbol{v}_2^*], [\boldsymbol{v}_1^* \times \boldsymbol{u}]) \end{aligned}$$

(and analogous formulae for the quantities without stars) which formulae are obtained from the general formulae of spherical trigonometry, using (N 6), the direction $\boldsymbol{u}$ being taken as the polar axis in a polar coordinate system. Theoretically we can from (N 14) and (N 22) obtain the transformation formulae for the differential cross-sections, but in praxis the resulting expressions are so complicated that they are quite unmanageable, with the exception of the special case where $\boldsymbol{u}$ has the same direction as one of the $\boldsymbol{v}^*$'s, in which case (N 22) reduces to (N 6). Further, if $\boldsymbol{u}$ lies in the plane of $\boldsymbol{v}_1^*$ and $\boldsymbol{v}_2^*$ we get $\Phi = \Phi^* = 0$, the formula for Θ being the same.

Note 3.[1]

For the eigenfunction of the one-dimensional oscillator we have[2]

$$\left.\begin{aligned} \psi_n(x) &= a^{-1/2} \pi^{-1/4} 2^{-\frac{n}{2}} (n!)^{-1/2} \exp\left(-\frac{1}{2}\frac{x^2}{a^2}\right) H_n\left(\frac{x}{a}\right) \\ a &= \left(\frac{\hbar}{M_p\, \omega}\right)^{1/2}, \quad E_n = \left(n + \frac{1}{2}\right) \hbar\, \omega \end{aligned}\right\} \quad \text{(N 23)}$$

where M_p is the reduced mass of the proton, ω the cyclical frequency of the proton and H_n the n'th Hermite polynomial. With these wave functions we shall now calculate the matrix element

$$\begin{gathered} \left(n \,|\, \exp\, (i k''_{mn_x} x) \,|\, m\right) = \\ \int \psi_n^* \cdot \exp \cdot \psi_m \, dx = \pi^{-1/2} 2^{-\frac{n+m}{2}} (n!\, m!)^{-1/2} e_{nm} \end{gathered} \qquad \text{(N 24)}$$

$$\left.\begin{aligned} e_{nm} = \bar{e}_{mn} &= \int_{-\infty}^{+\infty} H_n(y) \exp\, (i b y)\, H_m(y) \exp\, (-y^2)\, dy \\ b &= a k''_{mn_x}, \quad y = \frac{x}{a}. \end{aligned}\right\} \quad \text{(N 25)}$$

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[1] The matrix elements given in this note have been given previously by the author, cf. Nordiska Naturforskarmötet i Helsingfors 1936. The reports, p. 248.

[2] Cf. e. g. Ruark and Urey: "Atoms, Molecules and Quanta", p. 533.

By definition we have[1]

$$H_m(y) = (-1)^m \exp(y^2) \left(\frac{d}{dy}\right)^m \exp(-y^2). \tag{N 26}$$

If we put (N 26) into (N 25) and integrate by parts, we get due to the fact that $\exp(-y^2)$ and all its derivatives vanish in $\pm\infty$ faster than every power of y

$$e_{nm} = 2n\, e_{n-1,\, m-1} + ib\, e_{n,\, m-1} \tag{N 27}$$

using $H_n' = 2n H_{n-1}$, $n \geq 1$.[2] Using this recurrence formula l times on itself, we can show by induction that the result is

$$e_{nm} = \sum_{s=0}^{l} 2^{l-s} \binom{l}{s} \frac{n!}{(n-l+s)!} (ib)^s e_{n-l+s,\, m-l} \tag{N 28}$$

Here l is restricted by the condition that $n-l$ and $m-l$ must both be positive or zero, that is $l \leq \min(m, n)$. Assuming $m \leq n$ we can therefore put $l = m$. By reducing $e_{n-m+s,0}$ in the same way, we get

$$e_{n-m+s,0} = (ib)^{n-m+s} \cdot e_{00} = (ib)^{n-m+s} \pi^{1/2} \exp\left(-\frac{b^2}{4}\right) \tag{N 29}$$

due to

$$e_{00} = \int_{-\infty}^{+\infty} \exp(iby) \exp(-y^2)\, dy =$$

$$= \exp\left(-\frac{b^2}{4}\right) \int_{-\infty}^{+\infty} \exp\left(-\left(y - \frac{ib}{2}\right)^2\right) dy = \exp\left(-\frac{b^2}{4}\right) \pi^{1/2}.$$

Putting now (N 29) into (N 28) with $l = m$, we get

$$\left.\begin{aligned} e_{nm} = \pi^{1/2} 2^m (ib)^{n-m} n!\, m! \exp\left(-\frac{b^2}{4}\right) \sum_{s=0}^{m} \frac{(ib)^{2s}}{2^s s!\, (m-s)!\, (n-m+s)!} \\ (m \leq n). \end{aligned}\right\} \text{(N 30)}$$

For $n \leq m$ we get the same formula with n and m interchanged. (N 30) into (N 24) finally gives us

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[1] Cf. Courant-Hilbert: "Methoden der mathematischen Physik", p. 78.

[2] Cf. Courant-Hilbert, loc. cit. p. 78.

$$\left.\begin{aligned} &\left(n \,|\, \exp\left(i k''_{mn_x} x\right) \,|\, m\right) = \\ &= 2^{-\frac{n+m}{2}} (n!\, m!)^{1/2} (ib)^{|\,n-m\,|} \exp\left(-\frac{b^2}{4}\right) \sum_{s=0}^{l} \frac{(-1)^s\, b^{2s}}{2^s\, s!\, (l-s)!\, (|\,n-m\,|+s)!} \\ &l = \min(n, m), \quad b = a k''_{mn_x}. \end{aligned}\right\} \quad \text{(N 31)}$$

For the one state being just the groundstate we get

$$\left(n \,|\, \exp\left(i k''_{on_x} x\right) \,|\, 0\right) = (n!)^{-1/2}\, 2^{-\frac{n}{2}} (ib)^n \exp\left(-\frac{b^2}{4}\right). \quad \text{(N 32)}$$

For the 3-dimensional isotropic oscillator we can at once get the cross-sections from (N 32) since the eigenfunctions are only the products of three of the type (N 23). Due to the states being degenerate with the multiplicity $g_n = \frac{(n+1)(n+2)}{2}$ we must form

$$I_{mn} = q \cdot \frac{1}{g_n} \frac{k_{mn}}{k_0} \sum_{m_x+m_y+m_z=m} \;\; \sum_{n_x+n_y+n_z=n} \left|\left(n_x n_y n_z \,|\, \exp\left(i \boldsymbol{k}''_{mn} \boldsymbol{r}\right) \,|\, m_x m_y m_z\right)\right|^2 \quad \text{(N 33)}$$

This is very complicated unless $m = 0$ in which case we can at once perform the summations if we only choose the (arbitrary) coordinate system so that $\boldsymbol{k}''_{mn}$ is along one of the axes

$$\left.\begin{aligned} I_{on} &= q \cdot \frac{k_{on}}{k_0} \sum_{n_x+n_y+n_z=n} \left|\left(n_x |\exp\left(i k''_{on} x\right)| 0\right) \left(n_y |1| 0\right) \left(n_z |1| 0\right)\right|^2 = \\ &= q \cdot \frac{k_{on}}{k_0} \frac{1}{n!} \left(\frac{b^2}{2}\right)^n \exp\left(-\frac{b^2}{2}\right) \end{aligned}\right. \quad \text{(N 34)}$$

$$\frac{b^2}{2} = \frac{1}{2} k''^2_{on} a^2 = \frac{M_N}{M_p} \frac{E_0}{\hbar\omega} \left[2 - \frac{E_n - E_0}{E_0} - 2\left(1 - \frac{E_n - E_0}{E_0}\right)^{1/2} \cos\theta\right] \quad \text{(N 35)}$$

by (1). This is the formula found by FERMI[1]) apart from the factor $\left(\frac{M_N}{m_N}\right)^2$ in q (cf. eq. (4)) and from the factor $\frac{M_N}{M_p}$ in eq. (N 35) which by FERMI (and by BETHE) are both put equal to unity:

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[1]) loc. cit. Cf. also BETHE, loc. cit. Part B eq. (455). It should be noted that by the authors quoted m_S it put equal to infinity throughout.

$$\varepsilon = \frac{M_N}{M_P} = \left(\frac{m_N\, m_S}{m_N + m_S}\right)\left(\frac{m_P + m_B}{m_P\, m_B}\right) = \frac{m_S^2}{m_S^2 - m_N^2} \geqq 1 \quad \text{(N 36)}$$

where m_B is the mass of the binding center $m_B = m_S - m_P$, $m_P \cong m_N$. For our value of $m_S = 14\, m_N$, ε has the value 1.0051, which can be safely replaced by unity, so that we apart from the important factor in q are left with FERMI's formula.

It might be of interest to note that the formula (N 34) can also be obtained by writing the wave functions in polar coordinates. We only give the formulae for reference1)

$$\left.\begin{aligned}
&\Psi_{nlm}(r,\theta,\varphi) = \left[\frac{(2l+1)}{4\pi}\,\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} \exp(im\varphi)\, P_l^{|m|}(\cos\theta)\times \\
&\times a^{-3/2}\left[\frac{2\left(\frac{n+l+1}{2}\right)!}{\left(\frac{n-l}{2}\right)!}\right]^{1/2} \frac{\exp\left(-\frac{r^2}{2a^2}\right)}{\left(l+\frac{1}{2}\right)!}\cdot {}_1F_1\left(-\frac{n-l}{2};\, l+\frac{1}{2}+1;\, \frac{r^2}{a^2}\right) \\
&-l \leqq m \leqq +l, \quad l = n,\ n-2,\ n-4, \cdots \geqq 0, \quad E_n = \left(n+\frac{3}{2}\right)\hbar\omega
\end{aligned}\right\} \text{(N 37)}$$

P_l^m is the ordinary associated LEGENDRE polynomial2) and ${}_1F_1$ the confluent hypergeometric function.3) We find

$$\left.\begin{aligned}
&(n\,l\,m\,|\exp(i\boldsymbol{k}''_{on}\boldsymbol{r})|\,000) = \\
&= \delta_{om}\,\pi^{-1/4}\, i^l\, 2^{l+\frac{1}{2}}\left[\frac{(2l+1)\left(\frac{n+l+1}{2}\right)!}{\left(\frac{n-l}{2}\right)!}\right]^{1/2} \frac{\left(\frac{n+l}{2}\right)!}{(n+l+1)!}\, b^n \exp\left(-\frac{b^2}{4}\right) \\
&b = a k''_{on}\,.
\end{aligned}\right\} \text{(N 38)}$$

Putting (N 38) into the formula analogous to (N 33) we just find the expression in (N 34) for I_{on} due to the formula proved by the author4)

$$\sum_{l = n,\, n-2 \cdots \geqq 0} \pi^{-1/2}\, 2^{2l+1}\left[\frac{(2l+1)\left(\frac{n+l+1}{2}\right)!}{\left(\frac{n-l}{2}\right)!}\right]\left[\frac{\left(\frac{n+l}{2}\right)!}{(n+l+1)!}\right]^2 = \frac{1}{2^n\, n!} \quad \text{(N 39)}$$

1) The author, loc. cit.

2) COURANT-HILBERT, loc. cit., p. 282.

3) Cf. e. g. MOTT and MASSEY, loc. cit., p. 36.

4) See Matematisk Tidsskrift, Copenhagen 1937. "To Prof. H. BOHR on his 50th birthday", p. 42.

In the calculation leading to formula (N 38) we also get the matrix elements for the fixed rotator with two degrees of freedom whose eigenfunctions are just the first part of (N 37) multiplied by $\delta(r-r_0)$, r_0 being the dimension of the rotator. We find

$$(jm|\exp(i\boldsymbol{k}''_{oj}\boldsymbol{r})|00) = \delta_{om}\left(\frac{\pi}{2}\right)^{1/2}(2j+1)^{1/2}\, i^j (k''_{oj}r_o)^{-1/2} J_{j+1/2}(k''_{oj}r_o) \qquad \text{(N 40)}$$

$J_{j+1/2}$ being the Bessel function of order $j+\frac{1}{2}$.

Note 4.

It may be interesting to note that the formula for the total elastic cross-section for the isotropic oscillator can also be deduced by direct calculation of the Born phases and their summation which is indeed very seldom possible. We have, since the phases are all small,1)

$$Q = 4\pi k_0^{-2} \sideset{}{'}\sum_{n=0}^{\infty} (2n+1)\,\zeta_n^2 \qquad \text{(N 41)}$$

$$\zeta_n = -\frac{2M_N k_0}{\hbar^2}\int_0^\infty V'_{00}\left[\left(\frac{\pi}{2k_0 r}\right)^{1/2} J_{n+1/2}(k_0 r)\right]^2 r^2\, dr \qquad \text{(N 42)}$$

$$V'_{00} = \int |\psi_0|^2\, V'\, d\tau = |\psi_0(\boldsymbol{r}_N)|^2 (-D')\,\frac{4\pi}{3}\,\varrho'^3 \qquad \text{(N 43)}$$

due to $\varrho' << a$. If we put (N 43) into (N 42) using (N 37), we get

$$\zeta_n = \frac{M_N D'}{\hbar^2}\,\frac{4}{3}\,\pi^{1/2}\,\frac{\varrho^3}{a^3}\int_0^\infty \exp\left(-\frac{r^2}{a^2}\right) J_{n+1/2}^2(k_0 r)\, r\, dr. \qquad \text{(N 44)}$$

Now

$$\int_0^\infty \exp(-p^2t^2)\, J_\nu(at)\, J_\nu(bt)\, t\, dt = \frac{1}{2p^2}\exp\left(-\frac{a^2+b^2}{4p^2}\right) I_\nu\left(\frac{ab}{2p^2}\right) \quad ^{2)} \qquad \text{(N 45)}$$

$$I_\nu(x) = \exp\left(-\frac{\pi}{2}\, i\nu\right) J_\nu(ix) \quad ^{3)} \qquad \text{(N 46)}$$

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1) Cf. Mott and Massey, loc. cit. eq. (5), p. 138 and eq. (12), p. 90.

2) Watson: “Bessel functions”, eq. (1). p. 395.

3) Watson, loc. cit., eq. (2). p. 77.

$$\sum_{n=0}^{\infty}{}' \left(n+\frac{1}{2}\right) I^2_{n+1/2}(x) = -i \sum_{n=0}^{\infty}{}' \left(n+\frac{1}{2}\right)(-1)^n J^2_{n+1/2}(ix) = \tag{N 47}$$

$$= -i\frac{\sin 2ix}{2\pi} = \frac{e^{2x}-e^{-2x}}{4\pi}. \quad ^{1)}$$

Putting (N 42) — (N 47) into (N 41) we get, using $\frac{1}{2}k_0^2 a^2 = W$ [2]

$$Q = \left(\frac{M_N}{m_N}\right)^2 \frac{4\pi}{9} \frac{m_N^2}{\hbar^4} (D' \varrho'^3) \frac{1-\exp(-4W)}{W}$$

which is just eq. (21) remembering eq. (4).

Note 5.

We first prove the formula

$$\int_0^{\infty} \left[\exp\left(-\alpha^2 (x-\beta)^2\right) - \exp\left(-\alpha^2 (x+\beta)^2\right)\right] dx = \pi^{1/2} \alpha^{-1} \Phi(\alpha\beta) \tag{N 48}$$

where $\Phi(x)$ is the Gauss error function given by

$$\Phi(x) = 2\pi^{-1/2} \int_0^x \exp(-t^2)\, dt. \tag{N 49}$$

Taking in the first part $y = x-\beta$, in the second $y = x+\beta$ as new variable we get

$$\int_0^{\infty} = \int_{-\beta}^{\infty} - \int_{+\beta}^{\infty} = 2\int_0^{\beta} \exp(-\alpha^2 y^2)\, dy$$

so (N 48) follows at once. We can now work out the integral in (29). The two angle integrations being performed, we are left with

$$\frac{\pi q}{\mu' v_N^2} \left(\frac{\mu}{\pi}\right)^{1/2} \exp(-\mu v_N^2) \int_0^{\infty} \left[\exp(-\mu v^2) - \exp\left(-(\mu + 4\mu')v^2\right)\right] \times$$

$$\times \left[\exp(2\mu v_N v) - \exp(-2\mu v_N v)\right] dv.$$

The two integrals here are just of the type (N 48). In the first we have $\alpha^2 = \mu$, $\beta = v_N$, in the second $\alpha^2 = (\mu + 4\mu')$, $\beta = \frac{\mu v_N}{\mu + 4\mu'}$. Putting in these values in (N 48) we easily find (30).

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1) Watson, loc. cit. eq. (3). p. 152.

2) Cf. eqs. (1) and (15).

Note 6.

We prove here the formula

$$\int_0^\infty W^{-1/2}\exp\left(-\alpha^2 W\right)\Phi\left(\beta W^{-1/2}\right)dW = 2\pi^{-1/2}\alpha^{-1}\,\mathrm{Arctg}\,\frac{\beta}{\alpha} \qquad \text{(N 50)}$$

where $\Phi(x)$ is defined in eq. (N 49).

We put first $t = \beta W^{1/2}$ as new variable and get

$$\int_0^\infty = 2\beta^{-1}\int_0^\infty \exp\left(-\frac{t^2}{x^2}\right)\Phi(t)\,dt = 2\beta^{-1}f(x),\quad x = \frac{\beta}{\alpha}. \qquad \text{(N 51)}$$

If we now differentiate the function $f(x)$ we get

$$f'(x) = x^{-1}\int_0^\infty \left[\exp\left(-\frac{t^2}{x^2}\right)\frac{2t}{x^2}\right]\left[t\Phi(t)\right]dt.$$

Integrating by parts we can get the inhomogeneous differential equation for $f(x)$

$$f'(x) = x^{-1}f(x) + \pi^{-1/2}\frac{x}{1+x^2}$$

which by the ordinary methods can be solved to

$$f(x) = \pi^{-1/2}\cdot x\cdot \mathrm{Arctg}\,x + (\mathrm{constant}\cdot x).$$

The constant can be determined to be equal to zero by expanding $\Phi(t)$ and integrating term by term. For $x^2 < 1$ the resultant series is convergent to just $\pi^{-1/2}\cdot x\cdot \mathrm{Arctg}\,x$. This in (N 51) then proves (N 50).

Note 7.

We prove the formula

$$\begin{aligned}\int_0^\infty x^2\left[\exp\left(-\alpha^2(x-\beta)^2\right)-\exp\left(-\alpha^2(x+\beta)^2\right)\right]dx = \\ = \Phi(\alpha\beta)\left[\frac{\pi^{1/2}\beta^2}{\alpha}+\frac{\pi^{1/2}}{2\alpha^3}\right]+\frac{\beta}{\alpha^2}\exp\left(-\alpha^2\beta^2\right)\end{aligned} \qquad \text{(N 52)}$$

where $\Phi(x)$ is defined in eq. (N 49).

Putting $y = x \pm \beta$ we get

$$\int_0^\infty = \int_{-\beta}^{+\beta} y^2 \exp(-\alpha^2 y^2)\,dy + 2\beta \int_{-\beta}^{+\beta} y \exp(-\alpha^2 y^2)\,dy +$$

$$+ 4\beta \int_{\beta}^{\infty} y \exp(-\alpha^2 y^2)\,dy + \beta^2 \int_{-\beta}^{+\beta} \exp(-\alpha^2 y^2)\,dy.$$

The second integral is zero, the two last ones can be performed at once and the first one by integration by parts. The result is

$$\int_0^\infty = \left[-\frac{\beta}{\alpha^2}\exp(-\alpha^2\beta^2) + \frac{\pi^{1/2}}{2\alpha^3}\,\Phi(\alpha\beta)\right] + \frac{2\beta}{\alpha^2}\exp(-\alpha^2\beta^2) + \frac{\pi^{1/2}\beta^2}{\alpha}\,\Phi(\alpha\beta)$$

which immediately proves (N 52).

Note 8.

We prove the formula

$$\int_0^\infty W^{1/2}\exp(-\alpha^2 W)\,\Phi(\beta W^{1/2})\,dW = \pi^{-1/2}\alpha^{-3}\left[\frac{\alpha\beta}{\alpha^2+\beta^2} + \mathrm{Arctg}\,\frac{\beta}{\alpha}\right] \qquad \text{(N 53)}$$

where $\Phi(x)$ is defined in eq. (N 49).

We take as new variable $t = \beta W^{1/2}$ and get using (N 49).

$$\int_0^\infty = 2\beta^{-3}\,2\pi^{-1/2}\int_0^\infty dt\int_0^t du\, t^2 \exp\left(-\frac{\alpha^2 t^2}{\beta^2}\right)\exp(-u^2).$$

Now

$$\int_0^\infty dt\int_0^t du = \int_0^\infty du\int_u^\infty dt$$

and so we get, performing the $\int_u^\infty dt$ by integrating by parts

$$\int_0^\infty = 2\beta^{-3}\,2\pi^{-1/2}\int_0^\infty du\,\exp(-u^2)\times$$

$$\times\left\{\frac{\beta^3}{\alpha^3}\,\frac{1}{2}\left[\frac{\alpha u}{\beta}\exp\left(-\frac{\alpha^2 u^2}{\beta^2}\right) + \frac{\pi^{1/2}}{2}\left(1-\Phi\left(\frac{\alpha u}{\beta}\right)\right)\right]\right\}.$$

Here all integrations can be performed, using eq. (N 50). The result is

$$\int_0^\infty = \pi^{-1/2} \alpha^{-3} \left[\frac{\alpha \beta}{\alpha^2 + \beta^2} + \frac{\pi}{2} - \text{Arctg}\, \frac{\alpha}{\beta} \right]$$

which proves (N 53) because we have the elementary identity

$$\frac{\pi}{2} - \text{Arctg}\, \frac{1}{x} = \text{Arctg}\, x.$$

Summary.

In the present paper we discuss the scattering of thermal neutrons in hydrogeneous substances. In § 1 we discuss the binding model for the protons. We assume the protons to be bound independently in an anisotropic oscillator taking the largest oscillation energy equal to 0.37 volts, and the others equal to 0.4 times that. Further we take the lower frequencies into consideration by ascribing an effective mass, which we have chosen equal to fourteen times the neutron mass, to the system consisting of proton plus potential and assuming these "molecules" to move freely like gas molecules with a MAXWELL distribution. In §§ 2 and 3 the cross-sections are calculated. In §§ 4 and 5 we discuss the temperature effects. Firstly it is found that when both the neutrons and the scattering substance have room temperatures, the' cross-section is 2.7 times larger than the free cross-section. Secondly it is found that the cross-section for neutrons at liquid air temperature i. e. 90° abs is 34 % higher than at room temperature. These figures are compared with the experiments. Finally we in § 6 discuss which effective energy must be attributed to a beam of MAXWELL neutrons in regard to the *scattering* cross-section. It is found that for our model this effective energy lies between 0.7 kT and 1.1 kT depending on the tempera-

ture. In the mathematical notes we have further compiled various formulae for transformation of coordinate systems, matrix elements and integrals used in the text.

In conclusion I wish to thank Prof. Niels Bohr for his kind interest in this work and to express my appreciation to Prof. G. Placzek for suggesting the problem to me and for many valuable and helpful discussions in the course of the calculations. Further I wish to thank Dr. F. Kalckar, Dr. C. Møller and Dr. V. Weisskopf for many stimulating discussions.

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STUDIES IN THE PROPERTIES OF IONIC CRYSTALS

BY

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I.

THE DIELECTRIC CONSTANT OF ALKALINE EARTHS

DETERMINED BY AN IMMERSION METHOD DEPENDING ON THE VARIATION WITH TEMPERATURE OF THE DIELECTRIC CONSTANT OF THE IMMERSION LIQUID

BY

KRISTIAN HØJENDAHL

CONTRIBUTION FROM THE CHEMICAL
LABORATORY OF THE ROYAL VETERINARY AND AGRICULTURAL COLLEGE.
COPENHAGEN. DENMARK.

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APPENDIX

Introduction and Summary.

In order to elucidate the relationship between the dielectric constant and the structure of solid compounds, it is best to proceed on a definite plan, for instance based on the periodic system of the elements. Binary uni-univalent compounds of course constitute the simplest cases, by now the dielectric constants of nearly all alkali-halides have been measured by many investigators, and a comprehensive compilation of data and references is given in LANDOLT-BÖRNSTEIN's tables[1]. In our present work dielectric constants of KCl, RbCl, RbBr and RbI at about 70° C. have been determined; at lower temperatures these had been determined earlier by the writer as well as by other investigators as will be seen from table 3. The temperature coefficients have small positive values.

Proceeding next to di-divalent compounds, it is observed that only very few of these have been investigated earlier. The dielectric constant of ZnS was extrapolated from infra-red by LIEBISCH and RUBENS[2], and the dielectric constant of MgO was measured by GÜNTHERSCHULZE and KELLER[3] (see later). In the present work the determination of dielectric

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[1] LANDOLT — BÖRNSTEIN: Tabellen; Erg. Bd. III; 194 h-r. p. 1889—98.

[2] LIEBISCH T. and RUBENS H.: Sitzber. Preuss. Akad. d. Wiss. XLVIII (1919).

[3] GÜNTERSCHULZE A. and KELLER F.: ZS. f. Physik. **75**, 82 (1932).

constants for the alkaline earths was regarded the main object. Various samples of BeO, MgO, CaO and SrO were investigated. Beryllium compounds were prepared in a pure state following a method given by Hönigschmied and Birkenbach, and strontium compounds following a method by S. P. L. Sørensen.

The alkaline earths are obtained nearly always as fine powders consisting of porous particles, hence resort must be taken to an immersion method. The special type of immersion method proposed by the writer[1] was found particularly suited for the purpose. According to this method, powder and a suitable immersion liquid were mixed and boiled for an hour in vacuo in order to remove occluded air. The mixture was transferred to the dielectric cell which was heated or cooled to a suitable temperature and then inserted into a Dewar vessel. During the subsequent slow temperature variation, the capacity of the dielectric cell was determined at intervals, and a curve, recording the variation of capacity with temperature, was plotted in a diagram. Afterwards the mixture was filtered, and the filtrate put into the dielectric cell, whereupon the measurements were repeated, and a new curve plotted in the same diagram. Where these two curves intersect, i. e. at that temperature, the dielectric constants of mixture, liquid and solid are equal, and if the dielectric constant of the liquid is known, that of the solid is hereby determined.

The present dielectric cell was calibrated by the standard values of dielectric constant for certain pure liquids determined by Hartshorn and Oliver, and by Sugden (see later).

Similar methods have been proposed for the purpose of

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[1] Højendahl K.: ZS. physik. Chem. B. **20**, 54 (1933).

determining the refractive index or the density of a powder, but have not met with success, because these properties vary little with temperature. The dielectric constant of a polar liquid, however, varies a great deal with temperature, as will be seen from the diagram (Fig. 6) in which it is demonstrated, that the dielectric constant of acetylene tetrachloride varies from 4.5 to 14 inside the liquid region.

In an older method of STARKE[1] the dielectric constant was varied by altering the composition of the immersion liquid, which in that case was a mixture. The present method, however, is considered advantageous not only because it is easier, but also for other reasons. In the present method the dielectric cell is kept closed during the measurements, no moisture or carbon dioxide being allowed in; that would hardly be possible by the old method. In the present method the rapidity of measurements is hampered by the slow heat transfer inside the dielectric cell, in the old method the rapidity would be even more hampered by the slow diffusion of the liquid added into the pores of the particles.

The capacity of the dielectric cell was measured by means of a resonance apparatus which is described in detail. The wave-lengths used were 120, 134 and 142 meters. By means of switches the dielectric cell was substituted by a capacity box, which was adjusted until resonance was again obtained. Then the capacity of the dielectric cell was equal to that of the capacity box. The effect on the dielectric constant, arising from the electrical conductivity of the cell contents, is computed and in actual cases this effect is found to be negligible.

Chlorobenzene, ethylene dichloride, acetylene tetrachloride and mixtures of benzene with nitrobenzene or ethyl

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[1] STARKE H.: Wied. Ann. **60**, 629 (1897).

alcohol were used for immersion liquids. As a rule, the liquids were purified by means of silica gel and distillation. In the case of acetylene tetrachloride, few and conflicting data are found in the literature, therefore a number of its properties were investigated. Its melting point, determined in two ways, was found to be — 44° C. From the variation of boiling point with pressure the latent heat of evaporation was evaluated. The variation with temperature and frequency of the dielectric constants of liquid and solid acetylene tetrachloride was investigated, the resultant curves being given in Fig. 6. Just below the melting point solid acetylene tetrachloride exhibits anomalous dispersion, i. e. the dielectric constant varies considerably with frequency as well as with temperature.

The Apparatus used for Measuring Dielectric Constants.

In principle the apparatus was similar to the earlier apparatus[1] used at Universitetets kemiske Laboratorium and at Landbohøjskolens kemiske Laboratorium, both in Copenhagen; and to the apparatus used in the Physikal.-chem. Abt. des Chemischen Instituts der Universität Würzburg[2].

A number of improvements, however, have been introduced in the course of time. The present apparatus is shewn diagramatically in Fig. 1. The double set of switches S_3 and S_4 enabled measurements to be performed either by the substitution method or by the compensation method. When S_3 was in the upper position marked ‘in’, the adjustable capacity box C_3 was thrown into the oscillation circuit of

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[1] Højendahl K.: Studies of Dipole Moment (Dissertation). Copenhagen. (1928) p. 69.

[2] Højendahl K.: ZS. physik. Chem. B. **20**, 55 (1933).

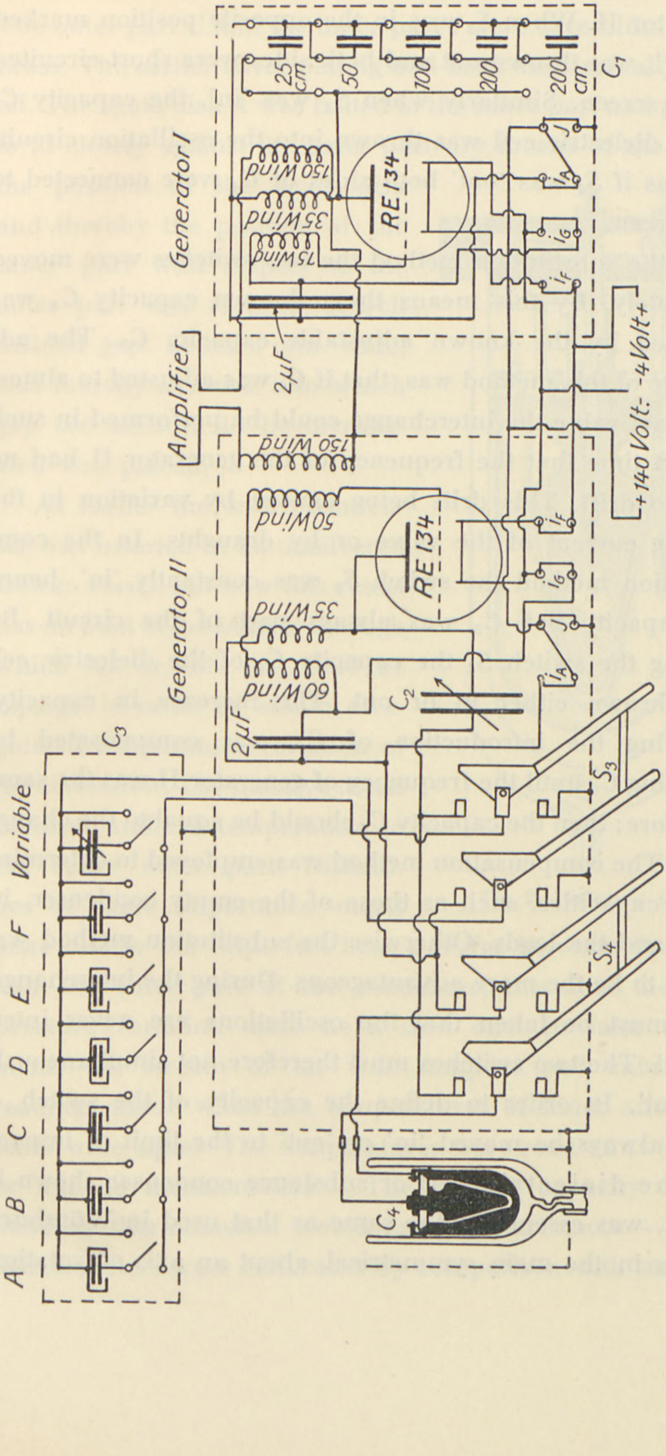

Fig. 1. Dielectric Apparatus

generator II. When S_3 was in the opposite position marked 'out', C_3 was thrown out and both sides were short-circuited to the screen. Similarly when S_4 was 'in', the capacity C_4 of the dielectric cell was thrown into the oscillation circuit, whereas if S_4 was 'out' both sides of C_4 were connected to the screen.

In the substitution method the two switches were moved alternately. By this means the unknown capacity C_4 was replaced by the known adjustable capacity C_3. The advantage of this method was, that if C_3 was adjusted to almost the exact value the interchange could be performed in such a short time that the frequency of the generator II had no time to drift. This drift being caused by variation in the heating current of the valve or by draughts. In the compensation method the switch S_3 was constantly 'in', hence the capacity box C_3 was always part of the circuit. By moving the switch S_4 the capacity C_4 of the dielectric cell was thrown either in or out. The increase in capacity, following the introduction of C_4, was compensated by adjusting C_3 until the frequency of generator II was the same as before; then the capacity C_4 should be equal to the change in C_3. The compensation method was employed to determine small capacities, such as those of the empty condenser, its parts and the leads. Otherwise the substitution method was found to be the more advantageous. During the interchange, care must be taken that the oscillations are never interrupted. The two switches must therefore not simultaneously be 'out'. In order to define the capacity of the switch, it must always be moved 'in' or 'out' to the limit of impact.

The dielectric cell or substance condenser shewn in Fig. 2, was essentially the same as that used in Würzburg. It was in the main symmetrical about an axis of rotation.

The outer part *U* and the inner part *I* were chromium plated brass. The earlier silver plating had been mechanically worn off. The agate disk *A* was bolted to the inner part and ground to fit closely against the outer part. By means of the nut *M* the position of the agate disk and thereby the position of the inner part with respect to the outer part was secured. A well defined gap, about 3 mm. wide, was thereby ensured, into which gap the mixture to be investigated was placed.

As earlier the entire condenser was inserted in an unsilvered Dewar vessel, but now this vessel has an inlet at the bottom through which hot or cold air could be injected in order to obtain a regulated temperature variation of the condenser. The massive metal ensured uniform temperature in the entire outer part. Difficulties of some importance might arise due to the imperfect heat transfer between the inner and the outer part of the condenser, therefore the temperature variation must be a slow one. In later experiments the stream of air was stopped, and subsequent readings made when the temperatures of inner and outer parts were equal. The temperatures were read on two nerol or toluene thermometers. — The mutual capacity of two mercury thermometers would cause disturbances. — These thermometers were calibrated by comparison with standard

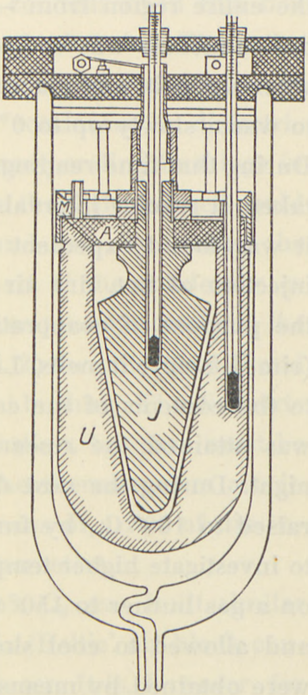

Fig. 2. Dielectric Cell.

thermometers, and in particular by the melting points of ice and mercury. The region of temperature considered was from —60° to +100° C. It was often sufficient to consider temperatures either above or below room temperature. If the entire region from —60 to 100° was to be considered, the condenser was cooled to —60° by means of CO_2-ether, whereupon it was placed in the Dewar vessel and allowed to warm slowly up to 0° C., taking about 5 hours to do so. During that time readings of capacity and temperature were taken at regular intervals. At a temperature just below zero it was found expedient to increase the rate of heating by injection of hot, dry air; the dry air was also injected for the purpose of evaporating and thereby removing any ice (rime), before it melts. Liquid water of course, was a danger to the contents of the condenser. When room temperature was attained, the research was generally interrupted over night. During the next day the temperature was gradually raised to 100° C., by further injection of hot air. In order to investigate higher temperatures the condenser was heated on a gas burner to 150° C., and placed in the Dewar vessel and allowed to cool slowly. Moderately low temperatures were obtained by means of common salt and ice, or better still, by placing the condenser in a dessicator in the open air on a cold winter night. Compressed air was procured from the plant of the college; it was dried through calcium chloride and heated in an electric oven.

As will be seen from Fig. 2 the condenser was suspended in the 'nokait' lid by means of three bolts of German silver (small thermal conductivity). One of these bolts was connected to one terminal and formed one lead. The second lead is directly visible in the figure; it consisted of bushing and plug, because the connected parts must be able to turn independently. The plug, which was perforated to take the thermometer, was connected to the second terminal. The 'nokait' lid fitted against the Dewar vessel, but it did not rest on it. It rested on a metal box, (not visible in the Fig. 2) forming a metal shield round the condenser. In this box the Dewar vessel was seated on a 'suberite' ring. The entire box with all could be tipped round a horizontal axis. In this way the terminal plugs of the condenser or dielectric cell could be removed from the corresponding bushings in the shield of generator II, whereupon the dielectric cell could be lifted out of the Dewar vessel and box. By turning the nut *M* with respect to the outer part *U* the condenser or dielectric cell could be taken into three pieces, namely 1) the nut *M* with nokait lid and terminals, 2) the outer part *U* and 3) the inner part *I* with agate disk and bushing. The dielectric cell was closed by the opposite operation, but care must be taken that the different holes for the thermometers are in alignment. This was ensured by means of a rod of dimensions similar to those of the thermometers.

The adjustable capacity box C_3 was built similar to a resistance box, from a set of six 'Baltic' air block condensers and a small variable condenser. It is, however, far more difficult to ensure independent additivity of capacities than of resistances. In order to secure additivity each component condenser was enclosed in a separate metal box. These boxes were connected together and connected to one terminal of the capacity box. One side of each component condenser was always connected to the box. The second side was brought through an opening in the box, and connected to a bushing in the ebonite top plate. By means of a special double plug or bridge, connection could be made, either to bushings connected to the second terminal in which case the capacity considered was 'in', or connection could be made to bushings connected to the first terminal in which case the condenser considered was short circuited and 'out'. In the above manner a capacity box which can be accurately set and read can be constructed from ordinary commercial radio articles. The entire capacity box was surrounded by a separate metal shield connected to the other shields of the apparatus.

The generators I and II were built from commercial radio articles when these were still abundant. Some parts were taken over from an older apparatus. The circuits will be seen from the diagram (Fig. 1). The valves were 'Telefunken R.E. 134'. The coils were 'Reactone Low Loss'. The variable condenser C_2 in generator II was an adjustable 'Torotor' condenser. In generator I a system of 'Baltic' block condensers was used for capacity. They could be thrown 'in' and 'out' from the outside in a similar way to those of the capacity box.

By this means it was ensured that the measurements were performed not at any frequency, but at a number of definite frequencies. The frequencies most often used correspond to the wave-lengths 120 m., 134 m., and 142 m.[1].

Each generator was placed in a separate box. Such a box consisted of front plate, bottom plate and framework of ebonite. The framework was rigidly bolted together by means of corners of brass plate. On top, bottom and three sides zinc plates were bolted on. The front plate was covered by a window fitted with brass network. The zinc plates and the brass network formed a closed Faraday cage or shield, which was connected to the shields mentioned before.

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[1] The wave meter was kindly lent to me by Mr. J. P. Christensen, Telephone and Telegraph Department of the Technical Highschool, Copenhagen.

If need be, the zinc plates could be removed to give access to the interior. Valves, coils etc. were mounted on the bottom plate. The front plate contained a number of control knobs, allowing the generator to be operated from the outside. The leads were all placed in the space between bottom and front plate, and hence they were all visible as soon as the zinc plates were removed. The leads were made of thick wire soldered on and drawn as far as possible straight through the intervening space from one support to another. The leads must be rigid and as remote as possible from everything else, in order that mechanical vibrations shall cause the smallest possible capacity or frequency changes (quivering).

The frequency of the electric oscillation set up in a generator depends largely on the effective capacity and inductance of the dominant oscillatory circuit, which in this case was placed in the anode circuit. In the case of generator II this dominant circuit was composed of a coil with 35 windings and the capacities C_2 and C_3 (or C_2 and C_4) in series. The use of capacities in series instead of in parallel gives the possibility of generating a larger variety of frequencies by means of the same condensers.

Auxiliaries. The two generators were coupled together by means of a link circuit, and the interference note set up was eventually made audible by means of a commercial radio receiver with loud speaker (Unica). If the frequencies of the two generators are close, an audible note will be heard in the loud speaker. The closer the frequencies, the more bass the note. The note will eventually be so bass that it becomes inaudible over a narrow interval. The two borders of this interval were used in the measurements in a manner similar to the borders of the sound minimum employed in the telephone-bridge method for determination of resistances. The procedure in the substitution method was then the following: A definite frequency or wave-length, say 142 m. was set up in generator I by throwing the 100 cm. condenser in the oscillation circuit of this generator. With the dielectric cell C_4 in, and the capacity box C_3 out of the oscillation circuit of generator II, the condenser C_2 was adjusted to one of the borders of the silent interval. C_4 was then replaced by C_3 which was adjusted to the two borders of the silent interval. The settings of these were read. Afterwards the procedure was repeated with C_2 set on the second border of the silent interval. The mean value of these four readings on the capacity box C_3 measured the capacity of the dielectric cell C_4.

The heating current for generators and receiver was supplied by an accumulator battery. The anode current for the receiver was taken from a high tension battery; that for the generators from a stabilizer (Fig. 3) the most important part of which was a discharge potential divider from

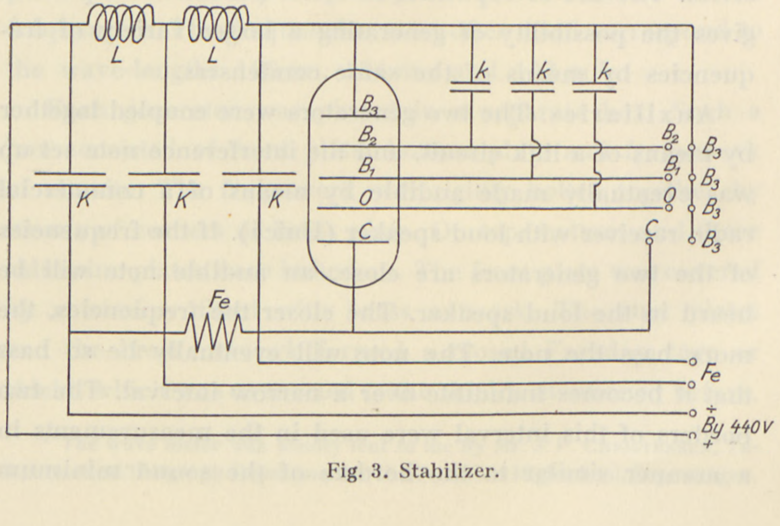

Fig. 3. Stabilizer.

G.m.b.H. Stabilovolt. The potential across the divider is nearly independent of the current passing through. This was combined with an iron-in-hydrogen resistance Fe., having just the opposite character in so far as the potential increases steeply with the current. The combination of these suppressed slow variations in the potential of the town supply to such an extent that the potential variations of the stabilized potential were found not to exceed 3 per cent. of those of the supply. In order to suppress oscillations as well, a filter chain consisting of chokes L and block condensers K were also introduced. The stabilizer was mounted in a box similar to those of the generators.

Calibration of the Apparatus.

The calibration of the adjustable capacity box was undertaken in a manner similar to the calibration of weights. The different block condensers A, B, etc. were expressed in terms of the degrees on the scale of the variable condenser. An unknown capacity x was measured by two different combinations of component condensers. For instance:

$$x = C + F + 14.8 = C + 88.1$$

from which was found: $F = 73.3$ degrees on scale

Similar equations were written down for other combinations. The different values varied due to the experimental error, which was up to 3 degrees on the scale, but there was no definite trend. As a mean value of 9 determinations it was found: $F = 71.2$ degrees on scale. In a similar manner the difference E—F was found from 10 determinations to be 72.9 and hence E was equivalent to 144.1

degrees on the scale and so on. That no definite trend was observed is a proof that the component capacities were independently additive within the experimental error. Furthermore by means of the standard instruments of the electrical laboratory of Nordisk Kabelfabrik the corresponding capacities were expressed in cm.[1]. As a result the following values for the different component condensers were obtained:

Table 1.

	degrees on scale	capacity in cm.
A	1093.0	222.2
B	1065.0	219.2
C	564.5	115.6
D	288.0	62.1
E	144.1	32.8
F	71.2	13.9
	1° equals	0.205 cm.

The calibration of the dielectric cell was undertaken to determine the true capacity of the cell. The apparent capacity of the cell was considered to consist of two parts, namely the true capacity which varied proportional to the dielectric constant of the contents, and the lead capacity which was constant. Four independent determinations were made:

1) By direct measurement of lead capacity. The capacity of the dielectric cell filled with air including leads to the switch S_4 was measured by the compensation method. It was found to be equivalent to 223.3 degrees on the scale or 45.7 cm. Afterwards the outer part was removed, i. e. it was

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[1] I therefore wish to express my thanks to Mr. J. Møllerhøj.

screwed out of the nut *M*. The capacity of what was left was considered to be that of the leads. It was found to be equivalent to 102.2 degrees on the scale or 20.9 cm. The difference of 121.1 degrees on the scale or 24.8 cm. was the true capacity of the dielectric cell.

2) Using benzene as a standard liquid. The purification of standard liquids is considered later. The capacity of the dielectric cell with benzene, leads included, by the compensation method was equivalent to 373.3 degrees on the scale at 17° C. According to the most accurate determination of Hartshorn and Oliver[1], the dielectric constant of benzene at 20° C. is 2.282, and at 17° C. it is 2.288. From this and the foregoing measurement on air one unit of dielectric constant was found to correspond to:

$$\frac{373.3-223.3}{2.288-1.001} = 116.6 \text{ degrees on the scale.}$$

3) Using chlorobenzene as a standard liquid. By now the most accurate value of the dielectric constant of chlorobenzene is presumably that of Sugden[2], i. e. $\varepsilon_{25^\circ} = 5.612$, whereas Ulich and Nespital[3] found $\varepsilon_{25^\circ} = 5.605$ and $\varepsilon_{20^\circ} = 5.685$. With the same temperature coefficient the Sugden value becomes 5.690 at 20° C., which was taken as a standard value. The capacity of the cell with chlorobenzene at 20° C. measured by the compensation method was found to be equivalent to 779.8 degrees on the scale. In a manner similar to that given for benzene it was found that one unit of dielectric constant corresponds to 118.7 degrees on the scale.

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[1] Hartshorn L. and Oliver D. A.: National Physical Laboratory. Collected Researches Vol. **22**, p. 342 (1930).

[2] Sugden S.: J. Chem. Soc. (1933) p. 773.

[3] Ulich H. and Nespital W.: ZS. physik. Chem. B. **16**, 229 (1932).

4) The above calibrations were carried out by the compensation method, the great majority of the measurements, however, were carried out by the substitution method. The dielectric constants measured were as a rule larger than that of chlorobenzene. Therefore a calibration was also carried out by the substitution method, using chlorobenzene and ethylene dichloride as standard liquids. Measurements on these two liquids were in fact carried out repeatedly during the entire series of measurements, in order to control the constancy of the true capacity of the dielectric cell. The following 16 readings referred to 20° C. were obtained on chlorobenzene in the course of time:

607.4; 609.1; 608.4; 611.9; 616.8; 616.9; 600.0; 600.8;

604.5; 605.2; 606.3; 606.3; 605.9; 611.0; 608.3 and 605.3.

all in degrees on the scale of the capacity box. It is seen that definite changes occur, which are somewhat larger than the hap-hazard error. The reason is the following:

The mixture of powder and liquid was sometimes so tough, that a certain violence was necessary in order to close the dielectric cell. On one occasion, towards the end of the series of researches, the pressure was so large, that a bit of the agate disk was broken off. The agate disk was mended by means of dental cement in a manner similar to the filling of a tooth. The change in capacity following this mishap, however, was not the largest. Other changes were caused by the giving way of the tin packings between the inner part *I* and the agate disk *A*, and by wear and tear on the different parts, which necessitated readjustment of the screws bearing against the upper surface of the agate disk.

Originally it was the intention to use the individual measurements on chlorobenzene to correct for these changes in the true capacity of the dielectric cell. This, however, was abandoned, since it was found that the dielectric constants of solids could not for other reasons be reproduced to more than 2—5 per cent. Hence the mean value of 607.7 at 20° C. was considered the standard reading for chlorobenzene.

In a similar manner the value of 1175.2 at 20° C. was obtained as an average of eight measurements on ethylene dichloride. The most accurate value of the dielectric constant of this compound as determined by SUGDEN: loc. cit. is: $\varepsilon = 10.36$ at 25° C., whereas ULICH and NESPITAL: loc. cit. found $\varepsilon = 10.24$ at 25° C. and $\varepsilon = 10.50$ at 20° C. Hence the value $\varepsilon = 10.62$ was taken as the standard value at 20° C. according to SUGDEN.

The difference in dielectric constant

$$10.62 - 5.69 = 4.93$$

corresponds to the difference in readings

$$1175.2 - 607.7 = 567.5.$$

The true capacity i. e. the number of degrees on the scale corresponding to one unit on dielectric constant therefore becomes:

$$\frac{567.5}{4.93} = 115.2 \text{ degrees on the scale}$$

$$\text{or } 115.2 \times 0.205 = 23.6 \text{ cm.}$$

As this value was obtained from repeated measurements by the more accurate substitution method it was taken as the standard value. The agreement with values obtained in other ways showed, that it was essentially correct and furthermore that linear inter- and extrapolation was allowable.

By such extrapolation the reading corresponding to zero dielectric constant was found to be —48 degrees on the scale. This was the difference in capacities of leads leading to C_3 and C_4, it includes the capacity of the capacity box with all block condensers out, and the scale of the variable condenser at zero.

Immersion Liquids.

In addition to the standard liquids mentioned above namely chlorobenzene and ethylene dichloride, we used acetylene tetrachloride and mixtures of benzene with nitrobenzene or ethyl alcohol as immersion liquids. These mixtures were used in order to evade an eventual decomposition of ethylene dichloride by the reactive compounds SrO and CaO.

Of the above liquids, benzene, chlorobenzene, ethylene dichloride, acetylene tetrachloride and nitrobenzene were purified by practically the same method. They were allowed to ooze through silica gel as proposed by Grimm and Wolff[1]. By selective adsorption more polar impurities such as water were retained on the gel. The adsorption apparatus was built from standard grounded parts (Normal Schliff), see Fig. 4. It was found convenient to have two columns (Hempel columns) one on top of the

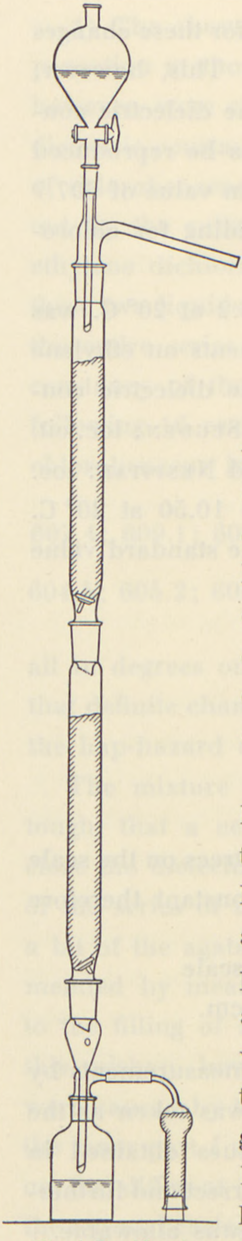

Fig. 4. Purification of Liq. by means of Silica Gel.

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[1] Grimm H. G. and Wolff H.: ZS. angew. Chem. 41, 98 (1928).

other. When the silica gel in the upper column was saturated, and the column therefore removed in order to refill it, the lower column was raised to the top and the refilled column attached below. In this manner a good purification could be obtained by means of the smallest amount of silica gel.

The liquids were afterwards distilled in the same distillation apparatus as used by LANNUNG[1] in his research on the solubilities of alkali-halides in alcohols and acetone. The apparatus is described and a figure is given by LANNUNG. The liquid containers were also those constructed by LANNUNG. They were stored in the dark and served their purpose well.

Nitrobenzene was distilled twice in a cheaper apparatus by slow surface evaporation in a vacuum of 20 mm. Hg.

The pure liquids were characterized by the following constants:

Benzene	melting point	5.10° C.
Nitrobenzene	melting point	5.76° C.
Chlorobenzene	refractive index $n_D =$	1.5224 at 23.6° C.
Ethylene dichloride	refractive index $n_D =$	1.4427 at 23.4° C.

Ethyl alcohol was purified by the method of LUND and BJERRUM[2] using magnesium and iodine. When it was due to be used the ethyl alcohol was distilled directly from the magnesium ethylate.

Various properties of acetylene tetrachloride were given special attention. Thus the refractive index for the D line was found to be 1.4937 at 22.0° C.[3].

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[1] LANNUNG A.: ZS. physik. Chem. A. **161**, 256 (1932).

[2] LUND H. and BJERRUM J.: Ber. D. Chem. Ges. **64**, 210 (1931).

[3] This value supercedes the value n_D = 1.4988 at 23° C. given by the writer in Kemisk. **16**, 54 (1935).

The melting point from the fusion curve is — 43° C. (thermometers calibrated by means of melting points of mercury and ice), but owing to the small heat of fusion and the slight heat conductivity of acetylene tetrachloride the melting point as determined from the fusion curve, i. e. temperature — time curve, is not very definite. A more definite value of — 44.5° C. is found from the variation of dielectric constant with temperature as will be considered later. The above values of the melting point agree well with that determined by Timmermans[1], namely — 43.8° C., but not with that found by Herz and Rathmann[2], namely — 36° C. The latent heat of vaporization of acetylene tetrachloride can be determined from the variation of boiling point with pressure. The above distillation apparatus used for the purification of the liquids was employed for the measurements. It was connected to a mercury-gauge. By the adjustment of the taps leading to the vacuum of a water jet aspirator and to dry air at atmospheric pressure, various pressures could be maintained, and the corresponding values of pressure and boiling point could be determined. Such values are plotted in diagram 5. Two samples were investigated. The crosses + + + refer to a purified sample and the circles to a still further purified sample. This second sample was the middle fraction obtained during the distillation of the first one. It is seen that there is no marked difference between the data obtained for the two samples, which indicates that these were sufficiently purified. The triangles represent earlier data of Herz and Rathmann[3], and the diamond data of Walden and Swinne[4]. In order to deter-

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[1] Beilstein: Handbuch org. Chem. Ergbd. I. p. 25.

[2] Herz W. and Rathmann W.: Chem. Zeitung, **37**, 621 (1913).

[3] Herz W. and Rathmann W.: Chem. Zeitung. **36**, 1417 (1912).

[4] Walden P. and Swinne R.: ZS. physik. Chem. **82**, 281 (1913).

mine the latent heat of vaporization, Briggsian logarithms of pressure are plotted as ordinates against the reciprocals of the absolute temperatures as abcisses. The X's are the values obtained from the first sample and the filled circles those obtained from the second sample. The data can be

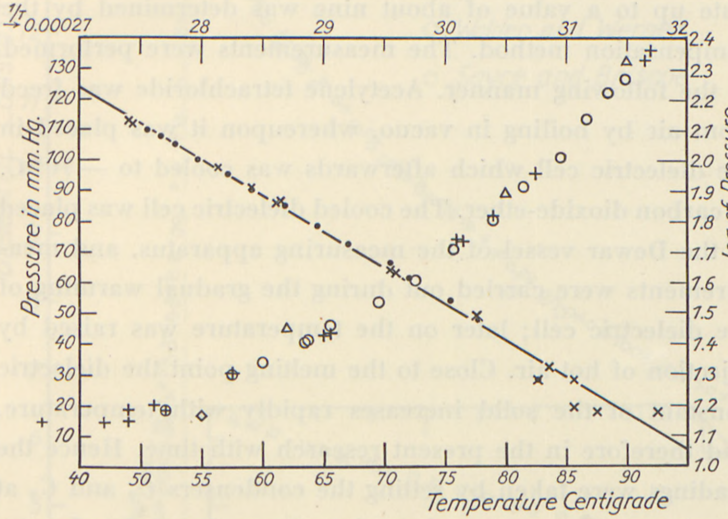

Fig. 5. Vapour Pressure of Acetylene Tetrachloride.

represented by a straight line within the experimental error, hence they can be expressed by the following "August" equation:

$$\log_{10} p = -\frac{A}{T} + B = -\frac{2375}{T} + 8.655;$$

According to the Clausius-Clapeyron relation the latent heat of evaporation is equal to:

$$l = \frac{A \times R}{\log e} = \frac{2375 \times 1.986}{0.4343} = 10850 \text{ cal/Mol.}$$

This is the value for a range of temperature around 70° C.;

Herz and Rathmann loc. cit. found 9134 cal/Mol at about 140° C.

The dielectric constant of acetylene tetrachloride in the liquid state was determined by the substitution method, whereas the dielectric constant in the solid state up to a value of about nine was determined by the compensation method. The measurements were performed in the following manner. Acetylene tetrachloride was freed from air by boiling in vacuo, whereupon it was placed in the dielectric cell which afterwards was cooled to — 70° C. in carbon dioxide-ether. The cooled dielectric cell was placed in the Dewar vessel of the measuring apparatus, and measurements were carried out during the gradual warming of the dielectric cell; later on the temperature was raised by injection of hot air. Close to the melting point the dielectric constant of the solid increases rapidly with temperature, and therefore in the present research with time. Hence the readings were taken by setting the condensers C_2 and C_3 at definite positions. In a short time the entire scale of notes was heard, and the temperatures corresponding to the two borders of the silent interval were read on the thermometers. The mean value of these readings gives the temperature corresponding to the setting of the condenser. Four series of measurements were carried out. In diagram 6 the resultant dielectric constants are plotted as ordinates against the (corrected) temperatures as abcisses. Data at 142 m. wave-length are denoted by triangles, those at 134 m. wave-length by X's, and those at 120 m. wave-length by circles.

Note that the dielectric constant varies considerably with temperature, and somewhat with frequency. The pointed maximum represents the melting point of — 44.5° C. The decrease of the dielectric constant of the liquid with rise of

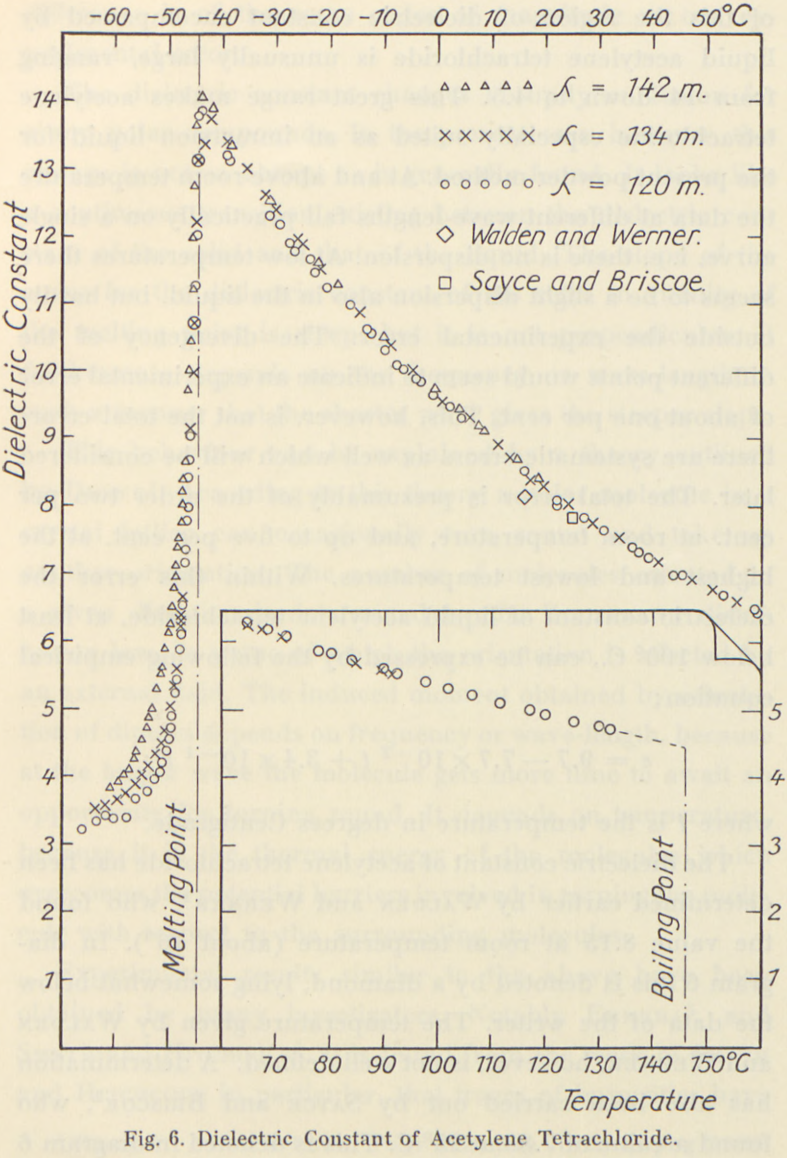

Fig. 6. Dielectric Constant of Acetylene Tetrachloride.

temperature is considerable. Furthermore the liquid region is wide, ranging from — 44.5° C. to 146° C. As a consequence of this the region of dielectric constant encompassed by liquid acetylene tetrachloride is unusually large, ranging from 14 down to 4.5. This great range makes acetylene tetrachloride especially suited as an immersion liquid for the present powder method. At and above room temperature the data at different wave-lengths fall practically on a single curve, i. e. there is no dispersion. At low temperatures there seems to be a slight dispersion also in the liquid, but hardly outside the experimental error. The divergency of the different points would seem to indicate an experimental error of about one per cent. This, however, is not the total error; there are systematic errors as well which will be considered later. The total error is presumably of the order two per cent. at room temperature, and up to five per cent. at the highest and lowest temperatures. Within this error the dielectric constant of liquid acetylene tetrachloride, at least below 100° C., can be expressed by the following empirical equation:

$$\varepsilon = 9.7 - 7.7 \times 10^{-2}\, t + 3.4 \times 10^{-4}\, t^2;$$

where t is the temperature in degrees Centigrade.

The dielectric constant of acetylene tetrachloride has been determined earlier by Walden and Werner[1], who found the value 8.15 at room temperature (about 16°). In diagram 6 this is denoted by a diamond, lying somewhat below the data of the writer. The temperature given by Walden and Werner, however, is not well defined. A determination has also been carried out by Sayce and Briscoe[2], who found a value of 7.83 at 25° C. This is denoted in diagram 6 by a square lying close below the data of the writer. The

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[1] Walden P. and Werner O.: ZS. physik. Chem. **111**, 469 (1924).

[2] Sayce L. A. and Briscoe H. V. A.: Journ. Chem. Soc. 2626 (1926).

difference is of the same order of magnitude as our experimental error.

The dielectric constant changes abruptly on fusion for many polar compounds. In the present case, however, this change is not so abrupt as is generally found. It looks like a continuous transition existing between the dielectric constant of the solid and that of the liquid. The slope of the curve for the dielectric constant of the solid in vicinity of the melting point is steep, but it is not perpendicular. It furthermore depends on the frequency or wave-length in such a manner that the shorter wave gives the steeper slope.

This behaviour can be explained by a theory outlined by DEBYE[1]. According to this theory a polar molecule in a crystal lattice can occasionally turn round and take up another orientation. The number of molecules oriented in a given direction is determined by the BOLTZMANN distribution law, in virtue of which the orientation is affected by an external field. The induced moment obtained by orientation of dipoles depends on frequency or wave-length, because at the longer wave the molecule gets more time to await an opportunity for turning round. It depends on temperature, because it is the thermal energy of the molecules which overcomes the potential barriers involved in turning the molecule with respect to the surrounding molecules.

Experimental results similar to the above have been obtained by many investigators. Notably ERRERA[2], and SMYTH and HITCHCOCK[3]. It is found from the work of SMYTH and HITCHCOCK in particular, that traces of impurities have

[1] DEBYE P.: Polare Molekeln, (Polar Molecules). Hirzel. Leipzig (1929). Paragraph 21. pp. 118—124.

[2] ERRERA J.: Journ. de Physique et le Radium. (6) **5**, 304 (1924).

[3] SMYTH C. P. and HITCHCOCK C. S.: Journ. Amer. Chem. Soc. **54**, 4631 (1932).

a considerable influence on the shape of the curve. This influence is such that the purer sample shows a more abrupt change in dielectric constant on fusion. As an explanation it is suggested that the molecules turned by the field in particular are those situated at places in the crystal where the continuity of the lattice is disturbed, for instance by the presence of foreign molecules.

Preparation and Analysis of solid Compounds.

KCl (Kahlbaum zur Analyse) was dried. RbCl, RbBr and RbI were those samples, which we had used earlier, recovered by recrystallization from water and dried[1]. They were prepared following a method by Lannung[2].

The beryllium compounds were prepared in a pure state following the method given by Hönigschmied and Birkenbach[3]. Commercial $Be(OH)_2$ was dissolved in acetic acid and the basic acetate formed was recrystallized twice in Soxhlet's apparatus from pure acetic acid. The crystals of basic beryllium acetate were placed in a tube of hard glass which was inserted into a larger glass tube placed in an electric oven. The basic acetate was sublimed from the narrow tube into the wider one at a vacuum of 10 mm. Hg in a stream of pure air. The sublimate was found to be free from iron. It was decomposed by nitric acid. From the beryllium nitrate, pure beryllium carbonate was prepared by precipitation with pure ammonium carbonate. By ignition of the hydroxide, the nitrate or the carbonate, different samples of beryllium oxide were obtained.

MgO (Kahlbaum zur Analyse) was analysed. A trace of

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[1] Højendahl K.: ZS. physik. Chem. B, **20**, 61 (1933).

[2] Lannung A.: ZS. physik. Chem. A, **161**, 259 (1932).

[3] Hönigschmied O. and Birkenbach L.: Ber. D. chem. Ges. **55**, 6 (1922).

carbonate and as much as 0.01 per mille chloride was found, but nothing else. The magnesium oxide was ignited. In one case the nitrate was formed by dissolving the oxide in nitrid acid. By ignition of the nitrate a special sample of magnesium oxide was obtained.

$CaCO_3$ (Merck pro Analysi) was analysed. No barium was found by the finest test of Sørensen (see later). A slight precipitate with $CaSO_4$ solution revealed a trace of strontium. A minute trace of iron and a minute trace of chloride were found, but nothing else. Calcium oxide was obtained by ignition.

SrO 'Kahlbaum', which had been ignited for four hours at 1000—1100° C., was analysed. Traces of Cl^- and Fe^{+++} were found. The dry residue of soluble sulphates amounted to 2.16 per cent. 2.8 per cent. CO_2 was found[1]. By spectral analysis about 1 per cent. Ca and rather less Ba were estimated to be present. Two series of measurements were carried out on the above SrO, whereas the subsequent two series were carried out on SrO purified following the method of Sørensen[2]. By this method iron and other metals were removed by heating an aqueous solution of strontium chloride and hydroxide with chlorine and filtering the ferric hydroxide formed. If large amounts of barium had been present, they could have been precipitated as barium chloride by addition of hydrogen chloride in the cold. In order to remove all other metals but barium, calcium, and lead, the sulphate was precipitated and washed. The sulphate was decomposed by ammonium carbonate and the carbonate by nitric acid. Barium was removed by fractional

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[1] I am indebted to Dr. K. J. Pedersen for using his apparatus which is described in: Journ. Amer. Chem. Soc. **53**, 20 (1931).

[2] Sørensen S. P. L.: ZS. anorg. Chem. **11**, 375 (1896).

precipitation of the sulphate from the nitrate solution. The remaining strontium nitrate solution was dried, and the residue repeatedly extracted with alcohol. Calcium nitrate, being considerably more soluble than strontium nitrate, was removed, and we were left with pure strontium nitrate. From this the carbonate was obtained by precipitation with ammonium carbonate. Different samples of strontium oxide were obtained by ignition of nitrate, carbonate, or hydroxide (obtained from oxide).

The pure strontium nitrate was analysed for barium and calcium by the finest tests given by Sørensen. No precipitate of barium chromate was visible after two days, which shows that the product contained less than 0.2 per mille barium. A slight precipitate of $CaNH_4AsO_4$ showed the presence of about 3 per mille calcium. On ignition strontium oxide was found to corrode the platinum crucible. The ignited product was gray, due to the platinum content, which was found to be about one per mille.

The ignition of the different compounds was performed in two electric furnaces. The first of these was a crucible furnace from Heraeus in which a temperature of 1000° C. could be attained. The second furnace was procured for the purpose. It was built by Sieverts in Stockholm and fitted with 'Globar' heating elements of carborundum. In this furnace a temperature of 1400° C. could be attained. The temperature was measured by means of a platinum — platinum-rhodium thermo-couple. The crucibles were generally of platinum except in the case of magnesium oxide where a magnesium oxide crucible of course was used. In order to avoid the formation of hydroxide or carbonate, due to the moisture and carbon dioxide in the air, and furthermore to prevent the formation of strontium peroxide, due to oxygen, a stream of pure nitrogen was conducted through the furnace until it was so cold that the crucible could be removed and placed in a dessicator.

Preparation of the Mixture of Powder and Immersion Liquid.

The ignited product was pulverized in a porcelain mortar. In the cases of calcium- and strontium oxide the mortar was placed in a manipulation chamber through which a stream of pure air was conducted. This chamber was similar to those in which balances are sheltered. Three openings, closed by shutters, are just large enough to allow a hand to be put into the chamber to perform the manipulation without introducing sensible amounts of moisture and carbon dioxide. The same chamber was also used for some of the following operations where moisture and carbon dioxide should likewise be avoided.

The powdered product was placed in a flask, belonging to the intermixture apparatus (Fig. 7). This was built similar to a vacuum distillation apparatus from standard ground parts — GREINER and FRIEDRICH Normalschliff. — It consisted of a round flask heated on an electric air bath. This was surmounted by an empty HEMPEL column, which served to catch the splashes — contrary to ordinary practice bumping is wanted. The column was attached to an Asher condenser, in the thermometer joint of which the leg of a tap-funnel was inserted. Through this tap-funnel the immersion liquid was introduced. The condenser was attached to a receiver, which in turn was connected to a water-jet aspirator. By tilting the apparatus the condenser could act as a reflux condenser.

The procedure was as follows: The powder — in particular the alkali-halides which were not dried in other ways — was dried by heating to about 200° C. in the highest

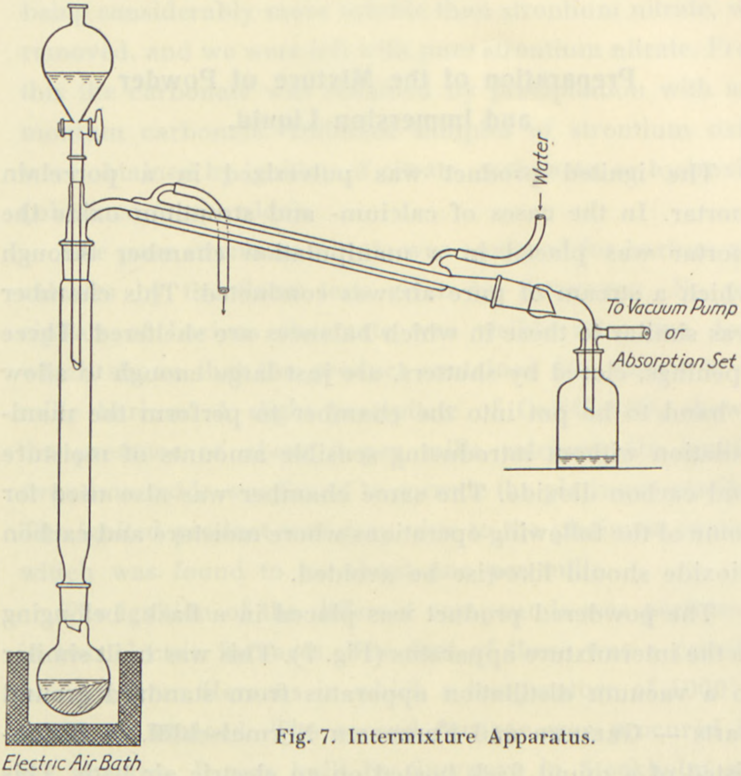

Fig. 7. Intermixture Apparatus.

vacuum attainable i. e. some 20 mm. Hg. After cooling the liquid was added, and the mixture boiled in vacuo — bumping — for two hours. By this operation occluded air should as far as possible have been removed from the powder. Finally the superfluos liquid was distilled off into the receiver, and pure air was allowed in. In the cases of strontium and calcium oxide, the immersion liquid was in most cases a mixture of nitrobenzene in benzene. To avoid heating the oxides with the less resistant nitrobenzene, the oxide was mixed with benzene in the above manner, and nitrobenzene was subsequently added. It was found necessary to allow the mixture to stand for some time, preferably over night, so that nitrobenzene might diffuse into the pores of the oxide.

The flask containing the mixture was placed in the manipulation chamber, and there the contents were poured into the outer part of the dielectric cell. The powder was allowed to precipitate to a certain degree, in so far this could be accomplished in a reasonable time, and the surplus liquid was drained off by means of a special pipette, having a plate of ebonite fixed on. By means of a libella this plate was placed level with the brim of the outer part of the dielectric cell, and by suction the liquid above a certain level was removed. The liquid drained off was employed later on. The inner part of the dielectric cell, filled to the defined height, contained 35 cubic centimeters of the mixture. The mixture was stirred, and the inner part of the dielectric cell was introduced. This was rocked and turned until the ground parts fitted together, and the nut *M* (see Fig. 2) could be screwed into the proper position. In order that the dielectric cell could be closed properly without violence, the fraction of solid powder must not exceed 30 per cent by volume of the mixture. This fraction of solid in the mixture was determined as follows: The amount of solid substance was originally weighed in the flask, and subsequently the liquid was added and mixed with the powder, whereupon the contents were poured into the dielectric cell. Here the powder precipitated, and the surplus liquid was drained off. It is now assumed that the total amount of solid was transferred into the dielectric cell, and knowing the density of the solid and the volume of the dielectric cell i. e. 35 cubic centimeter, the percentage by volume of solid in the mixture could be calculated. This percentage is not very definite, however, even if the solid could be quantitatively transferred, because the solid precipitated in the dielectric cell to an unknown extent.

Determination of the Dielectric Constant of Solids.

The dielectric cell was cooled as described on page 12, and then inserted into the Dewar vessel. During the subsequent slow rise in temperature, readings were carried out by the substitution method as described on page 10. The readings on the scale of the variable condenser in the capacity box were plotted against the corresponding readings on the thermometers. Such plots are given in the following diagrams.

The key is as follows:

△———△ i. e. the triangles denote measurements on the mixture at a wave-length of 120 meters;

+———+ i. e. the crosses, the same at a wave-length of 134 meters;

□——·——□ i. e. the squares, the same at a wave-length of 142 meters.

Curves, usually straight lines, have been drawn through the points of each set. Various combinations of block condensers were generally used, each combination giving a separate curve in the diagram. Such a curve for instance is denoted $A + F$, which means that, besides the variable condenser, the block condensers A and F were in the circuit.

After these measurements were finished the contents of the dielectric cell were filtered on a dry filter. The filtrate, together with the liquid drained off by the pipette (see page 35), was placed in the dielectric cell, and the capacities and temperatures were measured exactly as above. The readings have again been plotted in the diagram.

The key is as follows:

○———○ i. e. circles, denote measurements on the filtrate or the pure liquid at a wave-length of 120 meters;

×———× i. e. X's, the same at a wave-length of 134 meters;

◇——·——◇ i. e. diamonds, the same at a wave-length of 142 meters.

Curves (straight lines) have again been drawn through the points of each set. Where the corresponding curves for mixture and filtrate intersect, the dielectric constants of solid and liquid are equal. As described, the determination was made with the use of a single combination of block condensers only; by considering more combinations of block condensers, the accuracy was improved in the following manner: In a separate part of the diagram, the differences between corresponding readings on the scale for liquid and mixture, have been plotted against the readings on the thermometers. The temperature at which this difference was zero, records a much more accurate value of the intersection temperature, and the corresponding reading on the scale was found from the curve for the liquid (or mixture). The dielectric constant was then calculated in the following manner: To the reading on the scale of the variable condenser was added, 1) the value of the block condensers in scale degrees (see page 18), and 2) the value 48, representing the lead capacity (see page 22). The total, expressed in scale degrees, was divided by 115.2 (see page 21), whereby the dielectric constant of liquid and solid at the temperature of

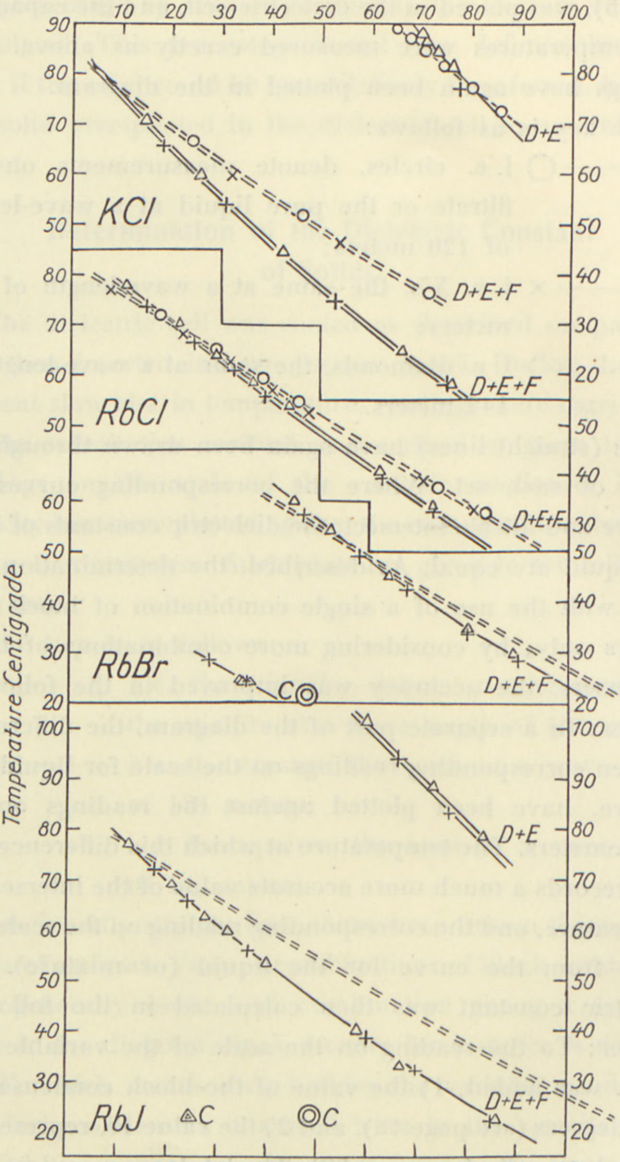

Fig. 8. Alkali Halides in Chlorobenzene.

intersection was determined. Above zero the thermometers gave the temperature in degrees centigrade with sufficient accuracy, but below zero a correction was found to be necessary. This correction was based on the melting points of ice and mercury. In the tables the corrected temperatures are quoted either in brackets or in a special column.

Data for alkali halides are given in diagram 8 and in table 2. The key is explained in the foregoing pages.

Table 2.

	Origin	Vol. per cent solid	Liquid	Wave-length	Intersection temperature	Condenser readings			Dielectric constant
						variable	fixed	total	
KCl	Kahlbaum	19.2	C_6H_5Cl	120	77.5	79.5	480.1	559.6	4.86
„	zur Anal.	same		120	80.0	4.8	551.3	556.1	4.83
„	„	sample		134	80.0	5.8	551.3	557.1	4.84
RbCl	purified	8.6	C_6H_5Cl	120	68.7	23	551	574	4.99
„	„	same sample		134	68.9	22	551	573	4.97
RbBr	purified	19.9	C_6H_5Cl	120	52.0	55	551	606	5.26
„	„	same sample		134	51.2	55	551	606	5.26
RbI	purified	17.7	C_6H_5Cl	120	77.5	12	551	563	4.89
„	„	same sample		134	75.8	14	551	565	4.90

The dielectric constant of KCl has been accurately determined by EUCKEN and BÜCHNER[1] whose measurements were carried out on plates cut from large single crystals. They found a value of 4.68 at 20° C. with a temperature coefficient $\frac{1}{\varepsilon}\frac{d\varepsilon}{dT} = 30.3 \times 10^{-5}$. This determination is considered the most accurate, and my determination above is only to be considered as a test of the total error involved

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[1] EUCKEN A. and BÜCHNER A.: ZS. physik. Chem. B, 27, 321 (1934).

in the present method. According to Eucken and Büchner the dielectric constant at 80° C. will be 4.77 which is about 1.5 per cent. smaller than the above values.

The dielectric constants of rubidium halides have likewise been determined earlier, and the different data have been compared in table 3.

Table 3.

	New dielectric constant	At temperature	Old dielectric constant	At temperature	Temperature coefficient	Dielectric constant at room temperature found by other investigators
RbCl	4.98	69	4.78[4]	1	6×10^{-4}	5.20[1]; 4.95[2]; 4.68[3]
RbBr	5.26	52	5.16[4]	−14	3×10^{-4}	4.70[1]; 4.87[2];
RbI	4.90	77	4.51[4]	12	13×10^{-4}	4.81[1]; 5.58[2];

[1] Errera J.: ZS. Elektrochemie. 36, 818 (1930).
[2] Kyropoulos S.: ZS. f. Physik. 63, 849 (1930).
[3] Schupp P.: ZS. f. Physik. 75, 100. (1932).
[4] Højendahl K.: ZS. physik. Chem. B. 20, 63 (1933).

There is fair agreement between my old and new values when it is remembered that there is a temperature difference of about sixty degrees. Old and new values are employed for the determination of temperature coefficients $\frac{1}{\varepsilon}\frac{d\varepsilon}{dT}$ which, however, cannot be considered accurate, because the error on the individual measurements is 2 per cent, giving rise to an error of some 50 per cent. on the temperature coefficient. The agreement between the data of the different investigators is not particularly good. I am aware that the plate method as developed by Eucken and Büchner is capable of greater accuracy than the powder methods, granted of course that sufficiently large crystals can be obtained. This is presumably the case with the alkali-halides, and therefore I suggest that any further measurements on these should be carried out by the plate method. But there are many cases where large single crystals cannot be obtained, and here the powder method in its present form will be of value. Such for instance is the case with most oxides.

BeO. Six mixtures of BeO of different origins and with different immersion liquids were investigated. For one of these mixtures the actual readings have been plotted into a diagram, Fig. 9. The diagrams for the other mixtures were

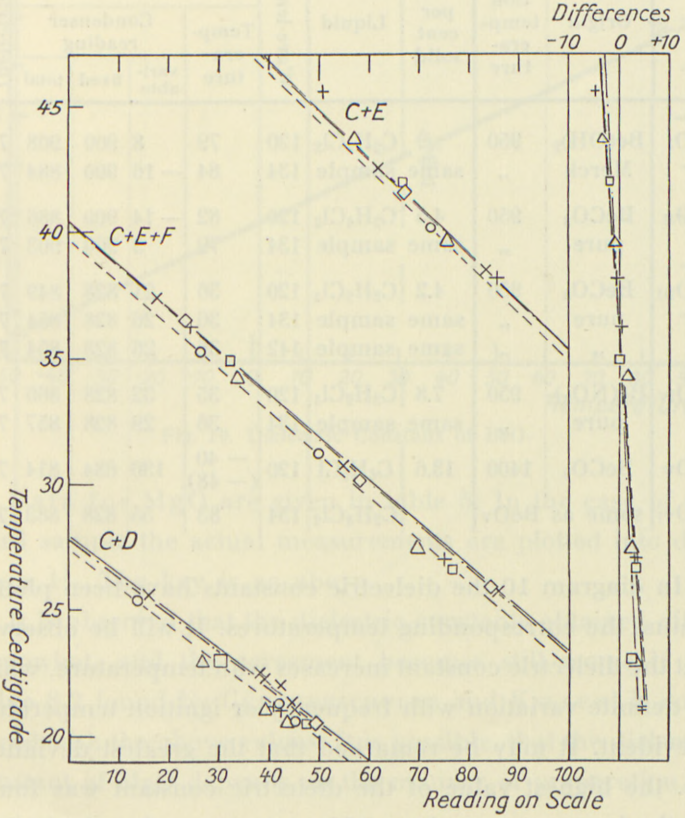

Fig. 9. BeO_{III} in $C_2H_2Cl_4$.

similar, and therefore they have been left out in order to save space, and only the intersection temperatures and the corresponding condenser readings are given in table 4. The sample considered in the diagram is the third one in the table. The key is largely as given earlier; 'pure' means purified as described on page 30; the ignition temperature is given in degrees Centigrade, and the duration of the ignition was some hours.

Table 4.

	Origin	Ignition temperature	Vol. per cent solid	Liquid	Wave-length	Intersection				Dielectric constant
						Temperature	Condenser reading			
							variable	fixed	total	
BeO_{I}	$Be(OH)_2$	950		$C_2H_4Cl_2$	120	79	8	900	908	7.89
„	Merck	„	same sample		134	84	— 16	900	884	7.68
BeO_{II}	$BeCO_3$	950	4.5	$C_2H_4Cl_2$	120	82	— 14	900	886	7.70
„	pure	„	same sample		134	79	3	900	903	7.84
BeO_{III}	$BeCO_3$	950	4.2	$C_2H_2Cl_4$	120	36	21	828	849	7.37
„	pure	„	same sample		134	36	26	828	854	7.41
„	„	„	same sample		142	36	26	828	854	7.41
BeO_{IV}	$Be(NO_3)_2$	950	7.8	$C_2H_2Cl_4$	120	35	32	828	860	7.46
„	pure	„	same sample		134	36	29	828	857	7.44
BeO_{V}	$BeCO_3$	1400	13.6	C_6H_5Cl	120	— 40 (— 48)	130	684	814	7.06
BeO_{VI}	same as BeO_{V}			$C_2H_4Cl_2$	134	83	55	828	883	7.67

In diagram 10 the dielectric constants have been plotted against the corresponding temperatures. It will be observed that the dielectric constant increases with temperature, whilst no definite variation with frequency or ignition temperature is evident. It may be remarked that the greatest deviation, i. e. the highest value of the dielectric constant was found for the less pure sample at 120 meters wave-length, but the corresponding value for 134 meters wave-length does not deviate, and hence we are not allowed to infer that impurities cause an increase in the dielectric constant. The value of the temperature coefficient is: $\frac{1}{\varepsilon}\frac{d\varepsilon}{dT} = 7 \times 10^{-4}$, as determined from the slope of the line drawn in the diagram, Fig. 10.

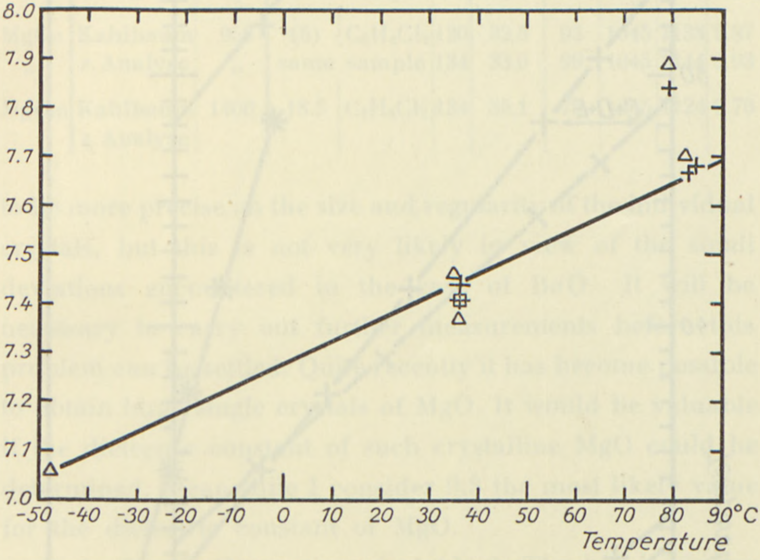

Fig. 10. Dielectric Constant of BeO.

Data for MgO are given in table 5. In the case of the third sample the actual measurements are plotted into diagram 11. The key is as above.

It is observed that the dielectric constants obtained differ somewhat, and the agreement becomes still worse if the value 8.2 found by Günterschulze and Keller[1] is compared with the above values. It is possible, that the dielectric constant of MgO depends on the manner of preparation, or

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[1] Günterschulze A. and Keller F.: ZS. f. Physik. **75**, 82 (1932).

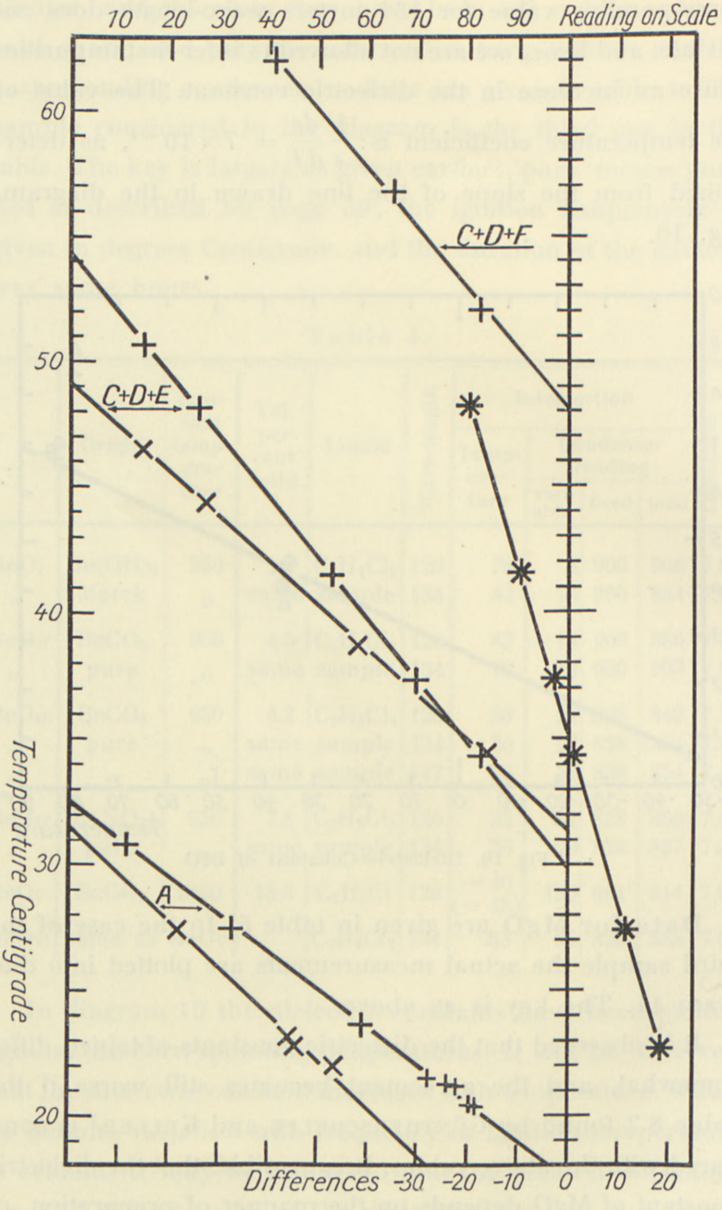

Fig. 11. MgO in $C_2H_4Cl_2$.

Table 5.

	Origin	Ignition temperature	Vol. per cent solid	Liquid	Wave-length	Intersection				Dielectric constant
						Temperature	Condenser reading			
							variable	fixed	total	
MgO_{I}	$Mg(NO_3)_2$	960	6.8	$C_2H_4Cl_2$	120	43.3	30	1045	1075	9.33
„	„	„	same	sample	134	45.8	21	1045	1066	9.25
MgO_{II}	Kahlbaum	950	(6)	$C_2H_4Cl_2$	120	32.5	93	1045	1138	9.87
„	z. Analyse	„	same	sample	134	33.0	99	1045	1144	9.93
MgO_{III}	Kahlbaum z. Analyse	1400	18.5	$C_2H_4Cl_2$	134	35.1	79	1045	1124	9.76

to be more precise on the size and regularity of the individual crystals, but this is not very likely in view of the small deviations encountered in the case of BeO. It will be necessary to carry out further measurements before this problem can be settled. Quite recently it has become possible to obtain large single crystals of MgO. It would be valuable if the dielectric constant of such crystalline MgO could be determined. Meanwhile I consider 9.8 the most likely value for the dielectric constant of MgO.

Data for CaO are given in table 6. The key is similar to that used in the foregoing cases, but now the immersion liquid is a mixture, and hence the table has been extended by the introduction of separate columns for the two liquids, and a column recording the percentage by weight of liquid II in the liquid mixture. Diagram 12 records two sets of measurements, made on two samples of the same mixture. The data of the first sample are denoted in the usual manner, whilst the data of the second sample are surrounded by circles, and lines are dotted. As it is not known in what proportion the powder distributes itself in the two samples,

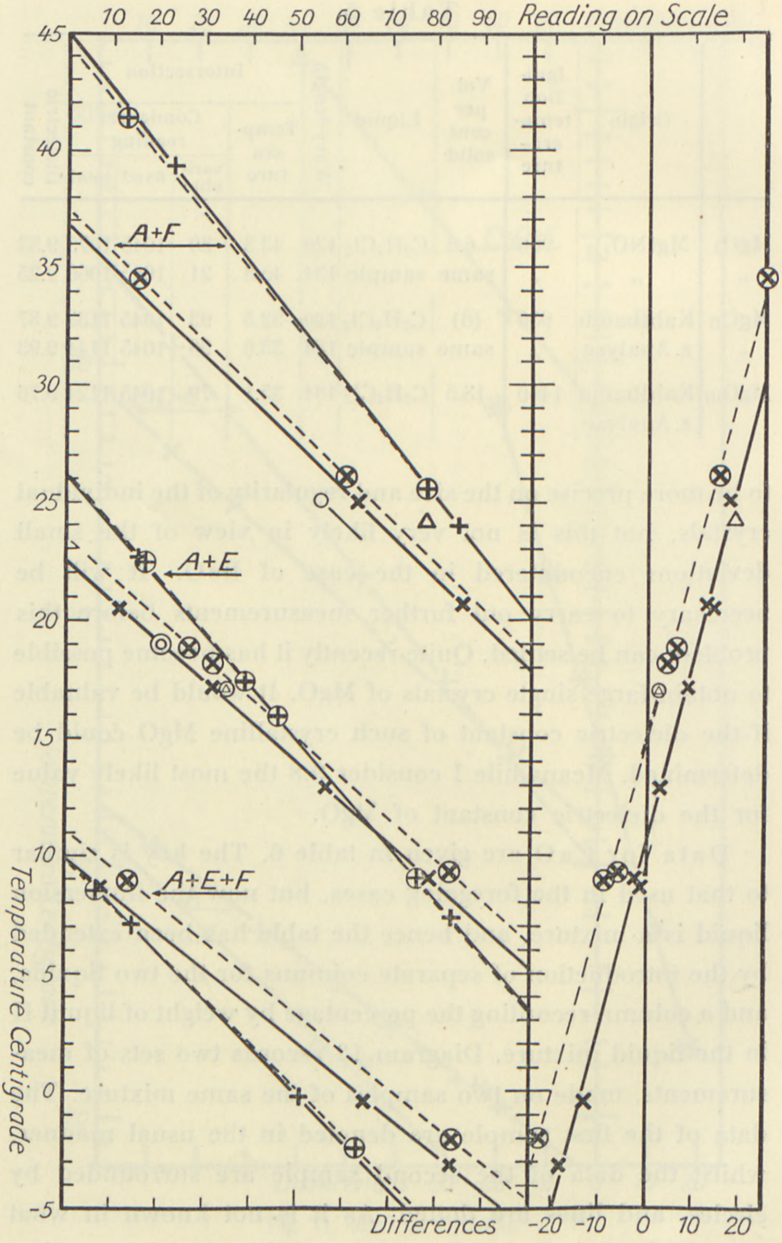

Fig. 12. CaO in Mixture of 45.0 % $C_6H_5NO_2$ and C_6H_6.

the percentage by volume of solid in the mixture have been left out. They are presumably about 27 per cent. in both cases.

Table 6.

	Origin	Ignition temperature	Vol. per cent solid	Liquid I	Liquid II	Per cent by weight of II
CaO_I	$CaCO_3$	1300	30	C_6H_6	$C_6H_5NO_2$	40.2
CaO_{II}	$CaCO_3$	1300		C_6H_6	C_2H_5OH	
CaO_{III}	$CaCO_3$	1300		C_6H_6	$C_6H_5NO_2$	45.0
CaO_{IV}	$CaCO_3$	1300	same mixture as CaO_{III}			

	Wave-length	Intersection: Temperature: read	Intersection: Temperature: correct	Intersection: Condenser reading: variable	Intersection: Condenser reading: fixed	Intersection: Condenser reading: total	Dielectric constant
CaO_I	134	−18	−22	175	1212	1387	12.04
CaO_{II}	134	13	13	3	1429	1432	12.44
CaO_{III}	120	9.8	9.8	74	1285	1359	11.80
”	134	10.7	10.7	68	1285	1353	11.74
CaO_{IV}	120	15.0	15.0	49	1285	1334	11.58
”	134	15.0	15.0	49	1285	1334	11.58

The data for the second sample are considered less safe because of a mishap; on closing the dielectric cell a bit of the agate disk was broken off. The mixture was then poured back into the flask and stored in a dessicator, whilst the agate disk was mended by means of dental cement. The effective capacity of the mended cell was checked as mentioned on page 20, whereupon the mixture was introduced anew, and measurements carried out. Owing to this mishap the percentages have not been quoted. Leaving this second sample out of consideration, the mean value 11.8 ± 0.3 is regarded as the best value of the dielectric constant at 10° C. of CaO prepared by igniting pure $CaCO_3$ at 1300° C.

The electrical conductivity of the filtrate was determined. 0.7×10^{-8} mho's was found for the first sample, and 60×10^{-8} mho's was found for the second sample. The considerably larger conductivity in the latter case was due to the presence of alcohol. According to the calculations in the appended paper, the conductivity causes an error which can be shown to be negligible, even in the case of the second sample. The residue of CaO obtained by the filtration was analysed for carbonate — due to air, and for nitrate — formed by decomposition of nitrobenzene. The residue was placed in the distilling flask of the apparatus (Fig. 7), and heated in vacuo to dryness, whereupon the dry residue was weighed in the flask. Afterwards an absorption system was connected to the outlet, the Hempel column was removed, and the apparatus was reconnected in such a way that the leg of the tap-funnel came close to the bottom of the flask. A sufficient amount of dilute hydrochloric acid was introduced, and a stream of CO_2-free air was injected through the tap-funnel. This air bubbled through the boiling solution in the flask, and drove the carbon dioxide into the absorption system; the absorbed carbon dioxide was then weighed. The contents of CO_2 in the different samples were as follows: in CaO_I 1.5 per mille, in CaO_{II} 1.5 per mille, in CaO_{III} 1.1 per mille. The solution in the flask was tested for nitrate or nitrite by means of concentrated sulphuric acid and ferrous sulphate, but no reaction was detected.

Data for SrO are given in table 7. The key is the same as for CaO.

Table 7.

	Origin	Ignition temperature	Vol. per cent solid	Liquid I	Liquid II	Per cent by weight of II
SrO_{I}	"Kahlbaum"		11.5	C_6H_6	$C_6H_5NO_2$	40.3
SrO_{II}	"Kahlbaum"		15.4	C_6H_6	$C_6H_5NO_2$	47.4
SrO_{III}	$Sr(NO_3)_2$	1350	13.4	C_6H_6	$C_6H_5NO_2$	49.7
SrO_{IV}	$Sr(OH)_2$	1350	21.5	C_6H_6	$C_6H_5NO_2$	44.8

	Wavelength	Intersection					Dielectric constant
		Temperature		Condenser reading			
		read	correct	variable	fixed	total	
SrO_{I}	134	— 18.5	— 23	179	1212	1391	12.08
SrO_{II}	134	25	25	39	1356	1395	12.12
SrO_{III}	134	10	10	118	1429	1547	13.43
SrO_{IV}	134	— 7	— 10	86	1429	1515	13.16

The readings are in the cases of SrO_{III} and SrO_{IV} given in the diagrams 13 and 14. The above samples of $Sr(NO_3)_2$ and $Sr(OH)_2$ were purified following Sørensen's method (see page 31). It will be seen that the values found for the dielectric constant are considerably higher in the case of the purified SrO than in the case of SrO "Kahlbaum". This discrepancy is explicable when it is borne in mind that, according to the analysis described on page 31, SrO "Kahlbaum" contains a large percentage of impurities, whereas, according to the analysis described on page 32, the purified

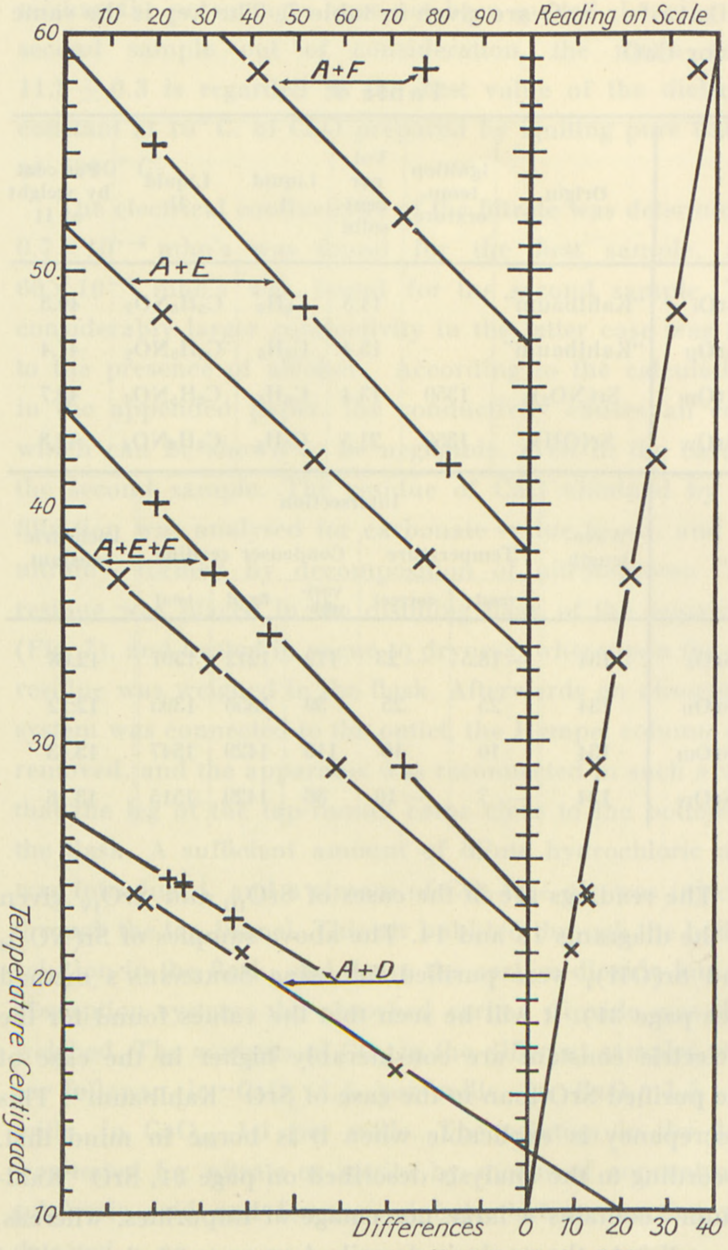

Fig. 13. SrO in Mixture of 49.7 % $C_6H_5NO_2$ in C_6H_6.

SrO contains only 3 per mille Ca and 1 per mille Pt. These data refer to the fresh SrO; after the measurements, however, the residual SrO was analysed for CO_3^{--} and NO_3^- in the same manner as described in the case of CaO; 1 per

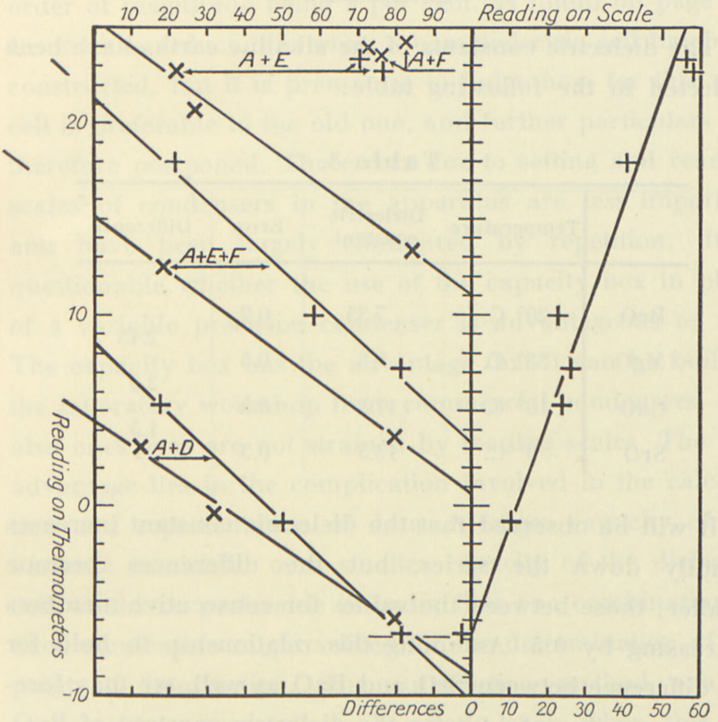

Fig. 14. SrO in Mixture of 44.8 % $C_6H_5NO_2$ in C_6H_6.

mille CO_2 and a faint trace of nitrate were found. The conductivity of the filtrate from SrO_{IV} was 1×10^{-8} mho's. It is evident that the purified strontium oxide is considerably purer than the "Kahlbaum" product, and hence the mean value of the two determinations on the purified compound, i. e. 13.3 ± 0.3 at 0° C. is regarded the most likely dielectric constant of strontium oxide.

A few, mainly preliminary, measurements have been omitted, either because of too far an extrapolation, or because of discrepancies which presumably were caused by air bubbles.

Conclusion.

The dielectric constants of the alkaline earths have been collected in the following table:

Table 8.

	Temperature	Dielectric constant	Error	Difference
BeO	20° C.	7.35	0.2	2.45
MgO	35° C.	9.8	0.5	2.0
CaO	10° C.	11.8	0.3	1.5
SrO	0° C.	13.3	0.3	

It will be observed that the dielectric constant increases steadily down the series, but the differences become smaller; those between the values for consecutive members decreasing by 0.5. Assuming this relationship to hold for the difference between SrO and BaO as well, we may foreshadow a value of 14.3 for the dielectric constant of BaO.

As regards the experimental procedure, the present immersion method, which depends on the variation with temperature of the dielectric constant of a polar liquid, has proved efficient. It is presumably the method to be used in the case of a powder consisting of porous particles. If single crystals of a reasonable size could be obtained, the plate method would be more accurate; and this method, using a compressed slug, may also be advantageous in the case of an extremely reactive compound such as barium oxide, for which it is difficult to find a sufficiently resistant immersion liquid.

Inability to reproduce the dimensions of the dielectric cell is probably the more important source of error; the order of magnitude being 2 per cent. as found on page 20. In order to reduce this error, a new dielectric cell has been constructed, but it is premature to judge how far this new cell is preferable to the old one, and further particulars are therefore postponed. The errors due to setting and reading scales of condensers in the apparatus are less important and have been largely eliminated by repetition. It is questionable whether the use of the capacity box in place of a variable precision condenser is advantageous or not. The capacity box has the advantage that it can be built in the laboratory workshop from commercial condensers, and also ones eyes are not strained by reading scales. The disadvantage lies in the complication involved in the calculation and representation of data. A larger capacity of the variable condenser or a smaller capacity of the dielectric cell would be preferable in order that one combination of fixed condensers might suffice for the determination of the point of intersection. The substitution method enables accurate measurements to be made even when the frequencies of the generators are drifting. At present methods for maintaining the frequency are known; still, the use of the substitution method enabled us to build an accurate apparatus at comparatively small expense.

Appendix.

Estimation of the Error caused by the Electrical Conductivity of the Contents of the Dielectric Cell.

In the case of a circuit as complicated as that of generator II in Fig. 1, it is not feasible to calculate exactly the effect on the dielectric constant determination arising from the electrical conductivity of the medium. In the present instance, however, we only want to know, whether such an effect may be neglected or not, and for that purpose we can simplify the problem considerably. We will therefore consider the simple circuit formed from a coil with the inductance L in series with a leaky condenser with capacity C and resistance R. In this circuit a sinusoidal potential is induced, and we are going to determine the conditions for resonance.

Similar problems have, of course, been treated in the literature previously, and the present calculation is based on that given by Jaeger in the Handbuch der Physik[1].

The induced potential V gives rise to a current i which results in a potential v across the leaky condenser and a potential v_1 across the inductance. The leaky condenser is considered to be composed of a capacity C and a resistance R in parallel, consequently the current can be written as the sum of two parts; one, a conduction current through the resistance and the other a displacement current through the condenser:

$$i = \frac{v}{R} + C\frac{dv}{dt}; \tag{1}$$

The induced potential V is counterbalanced by the potentials

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[1] Handbuch der Physik. **16**, chapter 7 by Jaeger W. pp. 201—224. (1927).

v and v_1, the latter being given by the usual expression. Hence:

$$V = L\frac{di}{dt} + v; \qquad (2)$$

or eliminating i:

$$V = LC\frac{d_2 v}{dt^2} + \frac{L}{R}\frac{dv}{dt} + v; \qquad (3)$$

This equation will be simplified in the manner proposed by JAEGER using a new unit of time defined by:

$$\tau = \omega_0 t \text{ where } \omega_0 = \sqrt{\frac{1}{LC}}; \qquad (4)$$

The modified equation then becomes:

$$V = \frac{d_2 v}{d\tau^2} + \frac{1}{R}\sqrt{\frac{L}{C}}\frac{dv}{d\tau} + v; \qquad (5)$$

$$\text{Putting } \frac{1}{2R}\sqrt{\frac{L}{C}} = \alpha;\ v = x; \text{ and } V = \varphi(\tau); \qquad (6)$$

the standard form of JAEGER's equation (10) is obtained, i. e.

$$(10) \qquad \frac{d_2 x}{d\tau^2} + 2\alpha\frac{dx}{d\tau} + x = \varphi(\tau); \qquad (7)$$

and from now on the treatment is concordant with his. JAEGER's equation numbers are given at the front of the equations.

The sinosoidal potential induced in the circuit is:

$$V = \varphi(\tau) = A\sin(\varkappa\tau + \delta); \qquad (8)$$

where A is the amplitude; δ the phase; and $\varkappa = \frac{\omega}{\omega_0}$ the pulsatance (on the new unit of time). The advent of this potential gives rise initially to complicated fluctuations of current and potentials in the circuit, but these are eventually damped, and the remaining potential across the condenser becomes a sinusoidal potential which can be written:

$$(50) \qquad v = x = \frac{A}{N} \sin(\varkappa\tau + \delta + \chi); \qquad (9)$$

where N is the ratio between the amplitude values of V and v. The expressions (8) and (9) are inserted in equation (7), and at the times $\tau = -\frac{\delta}{\varkappa}$ and $\tau = -\frac{\delta + \chi}{\varkappa}$ two expressions for the difference in phase χ are derived:

$$\tan\chi = -\frac{2\,\alpha\varkappa}{1-\varkappa^2}; \text{ and } \sin\chi = -\frac{2\,\alpha\varkappa}{N}; \qquad (10)$$

On elimination of χ is obtained:

$$(51) \qquad N^2 = (1-\varkappa^2)^2 + 4\,\alpha^2\varkappa^2; \qquad (11)$$

Resonance, i. e. a maximum value of v for a given value of V, will be obtained when N and also N^2 attain minimum values with respect to $\varkappa$, α being maintained constant. From the differentiation

$$(57) \qquad \frac{d(N^2)}{d(\varkappa^2)} = O; \text{ it is found: } \varkappa_m = \sqrt{1-2\,\alpha^2}; \qquad (12)$$

In the substitution method the leaky condenser with resistance R and capacity C was replaced by a perfect condenser of immense resistance and with capacity C_1, the latter condenser being adjusted until the pulsatance $\omega_1 = \sqrt{\frac{1}{LC_1}}$ was the same as that of the damped circuit. This is determined by the above resonance value $\varkappa_m$ or, reverting to the usual unit of time, by $\varkappa_m \cdot \omega_0$. Hence:

$$\varkappa_m = \frac{\omega_1}{\omega_0}; \tag{13}$$

Considering the definition of ω_1 given above and of ω_0 given by equation (4), and introducing the value of α from equation (6):

$$\varkappa_m = \frac{\omega_1}{\omega_0} = \sqrt{\frac{C}{C_1}} = \sqrt{1 - \frac{L}{2R^2C}}; \tag{14}$$

Eliminating L by means of the relation (4): $LC = \frac{1}{\omega_0^2}$ we obtain:

$$\frac{C}{C_1} = 1 - \frac{1}{2R^2C^2\omega_0^2}; \tag{15}$$

For practical purposes this expression is modified by the introduction of the dielectric constant ε in place of the capacity C; the specific electrical conductivity l in mho's in place of the resistance R, and the wave-length λ in cm. in place of the pulsatance ω. Thus the relative error in the dielectric constant, arising from the conductivity of the cell contents is determined as:

$$\frac{\Delta\varepsilon}{\varepsilon} = \frac{1800\, l^2\lambda^2}{\varepsilon^2}; \tag{16}$$

For correction purposes this expression is only strictly applicable to the idealized circuit considered, but it will give us the order of magnitude of any such error in our experimental circuit, and we shall see that a small conductivity has negligeable effect on our results.

As an illustration, consider the case of CaO in a mixture of benzene and ethyl alcohol for which the measured conductivity was by far the greatest, i. e. $l = 6 \times 10^{-7}$ mho's; $\varepsilon = 12.2$, and $\lambda = 13400$ cm.

$$\frac{\Delta\varepsilon}{\varepsilon} = \frac{1800 \times 6^2 \times 10^{-14} \times (1.34)^2 \times 10^8}{(12.2)^2} = 8 \times 10^{-4}. \quad (17)$$

Even in this exceptional case the error is negligible, although we are close to the limit.

Substances with larger conductivities should not in my opinion be measured by the interference note method, but by a bridge method.

The conductivities of the liquids (filtrates) were determined by means of direct current from an accumulator battery which passed through resistances, a conductivity cell and a galvanometer. The method was calibrated by means of conductivity water of known conductivity.

The conductivity was only measured when it was anticipated to be great. Thus from earlier measurements I knew the conductivity of chlorobenzene saturated with alkali halide to be of the order 10^{-10} mho's, and therefore the conductivity of these solutions were not measured. Similarly it was argued that BeO and MgO are chemically so resistant that any considerable rise in conductivity of the immersion liquid was not to be anticipated.

A similar circuit having capacities in parallel was considered by SUGDEN[1] who found the following expression for the deviation of a leaky condenser:

$$C = C\,\mathrm{obs}\left(1 - \frac{1}{R^2\omega^2 C^2} \cdot \frac{C}{C_0}\right); \quad (18)$$

The capacity of the dielectric cell C is smaller than the measured value C obs by a magnitude similar to that found above.

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[1] SUGDEN S.: Journ. Chem. Soc. (1933) p. 774.

II.

ON THE RELATIONSHIP BETWEEN DIELECTRIC CONSTANT, REFRACTIVE INDEX, ABSORPTION AND REFLECTION MAXIMA AND MINIMA IN THE FAR INFRA-RED, AND COMPRESSIBILITY OF REGULAR IONIC CRYSTALS

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a	amplitude	80	A	area	73
b	constant	96	B	constant ratio	101
c	velocity of light	83	C	numerical constant	112
d	distance in free space	114	D	proportionality factor	101
e	electronic charge	66			
f	elastic force	109	F	Faraday charge	83
g	lattice dimension	106	G	Cation	66
h	height	74	H	Anion	66
j	Madelung's constant	99	I	strength of the inner field of force	66, 76
k	number of neighbours	99	K	proportionality factor	81, 110
k_1	number of next neighbours	99			
l	change in ionic distance	97	L	distance between (neighbour) ions	97, 115
m	mass of one molecule (ion)	80	M	molecular weight	73, 91
n	refractive index	77, 91	N	Avogadro's number	73
o	constant ratio	98			
p	polarization	113	P	molar polarization	127
p_A	atomic polarization	113			
p_E	electronic polarization or refraction	113	P_E	molar refraction	127
			P_E^+, P_E^-	molar refraction of ions	122
p	pressure	102	Q	density of charge	74
r	radius	74	R	reflection ratio	86
r	distance	96			
r	ionic radius	114, 122			
s	displacement	66, 103			
t	time	80			
u	number of cations in molecule	66	U	electric moment of 1 cc.	73
v	number of anions in molecule	66	V	volume	101
x y z	components of displacement	104, 107	X Y Z	coordinates	104, 107

		page
α	polarizability	66
α_A	atomic polarizability	67
α_{A_0}	atomic polarizability (long waves)	82
α_E	electronic polarizablt.	66
α_E^+ α_E^-	,, ,, of ions	66
β	Heckmann's parameter	76, 120
γ	number of outer electrons	126
δ	density	73, 91
ε	dielectric constant	75, 91
Φ	total potential energy	100
φ	potential energy of repulsive forces	97
$\varphi, \varphi' \varphi''$	coefficients in the Taylor series of the potential energy of repulsive forces between neighbours	97
$\psi \psi' \psi''$	coefficients between next neighbours	98
$\varphi_{(B)}$	(Born)potential energy	97
$\varkappa$	compressibility	102, 116
λ	wave-length	83
μ	electric moment induced in a molecule	66
ν	valency of an ion	66
ω	frequency or pulsatance	80
ϱ	constant distance	97
θ	angle	73

Introduction.

Two classes of insulators have structures sufficiently simple to be amenable to theoretical treatment. The dilute gas, and to a certain extent the dilute solution (in non-polar solvents) fall in the first class. The dielectric constant and related properties of gases and dilute solutions were considered by DEBYE[1] in his theory of dipole moments. Ionic crystals form the second class; a theory of ionic crystals was worked out by BORN and co-workers in a number of papers. A survey is given in the Handbuch der Physik[2]. In these papers a number of relations between measurable properties were derived; at present a relation between the dielectric constant, the refractive index and the wave-length of the absorption or reflection maximum in the far infra-red (residual ray) interests us. Such a relation was first derived by DEHLINGER[3], and afterwards developed by BORN[4] and by HECKMANN[5]. Further contributions to the theory and to the experimental data were given by ERRERA[6] and by EUCKEN and BÜCHNER[7].

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[1] DEBYE P: Polar Molecules. Chemical Catalogue Company. New York.
„ „ Polare Molekeln. Hirzel. Leipzig. (1929))

[2] BORN M. and BOLLNOW O. F.: Hdb. d. Physik. **24**, 370 (1927).
BORN M. and GÖPPERT-MAYER M.: Hdb. d. Physik. (2 Aufl.) **24**, 11 (1933).

[3] DEHLINGER W.: Physik. ZS. **15**, 276 (1914).

[4] BORN M.: Physik. ZS. **19**, 539 (1918).

[5] HECKMANN G.: ZS. f. Kristall. **61**, 250 (1925).

[6] ERRERA J.: ZS. Elektrochemie. **36**, 818 (1930).

[7] EUCKEN A. and BÜCHNER A.: ZS. physik. Chem. B. **27**, 321 (1935).

As emphasized by **Heckmann** in particular, the above relation is subject to an inherent uncertainty originating in the 'Lorentz force'. It is the object of the present exposition to investigate from a theoretical, as well as from an experimental point of view, this uncertainty or deviation of the Lorentz force. In addition a further relation (also subject to the uncertainty of the Lorentz force) will be derived, connecting the dielectric constant, the refractive index and the compressibility[1]. A test of the theory and an evaluation of the deviations due to the Lorentz force can be made by means of this latter relation in particular, because of the large amount of experimental data available.

The theory is rendered as simply as possible; this simplicity is achieved by making at the start such assumptions as earlier investigators have been obliged to make in the course of their calculations. This also implies the advantage that the limitation of the deduction is clearly seen. The following are the necessary preliminary assumptions and restrictions.

1) *The ions must be arranged in a regular diagonal lattice. The NaCl, CsCl, ZnS and CaF_2 lattices are the only ones complying with this requirement.*
2) *The charge of an ion must be a whole multiple of the electronic charge. This means that there must be no sharing of electrons between the ions.*
3) *The lattice shall be perfect and the ions devoid of thermal motion. Actually the latter is not the case even at the absolute zero of temperature, but the amplitudes are generally small.*

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[1] An approach was made by the writer in 'Leipziger Vorträge' (1929) p. 114, or in English: 'The dipole moment and chemical structure' (1931) p. 108, both edited by P. Debye.

4) *The forces between the ions can be separated into two types. a) the electrostatic force which follows Coulomb's law, and b) a short range intrinsic repulsive force which keeps the ions apart.*
5) *This intrinsic repulsive force is assumed to be central, and this implies that the electron cloud of the ion has spherical symmetry.*
6) *Since the intrinsic repulsive forces are short range, only such forces between neighbours and eventually between next neighbours need consideration.*
7) *Dissipative forces are disregarded, i. e. the damping of the ionic motion is neglected.*
8) *Classical mechanics and not quantum mechanics are employed.*

By means of the above restrictions and assumptions an idealized state is defined for which certain relations can be derived. These relations, however, will only hold with approximation to the actual ionic crystal. The theory may be refined by omitting certain of the restrictions, but as long as the uncertainty of the Lorentz force remains, much better agreement cannot be expected.

Induced Moments and Polarizabilities.

If the ionic lattice as considered above is placed in an electric field it will suffer deformation arising from two different causes.

The first effect to be considered takes place inside each ion. The applied field causes the electrons in the ion to be displaced relative to the nucleus. By the displacement forces between electrons and nucleus come into play, which eventually will balance the external force. The displacement of charges gives rise to an electric moment, the "charge-centre" of the electrons no longer being situated at the nucleus. The displacement of the charge-centre relative to the nucleus multiplied by the total charge of the electrons is defined as the electric moment induced in the ion in question. It is an assumption verified by experiment, that for the small field strengths commonly used, the displacement, and thereby the induced moment, is proportional to I the strength of the electric field of force. Hence we will write:

$$\overset{+}{\mu}_E = I\overset{+}{\alpha}_E \text{ and } \overset{-}{\mu}_E = I\overset{-}{\alpha}_E; \tag{1}$$

for the moments induced in cation and anion respectively, $\overset{+}{\alpha}_E$ and $\overset{-}{\alpha}_E$ are the constant "internal or electronic polarizabilities" of the ions. The total electronic moment of the molecule $G_u H_v$ is the sum:

$$\mu_E = I\alpha_E = I(u\overset{+}{\alpha}_E + v\overset{-}{\alpha}_E); \tag{2}$$

The second effect consists of a deformation of the lattice itself. The ion considered as an entirety is a charged body. Owing to the action of the electric field, positive ions retire from negative ions on one side, whilst approaching them on the other side and vice versa. Due to the change in distance forces of the types considered in assumption 4) come into play. These forces will eventually balance the external force.

The electric moment arising when the ion of charge + ve is displaced the distance s is:

$$\overset{+}{\mu}_A = ves; \tag{3}$$

Again the displacement and the induced moment is assumed to be proportional to the force. This is so much more likely because the same forces come into action when the body is externally deformed, and then the deformation is known to be proportional to the force applied. The reason for the proportionality is considered on pages 106 and 109, it is found to be valid for small displacements only. Hence for ordinary small displacements we have:

$$\overset{+}{\mu}_A = I\,\overset{+}{\alpha}_A; \tag{4}$$

where $\overset{+}{\alpha}_A$ is the constant "atomic polarizability"[1]. The moment induced in the molecule $G_u\,H_v$ is the sum of those of the constituent ions. Hence:

$$\mu_A = I\,\alpha_A = I(u\overset{+}{\alpha}_A + v\overset{-}{\alpha}_A); \tag{5}$$

By superposition of the two types of moment the total moment induced in a molecule is obtained:

$$\mu = \mu_E + \mu_A = I(\alpha_E + \alpha_A); \tag{6}$$

This is only allowable if these moments are independent of each other, which is only true to a certain degree. The considerations on pages 124—28 have some bearing on this question.

By the ionic shift considered above it is mainly the distances between unlike ions that are altered. In some cases, however, the distances between like ions are changed as well. This means that the dimensions of the crystal are altered by the field, or from the converse point of view, that the crystal is piezoelectric. Piezoelectricity in itself is an important property, the theory of which has been elucidated by Born and Heckmann. To the present exposition it means

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[1] This mode of designation was proposed by L. Ebert: ZS. physik. Chem. **113**, 1 (1924).

a complication, which, however, can be eliminated by a simple experimental artifice.

If the electric field applied is alternating, the values of the polarizabilities α_E and α_A will vary with the frequency or wave-length of the electric field. The variation is due to the inertia of the electrons, the ions or the entire crystal. The inertia of the vibrating parts depends mainly on their masses which are very different in magnitude, thus the mass of an ion is some thousand times as large as that of the electron, and the parts vibrating in the piezoelectric crystal contain a huge number of ions. Due to these great differences in mass and inertia, the natural frequencies of the different vibrations are widely separated in the spectrum.

In the vicinity of the natural frequency, the polarizability or the dielectric constant or the refractive index (these are related as will be shown later) vary much to both sides; and at a frequency which is considerably higher than the natural frequency in question, the corresponding part of the polarizability vanishes. The shape of the dispersion curve in the vicinity of the natural frequency of the ionic vibration will be considered in details on pages 78—90.

The lowest natural frequencies are those of the vibrations arising in piezoelectric crystals. It is well known that piezoelectric quartz crystals are employed in the broadcasting stations for adjusting the frequency. The natural acoustic frequencies depend on the rigidity and the size of the crystal, they are often close to the ordinary radio frequencies of 10^6. At frequencies considerably higher than this the acoustic vibrations vanish, for instance this is the case at a frequency of 10^8. At such a frequency we are also far from the natural frequency of the vibration of positive and negative ions in the crystal. This natural frequency which manifests itself in the residual ray is of the order 10^{13}. The dispersion is only great close to the natural frequencies. If therefore the dielectric constant of a piezoelectric crystal (which shall be large) is measured at a suitable frequency of the order 10^8 or wave-length of some meters, the effect of piezoelectricity will be eliminated. This means that the dimensions of the crystal and furthermore the distances between like ions are not altered during the vibration. It is this value of the dielectric constant which has to be introduced in the following formulae. It is evident that this is not necessarily the same as the static value which means that the dielectric constant of piezoelectric crystals shows dispersion at radio frequencies. This is probably one of the reasons why the dielectric constants of solids hitherto have not been determined with conformity.

At a sufficiently high frequency α_A vanishes and only α_E is left. α_E has remained nearly constant throughout the entire range of frequency encountered so far, its natural frequency being situated in the ultra-violet region. In the visible region there is a sensible dispersion known of old, but α_E determined in the near infra-red at a frequency of 10^{14} is considered a good representative of the static value.

The Lorentz Force.

We require to find the electric force I which acts on the charges inside the body. The electric force, however, is defined as the force exerted on a unit charge of electricity situated in empty space; hence to measure the electric force inside a body, we must make a small cavity surrounding the point at which the unit charge is placed. It is now observed that the force obtained depends on the shape of the cavity. For a continuum or an isotropic body it is reasonable to assume that a spherical cavity gives the correct value of the force. Seen from the centre the sphere is isotropic i. e. it has the same properties in all directions which is not the case with any other surface. Furthermore the force at the centre does not depend on the dimensions of the spherical cavity. This is most easily realized by an argument given by N. Bohr:

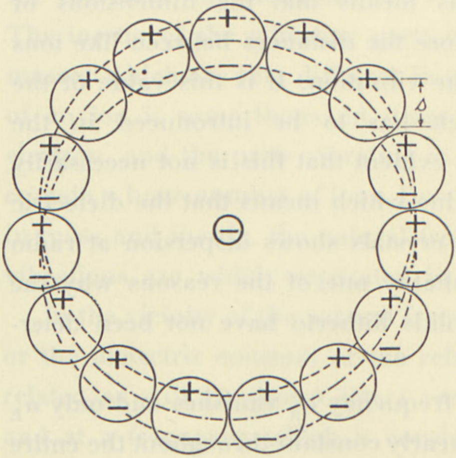

Fig. 1.

Consider a spherical shell, for instance one molecule thick, cut out of the bulk of polarized substance. (Fig. 1). In each molecule a moment is induced which can be considered as two charges at a small distance *s*. As the centres of the molecules lie on the surface of a sphere it is seen that the positive and the negative charges respectively lie on two spheres mutually displaced the distance *s*. Both of these spheres surround the measuring charge placed at the centre of the first sphere. Now in the interior of a sphere with evenly distributed charge the force is zero, hence it will be realized that this also is the case at the centre of a spherical polarized shell.

Similar considerations can also be applied to the regular crystals. If an arbitrary ion in the lattice is considered the "central ion", it is seen that the surrounding substance can be divided up into concentric shells, each shell containing a number of four or more ions all having the same distance from the central ion. The ions in such a shell have like charges, and they are regularly and to a certain extent also evenly distributed on a sphere. By the action of a homogeneous field of force the ions are displaced, furthermore dipoles are induced in them. We remark however, that the different charges still form regular polyhedra having the "central ion" pretty close to the centre. Now the electric force close to the centre of a regular configuration of charges is not quite zero, but it is negligibly small. Later, on page 109 this will be shewn to be the case for certain important regular configurations.

In this manner it is realized that we are not altering sensibly the force on the central ion, if shell by shell we remove the surrounding ions, thus forming a spherical cavity around the central ion. This is the basis of the classical theories of CLAUSIUS-MOSOTTI and LORENZ-LORENTZ as given by DEBYE[1].

HECHMANN[2], however, discards the above argument for the following reason: The ion is an extended structure, the distance between the nucleus and one of the outer electrons is comparable to the distance between the ions. The nuclei of the neighbouring ions form a regular polyhedron around the nucleus of the central ion which even if displaced remains close to the centre. Hence the argument is valid as regards the nuclei. The outer electrons in the central ion however, are often remote from the nucleus and thereby also from the centre of the polyhedron of neighbouring ions. Therefore the above argument is not valid as regards the electrons. This can also be expressed in another manner:

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[1] DEBYE P.: Polare Molekeln. p. 4.

[2] HECKMANN G.: ZS. f. Kristal. **61**, 253 (1925).

The field of force due to the neighbouring ions is inhomogeneous. We are not allowed to consider the strength of the field where the electrons move to be given by the value at the centre of the polyhedron i. e. close to the nucleus. That there is a deviation is evident, the question is, how great is it, and on what does it depend? To evaluate the deviation from theory alone is not feasible as it would require an intimate knowledge of the distribution and motion of electrons in the ions. What is attempted is an empirical investigation regarding the manner in which the deviation varies from compound to compound, especially in the system of alkali-halides. We should expect the deviation to depend on the dimensions of the ions and on their internal polarizabilities. On page 122 in table 7 we find that actually it depends mainly on the internal polarizability of the anion. As a measure of the deviation the proportionality factor β proposed by HECKMANN can be employed (see later).

ONSAGER[1] likewise discards the classical theory of CLAUSIUS-MOSOTTI, his problem however, is a different one. He computes the action of a dipole molecule on its surroundings and vice versa, and concludes that the strength of the electric field due to the surroundings must not in general be averaged into the familiar Lorentz force. In the present theory dipoles are not considered, hence the problem treated by ONSAGER does not appear.

We are now changing from an atomic to a continuous viewpoint, and will calculate how the strength of the field of force inside a spherical cavity of macroscopic dimensions depends on the induced moment.

Inside the body there are equal amounts of positive and negative electricity in any space element, hence uncom-

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[1] ONSAGER L.: J. Amer. Chem. Soc. 58, 1486 (1936).

pensated charges will appear on interfaces only. To determine the density of charge on such an interface, two cylinders are cut out of the bulk of polarized substance (see Fig. 2). They are bounded by the same cylinder surface which is a tube of force. The only difference is that in one case the flat ends are perpendicular to the lines of force forming its curved surface, and in the other cases the flat ends are inclined to them at an angle θ. Since they have the same diameter and height d, their volumes will be the same and equal to Ad where A is the area of cross section perpendicular to the lines of force. All the electric moments induced in the constituent molecules are parallel to the lines of force and consequently they are simply additive. Considering expression (6) the moment of one cubic centimeter becomes:

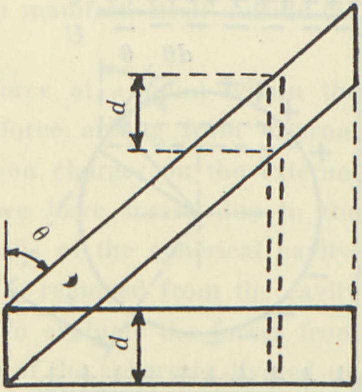

Fig. 2.

$$U = \frac{\mu N \delta}{M} = \frac{I N \delta}{M} (\alpha_E + \alpha_A); \qquad (7)$$

where δ is the density; M the molecular weight; N Avogadro's number; μ the moment induced in one molecule; I the strength of the electric force; α_E the electronic polarizability and α_A the atomic polarizability. The total moment of each cylinder becomes the same, and each is equal to UAd. The cylindrical bounding surfaces are not charged, since they are parallel to the lines of force and thereby to the induced moments. The only uncompensated charges are to be found on their end surfaces. As the distances between corresponding charges are always d, it is seen that the total charges on the end surface in both cases becomes UA. The area of the inclined end is $\frac{A}{\sin\theta}$, and the density of charge therefore becomes: $U\sin\theta$. The area of the perpendicular end is A, hence the density of charge becomes U.

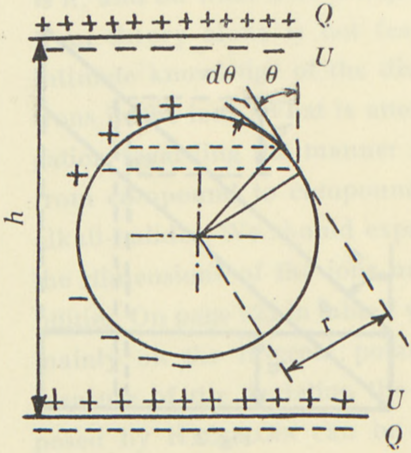

Fig. 3.

The induced moments and polarizabilities are not directly measurable. What can be measured is the dielectric constant and the refractive index. The dielectric constant is generally measured by means of a condenser which can be used as a convenient mental picture in the following deduction (see Fig. 3). The metal plates are charged with electricity of density Q. Thereby a homogeneous field of force is set up which induces the moment U in each cubic centimeter of the dielectric placed between the plates. As argued above, the interface between metal plate and dielectric is charged with electricity of density U. These charges are very close to those of the plates themselves and of opposite sign. Seen from the outside there are no charges within the bulk, and so from the outside the condenser behaves like an empty condenser charged with electricity of density $Q—U$. This also holds with regard to the potential. For the condenser the potential is proportional to this apparent charge, and the dielectric constant ε of the dielectric is the ratio between the amount of electricity required to give the condenser a certain potential, when the dielectric fills it, and the amount to give it the same potential when empty. Hence:

$$\varepsilon = \frac{Q}{Q-U}; \tag{8}$$

This is how the polarization manifests itself outside the dielectric.

To evaluate the field of force at a point within the dielectric in addition to the force arising from external charges Q and from polarization charges on the external surface of the dielectric U, we have forces due to the polarization charges on the walls of the spherical cavity. The forces due to the molecules removed from the cavity were discussed on p. 70—72. To evaluate the forces from the spherical cavity the surface of the sphere is divided up in rings, the boundaries of such a ring being given by the angles θ and $\theta + d\theta$ see Fig. 3. The area of this ring surface is:

$$2\pi r \cos\theta r d\theta;$$

As considered earlier the density of charge on an inclined surface is $U \sin\theta$. Each element of the ring reacts upon the measuring unit at the centre with a Coulomb force, and the components of this force in the direction of the external field, when added together give the force arising from the ring, i. e.

$$\frac{2\pi r^2 \cos\theta\, d\theta\, U \sin\theta \sin\theta}{r^2} = 2\pi U \sin^2\theta \cos\theta\, d\theta;$$

The total force due to the charges on the sphere is found by integration over the total surface of the sphere.

$$2\pi U\int_{-\frac{\pi}{2}}^{+\frac{\pi}{2}}\sin^2\theta\, d(\sin\theta) = 2\pi U\left|\frac{\sin^3\theta}{3}\right|_{-\frac{\pi}{2}}^{+\frac{\pi}{2}} = \frac{4\pi}{3}U; \qquad (9)$$

This is the classical Lorentz force, but according to Heckmann it is not necessarily the force acting on the electrons in an ion. The uncertainty may be expressed by multiplying the Lorentz force by a proportionality factor β. This β is an average value regarding the different electrons and nuclei. It is doubtful whether β is independent of frequency, any change will probably affect α_E and α_A to different degrees. The assumption that β is independent of frequency is presumably equivalent to Heckmann's[1] assumption that $\beta_1 = \beta_2 = \beta$, at all events it leads to the same result. Adding to this modified Lorentz force, the forces arising from the true charge density Q on the plates and the polarization charge density U on the dielectric interface, we get for the total strength of the inner field of force:

$$I = 4\pi(Q-U) + \frac{4\pi U\beta}{3}; \qquad (10)$$

Using (8) to eliminate Q we obtain:

$$I = 4\pi U\left(\frac{\varepsilon}{\varepsilon-1} - 1 + \frac{\beta}{3}\right) = 4\pi U\frac{1+\frac{\beta}{3}(\varepsilon-1)}{\varepsilon-1}; \qquad (11)$$

This gives an expression for the ratio U/I, the same ratio can be found from equation (7):

$$\frac{U}{I} = \frac{\varepsilon-1}{4\pi\left[1+\frac{\beta}{3}(\varepsilon-1)\right]} = \frac{N\delta}{M}(\alpha_E+\alpha_A);$$

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[1] Heckmann G.: ZS. f. Kristal, **61**, 254 middle of the page (1925).

Hence:

$$\alpha_E + \alpha_A = \frac{M}{4\,\pi N \delta} \cdot \frac{\varepsilon - 1}{1 + \frac{\beta}{3}(\varepsilon - 1)}; \tag{12}$$

Two important cases are to be considered: When $\beta = 1$; the classical Clausius-Mosotti equation is obtained:

$$\alpha_E + \alpha_A = \frac{3\,M}{4\,\pi N \delta} \cdot \frac{\varepsilon - 1}{\varepsilon + 2}; \tag{13}$$

and when $\beta = 0$, i. e. no Lorentz force whatever, we get:

$$\alpha_E + \alpha_A = \frac{M}{4\,\pi N \delta}(\varepsilon - 1); \tag{14}$$

Maxwell[1], in his work on the electromagnetic theory of light, deduced the relation:

$$n^2 = \varepsilon; \tag{15}$$

between the refractive index n and the dielectric constant ε. The relation has been verified by many investigators, notably by Drude[2], [3] but n and ε must be measured at the same frequency, and the damping must be negligible.

If Maxwell's relation is introduced in equation (12) the following expression is derived:

$$\frac{M}{4\,\pi N \delta} \cdot \frac{n^2 - 1}{1 + \frac{\beta}{3}(n^2 - 1)} = \alpha_E + \alpha_A \text{ at high frequency} = \alpha_E; \tag{16}$$

If β is equal to unity the familiar Lorenz-Lorentz ex-

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[1] Maxwell J. C.: Treatice on Electricity and Magnetism. 2, 396 (1881).

[2] Drude P.: ZS. physik. Chem. 23, 267 (1897).

[3] In Fysisk Tidsskrift (1936) 86, the writer has given a simple derivation of Maxwell's relation based on Drude's first method.

pression results. The refractive index is generally measured at the frequency of visible light, and as argued on page 69. α_A vanishes at such a frequency, when only α_E remains. Now in the visible region there is sensible dispersion of n and α_E, we therefore extrapolate them to zero frequency. Plotting n against the square of frequency, we expect and find an almost straight line. Instead of extrapolating, we may use directly the value of n in the near infra-red, where it has become almost constant. Hence if (16) represents the value of α_E when n is measured at a suitable infra-red frequency, and (12) the value of $\alpha_E + \alpha_A$ when ε is measured at a frequency considerably lower than the natural frequency of the atomic vibration, the value of α_A can be obtained by subtracting (16) from (12).

$$\alpha_A = \frac{M}{4\pi N\delta}\left[\frac{\varepsilon - 1}{1 + \frac{\beta}{3}(\varepsilon - 1)} - \frac{n^2 - 1}{1 + \frac{\beta}{3}(n^2 - 1)}\right]$$

$$= \frac{M}{4\pi N\delta} \cdot \frac{\varepsilon - n^2}{\left[1 + \frac{\beta}{3}(\varepsilon - 1)\right]\left[1 + \frac{\beta}{3}(n^2 - 1)\right]}; \qquad (18)$$

From which again two important values are derived namely:

$$\text{for } \beta = 1; \qquad \alpha_A = \frac{9M}{4\pi N\delta} \cdot \frac{\varepsilon - n^2}{(\varepsilon + 2)(n^2 + 2)}; \qquad (19)$$

$$\text{and for } \beta = 0; \qquad \alpha_A = \frac{M}{4\pi N\delta}(\varepsilon - n^2); \qquad (20)$$

Dispersion in the Infra-Red Region.

As stated on page (68) the shape of the dispersion curve in the vicinity of the natural frequency of the ionic vibration will be given a special consideration. For the sake of simplicity the NaCl, CsCl and ZnS lattices only will be explicitly considered, but the CaF_2 lattice can be considered in a similar though more complicated manner.

Owing to the action of the alternating electric field, the ions are forced into vibrations; besides this 'forced' vibration we must also consider the 'free' vibration which in fact constitutes the thermal motion of the ions. There is one principal difference between this forced vibration and the thermal motion, which is not encountered in the simple case of forced and free vibration of one single particle. The thermal motion is disorderly, i. e. the single ions are vibrating independently in every direction, whereas the forced vibration is orderly, because it is regulated by the external field. The ions must move in the direction of the field and with the same frequency. The wave-length of the residual ray is of the order 10^{-3} cm., whereas the distance between neighbouring ions is of the order 10^{-8} cm., it will thus be realized that the force and thereby the displacements of the ions is uniform in large sections of the crystal. This means in fact that by the 'forced' vibration the entire lattice of positive ions vibrates with regard to the entire lattice of negative ions. The disorderly thermal motion has a much larger probability or entropy than has the the orderly forced vibration, consequently the radiant energy causing the forced vibration will steadily be transformed into heat energy. The rate at which this transformation proceeds determines the damping or absorption coefficient of the crystalline substance. In classical theory the damping is described by introducing, in the equation of motion of the ion, a dissipative force proportional to the velocity of the ion; but on the quantum theory the energy transfer must take place in quanta, and as far as I know an adequate mechanism of the damping process has not been described. It is realized, that further assumptions and unknown quantities must be introduced should the damping be considered. Therefore in accordance with Dehlinger, Born and Heckmann, we have introduced the assumption 7) to the effect that "dissipative forces are disregarded, i. e. the damping of the ionic motion is neglected" and also assumption 3) that "the ions shall be devoid of thermal motion". I am not sure to what extent this latter assumption is necessary for the present, but if it is introduced now the problem becomes very simple; we are in fact left with the forced vibration of the lattice of positive ions with regard to the lattice of negative ions. It is found convenient to consider the simple-harmonic vibration of the ions as the primary motion, and afterwards to discuss the forces acting on the ions.

Consider an ion of charge $+ ve$ and mass m_1 performing a simple-harmonic vibration of frequency ω. The displacement at time t is:

$$s_1 = a_1 \cos(\omega t); \tag{21}$$

where a_1 is the amplitude. An ion of opposite charge $- ve$ with mass m_2 will perform a similar vibration with the same frequency, the opposite phase and with the amplitude a_2. The restoring force necessary for maintaining the vibration is equal to the acceleration multiplied by the mass.

$$m_1 \frac{d^2 s_1}{dt^2} = - m_1 a_1 \omega^2 \cos(\omega t); \tag{22}$$

This force must result from the other forces acting on the ion. These may be separated into: a) the intrinsic repulsive force which according to assumption (5) is a central force depending solely on the distance between the (nuclei of the) ions. The change in this force we will for the present assume to be proportional to the relative displacement of the ions, this assumption is proved later on page (110). The proportionality factor we term K.

$$K(s_1 - s_2) = K(a_1 + a_2)\cos(\omega t); \tag{23}$$

b) the total electrostatic force due to the action of the inner field of force on the ion. As considered on page (75) this force is composed by external and internal forces. Since the restoring force and the intrinsic repulsive force both vary with $\cos(\omega t)$ the electrostatic force must also vary with $\cos(\omega t)$ i. e., it must be in phase with the motion of the ion; if damping be present this will no longer be the case.

It is to be remarked that the calculation on page (76) of the strength of the inner field of force is only valid when the damping is negligible. U being the moment of one cubic centimeter of the dielectric, is necessarily in phase with the motion of the charged particles (ions or electrons) composing the dielectric, but if damping be present it is not in phase with Q which expresses the external force.

As a consequence of what has been said, the electrostatic force on the ion can be written:

$$\nu e I \cos(\omega t); \tag{24}$$

where I stands for the amplitude value of the strength of the inner field. The factor $\cos(\omega t)$ which appears in all terms can be omitted and hence the total balance of forces becomes:

$$-m_1 a_1 \omega^2 = \nu e I - K(a_1 + a_2) \tag{25}$$

The expression for the oppositely charged ion is similar. Only $m_1 a_1$ has to be replaced by $m_2 a_2$. It is seen that the right hand side of the equation is unaltered, consequently $m_1 a_1$ must be equal to $m_2 a_2$. This means that the centre of gravity is not moved during the vibration. It follows that:

$$a_1 = \frac{m_2}{m_1 + m_2}(a_1 + a_2); \tag{26}$$

Introducing this in equation (25) and rearranging:

$$(a_1 + a_2)\left[K - \frac{m_1 m_2}{m_1 + m_2}\omega^2\right] = \nu e I; \tag{27}$$

According to equation (3) the moment μ_A, obtained by displacing the ions in a molecule, is equal to the charge νe multiplied by the relative displacement of the ions. Furthermore it follows from equation (5) that this induced moment is proportional to the strength of the inner field of force, the constant proportionality factor being α_A. Hence:

$$\frac{a_1 + a_2}{I} = \frac{\nu e(a_1 + a_2)}{\nu e I} = \frac{\mu_A}{\nu e I} = \frac{\alpha_A}{\nu e}; \tag{28}$$

Introducing this in equation (27);

$$K - \frac{m_1 m_2 \omega^2}{m_1 + m_2} = \frac{\nu^2 e^2}{\alpha_A}; \tag{29}$$

K can be evaluated by extrapolating to low frequencies. (Not always zero frequency as the complication due to acoustic vibrations may then arise.) The term containing ω^2 rapidly becomes negligible and we have:

$$K = \frac{\nu^2 e^2}{\alpha_{A_0}}; \tag{30}$$

where α_{A_0} is the constant value of the ionic polarizability holding at low frequency. This value of K is introduced:

$$\omega^2 = \frac{(m_1 + m_2)\,\nu^2 e^2}{m_1 m_2}\left[\frac{1}{\alpha_{A_0}} - \frac{1}{\alpha_A}\right]; \tag{31}$$

Here the frequency ω is expressed by the atomic polarizabilities α_{A_0} and α_A. These are not directly measurable quantities, but by means of equation (18) they can be expressed in terms of dielectric constants and refractive indices. It will be convenient first to reduce the difference:

$$\frac{1}{\alpha_{A_0}} - \frac{1}{\alpha_A} = \frac{4\,\pi N \delta}{M}\left[1 + \frac{\beta}{3}(n^2 - 1)\right]\left[\frac{1 + \frac{\beta}{3}(\varepsilon_0 - 1)}{\varepsilon_0 - n^2} - \frac{1 + \frac{\beta}{3}(\varepsilon - 1)}{\varepsilon - n^2}\right];$$

to:

$$\frac{1}{\alpha_{A_0}} - \frac{1}{\alpha_A} = \frac{4\,\pi N \delta}{M}\,\frac{\left[1 + \frac{\beta}{3}(n^2 - 1)\right]^2 \left[\varepsilon - \varepsilon_0\right]}{\left[\varepsilon_0 - n^2\right]\left[\varepsilon - n^2\right]}; \tag{32}$$

This is introduced into equation (31).

$$\omega^2 = \frac{(m_1 + m_2)\,\nu^2 e^2}{m_1 m_2} \cdot \frac{4\,\pi N \delta}{M} \cdot \frac{\left[1 + \frac{\beta}{3}(n^2 - 1)\right]^2 \left[\varepsilon - \varepsilon_0\right]}{\left[\varepsilon_0 - n^2\right]\left[\varepsilon - n^2\right]}; \tag{33}$$

Certain reductions are made. $\frac{M}{N}$ is the mass of one molecule which is also expressed by $m_1 + m_2$, these terms therefore cancel out. Furthermore $\frac{e}{m_1}$ is equal to $\frac{F}{M_1}$ where F is one Faraday, and M_1 the atomic weight (gram-atom) of the ion. It is also found expedient to replace the frequency by the wave-length $\lambda = \frac{2\,\pi c}{\omega}$ where c is the velocity of light.

As a result of these changes the following general expression is obtained:

$$\lambda^2 = \frac{\pi c^2 M_1 M_2 [\varepsilon_0 - n^2][\varepsilon - n^2]}{\nu^2 F^2 \delta \left[1 + \frac{\beta}{3}(n^2 - 1)\right]^2 [\varepsilon - \varepsilon_0]}; \tag{34}$$

It will be convenient to recall the symbols not stated above: ν is the valency: δ the density; n the constant refractive index (in the near infra-red); ε_0 the constant dielectric constant for long waves (not always infinitely long waves); ε the variable dielectric 'constant' at the wave-length λ. β is a parameter (see page 76). The above expression (34) is a very general one, dependent as it is on two independent variables namely ε and β.

Certain characteristic wave-lengths will now be deduced by ascribing characteristic values to ε and β. In the first place the wave-length corresponding to ε equals infinity and β equals zero is determined:

$$\lambda_B^2 = \frac{\pi c^2 M_1 M_2}{\nu^2 F^2 \delta} [\varepsilon_0 - n^2]; \tag{35}$$

This is the same relation as derived by Born[1]. This Born wave-length will be used for reference.

If ε is equal to infinity and β equal to unity an expression similar to that of Dehlinger[2] is obtained:

$$\lambda_D^2 = \lambda_B^2 \frac{9}{(n^2+2)^2}; \tag{36}$$

The more general case of ε equal to infinity and β arbitrary leads to the same relation as derived by Heckmann[3]:

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[1] Born M. and Bollnow O. F.: Handbuch d. Physik. **24**, 390 (1927) Eq. 43'.

[2] Dehlinger W.: Physik. ZS. **15**, 276 (1914).

[3] Heckmann G.: ZS. Kristall. **61**, 265 (1925).

$$\lambda_H^2 = \lambda_B^2 \frac{1}{\left[1+\frac{\beta}{3}(n^2-1)\right]^2}; \tag{37}$$

In the second place the wave-lengths corresponding to ε equals zero are considered. Again we have one characteristic wave-length for β equals zero;

$$\lambda_I^2 = \lambda_B^2 \frac{n^2}{\varepsilon_0}; \tag{38}$$

and another for β equals unity:

$$\lambda_E^2 = \lambda_B^2 \frac{n^2}{\varepsilon_0} \cdot \frac{9}{(n^2+2)^2}; \tag{39}$$

In the third place we will consider the wave-lengths corresponding to ε equal to unity. This means that the dielectric constant and the refractive index are equal to those of the vacuum and practically to those of air. At such a wave-length the radiation therefore passes unrefracted, and, as will be seen shortly, unreflected through the powder in air. Hence, this corresponds to the CHRISTIANSEN[1] wave-length λ_C which for a number of compounds has been measured by BOWLING BARNES and BONNER[2]. As before we have one theoretical wave-length for β equals zero:

$$\lambda_J^2 = \lambda_B^2 \frac{n^2-1}{\varepsilon_0-1}; \tag{40}$$

and another for β equals unity:

$$\lambda_K^2 = \lambda_B^2 \frac{n^2-1}{\varepsilon_0-1} \cdot \frac{9}{(n^2+2)^2}; \tag{41}$$

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[1] CHRISTIANSEN C.: Ann. d. Physik. **23**, 298 (1884).

[2] BOWLING BARNES R. and BONNER L. G.: Physical Rev. **49**, 732 (1936).

Absorption and Reflection in the Infra-Red Region.

In principle the dielectric constant is a measurable quantity, still measurements in the infra-red region are not practicable. Of related properties the coefficient of absorption and the reflection ratio are those more frequently measured.

In our assumption (7) we have neglected the damping and thereby also the absorption. The occurrence of sensible absorption shows that this assumption can only be approximately correct. In the cases of slight damping the absorption maximum is situated close to the wave-length at which ε becomes infinite, which means that λ_A has to be compared with λ_B or λ_D.

The relation between the reflection ratio R, and the dielectric constant ε or the corresponding refractive index n is, in the case of perpendicular incidense and no damping, given by FRESNEL's[1] formula:

$$R = \left[\frac{n \pm 1}{n + 1}\right]^2 = \left[\frac{\sqrt{\varepsilon} \pm 1}{\sqrt{\varepsilon} + 1}\right]^2 \tag{42}$$

Generally the negative sign has to be used, but if ε is negative and consequently n imaginary the positive sign must be employed in order that a real value of R, namely unity, may be obtained. This means that the reflection is total for all negative values of ε. Now ε has negative values within a certain region of wave-length; the wave-lengths corres-

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[1] This formula was derived by FRESNEL: Œuvres, tom **1**, pp 441. on the basis of the undulatory theory. It has since been derived on the basis of Maxwell's electromagnetic wave theory, see for instance: KÖNIG W. in Handbuch d. Physik. Bd. **20**, p 200 and 214. It is found as the solution of a second order equation, whence the sign ± appears.

ponding to values of ε of zero and minus infinity are the border values of the region inside which reflection is total.

The variation of the reflection ratio with wave-length is probably demonstrated better if a special case, for instance NaCl, is considered in a diagram. In Fig. 4 the circles and the unbroken curve represent the experimental reflection curve determined by Rubens[1]. The triangles give the reflection measured by Czerny[2] and Cartwright and Czerny[3]. The Christiansen wave-length as determined by Bowling Barnes and Bonner l. c. is also shown in the diagram. Two theoretical reflection curves are drawn. The dotted curve is obtained when β is put equal to zero and

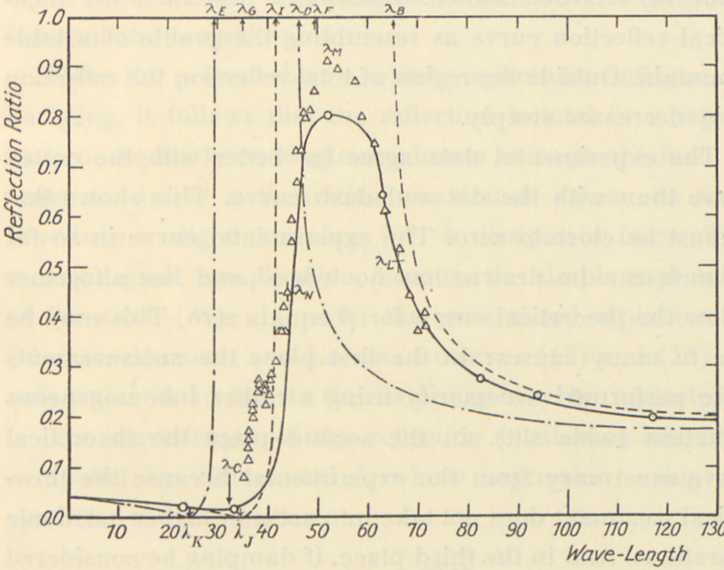

Fig. 4.

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[1] Rubens H.: Sitzber. Preuss. Akad. d. Wiss. II (1915).

[2] Czerny M.: ZS. f. Physik. **65**, 600 (1930).

[3] Cartwright C. H. and Czerny M.: ZS. f. Physik. **85**, 269 (1933). Cartwright C. H. and Czerny M.: ZS. f. Physik. **90**, 457 (1934).

the dot and dash curve is obtained when β is equal to unity. The curves are obtained using ε as a parameter. From Fresnel's relation (42) the reflection ratio R corresponding to a selected value of ε is calculated, and from equation (34) the wave-length corresponding to the same value of ε is determined. Heckmann described the theoretical reflection curve as resembling the profile of a table mountain. Outside the region of total reflection the reflection ratio decreases steeply.

The experimental data agree far better with the dotted curve than with the dot and dash curve. This shows that β must be close to zero. The experimental curve in so far as such can be drawn, has no 'edges' and lies altogether below the theoretical curve for β equals zero. This may be due to many causes: In the first place the measurements were performed necessarily using a rather inhomogeneous radiation (wide slit). In the second place the theoretical curve must vary from the experimental because the theoretical treatment does not take into account higher harmonic vibrations. And in the third place, if damping be considered the theoretical curve will be still further altered.

Reflection curves similar to the above have been determined for more compounds, but since the representation by curves takes too much space, characteristic wave-lengths are quoted in table (3). As there are no distinguishable 'edges' on the experimental curves some other characteristic points must be chosen for representation. The values taken are the wave-length λ_M corresponding to maximum of reflection and those corresponding to the half height of the reflection mountain. The latter are those at which the reflection ratio is the mean of the maximum value and the value representing the level to the same side of the mountain. It will be seen from Fig. 4 that the 'half height' wave-lengths are well defined, and furthermore that each of these is close to an 'edge' on the theoretical curve. λ_L being close to λ_B, and λ_N close to λ_I. The breadth of the experimental mountain as measured between the 'half height' wave-lengths is thus equal to the breadth of the theoretical mountain as measured between the 'edges'.

From the present theory, which neglects the influence of damping, it follows that the reflection is total in a region, and consequently no single maximum value is obtained. In order to derive a theoretical maximum value one must introduce a slight damping, i. e. a dissipative force. This means a great complication, because the simple expression of FRESNEL (42) and even the generalized equations of CLAUSIUS-MOSOTTI and LORENZ-LORENTZ (12) and (16) are only valid in so far as the damping may be neglected.

The wave-length of the reflection maximum has been computed by FÖRSTERLING[1], whose expression, using our symbols, can be written:

$$\frac{1}{\lambda_F^2} = \frac{1}{\lambda_B^2} + \frac{F^2 \delta^2}{2\, n^2 \pi c^2 M_1 M_2};$$

which can be reduced to:

$$\lambda_F^2 = \lambda_B^2 \frac{2\, n^2}{\varepsilon_0 + n^2} \tag{43}$$

This holds for $\beta = 0$; the corresponding expression for $\beta = 1$ is:

$$\lambda_G^2 = \lambda_B^2 \frac{2\, n^2}{\varepsilon_0 + n^2} \cdot \frac{9}{(n^2+2)^2}; \tag{44}$$

Values of λ_F and λ_G are quoted in table 3.

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[1] FÖRSTERLING K.: Ann. d. Physik. **61**, 577 (1920).

Havelock[1] derived an expression different from that of Försterling. According to O. Fuchs and K. L. Wolf[2] Havelock's expression is the more accurate one. The calculations of Försterling and Havelock were carried out on the classical theory of absorption; but as remarked on page (79) the very basis of this theory is invalid, and therefore neither of the two expressions are considered safe. Our only purpose in quoting Försterling wave-lengths is to obtain a comparison with Heckmann's data.

It is found that the equations (34) to (44) may also be applied to the CaF_2 lattice if ν^2 is replaced by the product $\nu_1\nu_2$ of the valencies of the ions. Hence for CaF_2 ν^2 is put equal to 2.

Experimental Test.

Experimental data used in the formulae are given in table 1 in which M_1 and M_2 are the atomic weights of the ions; ε_0 is the dielectric constant for long waves. The density δ is quoted, and the refractive index n is extrapolated to the near infra-red, using data from Landolt-Börnsteins tables[3]. In a few cases n^2 is quoted from the paper of Eucken and Büchner (cited next page) all data applies to room temperature.

In table 2 theoretical wave-lengths as given by the expressions (35) and (36) are compared to the wave-length of the absorption maximum; note that the experimental wave-length in all cases but one is situated between the two

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[1] Havelock T. H.: Proc. Roy. Soc. London. A. **105**, 488 (1924).

[2] Fuchs O. and Wolf K. L.: ZS. f. Physik. **46**, 506 (1928).

[3] Landolt-Börnstein: Tabellen. Tables 81 and 170 in the Erg. Bd. I, II and III in particular.

Table 1. Experimental Data used in the Formulae.

	M_1	M_2	ν	δ	ε_0	n	n^2
LiF	6.94	19.0	1	2.64	9.27 E. B.	1.39	1.92 E. B.
NaF	23.0	19.0	1	2.80	6.0 K.	1.32	1.74
NaCl ...	23.0	35.46	1	2.16	5.62 E. B.	1.50	2.25
NaBr ...	23.0	79.9	1	3.20	5.99 E.	1.62	2.62
NaI	23.0	126.9	1	3.67	6.60 E.	1.71	2.91
KCl	39.1	35.46	1	1.99	4.68 E. B.	1.46	2.13
KBr	39.1	79.9	1	2.74	4.78 E.	1.53	2.33
KI	39.1	126.9	1	3.12	4.94 E.	1.64	2.69
RbCl ...	85.4	35.46	1	2.76	5.0 A.	1.48	2.19
RbBr ...	85.4	79.9	1	3.36	5.0 A.	1.53	2.33
RbI	85.4	126.9	1	3.55	5.0 A.	1.62	2.63
CsCl	132.8	35.46	1	3.98	7.20 H_1	1.61	2.60
CsBr ...	132.8	79.9	1	4.45	6.51 H_1	1.67	2.78
CsI	132.8	126.9	1	4.51	5.65 H_1	1.74	3.03
NH_4Cl ..	18.04	35.46	1	1.53	6.96 J.	1.62	2.63
TlCl	204.4	35.46	1	7.02	31.9 E. B.	2.26	5.10 E. B.
TlBr	204.4	79.9	1	7.54	29.8 E. B.	2.33	5.41 E. B.
AgCl	107.9	35.46	1	5.56	12.3 E. B.	2.02	4.04 E. B.
AgBr ...	107.9	79.9	1	6.4	13.1 E. B.	2.15	4.62 E. B.
BeO	9.02	16.0	2	3.00	7.35 H_2	1.72	2.95
MgO	24.32	16.0	2	3.65	9.8 H_2	1.72	2.95
CaO	40.08	16.0	2	3.4	11.8 H_2	1.81	3.28
SrO	87.63	16.0	2	5.0	13.3 H_2	1.82	3.31
ZnS	65.38	32.06	2	4.06	8.3 L. R.	2.25	5.07
CaF_2 ...	40.08	19.0	2—1	3.18	8.43 E. K.	1.411	1.99
SrF_2 ...	87.63	19.0	2—1	4.28	7.69 E. K.	1.441	2.08
BaF_2 ...	137.36	19.0	2—1	4.89	7.33 E. K.	1.444	2.09

The dielectric constants were measured by:

E. Errera J.: ZS. Elektrochemie. **36,** 818 (1930).
E. K. Errera J. and Ketelaar H.: J. Phys. et Radium. (7) **3,** 240 (1932).
E. B. Eucken A. and Büchner A.: ZS. physik. Ch. B. **27,** 321 (1935).
H_1 Højendahl K.: ZS. physik. Ch. B. **20,** 63 (1933).
H_2 „ „ This work.
J. Jaeger R.: Ann. d. Physik. (4) **53,** 409 (1917).
L. R. Liebisch Th. and Rubens H.: Sitzber. Preuss. Akad. Wiss. XLVIII (1919).
K. Kyropoulos S.: ZS. f. Physik. **63,** 849 (1930).
A. Average of measurements by Errera, Kyropoulos and myself.

Table 2. Test on Infra-Red Transmission Data.

	Absorption maximum				Christiansen wave-length			
	theoretical		experimental		theoretical		experimental	
	λ_B	λ_D	λ_A	β_A	λ_J	λ_K	λ_C	β_C
LiF . . .	35.2	27.0	32.6 B_1	0.26	11.7	9.0	11.2 B_2	0.15
NaF . .	47.4	38.0	40.6 B_1	0.68				
NaCl .	65.6	46.3	61.1 B.C.	0.18	34.2	24.1	32.0 B_2	0.16
NaBr .	80.8	52.5	74.7 B_1	0.15	46.1	29.9	37 B_2	0.45
NaI . . .	99.3	60.7	85.5 B_1	0.25	58.0	35.4	49 B_2	0.29
KCl . . .	77.6	56.3	70.7 B.C.	0.26	43.0	31.2	37 B_2	0.43
KBr . .	97.2	67.4	88.3 B_1	0.23	57.7	40.0	52 B_2	0.25
KI	110.0	70.4	102.0 B_1	0.13	72.0	46.1	64 B_2	0.22
RbCl .	102.1	73.2	84.8 B_1	0.52	55.7	39.9	45 B_2	0.60
RbBr .	135.3	93.7	114.0 B_1	0.42	78.1	54.1	65 B_2	0.45
RbI . . .	156.0	101.1	129.5 B_1	0.38	99.4	64.4	73 B_2	0.67
CsCl . .	136	89	102.0 B_1	0.63	69.2	45.1	50 B_2	0.72
CsBr . .	173	109	134.0 B_1	0.49	98.2	61.6	60 B_2	1.07
TlCl . .					111	47	45 B_2	1.07
TlBr . .					165	67	64 B_2	1.07
BeO . .	13.2	8.0	13.5 T.	— 0.03	7.3	4.5	8 T.	— 0.13
MgO . .	24.8	15.1	14.2 T.	1.14	11.6	7.1	12.2 B_2	— 0.06
CaO . .	36.8	20.9	22.1 T.	0.87	17.0	9.6	16 T.	0.08

Transmission in infra-red was measured by:

B. C.	Bowling Barnes R. and Czerný M.: ZS. f. Physik. **72,** 447 (1931).
B_1	Bowling Barnes R.: ZS. f. Physik. **75,** 723 (1932).
B_2	Bowling Barnes R. and Bonner L. G.: Physical Rev. **49,** 732 (1936).
T.	Tolksdorf S.: ZS. f. physik. Ch. **132,** 161 (1928).

corresponding theoretical wave-lengths. MgO and BeO are exceptions, but the discrepancy is not larger than what may be due to experimental error. Hence the two theoretical values define a region within which the experimental absorption maximum is found.

The above theoretical wave-lengths λ_B and λ_D are those obtained for β equals unity and zero. It is of interest to see what value shall be ascribed to β in order that relation (37) shall hold with accuracy. For this purpose the wave-length of the absorption maximum λ_A is introduced in place of λ_H, hence:

$$1+\frac{\beta}{3}(n^2-1)=\frac{\lambda_B}{\lambda_A};$$

from which β can be determined:

$$\beta=\frac{3\left(\frac{\lambda_B}{\lambda_A}-1\right)}{n^2-1}; \qquad (45)$$

By means of this expressions the β_A values in column (5) are calculated. Considering the alkali-halides it will be realized that the variation of β_A with the inner polarizability of the anion, so marked in the case of the β determined from the relation between compressibility and dielectric constant and refractive index, is far less pronounced in the present case. (Compare p. 122).

In the second section of table 2 theoretical wave-lengths as given by the expressions (40) and (41) are compared to the experimental Christiansen wave-length measured by Bowling Barnes. This Christiansen wave-length constitutes the transmission maximum in the case of a powder, hence, such transmission maxima measured by Tolksdorf are also quoted. For MgO Bowling Barnes found the same maximum as Tolksdorf. Values of the parameter β_C are calculated by means of the above formula (45), replacing λ_B/λ_A by λ_J/λ_C. For the alkali-halides the agreement in most cases is fair; note that the absorption curves determined by Bowling Barnes and Czerny are measured on plates or films. For the oxides the agreement between the two different values of β is bad. The explanation is presumably the following. TOLKSDORF actually measured the transmission minimum, but because the radiation may be scattered owing to reflection on the surfaces of the single particles in the powder, the transmission minimum and the true absorption maximum are not identical.

The characteristic wave-lengths of each reflection curve are quoted in table 3. In the cases of NaCl, KCl, KBr, KI, ZnS and CaF_2 it will be noticed that the half height — maximum — half height' wave-lengths of the experimental reflection curve agree well with the corresponding 'edge — maximum — edge' wave-lengths of that theoretical curve which is obtained using the value β equals zero (expressions (35) (43) and (38)). This also shows that the breadth of the experimental reflection mountain is equal to the theoretical breadth, which is considered a verification of the theory. If the theory is correct the absorption maximum should be situated close to the larger of the 'half height wave-lengths'. This holds fairly well for NaCl, KCl, KBr and KI but not at all for LiF.

An empirical value of β can be evaluated from reflection data by a method similar to that applied to transmission data. Such a calculation was in fact first undertaken by HECKMANN[1], and his values of β are quoted in the last column. Our calculation is performed using equation (45). In place of the ratio λ_B/λ_A the ratio λ_F/λ_M is introduced. According to theory these ratios should be equal, granted of course that the FÖRSTERLING expression is sufficiently accurate. Values of β_R evaluated from reflection data are quoted in the column next to the last. That the experimental

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[1] HECKMANN G.: ZS. Kristall. 61, 266 (1925).

Table 3. Test on Reflection Data.

	Theoretical						Experimental Reflection				Heckmann
	$\beta = 0$			$\beta = 1$							
	Edge (35)	Max (43)	Edge (38)	Edge (36)	Max (44)	Edge (39)	half height	Max	half height		
	λ_B	λ_F	λ_I	λ_D	λ_G	λ_E	λ_L	λ_M	λ_N	β_R	β_H
LiF	35.2	20.6	16.1	27.0	15.8	12.3	20.0	17.1	14.6 Re.	0.67	
NaF	47.4	31.9		38.0	25.5			35.8	Re. B.	− 0.40	
NaCl ...	65.6	49.6	41.5	46.3	35.0	29.3	66.5	51.7	43.5 C.	− 0.10	− 0.15
KCl	77.6	62.0	52.4	56.3	44.5	38.0	78	62	53 C.	0.00	− 0.16
KBr	97.2	78.6	68.0	67.4	55.0	47.2	95	83	68 R.	− 0.12	− 0.28
KI	110.0	92.0	81.2	70.4	59.1	52.0	104	94	85 R.	− 0.03	+ 0.09
RbCl ...	102	80	68	73	57	48		74	Re.	0.19	
NH_4Cl ..	78	58	48	51	37	32	64	52	45 R.	0.21	
TlCl	306	160	122	129	68	52	150	100	65 R.	0.44	0.69
TlBr	422	234	180	171	95	73	200	117	95 R.	0.68	0.75
AgCl	139	98	80	69	49	40	120	90	58 R.	0.09	0.14
AgBr ...	197	142	117	89	65	53	200	110	83 R.	0.24	0.17
ZnS	37.7	32.8	29.4	16.0	13.9	12.5	40.5	31.8	27.5 L.R.	0.02	0.13
CaF_2	51.0	31.5	24.8	38.4	23.7	18.4	40	32.8	21 K.S.	− 0.11	
SrF_2	61.5	39.7	31.6	45.2	29.2	23.2		40.7	Re. B.	− 0.07	
BaF_2	68.7	45.8	36.7	50.4	33.6	26.9		50.7	Re. B.	− 0.27	

Reflection data were measured by:

C. Czerny M.: ZS. f. Physik. **65**, 600 (1930).

K. S. Kellner L.: ZS. f. Physik. **56**, 231 (1929).

R. Rubens H.: Sitzber. Preuss. Akad. Wiss. II (1915).

L. R. Liebisch T. and Rubens H.: Sitzber. Preuss. Akad. Wiss. XLVIII (1919).

Re. Reinkober O.: ZS. f. Physik. **39**, 439 (1926).

Re. B. Reinkober O. and Bluth M.: Ann. d. Physik. (5) **6**, 785 (1930).

error is considerable is appreciated if the β values from reflection data are compared with those found from transmission data. Especially in the cases of LiF and NaF the error must be large. In the case of other alkali-halides, besides a large experimental error there can also be distinguished a systematic deviation, in that the β values found from transmission are as a rule larger than those found from reflection. This systematic deviation is an indication of the limitation of the theory.

Although data, more extensive and in some respects more accurate than those employed by Heckmann have here been considered, we are not able to derive further conclusions than he did. This, however, will be possible by means of our second relation, namely that between dielectric constant, refractive index and compressibility. Further discussion will therefore be postponed till this relation has been derived and tested.

The Interionic Forces.

The forces between the ions have hitherto been treated in a very general manner, the only assumption being, that for small displacements the force arising shall be proportional to the relative displacements of the ions (strictly the nuclei). In order to carry out a theoretical calculation of the compressibility, the mathematical form of the potential between two ions must be considered more specifically. The calculation is based upon assumptions 4, 5, and 6 on page 65. According to assumption 4) the forces between the ions can be separated into two types: a) the electrostatic force which follows Coulomb's law, and b) a short range intrinsic repulsive force which keeps the ions apart. The nature of and mathematical form of the latter is not quite settled.

Born and Lande[1], who first encountered the problem, considered the potential of intrinsic repulsive force between two ions to be given by the expression $b \times r^{-n}$, where r is

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[1] Born M. and Lande A.: Verh. D. physik. Ges. **20**, 210 (1918).

the distance between the ions and b and n are constants for the same combination of ions. According to modern theory the intrinsic force arises from a certain quantum-mechanical interaction (antisymmetric coupling) of the electrons in the two ions[1,2], and as a consequence an exponential relation is to be expected. BORN and MAYER[3] write this:

$$\varphi_{(B)} = b e^{\frac{r_1 + r_2 - r}{\varrho}}$$

where r_1 and r_2 are the ionic radii; r the distance; ϱ equals 0.345×10^{-8} cm. the same constant for all alkali-halides, and b a constant for the same salt. According to PAULING[4] b has to be replaced by a polynomial. In recent papers which have been obtained since the major part of the present paper was written, WASASTJERNA[5,6,7] makes efforts to evaluate this polynomial from experimental data. He finds that the dominant terms are those containing r to the sixth or eigth power.

All investigators agree in considering the intrinsic repulsive force as a short range central force. In the present exposition it is attempted to make this the only assumption regarding this force, therefore the potential of the intrinsic repulsive force between two ions is considered to be given by the TAYLOR series:

$$\varphi_{(L \pm l)} = \varphi_L \pm \varphi' l + \frac{\varphi''}{2} l^2 \pm \dots \qquad (46)$$

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[1] HEITLER W. and LONDON F.: ZS. f. Physik. **44**, 455 (1927).

[2] LONDON F.: Naturwissenschaften. **17**, 516 (1929).

[3] BORN M. and MAYER J. E.: ZS. f. Physik. **75**, 1 (1932).

[4] PAULING L.: ZS. f. Krist. **67**, 377 (1928).

[5] WASASTJERNA J. A.: S. Sc. Fennica. C. Phys. Mat. VI. **22** (1932).

[6] WASASTJERNA J. A.: S. Sc. Fennica. C. Phys. Mat. VIII. **20** (1935).

[7] WASASTJERNA J. A.: S. Sc. Fennica. C. Phys. Mat. VIII. **21** (1935).

where L is the mutual distance, l the change in it, and φ_L, φ' and φ'' are constants. The Taylor series is practicable because l as a rule is very small compared to L, whence only the first few (three) members of the series need consideration.

If now the ionic lattice be deformed, the forces mentioned come into play. There are two types of deformation of special interest, which will be discussed in the following. The first type of deformation is the homogeneous contraction resulting from a compression of the crystal. The second type of deformation is the relative displacement of the lattices of oppositely charged ions contemplated on page 66.

The Compressibility of Regular Crystals.

According to restriction 6) on page 65 not only the forces between neighbours, but also the forces between next neighbours are to be considered. The above Taylor series (46) with the constants φ_L, φ' and φ'' is considered to represent the potential between neighbour ions. The potential of intrinsic repulsive forces between next neighbours is considered to be given by another Taylor series:

$$\psi_{(L_1 \pm l_1)} = \psi_{L_1} \pm \psi' o l + \frac{\psi''}{2} o^2 l^2 \pm \dots \qquad (47)$$

where ψ_{L_1}, ψ' and ψ'' are new constants. The normal distance L_1 between next neighbours is different from L, it is actually equal to oL where o is a constant factor. Hence the change in distance is equal to ol. There are two different combinations of next neighbours present namely $(+\,+)$ and $(-\,-)$, but as a rule the intrinsic repulsive force between cations is negligible and only that between anions needs consideration.

The total potential energy due to intrinsic repulsive forces between one ion and its neighbours is obtained by multiplying expression (46) by the coordination number k, i. e. the number of neighbours of any one ion. Similarly the potential energy between one ion and its next neighbours is obtained by multiplying expression (47) by k_1 which is the number of next neighbours of an ion.

Besides the intrinsic repulsive forces considered, electrostatic forces between ions are also present. The electrostatic potential energy of two ions of charges νe and $\nu_1 e$ at a distance L is:

$$\varphi_E = \frac{\nu \nu_1 e^2}{L};$$

The electrostatic potential energy of one ion with respect to all other ions in the lattice is obtained by multiplying the above expression by a constant j which is:

$$j = \sum \frac{L_0}{L_1}; \tag{48}$$

where L_1 is the distance between the ion considered and any other ion, and L_0 that between neighbour ions. The summation shall be extended over all ions, counting each ion once and considering the sign of the ion.[1]

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[1] MADELUNG E.: Physik. ZS. **19**, 524 (1918), applied a mathematical artifice in order to determine the constant j, because a direct summation was not found feasible. — The writer should like to point out that a direct summation still may be practicable if only it proceeds on a definite plan: Consider for instance a crystal growing by the successive addition of neutral ionic layers. If now the potential energy of one ion in the crystal with respect to those in the layer is computed, it will be found that this increment of energy decreases rapidly as the crystal grows, and hence the total potential energy between one ion and all other ions can be evaluated. A profound treatment will be given later on pages 133—54.

Hence the total potential energy of one ion with respect to all other ions in the lattice is given by:

$$\phi_L = -\frac{j\nu\nu_1 e^2}{L} + k\varphi_L + k_1\psi_L; \tag{49}$$

L is the normal i. e. the equilibrium distance between neighbour ions. This means that:

$$\frac{d\phi}{dL} = \frac{j\nu\nu_1 e^2}{L^2} + k\varphi' + k_1 o\psi' = 0; \tag{50}$$

The change in distance between next neighbours dL_1 being odL. By compression the distance between neighbours is altered from L to $L-l$. By this change the potential energy is altered to:

$$\phi_L + \Delta\phi = -\frac{j\nu\nu_1 e^2}{L-l} + k\left[\varphi_L - \varphi' l + \frac{\varphi''}{2} l^2 \dots\right] + \\ + k_1\left[\psi_{L_1} - \psi' o l + \frac{\psi''}{2} o^2 l^2 \dots\right];$$

ϕ_L as given by expression (49) is subtracted. Furthermore by means of expression (50)

$$-j\nu\nu_1 e_2 \text{ is replaced by } (k\varphi' + k_1 o\psi')L^2;$$

Hence an expression for the energy change is obtained:

$$\Delta\phi = (k\varphi' + k_1 o\psi')L^2\left[\frac{1}{L-l} - \frac{1}{L}\right] - k\varphi' l + \frac{k\varphi''}{2} l^2 - \\ - k_1 o\psi' l + \frac{k_1 o^2 \psi''}{2} l^2 \dots .$$

Neglecting the third power terms of l the expression:

$$L^2\left[\frac{1}{L-l} - \frac{1}{L}\right] \text{ reduces to } l + \frac{l^2}{L};$$

This is introduced:

$$\Delta\phi = k\varphi' l + k_1 o\psi' l + k\varphi' \frac{l^2}{L} + k_1 o\psi' \frac{l^2}{L}$$

$$- k\varphi' l - k_1 o\psi' l + k\varphi'' \frac{l^2}{2} + k_1 o^2 \psi'' \frac{l^2}{2};$$

It is seen that first power terms cancel.

$$\Delta\phi = \left[k\left(\frac{\varphi'}{L} + \frac{\varphi''}{2}\right) + k_1\left(\frac{o\psi'}{L} + \frac{o^2\psi''}{2}\right)\right] l^2 = Dl^2; \qquad (51)$$

The change in energy is thus proportional to the square of the change in distance between the ions, this means that HOOKE's law is valid. In case l is so large that third power terms become significant, HOOKE's law will no longer be valid. In the following treatment it is found practical to make use of the proportionality factor D as a parameter. $\Delta\phi$ is the change in potential energy due to changes, arising from compression, in forces between one ion and all other ions. The energy of N ions is not N times but only $\frac{N}{2}$ times as great, for in our summation we count each distance twice, i. e. count both ba and ab. Hence the energy change to be ascribed to any one ion is only half of $\Delta\phi$. As the molecule (in the cases of the NaCl, CsCl and ZnS lattices) contains two ions, $\Delta\phi$ represents the energy change per molecule.

Owing to the change in distance from L to $L-l$ the volume occupied by a molecule is diminished. In the normal state this volume is $V = BL^3$ where the constant B is 2 for the NaCl lattice, $\frac{8}{3\sqrt{3}}$ for the CsCl lattice and $\frac{16}{3\sqrt{3}}$ for the ZnS lattice. (52)

The change due to compression in the volume occupied by a molecule is:

$$\varDelta V = BL^3 - B(L-l)^3 = B[3L^2l - 3Ll^2 + l^3] \backsim 3BL^2l; \quad (53)$$

the two latter terms being negligible compared to the first one.

The external pressure p necessary to perform the compression is equal to $-\frac{\delta(\varDelta\phi)}{\delta(\varDelta V)}$. Thus combining (51) and (53):

$$p = -\frac{\delta(\varDelta\phi)}{\delta(\varDelta V)} = -\frac{\frac{\delta(\varDelta\phi)}{\delta l}}{\frac{\delta(\varDelta V)}{\delta l}} = -\frac{2Dl}{3BL^2}; \quad (54)$$

from which:

$$\frac{\delta p}{\delta(\varDelta V)} = \frac{\frac{\delta p}{\delta l}}{\frac{\delta(\varDelta V)}{\delta l}} = -\frac{2D}{9B^2L^4};$$

The compressibility is defined as:

$$\varkappa = -\frac{1}{V}\frac{\delta(\varDelta V)}{\delta p};$$

introducing the values of V and $\frac{\delta p}{\delta(\varDelta V)}$, this becomes:

$$\varkappa = \frac{1}{BL^3} \cdot \frac{9B^2L^4}{2D} = \frac{9BL}{2D}; \quad (55)$$

Putting in the value of D, the following general expression for the compressibility is obtained:

$$\varkappa = \frac{9B}{k\left(\frac{2\varphi'}{L^2} + \frac{\varphi''}{L}\right) + k_1\left(\frac{2o\psi'}{L^2} + \frac{o^2\psi''}{L}\right)}; \quad (56)$$

where B is a constant characteristic of the lattice type; k is the number of neighbours of any one ion; k_1 the number of next neighbours; L the distance between neighbours; o the ratio of the distances between neighbours and next neighbours. φ', φ'' and ψ', ψ'' are constants in the TAYLOR series (46) and (47).

The second term containing k_1 in the denominator is due to forces between next neighbours. As a rule it is considerably smaller than the first one. If it be neglected the expression reduces to:

$$\varkappa = \frac{9\,BL}{k\left(\frac{2\,\varphi'}{L} + \varphi''\right)}; \tag{57}$$

This expression will be used in the following discourse. The error introduced by disregarding the intrinsic repulsive force between next neighbours will be discussed later.

Relative Displacement of Positive and negative Ions.

Although the problem of the interaction of a crystal lattice with an electric field has been shown on pages 70—72 to depend on assumptions concerning the Lorentz force; nevertheless, the problem can be treated on the same general lines as the compressibility was in the last section. In addition the problems of dielectric polarization and compressibility may be linked together.

Consider a regular ionic crystal, and suppose the lattice of positive ions as an entirety is displaced with regard to the lattice of negative ions. The relative displacement of the force-centres (not necessarily the nuclei) is s. Next neighbours, always having the same sign, are not displaced relative to each other. The forces between next neighbours therefore are not altered, whence, according to restriction 6), the total change in the potential energy of the intrinsic repulsive forces is due to changes in distances between neighbours. The neighbours of any one ion in a regular diagonal lattice form either a regular tetrahedron, a regular octahedron or a cube.

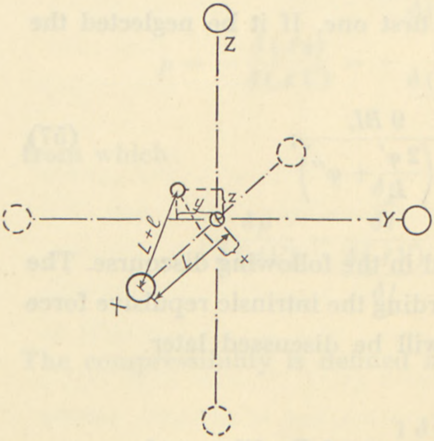

Fig. 5.

The octahedric arrangement which is found in the NaCl lattice is considered first. In figure 5 the central ion is placed at the origin of Cartesian coordinates, and the neighbour ions are placed on the coordinate axes at the distances L. The potential energy of the intrinsic repulsive force between the central ion and one of its neighbours is given by the Taylor series (46). We shall now determine the change in this potential energy and the force which will arise when the central ion is displaced the distance s with the components x, y and z.

It is found that the first power terms of x, y, z cancel one another, therefore terms containing x, y, z to the second power are significant. Terms to the third and fourth power are neglected.

First consider the change l in L the distance between the central ion and one of its neighbours situated on the X axis. This change is:

$$l = \sqrt{(\pm L - x)^2 + y^2 + z^2} - L; \qquad (58)$$

or

$$l = (L \pm x)\sqrt{1 + \frac{y^2 + z^2}{(L \pm x)^2}} - L;$$

The numerator contains y and z to the second power, hence third power terms will only be neglected if x in the denominator is discarded. Furthermore the reduction $\sqrt{1 + \Delta} = 1 + \frac{\Delta}{2}$ is used, the error introduced thereby is in the fourth power of y and z, and we get:

$$l = (L \pm x)\left[1 + \frac{y^2 + z^2}{2L^2}\right] - L;$$

In the multiplication the third power term is neglected. Hence:

$$l = \pm x + \frac{y^2 + z^2}{2L}; \qquad (59)$$

and neglecting terms to the third and fourth power we obtain:

$$l^2 = x^2. \qquad (60)$$

These values are introduced into the TAYLOR series (46), whence the potential energy due to one neighbour ion on the X axis is found to be:

$$\varphi_{L+l} = \varphi_L + \varphi'\left[\pm x + \frac{y^2 + z^2}{2L}\right] + \frac{\varphi''}{2}x^2;$$

When we consider both neighbour ions on the X axis, the first power terms (having opposite sign) cancel, and we have the change in potential energy due to the displacement:

$$\Delta\varphi_x = \varphi'\frac{y^2 + z^2}{L} + \varphi'' x^2.$$

Similar expressions are found for the ions on the y and z axes. By summation the potential energy change due to all six neighbours is:

$$\Delta\phi = \varphi' \frac{2(x^2+y^2+z^2)}{L} + \varphi''(x^2+y^2+z^2);$$

$x^2+y^2+z^2$ is equal to s^2, hence the above expression reduces to:

$$\Delta\phi = \left[\frac{2\varphi'}{L} + \varphi''\right] s^2 \quad . \qquad (61)$$

It is seen that the change in energy $\Delta\phi$ is proportional to the square of the displacement, and furthermore that the proportionality factor is independent of the direction of the displacement. These results are only valid for small displacements. If the displacement is so large that third power terms become significant, the elastic energy will no longer be proportional to the square of the displacement, and the proportionality factor no longer the same in all directions. Just as was the case for compression, Hooke's law will no longer be valid.

The tetrahedric and cubic arrangements.

In the ZnS lattice the neighbours of any one ion form a regular tetrahedron, in the CsCl lattice they form a cube, and in the CaF_2 lattice the F^- ions form a cube round the Ca^{++} ion, and the Ca^{++} ions form a tetrahedron round any F^- ion. As shown in figure 6 a regular tetrahedron is formed from ions placed at every second corner of a cube. Hence the cases of the regular tetrahedron and the cube can be treated together. Cartesian coordinate axes are placed in the lattice as shown in the figure. The coordinates of the neighbour ions are $X = \pm g$; $Y = \pm g$ and $Z = \pm g$. In the case of the cubic arrangement all combinations of + and — have to be considered, in the case of the tetrahedric arrangement the combinations $(---)$, $(-++)$, $(+-+)$ and $(++-)$ only. The distance L between one corner of the cube and the centre, i. e. that between one neighbour ion and the central ion in its initial position is $L = \sqrt{3}g$.

Consider as before the central ion to be displaced the small distance s. The general case of the ion being displaced in any direction has been considered by the writer. The calculations are similar to those regarding the octahedron. Just as was found for the octahedron, the change in potential energy is proportional to the square of the displacement and the proportionality factor is independent of the direction of the displacement in the crystal. The calculations for the general case, however, are lengthy, but they are simplified if the displacement considered takes place in the direction of one of the axes. This therefore is considered here. The coordinates of the displaced central ion are x, o, o. The change in distance between the central ion and any one of its neighbour ions is:

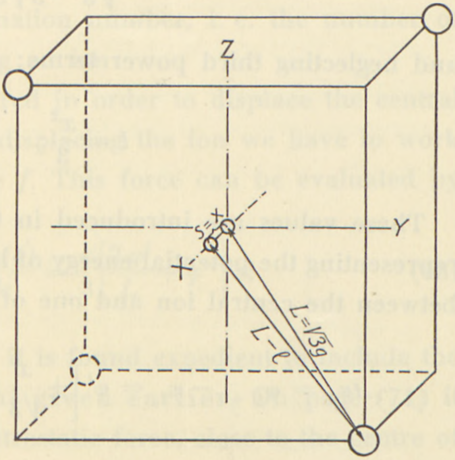

Fig. 6.

$$l = \sqrt{(\pm g - x)^2 + g^2 + g^2} - \sqrt{3}\,g; \qquad (62)$$

which can also be written:

$$l = \left(\sqrt{3}\,g \pm \frac{x}{\sqrt{3}}\right) \sqrt{1 + \frac{\frac{2}{3}x^2}{\left(\sqrt{3}\,g \pm \frac{x}{\sqrt{3}}\right)^2}} - \sqrt{3}\,g;$$

This is reduced, firstly by omitting the second term in the denominator, secondly by the familiar reduction $\sqrt{1+\Delta} = 1 + \frac{\Delta}{2}$, and thirdly by neglecting third power terms in the multiplication. As a result we obtain:

$$l = \pm \frac{x}{\sqrt{3}} + \frac{x^2}{3\sqrt{3}\,g}; \qquad (63)$$

and neglecting third power terms:

$$l = \frac{x^2}{3}; \qquad (64)$$

These values are introduced in the Taylor series (46) representing the potential energy of intrinsic repulsive forces between the central ion and one of its neighbours; hence:

$$\Delta\varphi_1 = \varphi_{L+l} - \varphi_L = \varphi' \left[\pm \frac{x}{\sqrt{3}} + \frac{x^2}{3\sqrt{3}\,g}\right] + \varphi'' \frac{x^2}{6};$$

By the summation over all neighbour ions the terms containing x to the first power cancel, and for the tetrahedric arrangement it is found:

$$\Delta\phi = \varphi' \frac{4x^2}{3\sqrt{3}\,g} + \varphi'' \frac{2x^2}{3};$$

It is advantageous to introduce L in place of $\sqrt{3}$g, furthermore $x = s$.

$$\Delta\phi = \frac{2}{3}\left[\frac{2\varphi'}{L} + \varphi''\right] s^2; \qquad (65)$$

Similarly for the cubic arrangement:

$$\Delta\phi = \frac{4}{3}\left[\frac{2\varphi'}{L} + \varphi''\right] s^2; \qquad (66)$$

Regular arrangements in general.

If we compare these equations with (61) it will be seen that the different equations can be replaced by:

$$\Delta\phi = \frac{k}{6}\left[\frac{2\,\varphi'}{L} + \varphi''\right] s^2; \qquad (67)$$

where k is the coordination number, i. e. the number of neighbours surrounding an ion.

$\Delta\phi$ is the energy required in order to displace the central ion the distance s. In displacing the ion we have to work against an elastic force f. This force can be evaluated by differentiation:

$$f = \frac{d(\Delta\phi)}{ds} = \frac{k}{3}\left[\frac{2\,\varphi'}{L} + \varphi''\right] s; \qquad (68)$$

At the present stage it is found expedient to include the proof of a statement given earlier. On page (71) it was stated that the electrostatic force, close to the centre of a regular configuration of ions placed on a spherical surface, is negligibly small. The electrostatic potential energy between two ions of charges νe and $\nu_1 e$ and distance L apart is:

$$\varphi_E = \frac{\nu\nu_1 e^2}{L};$$

$$\text{Hence: } \varphi' = \frac{d\varphi_E}{dL} = -\frac{\nu\nu_1 e^2}{L^2} \text{ and } \varphi'' = \frac{2\,\nu\nu_1 e^2}{L^3};$$

$$\text{Thus: } \frac{2\,\varphi'}{L} + \varphi'' = 0; \qquad (69)$$

If this is introduced in equation (68), it is seen that the force near the centre of the configuration becomes zero independent of direction of displacement. This of course only holds for small displacements, since it is subject to the same restriction, as the entire calculation above, namely that the cube of the displacement shall be small compared to the square of it. We have demonstrated the correctness of our assumption in the cases of the octahedron, tetrahedron and cube, but in all probability it will hold for other regular configurations. (Regular is to be taken in the crystallographic sense of the word.) For the limiting case of the evenly charged spherical surface our assumption is valid for all displacements smaller than the radius.

A Relation between Compressibility and Atomic Polarizability.

Equation (68) as derived considers elastic forces between neighbour ions only. In the case considered on page 103 where the lattices of positive and negative ions are relatively displaced, the contribution of force due to ions at greater distances than L is negligible, and f can be considered the total elastic force exerted on one ion by the entire lattice.

This force was also considered on page 81; there it was assumed that the force was proportional to the relative displacement of the ions. Now we have actually found, that this assumption holds good, and furthermore that the proportionality factor, which was then termed K, has the value:

$$K = \frac{k}{3}\left[\frac{2\,\varphi'}{L} + \varphi''\right]. \tag{70}$$

There is one objection to be made: the relative displacement considered in defining K was that of the nuclei, whereas the displacement s in the above calculations is that of the force-centres of intrinsic repulsive forces. By action of the field the electrons in the ion are shifted with regard to the nucleus. The intrinsic repulsive force between two ions, however, is dependent not only on the relative distances of the nuclei, but also and probably more on the location and motion of the electronic systems in the two ions. Hence it will be realized that the above equation (70) is not absolutely exact, still we will use it for the present. A modified expression will be derived later on pages 124—28,

The constant K can be determined by means of equation (30). In this way the field constants φ' and φ'' may be expressed in terms of the atomic polarizability α_{A_0}. Hence:

$$K = \frac{k}{3}\left[\frac{2\,\varphi'}{L} + \varphi''\right] = \frac{\nu^2 e^2}{\alpha_{A_0}}; \tag{71}$$

The same function of φ' and φ'' also appears in the equations (56) and (57). At present we will consider equation (57). It may be rearranged as follows:

$$K = \frac{k}{3}\left[\frac{2\,\varphi'}{L} + \varphi''\right] = \frac{3\,BL}{\varkappa}; \tag{72}$$

Putting the two values of K equal it is seen that a simple relation between the compressibility $\varkappa$ and the atomic polarizability α_{A_0} can be derived. Hence:

$$\varkappa = \frac{3\,BL\,\alpha_{A_0}}{\nu^2 e^2}. \tag{73}$$

Experimental Test.

With a view to numerical calculation, the value of α_{A_0} from expression (18) is introduced:

$$\varkappa = \frac{3\,BL}{\nu^2 e^2} \cdot \frac{M}{4\,\pi N \delta} \cdot \frac{\varepsilon_0 - n^2}{\left[1 + \frac{\beta}{3}(\varepsilon_0 - 1)\right]\left[1 + \frac{\beta}{3}(n^2 - 1)\right]}; \quad (74)$$

It is not necessary to consider both L and δ as these are related. The volume occupied by a molecule can be expressed both by $\frac{M}{N\delta}$ and by BL^3 (this is the definition of B). Either L or δ, N and M can be eliminated, the latter is found the more advantageous. Hence:

$$\varkappa = \frac{3\,B^2 L^4}{4\,\pi \nu^2 e^2} \cdot \frac{\varepsilon_0 - n^2}{\left[1 + \frac{\beta}{3}(\varepsilon_0 - 1)\right]\left[1 + \frac{\beta}{3}(n^2 - 1)\right]}; \quad (75)$$

It is convenient to unite such magnitudes as are constant for the same valency and lattice type into one numerical constant.

$$C = \frac{9\,B^2}{4\,\pi \nu^2 e^2};$$

(why the number 3 is replaced by the number 9 will appear later).

Two limiting values of β in particular are to be considered. First β equals unity which gives:

$$\varkappa_1 = \frac{CL^4}{3} \cdot \frac{[\varepsilon_0 - n^2]}{\left[1 + \frac{1}{3}(\varepsilon_0 - 1)\right]\left[1 + \frac{1}{3}(n^2 - 1)\right]} = \frac{3\,CL^4 [\varepsilon_0 - n^2]}{[\varepsilon_0 + 2]\,[n^2 + 2]}$$

$$\varkappa_1 = CL^4 \left[\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} - \frac{n^2 - 1}{n^2 + 2}\right] = CL^4 p_A. \quad (77)$$

The latter transformation is convenient because in the thesis on dipole moment[1], there was calculated a table of the familiar polarization and refraction functions:

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[1] HØJENDAHL K.: Studies of Dipole-Moment. Copenhagen (1928) p. 152.

$$p_A = p - p_E;\ p = \frac{\varepsilon - 1}{\varepsilon + 2};\ \text{and}\ p_E = \frac{n^2 - 1}{n^2 + 2};$$

The last calculation also explains why the particular value of C was chosen.

The second limiting value of the compressibility obtained for β equals zero is:

$$\varkappa_2 = \frac{1}{3} CL^4 [\varepsilon_0 - n^2]; \tag{78}$$

In table 5 columns 4 and 5 such limiting values of the compressibility are compared with the experimental compressibility quoted in column 6. The data are mainly recent ones by BRIDGMAN (marked B.) and by SLATER (marked S.); in a few cases earlier data of RICHARDS and JONES (marked R. J.) are employed. As the different investigators used different units, the data from LANDOLT-BÖRNSTEIN'S tables are quoted, and further references are also given there[1].

Experimental data used in the formulae are collected in table 4. ν is the valency; L the distance between neighbour ions, the values quoted are taken for the most part from a survey by EWALD[2] supplemented by recent data from LANDOLT-BÖRNSTEIN'S tables[3]. The dielectric constant ε_0, and the square of the refractive index n^2 are transferred from table 1. The few values not given there, if marked by E. were measured by ERRERA[4], and if marked by E. B. were measured by EUCKEN and BÜCHNER[5].

The above theoretical values of $\varkappa$ (77) and (78) are the

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[1] LANDOLT-BÖRNSTEIN: Tabellen. Ergbd. I and III; table 26 p.

[2] Handbuch d. Physik. Bd. 24., 334—5 and 339, by P. P. EWALD.

[3] LANDOLT-BÖRNSTEIN: Tabellen. Ergbd. I, II, III; table 155 d.

[4] ERRERA J.: ZS. Elektrochemie **36**, 818 (1930).

[5] EUCKEN A. and BÜCHNER A.: ZS. physik. Ch. (B) **27**, 321 (1934).

limiting values corresponding to β equals unity or zero. It is also of interest to see what value must be ascribed to β in order that equation (75) shall hold with accuracy. To derive this value, $\varkappa$ in equation (75) is put equal to the experimental value $\varkappa_3$. Dividing equation (78) by equation (75) the constant C, the distance L and the term $\varepsilon_0 - n^2$ cancel, and we have:

$$\left[1+\frac{\beta}{3}(\varepsilon_0-1)\right]\left[1+\frac{\beta}{3}(n^2-1)\right]=\frac{\varkappa_2}{\varkappa_3}; \qquad (79)$$

This is a quadratic equation the solution of which is:

$$\beta=-\frac{3(\varepsilon_0+n^2-2)}{2(\varepsilon_0-1)(n^2-1)}\left[1\pm\sqrt{1+\frac{4(\varepsilon_0-1)(n^2-1)\left(\frac{\varkappa_2}{\varkappa_3}-1\right)}{(\varepsilon_0+n^2-2)^2}}\right] \qquad (80)$$

The positive sign in front of the surd always leads to numerically large negative values of β. In tables 2 and 3 we found from transmission and reflection data that β as a rule is positive or eventually has a small negative value. Therefore the negative sign in front of the surd is the only one considered, and values of β obtained in this manner are quoted in table 5 column 7.

The variation in β is compared with the variation in some other properties; for instance with d, in column 8, which is the distance of free space between the anions. If these are considered as spheres of radius r and the distance between the centres of the anions is oL where o is a factor, which is constant to the lattice type (see p. 98) we have:

$$d = oL - 2r \qquad (81)$$

In the case of the NaCl lattice o is $\sqrt{2}$; in the case of the CsCl lattice it is $\frac{2}{\sqrt{3}}$. Values of the ionic radii are given later in table 7.

Table 4. Experimental Data used in the Formulae.

	Lattice	ν	$L\cdot 10^8$ cm	ε_0	n^2	p_E	p_A	$\frac{\varepsilon_0 - n^2}{3}$
LiF	NaCl	1	2.07	9.27	1.92	0.235	0.500	2.45
LiCl	„	1	2.57	11.05 E.	2.75	0.368	0.401	2.77
LiBr	„	1	2.74	12.1 E.	3.16	0.419	0.369	2.98
LiI	„	1	3.03	11.03 E.	3.80	0.483	0.288	2.41
NaF	„	1	2.31	6.0	1.74	0.198	0.427	1.42
NaCl ...	„	1	2.81	5.62	2.25	0.294	0.313	1.12
NaBr ...	„	1	2.97	5.99	2.62	0.351	0.274	1.12
NaI	„	1	3.23	6.60	2.91	0.389	0.260	1.23
KF	„	1	2.66	6.05 E.	1.85	0.221	0.407	1.40
KCl	„	1	3.14	4.68	2.13	0.274	0.277	0.85
KBr	„	1	3.29	4.78	2.33	0.307	0.249	0.82
KI	„	1	3.53	4.94	2.69	0.360	0.208	0.75
RbF	„	1	2.82	5.91 E.	1.93	0.237	0.383	1.33
RbCl ...	„	1	3.27	5.0	2.19	0.284	0.287	0.93
RbBr ...	„	1	3.42	5.0	2.33	0.307	0.274	0.89
RbI	„	1	3.66	5.0	2.63	0.352	0.219	0.79
AgCl	„	1	2.77	12.3	4.04	0.503	0.288	2.75
AgBr ...	„	1	2.88	13.1	4.62	0.547	0.254	2.83
MgO	„	2	2.10	9.8	2.95	0.394	0.352	2.28
CaO	„	2	2.40	11.8	3.28	0.432	0.353	2.86
SrO	„	2	2.57	13.3	3.31	0.435	0.366	3.33
CsCl	CsCl	1	3.56	7.20	2.60	0.348	0.327	1.53
CsBr	„	1	3.71	6.51	2.78	0.372	0.275	1.24
CsI	„	1	3.95	5.65	3.03	0.404	0.204	0.87
NH_4Cl ..	„	1	3.34	6.96	2.62	0.351	0.314	1.45
TlCl	„	1	3.33	31.9	5.10	0.578	0.334	8.90
TlBr	„	1	3.44	29.8	5.41	0.595	0.311	8.13
CuCl	ZnS	1	2.34	10.0 E. B.	3.57	0.461	0.289	2.14
CuBr ...	„	1	2.46	8.0 E. B.	4.08	0.507	0.193	1.31
ZnS	„	2	2.33	8.3	5.07	0.576	0.133	1.08
BeO	ZnO	2	1.65	7.35	2.95	0.394	0.285	1.47
CaF_2	CaF_2	2—1	2.36	8.43	1.99	0.248	0.465	2.15
SrF_2	„	2—1	2.50	7.69	2.08	0.265	0.426	1.87
BaF_2	„	2—1	2.69	7.33	2.09	0.266	0.412	1.75

Table 5. Comparison between Theoretical and Experimental Compressibility.

	B	C	theoretical		experimental		β	d
			$\varkappa_1$	$\varkappa_2$	$\varkappa_3$			
			all × 10^6		cm²/kg.			× 10^8 cm.
LiF	2	12.3	1.13	5.5	1.50	S.	0.73	0.27
LiCl	„	„	2.16	14.9	3.34	S.	0.66	0.01
LiBr	„	„	2.56	20.7	4.23	S.	0.64	— 0.04
LiI	„	„	2.99	25.0	5.889	B.	0.54	— 0.11
NaF	„	„	1.50	5.0	2.07	B.	0.65	0.61
NaCl	„	„	2.40	8.6	4.182	B.	0.47	0.37
NaBr ...	„	„	2.63	10.7	4.98	S.	0.44	0.28
NaI	„	„	3.48	16.5	6.936	B.	0.45	0.17
KF	„	„	2.51	8.6	3.25	S.	0.71	1.10
KCl	„	„	3.32	10.2	5.53	S.	0.46	0.82
KBr	„	„	3.60	11.9	6.56	S.	0.42	0.73
KI	„	„	3.98	14.4	8.37	S.	0.34	0.59
RbF	„	„	2.99	10.4				
RbCl	„	„	4.04	13.1	6.52	B.	0.51	1.00
RbBr ...	„	„	4.61	15.0	7.78	S.	0.45	0.92
RbI	„	„	4.83	17.4	9.39	S.	0.39	0.78
AgCl	„	„	2.09	19.9	2.4	R. J.	0.89	0.30
AgBr	„	„	2.16	24.0	2.7	R. J.	0.85	0.15
MgO	„	3.08	0.211	1.37	0.5904	B.	0.32	0.33
CaO	„	„	0.360	2.93	4.57	B.	— 0.09	0.76
SrO	„	„	0.492	4.47				
CsCl	$\frac{8}{3\sqrt{3}}$	7.30	3.84	18.0	5.829	B.	0.63	0.49
CsBr ...	„	„	3.81	17.2	6.918	B.	0.50	0.36
CsI	„	„	3.63	15.5	8.403	B.	0.33	0.16
NH_4Cl ..	„	„	2.86	13.1	5.9	B.	0.41	0.24
TlCl	„	„	3.00	80.0	4.8	R. J.	0.74	0.23
TlBr	„	„	3.18	83.1	5.2	R. J.	0.71	0.05
CuCl ...	$\frac{16}{3\sqrt{3}}$	29.21	2.53	18.7	2.463	B.	1.02	0.20
CuBr ...	„	„	2:06	14.0	2.87	B.	0.75	0.10
ZnS	„	7.30	0.286	2.32	1.281	B.	0.18	0.32
BeO	„	„	0.154	0.79				
CaF_2	$\frac{16}{3\sqrt{3}}$	7.30	1.05	4.87	1.206	B.	0.87	0.07
SrF_2	„	„	1.21	5.33	1.58	B.	0.75	0.23
BaF_2	„	„	1.58	6.68	2.07	B.	0.74	0.45

Discussion.

It will be seen that the experimental compressibility has a value which in nearly all cases lies between the two corresponding theoretical values. The only exceptions are CuCl and CaO.

In the case of CuCl the experimental value is so close to the region of the theoretical values, that it is safe to say that here the experimental value is equal to the theoretical value obtained when β is equal to unity, i. e. when the entire LORENTZ force is taken to be present.

The value found for CaO is far outside the region of the theoretical values. It is very hard at first sight to understand why CaO alone should show this large discrepancy. An explanation however, is found when the original paper of BRIDGMAN is consulted[1]. Some parts of interest are quoted verbatim: About MgO BRIDGMAN writes:

> "*I was most fortunate to obtain a water-clear transparent crystal of artificial origin*". . . . For this the compressibility at 30° and pressure zero was found to be 5.904×10^{-7}.

(This is the experimental compressibility quoted in table 5 column 6.)

> "*Before the sample of clear crystal MgO was obtained, measurements had been carried through in the regular way on a compressed slug of powdered MgO, made from Kahlbaum's MgO, zur Analyse. . . . The absolute value of the compressibility was of the order of twice that of the crystal, however.*"

It was now found by BRIDGMAN that although the slug had been compressed by an immense pressure it was still porous.

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[1] BRIDGMANN P. W.: Proc. Amer. Acad. **67**, 345 (1932).

Due to the pores and to the irregular "amorphous" arrangement of the ions in the slug, the compressibility is considerably larger in the slug than in the crystal. About CaO Bridgman writes:

> "*The compressibility of CaO appears not to have been determined previously. The enormously greater value than for MgO is noteworthy and would seem to demand explanation. The crystal structure of MgO and CaO is the same and of the NaCl type. It is highly probable that if clear crystallized CaO could be obtained the same differences as compared with the compressed slug would be found as were shown by MgO.*"

The quotation leaves little to be added. The experimental compressibility of CaO quoted in table 5 column 6 is that of the slug. This is probably more than twice as large as that of crystalline CaO. It is to the crystalline state however, that our relations should be applied. Hence, if the true compressibility be only 2.78×10^{-6}, namely half the compressibility of the slug, it enters into the region of the theoretical values, and the discrepancy of CaO has disappeared.

The above quotation indicates what is the greatest difficulty at present attached to the measurements of compressibility of oxides. It is not in the experimental procedure, although the difficulties overcome by Bridgman undoubtedly are numerous, but it is in the provision of large and perfect crystals, where the difficulty lies.

The same remarks can also be applied to the dielectric constants of oxides. Here the experimental difficulties are admittedly smaller, and discrepancies of the above magnitude are not found. Still the discrepancies of dielectric constants are considerable and hardly due to experimental error. In the cases of three different samples of MgO powder of different origins I found the dielectric constants to be: 9.9; 9.3 and 9.8 respectively, whereas GÜNTHERSCHULZE and KELLER[1] found the value 8.2. This means a discrepancy of about 20 per cent. To elucidate the problem of relative errors in dielectric constants of oxides, it would be valuable if the dielectric constant of clear crystalline MgO were measured using EUCKEN and BÜCHNER's method, which presumably would be the most accurate one in this case.

If the theories of CLAUSIUS-MOSOTTI and LORENZ-LORENTZ were absolutely true, and the other assumptions we have introduced were also strictly permissible, the experimental compressibility should be given by equation (77), i. e. it should be equal to $\varkappa_1$. Actually a deviation is found. As a measure of this deviation the factor β was introduced. This factor which represents the virtual fraction of the LORENTZ force has been calculated by means of equation (80) and is given in table 5 column 7.

It is interesting to compare the present values of β_K as obtained from compressibility with those earlier values obtained from infra-red data. This comparison is made in table 6.

The values of β_A from absorption agree well with the corresponding values of β_K from compressibility in the cases of the Rb and Cs-halides, whilst β_A is somewhat smaller than β_K in the cases of the Li, Na and K-halides. The values of β_C from the CHRISTIANSEN wave-length on the average agree with the corresponding values of β_K from compressibility; still large values of β_C are often larger, and small values smaller, than the corresponding values of β_K; but this may well be due to experimental error. It appears on the whole that the haphazard error on the β values from

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[1] GÜNTHERSCHULZE A. and KELLER F.: ZS. f. Physik. **75**, 82 (1932).

Table 6. Comparison between β values of different origin.

	Compressibility β_K	Absorption β_A	Christiansen β_C	Reflection β_R
LiF	0.73	0.26	0.15	0.67
NaF	0.65	0.68		− 0.40
NaCl	0.47	0.18	0.16	− 0.10
NaBr	0.44	0.15	0.45	
NaI	0.45	0.25	0.29	
KCl	0.46	0.26	0.43	0.00
KBr	0.42	0.23	0.25	− 0.12
KI	0.34	0.13	0.22	− 0.03
RbCl	0.51	0.52	0.60	0.19
RbBr	0.45	0.42	0.45	
RbI	0.39	0.38	0.67	
CsCl	0.63	0.63	0.72	
CsBr	0.50	0.49	1.07	
NH_4Cl	0.41			0.21
TlCl	0.74		1.07	0.44
TlBr	0.71		1.07	0.68
AgCl	0.89			0.09
AgBr	0.85			0.24
MgO	0.32	1.14	− 0.06	
ZnS	0.18			0.02
CaF_2	0.87			− 0.11
SrF_2	0.75			− 0.07
BaF_2	0.74			− 0.27

infra-red measurements is considerable and larger than the error on the β_K values from compressibility. The values of β_R from reflection are definitely smaller than the other values of β; this deviation, however, may well be due to assumptions involved in Försterling's relation.

On the whole we may conclude, that the values of β_K, β_A and β_C agree inside the experimental error, and hence the deviation from a simple relationship may solely be ascribed to the uncertainty of the LORENTZ force. Whether the deviation actually is due to this one cause is another question.

A question of interest is, whether it is possible to find regularity in the variation of β with the periodical system of elements, and whether this variation can be related to other properties of the ions or of the lattice. Important properties of the ions are: the charge; the size as expressed by the ionic radius, and the inner polarisability as expressed by the molar refraction of the ion. In order that properties other than those considered shall not complicate the matter, it is desirable that the ions all should have similar electronic structures. This is achieved in the case of the alkali-halides, because then all component ions have similar noble gas structures with two s. and six p. electrons in the outer electron shell. In this case the charge on the ions is always the same, namely plus or minus one electronic charge. Furthermore the ionic radius and the inner polarizability are related, because they are both dependent on the dimensions of the outer electronic orbit, or in modern language on the distribution of electrons in the outer shell.

In table 7 values of β, as found from compressibility and dielectric constant, are compared with the ionic radii given by GOLDSCHMIDT[1], and with the "molar" refraction of the ion as given by FAJANS and JOOS[2]. A twofold variation is of course to be considered, one with the cation, and one with the anion. It is perceived that the variation of β_K is not

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[1] GOLDSCHMIDT V. M.: Ber. D. chem. Ges. **60**, 1270 (1927).

[2] FAJANS K. and JOOS G.: ZS. f. Physik. **23**, 20 (1924).

completely haphazard, but a regular variation is found. The variation with size and polarizability of the anion (the cation being maintained constant) is the larger and is one way only, i. e. β_K always decreases with increasing size and refraction of the anion. The variation with the cation is not so large, apparently β_K is a minimum for the sodium or potassium ion.

In the β values obtained from absorption, transmission or reflection measurements, similar regularities can only just be traced, but no more than that. The experimental error is probably so large that any regularities are masked.

Table 7. Variation of β_K in the System of Alkali-Halides.

		F	Cl	Br	I	
	Radius → ↓	1.33	1.81	1.96	2.20	P_E^+ ↓
Li	0.78	0.73	0.66	0.64	0.54	0.20
Na ...	0.98	0.65	0.47	0.44	0.45	0.50
K.....	1.33	0.71	0.46	0.42	0.34	2.23
Rb....	1.49		0.51	0.45	0.39	3.58
Cs	1.65		0.63	0.50	0.33	6.24
	P_E^- →	2.50	9.00	12.67	19.24	← Refraction ↑

Besides the influence of these ionic properties, influences due to the nature of the lattice must also be considered. One of these is important. By the reduction of expression (56) to give (57) the intrinsic repulsive forces between next-neighbours were neglected. In doing this a systematic error is introduced in the calculation which followed, and this also affects β_K. The repulsion between next-neighbours depends largely on the degree of contact between them. We have introduced the free distance d quoted in the last column of table 5 as a measure of the degree of contact between anions. Contact between cations is not found. If there is no contact, i. e. if the free distance is large, the repulsion between next-neighbours is presumably negligible. This will be seen if the values of β_K found for RbCl, RbBr and RbI are compared with those found for CsCl, CsBr and CsI. These salts crystallize in two different lattice-structures, having largely different distances between anions, which distances however, are all so large that no contact occurs. As will be seen from table 7 this sudden change in distances between anions is not followed by any large change in β_K. The closest contact is found for LiCl, LiBr and LiI, it seems likely that the remarkable increase in β_K found for these compounds is probably caused by the effect of anions in contact. The effect of repulsion between anions will be such that the compressibility is diminished. According to equation (75) a decrease in $\varkappa$ all other things being equal will manifest itself as an increase in β.

This probably explains the peculiar variation of β_K with size and polarizability of the cation. It is likely that β always decreases with decreasing size and polarizability of the cation; in the case of the lithium salts, however, this decrease is more than compensated by the increase due to anion contact.

The effect of other changes in the nature of the ions can be estimated if salts other than the alkali-halides are compared with them. The effect of valency for instance, is estimated if values of β_K for the oxides of the metals of the second group are compared with those of the alkali-halides.

Now it must be borne in mind that in the calculation of β_K the valency has already been taken into account, and so the present estimation is to some extent a proof of the relationship. The value of β_K for MgO is 0.31, which is somewhat smaller than that for NaCl namely 0.47, with which it is reasonable to compare it, since the O^{--} ion has a refraction similar to that of the Cl^- ion. The experimental error in the value of β_K for CaO is too large for a test. The small value of β_K for ZnS is probably caused by the large polarizability of the S^{--} ion, furthermore the Zn^{++} ion has not noble gas structure. Otherwise it is found that salts whose cations have not noble gas structure, exhibit comparatively large values of β_K. Such for instance is the case of the Cu^+, Ag^+ and Tl^+ chlorides and bromides. The ionic radii of these cations are comparable with those of the alkali ions, whereas the refractions are considerably larger. Hence it is argued, that the internal polarizability rather than the ionic radius has the principal influence on β. This influence can be generalized as follows: "β increases with increasing internal polarizability or refraction of the cation, and decreases with increasing refraction of the anion!" So far the relationship is empirical. In this respect and in others, it is similar to the relationship holding for the variation of the molar refraction of salts as dealt with by Fajans and Joos[1].

The Force-Centre of the Intrinsic Repulsive Force.

The deviation from equation (77) is not to be ascribed to the uncertainty of the Lorentz force alone, the irrelevance

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[1] Fajans K. and Joos G.: ZS. f. Physik. **23**, 1 (1924).

of some other assumption involved in the treatment may also contribute.

A possible cause of discrepancy has been introduced by the assumption that the nucleus is the force-centre of the polarized ion. This assumption was introduced in order to derive expression (70), but an objection was made then. In view of the theory of HEITLER and LONDON[1] it is evident that the above assumption cannot be correct. The intrinsic repulsive force is caused by an interaction of the electrons rather than of the nuclei, it must therefore depend on the relative location of the electrons rather than on that of the nuclei. Now it is a question whether the intrinsic repulsive force can be in any way regarded as a central force. But as calculation will be rendered much more difficult without this assumption, we will try to retain it. The force-centre cannot always be situated at the nucleus, it must be shifted in the same direction as are the electrons. As a reasonable conception we will now assume the force-centre to be represented by the mass- or charge-centre of the outer electron shell.

The separation into outer and inner electrons is arbitrary, especially as it is not granted that the number of outer electrons is an integer, because the electron cannot be considered 'outer' in all parts of its orbit. Since the number of outer electrons is thus unsettled, it is suggestive to consider this as the unknown magnitude which is to be determined on the assumption that the present cause of discrepancy is the preponderant one. It is assumed that only the outer electrons contribute to the internal polarizability α_E of the ion. If now the strength of the inner field of force is unity the displacement of the outer electron shell with regard to the nucleus becomes:

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[1] LONDON F.: Naturwissenschaften. **17**, 516 (1929).

$$s_1 = \frac{\alpha_E^+}{\gamma_1 e} \text{ for the cation, and } s_2 = \frac{\alpha_E^-}{\gamma_2 e} \text{ for the anion} \quad (82)$$

The numbers of outer electrons γ_1 and γ_2 are assumed to be equal in the following, and the suffixes are therefore omitted.

By action of the field the ions as such are also displaced. According to equations (3—5) the relative displacement of the nuclei is given by:

$$s_3 = \frac{\alpha_A}{\nu e};$$

The electrons of both anion and cation are displaced in the same direction as the anion as such, whereas the cation as such is displaced in the opposite direction. It follows that the relative displacement of the two outer electron shells is given by:

$$s_4 = s_3 + s_2 - s_1 = \frac{\alpha_A}{\nu e} + \frac{\alpha_E^- - \alpha_E^+}{\gamma e}; \quad (83)$$

As argued above the intrinsic repulsive force depends on the relative displacement s_4 of the electron shells, and not on that of the nuclei, namely s_3; hence it will be realized that s_4 and not s_3 ought to be introduced in equation (68). In order to correct equation (70) and the equations which followed we may introduce the correction factor:

$$\frac{s_4}{s_3} = 1 + \frac{\nu}{\gamma} \cdot \frac{\alpha_E^- - \alpha_E^+}{\alpha_A}; \quad (84)$$

This correction factor can be applied to the theoretical compressibility $\varkappa_1$ obtained from equation (77). If the present cause of discrepancy is the preponderant one the experimental compressibility $\varkappa_3$ should be obtained thereby. This means that the ratio ${}^{s_4}/_{s_3}$ should be equal to the ratio ${}^{\varkappa_3}/_{\varkappa_1}$. With a view to numerical calculation the following transformations are performed.

$$\frac{\varkappa_3}{\varkappa_1} - 1 = \frac{\nu}{\gamma}\cdot\frac{P_E^- - P_E^+}{P_A} = \frac{\nu}{\gamma}\cdot\frac{P_E}{P_A}\cdot\frac{P_E^- - P_E^+}{P_E} = \frac{\nu}{\gamma}\cdot\frac{p_E}{p_A}\cdot\frac{P_E^- - P_E^+}{P_E^- + P_E^+};$$

From this again γ can be calculated.

$$\gamma = \frac{\nu}{\frac{\varkappa_3}{\varkappa_1} - 1}\cdot\frac{p_E}{p_A}\cdot\frac{P_E^- - P_E^+}{P_E^- + P_E^+}; \tag{85}$$

The reason why the transformation was made in the above manner is that ν, p_E and p_A have already been quoted in table 4; $\varkappa_1$ and $\varkappa_3$ in table 5; and P_E^+ and P_E^- in table 7. The values of γ calculated for the alkali-halides by means of the above equation are tabulated in table 8. The arrangement is similar to that of table 7.

Table 8. Number of Effective Outer Electrons γ.

	F	Cl	Br	I
Li	1.21	1.61	1.69	1.69
Na	0.82	1.13	1.33	1.47
K	0.10	0.90	1.06	1.25
Rb		0.66	0.91	1.17
Cs		0.37	0.56	0.77

As will be seen from the table 8, γ is not found to be the same for all salts. It is furthermore considerably smaller than six, the number of electrons in the loosely held *p*-subgroup. Thus it is likely that the present cause of discrepancy is not the only one. On the other hand it cannot be neglected as being inconsiderable. As argued above, all six *p* electrons cannot be considered 'outer' electrons at the same time. They presumably describe orbits round the nucleus. The deflection caused by an external field is considerably larger at an outer, than at an inner loop of an orbit. Hence electrons in inner loops do not contribute nearly as much as those in outer loops. We may express this by asserting that the electrons in inner loops do not count at all. As a consequence of this the number of effective outer electrons may be considerably smaller than six; still one can hardly expect it to be as small as unity.

Too small values for the number of outer electrons are also found from the relation of Drude and Voigt, concerning the dispersion in ultra-violet. By means of this relation, the number of outer electrons in the noble gases were determined by Cuthbertson and Quarder. The resultant numbers quoted from Handbuch der Physik are[1]:

He 1.11; Ne 2.37; A 4.58; Kr 4.90; Xe 5.61.

It will be seen that these numbers are also smaller than the number of electrons usually taken to be in the outer shell. The explanation is similar to that given above.

Note on the Effect of Thermal Motion.

Professor J. A. Wasastjerna (in a discussion following his reading of the present manuscript) commented on assumption 3) on page 64 i. e.:

The lattice shall be perfect and the ions devoid of thermal

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[1] Handbuch der Physik: **20**, 490—91. Wolf K. L. and Herzfeld K. F.

motion. Actually the latter is not even the case at the absolute zero of temperature, but the amplitudes are generally small.

Wasastjerna remarked that the amplitudes are not small under any circumstances. At room temperature the amplitudes are of the order ten per cent of the distance between the ions, and at the absolute zero of temperature they are of the order five per cent. of the distance. He pointed out that the neglect of thermal motion is an important cause of discrepancy.

It is admitted that the neglect of thermal motion contributes to the discrepancy; but it is another question how great this contribution would be and how it may be evaluated. In the writers opinion the proper procedure would be, to measure the property in view at a variety of temperatures, to plot in a diagram the measured values against the corresponding amplitudes, and to extrapolate to zero amplitude. (Not to the absolute zero of temperature.) The present experimental data, however, are too scant and inexact for performing such an extrapolation with any degree of accuracy. Possibly the compressibility can be extrapolated by means of the procedure proposed by Hildebrand[1], Born and Mayer[2] and Wasastjerna[3,4]; but as regards the dielectric constant and the residual ray, new experiments must be undertaken at various temperatures, before the effect of thermal motion can be evaluated.

Summary.

1) The entire treatment is restricted to regular ionic lattices, and is subject to certain assumptions which are stated in the preliminary pages.

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[1] Hildebrand J. H.: ZS. f. Physik. **67**, 127 (1931).

[2] Born M. and Mayer J. E.: ZS. f. Physik. **75**, 1 (1932).

[3] Wasastjerna J. A.: Soc. Sc. Fennica. Com. Phys. Mat. VIII. **20** (1935).

[4] Wasastjerna J. A.: Soc. Sc. Fennica. Com. Phys. Mat. VIII. **21** (1935).

2) The theory of the "Lorentz" force is put forward in a simple manner mainly following Debye, but emphasizing the inherent uncertainty pointed out by Heckmann. As a measure of the uncertainty the parameter β is introduced which denotes the virtual fraction of the classical Lorentz force.
3) By means of a simple statement, regarding the inertia of a vibrating ion and the forces acting on it, an expression for the dispersion of the dielectric constant in the far infra-red is derived. The influence of damping being neglected, the dielectric constant becomes infinite at the natural frequency of the ionic motion. The corresponding wave-length is found to be given by Heckmann's relation, which includes Born's relation as a special case.
4) The natural frequency is approximately equal to the frequency of the absorption maximum, but not to that of the reflection maximum. (The residual ray.) The shape of the reflection curve is discussed.
5) The various relations are tested on the experimental data available. The discrepansies may be ascribed solely to the uncertainty of the Lorentz force, whence reasonable values of β have been determined.
6) The intrinsic repulsive force between two ions is assumed to be a short range central force. It is found convenient to expand it into a Taylor series.
7) The compressibility can be expressed as a function of the second and the third coefficient of this Taylor series.
8) The change in potential energy of intrinsic repulsive forces arising from a relative displacement of the lattices of positive and negative ions respectively is

computed. For small displacements the resultant elastic force is proportional to the displacement and independent of the direction in the crystal. The proportionality factor is expressed by the same function of the second and the third coefficient of the TAYLOR series as is the compressibility.

9) Both coefficients therefore can simultaneously be eliminated whereby a relation connecting measurable quantities is derived. These are: the compressibility, the lattice dimensions, the dielectric constant and the refractive index.

10) The parameter β is the only arbitrary magnitude involved. It can therefore be determined by means of the experimental data. Values between unity and zero are found in nearly all cases. The values of β found from compressibility data are similar to those found from the absorption maximum in the far infra-red, and to those found from the CHRISTIANSEN wave-lengths (measured by BOWLING BARNES and BONNER), but somewhat larger than those found from reflection data.

11) The compressibility as a rule is measured with greater accuracy and for more compounds than is the absorption, transmission or reflection in the far infra-red. As a consequence the values of β found from compressibility data are employed in an empirical manner to elucidate the relationship between the deviation of the LORENTZ force and various properties of the ionic lattice.

12) Thus it is found that β increases with increasing internal polarizability of the cation, and decreases with increasing internal polarisability of the anion.

13) Intrinsic repulsive forces between next-neighbours are

found to be insignificant except in the case of anion contact which causes an increase in β.

14) The deviation expressed by β may also be ascribed partly to an irrelevance of some of the other assumptions involved. For instance it is likely that the intrinsic repulsive force is not a central force, and if it has to be described as such, then the force-centre of the polarized ion cannot be situated at the nucleus. The alternate conception of the force-centre as situated at the charge-centre of the outer electron shell is considered. It is likely that part of the deviation has to be explained in some such way.

15) The neglect of thermal motion may also contribute to the deviation.

III.

ON AN ELEMENTARY METHOD OF CALCULATING MADELUNG'S CONSTANT

WITH A DETERMINATION OF THE ELECTROSTATIC LATTICE ENERGY OF THE IDEALIZED CALCITE LATTICE

BY

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The lattice energy of a salt is defined as the energy necessary to form free gas ions from one grammolecule of the crystal; it is not to be confused with the heat of vaporisation of the salt crystal; salt vapours, at attainable temperatures at all events, do not consist of separate ions, but of clusters of associated ions, these being the molecules in the ordinary sense. The difference between the heat of vaporization and the lattice energy, which is the energy gained by the association and mutual polarization of the ions in forming the cluster, has been calculated by BORN and HEISENBERG[1] who, computing also the lattice energy, were able to evaluate the heat of vaporization of the alkali-halides in fair agreement with experimental data.

The lattice energy is also of great importance as regards the solubility of salts in various solvents. According to FAJANS[2] the heat of solution of a salt in a solvent is equal to the difference between the heat of solvation of the gas ions, and the lattice energy of the salt crystal. This has been emphasized by BJERRUM[3]. In a more qualitative manner the lattice energy is related to the hardness, the melting point, and several other properties of the salt crystal.

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[1] BORN M. and HEISENBERG W.: ZS. f. Physik. **23**, 388 (1924).

[2] FAJANS K.: Naturwissenschaften. Heft **37**, 1 (1921).

[3] BJERRUM N.: Ber. D. chem. Ges. **62**, 1091 (1929).

The lattice energy can be determined by means of Born's cycle[1], this method, however, has the disadvantage that the electron affinity of the anion is implied, and as a rule this energy term is badly known. The lattice energy can also be calculated directly on the basis of certain assumptions regarding the forces between the ions. These forces can be separated into two types; a) the electrostatic force which follows Coulomb's law, and b) a short range repulsive force which keeps the ions apart; and the lattice energy can accordingly be separated into a major electrostatic part, and a minor repulsive part. A calculation of the repulsive part was first carried out by Born and Landé[2], and afterwards refined by Born and Mayer[3] and Wasastjerna[4]; this part amounts to about one tenth of the electrostatic part; it cannot be determined with any great accuracy, since an accurate expression for the relation between repulsive force and distance of ions is not known.

The calculation of the electrostatic part of the lattice energy is the theme of the present investigation, and in what follows we will restrict ourselves to that item: The electrostatic potential energy of two ions of charges νe and $\nu_1 e$ at a distance L is:

$$\varphi = \frac{\nu \nu_1 e^2}{L}; \tag{1}$$

To obtain the potential energy ϕ of an ion with respect to all other ions in the lattice we must sum up over all distances with due regard to the signs of the ions. It is convenient to introduce a standard distance L_0.

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[1] Born M.: Verh. d. D. Physik. Ges. **21**, 679 (1919).

[2] Born M. and Landé A.: Verh. d. D. Physik. Ges. **20**, 210 (1918).

[3] Born M. and Mayer J. E.: ZS. f. Physik. **75**, 1 (1932).

[4] Wasastjerna J. A.: S. Sc. Fennica. C. Phys. Mat. VI. **22**; VIII. **20**; VIII. **21**.

$$\phi = \frac{\nu\nu_1 e^2}{L_0} \sum \frac{L_0}{L} = \frac{\nu\nu_1 e^2}{L_0} j; \qquad (2)$$

The factor j is termed MADELUNG's constant, the numerical value of it is proportional to the particular value chosen for L_0, but for a given standard distance it is a constant number characteristic of the lattice. The electrostatic lattice energy of a grammolecule Φ is only half the sum of the ϕ values of the constituent ions, for in our summation we count each distance twice, counting both *a—b* and *b—a*.

$$\Phi = \frac{N}{2} (\phi_1 u + \phi_2 v + \ldots.); \qquad (3)$$

N is AVOGADRO's constant, and u and v are the numbers of ions of different types in the molecule. The constant j cannot be evaluated by an uncritical summation, because the ratio $\frac{L_0}{L}$ decreases only slowly, and the number of ions increases rapidly with the distance; it is therefore necessary to proceed on a definite plan.

MADELUNG[1], who first calculated the value of j for the NaCl lattice, considered at the first instance the potential of an ion with respect to a linear, equidistant row of alternately charged ions. If the reference ion is one of the row, the summation gives a well known series, namely:

$$2\left(1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} \ldots\ldots\right) = 2\, ln.\, 2. = 1.3863 \qquad (4)$$

If, however, the ion is outside the row, the summation is by no means so simple. MADELUNG evolved the distribution of electric charge along the line of the row into a FOURIER

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[1] MADELUNG E.: Physik. ZS. **19**, 524 (1918).

series, which means that he replaced the discrete charges by a number of superimposed continuous charges, having charge densities varying as cosine functions. In practice only two members of the Fourier series need consideration, namely that having the ionic distance as period, and that having one third of this distance as period. The problem is now reduced to the determination of the potential energy of an ion with respect to a linear charge the density of which varies as a cosine function. This problem can be solved by means of high mathematics, the solution involving a cylinder function, namely Hankel's function that is tabulated in Jahnke and Emde's Funktionentafel[1]. The potential energy was found to decrease considerably with the distance between the ion and the row, and hence the summing up of the contributions of comparatively few rows sufficed to give a reasonably accurate value of Madelung's constant for the entire lattice. Ewald[2] has proposed another method which, however, is still less understandable to persons not acquainted with the highest of mathematics.

Now it is not my opinion that the use of high mathematics to physical chemical problems should be abandoned, since in many cases there is no other way, still if a more elementary way can be found this is worth while, because a considerably greater number of persons will then be able to understand the derivation. That an elementary method of calculating Madelung's constant can be derived, which is even less cumbersome as regards the numerical calculation than the above methods, I should like to show:

It is a familiar fact that crystals, growing from a solution, as a rule acquire a nearly perfect external shape. This is

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[1] Jahnke F. and Emde E.: Funktionentafel. Leipzig (1909) p. 135.

[2] Ewald P. P.; Ann. d. Physik. **64**, 253 (1921).

not accidental, on the contrary, we must infer that the perfect crystal is more probable, and this again can only be explained by the internal energy or the lattice energy of the perfect crystal attaining a maximum value. This value depends on the size of the crystal, but only slightly, as will be seen later; this is in agreement with the fact that the solubility of small crystals is only slightly greater than that of large crystals, granted of course that the crystals are perfect. In order that the lattice energy of even a small crystal shall approach closely to that of an infinite crystal, the crystal must not only be perfect in every way, but it must presumably also be electro-neutral, i. e. it must contain equal numbers of positive and negative charges. The fact that a maximum of lattice energy has been attained, means that the forces on the outside charge neutralize each other, which can only be the case if the crystal is electro-neutral.

The new method of calculating electrostatic lattice energy is the following: In the case of the smallest possible perfect and electro-neutral crystal we sum up the reciprocals of the relative distances between one reference ion and all other ions in the crystal whereby a value j_1 of the MADELUNG constant for the minute crystal is obtained. Afterwards the crystal is allowed to grow equally in all directions by deposit of a mono-ionic layer or a layer of crystal units, and in this way a larger perfect and electro-neutral crystal is built. Now the reciprocals of the distances between the above reference ion and the ions of the newly deposited layer are summed up as before, and a value j_2 is obtained which is termed the contribution of the second division. In a similar manner we determine the contributions of the subsequent divisions. Now it will be observed that these contributions diminish exceedingly with the distance from the reference ion, and as a rule only few contributions need be summed up to give practically the entire electrostatic lattice energy of the infinite lattice.

In order to demonstrate the method by the simplest example we will consider a two-dimensional lattice, for

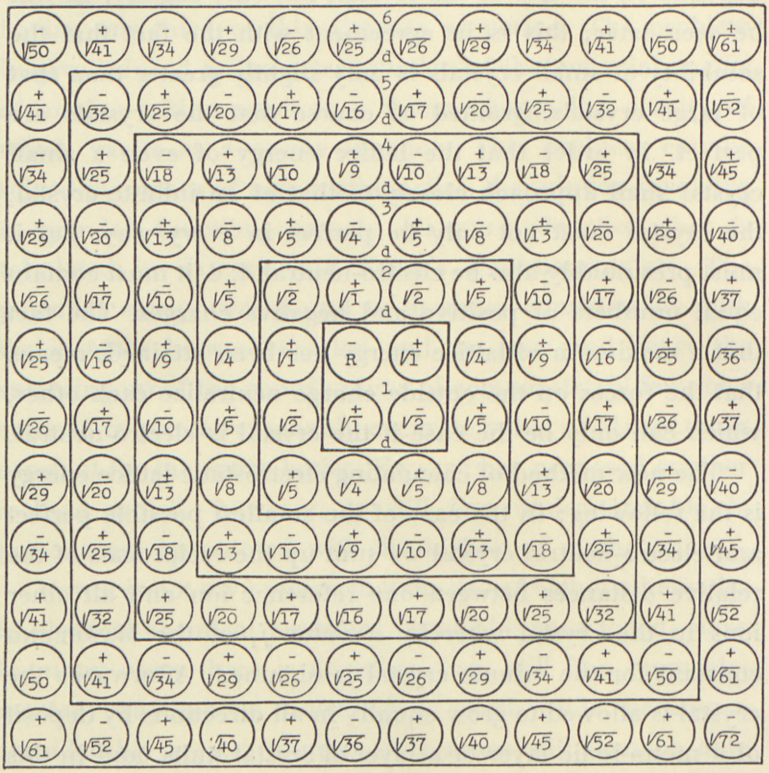

Fig. 1.

instance, an ion bearing (1, 0, 0) plane of the NaCl lattice, see Fig. 1. In this the reference ion is marked *R*, and the relative distances from the reference ion are written in the circles representing the other ions. This relative distance can always be expressed by $\sqrt{n}$ where *n* is a whole number, which facilitates the calculus, as $1/\sqrt{n}$ is tabulated in Barlow's tables of squares and cubes. The ions are classified into divisions as will be seen from the figure, each new division forming a frame around the former one. The summation was carried out on a calculating machine, and the following contributions were found.

1 division: $\frac{2}{1}-\frac{1}{\sqrt{2}}$ $= 1.29289$

2 division: $\frac{2}{1}-\frac{3}{\sqrt{2}}-\frac{2}{\sqrt{4}}+\frac{4}{\sqrt{5}}-\frac{1}{\sqrt{8}}$ $= 0.31398$

3 division: $= 0.00365$

4 division: $= 0.00299$

5 division: $= 0.00098$

6 division: $= 0.00044$

Total 1.61493 ± 0.001

The electrostatic lattice energy of the entire NaCl lattice is more important. The smallest possible crystal of NaCl consists of eight ions forming a cube. The reference ion is one corner of this cube. The subsequent divisions form something similar to a system of Chinese boxes. The calculation was carried out as above using Barlow's tables and the calculating machine. The following contributions were obtained:

1 division: $\frac{3}{1}-\frac{3}{\sqrt{2}}+\frac{1}{\sqrt{3}}$ $= 1.456030$

2 division: $\frac{3}{1}-\frac{9}{\sqrt{2}}+\frac{7}{\sqrt{3}}-\frac{3}{\sqrt{4}}+\frac{12}{\sqrt{5}}-$

$-\frac{12}{\sqrt{6}}-\frac{3}{\sqrt{8}}+\frac{6}{\sqrt{9}}-\frac{1}{\sqrt{12}}$ $= 0.295739$

3 division: $= -0.004729$

4 division: $= 0.000679$

5 division: $= -0.000221$

Total 1.747498 ± 0.0005

Note! that a value of 1.7518, which is only 3 per mille in error, can be obtained from the first two divisions. This will suffice to demonstrate for students how Madelung's constant may be determined. In order to approximate Madelung's constant as closely as possible from the above data, the contributions of the subsequent divisions have been evaluated by extrapolation. In diagram 2 the logaritms of the numerical values of the above contributions are plotted against the numbers of the divisions, and the logaritms of the subsequent contributions are graphically extrapolated. In this manner we found:

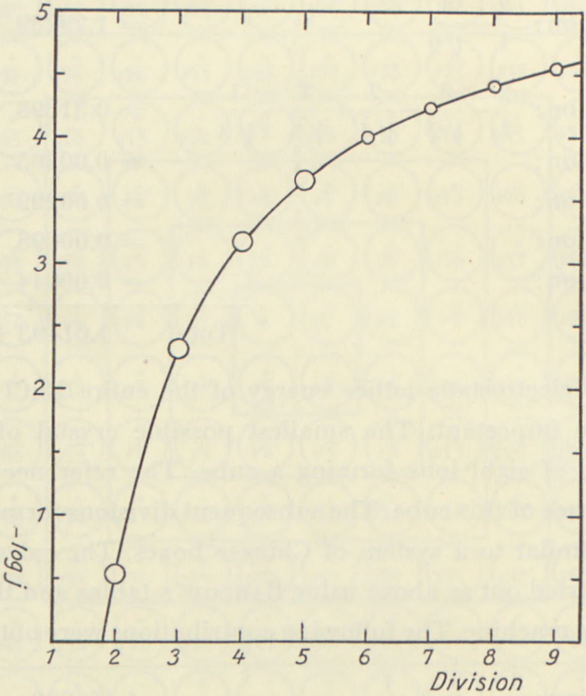

Fig. 2.

6 division: = 0.000100
7 division: = −0.000059
8 division: = 0.000040
9 division: = −0.000028
estimated for further divisions = 0.000007

Total 0.000060
added to the above 1.747498

we obtain as our most accurate value 1.747558

This is very close to the values found by MADELUNG l. c. and by EMERSLEBEN[1] who found: 1.747557.

KOSSEL[2] has calculated the energy involved in placing an ion anywhere at the surface of a NaCl crystal. He found that this energy depends, in a large measure, on the position of the ion, and thus explains why crystals grow in a definite habit. The different energy terms determined by KOSSEL can easily be derived from the above values of the electrostatic energy of an ion with respect to a row, a plane layer, or a three-dimensional lattice of ions. We can, for instance, determine the energy gained by placing an ion in the proper position outside a plane (1, 0, 0) surface of a large NaCl crystal. In order to do that we will consider an ion inside a large NaCl crystal, its electrostatic energy with respect to all other ions being expressed by MADELUNG's constant 1.7476. We are now removing all ions except the reference ion in a (1, 0, 0) layer. The energy required for removing these ions from the reference ion was determined above to be 1.6149. The energy left, i. e. 1.7476 — 1.6149 = 0.1327 is the energy of the reference ion placed properly outside

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[1] EMERSLEBEN O.: Physik. ZS. **24**, 104 (1923).

[2] KOSSEL W. in a monograph edited by FALKENHAGEN: Quantentheorie und Chemie.

the (1, 0, 0) surfaces of two crystals, hence this energy is just twice the energy to be determined. We find 0.0663, whereas Kossel found 0.0662. In a similar manner we find the energy gained by placing an ion properly outside the edge of a (1, 0, 0) layer to be equal to: $^1/_2(1.6149 - 1.3863) = 0.1143$, whilst Kossel found 0.1144. We are thus able to confirm Kossel's data.

The Electrostatic Lattice Energy of the Calcite and the Sodium Hydrofluoride Lattices.

The electrostatic lattice energy has, as far as I know, only been calculated for the NaCl lattice, the CsCl lattice, the ZnS lattices (both blende and wurtzite), the CaF_2 lattice, the Cu_2O lattice and the two TiO_2 lattices (rutile and anatase)[1]. The calcite lattice is one of the simplest and most important among the lattices which, as I believed, had not been considered earlier; afterwards, however, I perceived that Evjen[2] had already considered the idealized calcite lattice. Later on Evjens data will be compared with mine. As we do not know how the electric charge of the carbonate ion is distributed, the lattice will be idealized in such a way that the total charge becomes located at the centre of the ion, i. e. on the carbon atom. It is not likely that the distribution of electricity inside the carbonate ion will affect the lattice energy to any great extent. By this idealization the calcite lattice becomes equivalent to a NaCl lattice, compressed along a trigonal axis. In a similar manner the $NaHF_2$ lattice corresponds to a NaCl lattice, expanded along

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[1] For references see: Born M. and Bollnow O. F.: Hdb. d. Physik. **24**, 438 (1927).

[2] Evjen H. M.: Physical Review. **39**, 680 (1932).

a trigonal axis. The ions in the planes perpendicular to the trigonal axis are all alike, and form a net-work of equilateral triangles; the distances between ions in such a plane are not altered by compression or expansion, but so are the distances between the ionic layers. The distance between neighbouring layers, which is the smallest intercept on the principal axis, will be employed for a standard distance L_0. The distances within the layer can be expressed by $L_1 \sqrt{m}$, where m is a whole number, and L_1 the radius of a circle circumscribing the equilateral triangle. The ratio $p = \frac{L_1}{L_0}$ is used for the parameter of the lattice. We are going to calculate the values of Madelung's factor j for a number of parameters, and in order to facilitate the calculation the parameters chosen are square roots of whole numbers; the distance between any two ions may then be expressed by $L_0 \sqrt{n}$ where n is a whole number, whence Barlow's tables can be employed as before.

The ions in the lattice are classified into divisions as before, but now these divisions are rhombohedral shells, and as a rule not cubical. A model of the NaCl lattice, and drawings of its (1, 1, 1) planes, were of great use in classifying and calculating relative distances. These drawings, however, are not reproduced, as they would occupy too much space, it is considered sufficient to give the (squares of) the relative distances between the reference ion and the other ions in the inner rhombohedron (Table 1) and those between the reference ion and the ions in the second division (Table 2).

The squares of the distances from the principal axis through the reference ion is given in the first column, and the square of the distance from the layer containing the reference ion is given in the second column. The last column gives the

Table 1. Inner Rhombohedron or 1st Division.

dist. from axis	dist. from layer	parameter						number
		1	$\sqrt{2}$	$\sqrt{3}$	$\sqrt{4}$	$\sqrt{5}$	$\sqrt{8}$	
		square of distance						
1	1	2	3	4	5	6	9	+ 3
1	4	5	6	7	8	9	12	− 3
0	9	9	9	9	9	9	9	+ 1

Table 2. 1st Rhombohedral Shell or 2d Division.

dist. from axis	dist. from layer	parameter						number
		1	$\sqrt{2}$	$\sqrt{3}$	$\sqrt{4}$	$\sqrt{5}$	$\sqrt{8}$	
		square of distance						
1	1	2	3	4	5	6	9	+ 3
1	4	5	6	7	8	9	12	− 3
0	9	9	9	9	9	9	9	+ 1
4	1	5	9	13	17	21	33	+ 3
3	0	3	6	9	12	15	24	− 6
9	0	9	18	27	36	45	72	− 3
4	1	5	9	13	17	21	33	+ 3
7	1	8	15	22	29	36	57	+ 6
4	4	8	12	16	20	24	36	− 3
7	4	11	18	25	32	39	60	− 6
3	9	12	15	18	21	24	33	+ 6
9	9	18	27	36	45	54	81	+ 3
1	16	17	18	19	20	21	24	− 3
4	16	20	24	28	32	36	48	− 3
1	25	26	27	28	29	30	33	+ 3
0	36	36	36	36	36	36	36	− 1

number of ions having the same distance, the sign plus indicating attraction, and the sign minus repulsion.

The cases considered above were those in which the parameter p is the square root of a whole number. A calculation has, however, also been carried out in some cases where the number under the surd was a simple fraction $\sqrt{\frac{k}{l}}$.

In order to make use of Barlow's tables, we were here obliged to choose another standard distance, namely one which is a $\sqrt{l}$ part of the distance between the layers. In this way the relative distances between the ions become expressed by square roots of whole numbers. Afterwards when the reciprocals have been summed up to give the contribution of the division, we may transfer to the usual value of L_0 by multiplying the total by $\sqrt{l}$. Such transferred values for the contributions are quoted in the following table 3 together with the values obtained by means of the above tables 1 and 2.

Table 3. Madelung's Factor for the Idealized Calcite Lattice.

Parameter	$\sqrt{\frac{1}{2}}$	$\sqrt{\frac{2}{3}}$	1	$\sqrt{\frac{3}{2}}$
1 division........	+ 1.3686	+ 1.2684	+ 1.1130	+ 0.9515
2 division........	− 0.4178	− 0.1651	+ 0.0462	+ 0.1441
3 division........	+ 0.0761	+ 0.0505	+ 0.0211	+ 0.0040
4 division........	− 0.0284	− 0.0198	− 0.0098	− 0.0029
Total	+ 0.9985	+ 1.1340	+ 1.1705	+ 1.0967

Parameter	$\sqrt{2}$	$\sqrt{3}$	$\sqrt{4}$	$\sqrt{5}$	$\sqrt{8}$
1 division........	+ 0.8406	+ 0.6994	+ 0.6143	+ 0.5581	+ 0.4673
2 division........	+ 0.1707	+ 0.1747	+ 0.1660	+ 0.1572	+ 0.1416
3 division........	− 0.0027	− 0.0092	− 0.0137	− 0.0175	− 0.0264
4 division........	+ 0.0004	+ 0.0035	+ 0.0049	+ 0.0058	+ 0.0075
Total	+ 1.0090	+ 0.8684	+ 0.7715	+ 0.7036	+ 0.5900

The parameter value $\sqrt{2}$ corresponds to the undeformed NaCl lattice considered page 141; hence it is an important check on the calculation to compare the present values of the contributions, division by division, with those found before. The earlier standard distance is $\sqrt{3}$ times as large as the present one, and hence each of the former contributions should be $\sqrt{3}$ times as large as the present one. For the total we find: $1.0090 \times \sqrt{3} = 1.74764$, whereas the first four divisions on page 141 gave a total of 1.74772. The discrepancy of 0.05 per mille gives a measure of the inaccuracy of the calculation itself. In the case of the NaCl lattice, i. e. for the parameter value $\sqrt{2}$, the electrostatic potential energy of an inner ion in a minute crystal consisting of 512 ions is practically equal to that of an ion in an infinite crystal, for other values of the parameter this will not be the case. A measure of the error, due to the neglection of outside ions, can be obtained in the case of the parameter value $\sqrt{8}$. For this value the deformed NaCl lattice becomes a CsCl lattice, as will be observed when the values of relative distances in tables 1 and 2 are examined. An accurate value of Madelung's constant for the infinite CsCl lattice has been calculated by Emersleben l. c. who (on Ewald's method) found a value of 2.035356 using the lattice spacing for a standard distance; transferring this to our standard distance by dividing by $\sqrt{12}$ we obtain a value of 0.587557. The difference of 4.1 per mille between this value and our corresponding value of 0.5900 is a measure of the error arising from our neglection of the outside ions. This is the case with the parameter value $\sqrt{8}$, for the value $\sqrt{2}$ the error is insignificant, hence we expect this error not to exceed, at any rate, one per cent, not only in the interval between the parameter values of $\sqrt{2}$ and $\sqrt{8}$, but also between those of $\sqrt{2}$ and $\sqrt{\frac{1}{2}}$. In the case of the CsCl lattice we have not approached the accuracy of Emersleben's calculations, as we did in the case of the NaCl lattice, still it is of pedagogical interest that a reasonably accurate value of MADELUNG's constant can be calculated by the elementary method also in the case of the CsCl lattice.

The following empirical formula was derived using the values of the totals from table 3 corresponding to the parameters $\sqrt{\frac{1}{2}}$, $\sqrt{\frac{2}{3}}$, 1, $\sqrt{2}$ and $\sqrt{5}$:

$$j = +0.3573 + 2.085\frac{1}{p^2} - 1.9185\frac{1}{p^4} + 0.7754\frac{1}{p^6} - 0.1286\frac{1}{p^8}; \quad (5)$$

The parameters not employed in the adjustment of the formula showed the following deviations: for $p = \sqrt{\frac{3}{2}}$, -2.2 per mille; for $p = \sqrt{3}$, $+2.5$ per mille; for $p = \sqrt{4}$, $+1.5$ per mille, and for $p = \sqrt{8}$, $+1.8$ per mille. To this must be added the more significant error due to the neglection of outside ions, whence the total error becomes of the order of one per cent.

The electrostatic part of the lattice energy of one gram-molecule can be calculated by means of the equations (2) and (3). In the present case ν and ν_1 are equal, and Φ_1 and Φ_2 are equal, whereas u and v are both equal to unity, and hence these equations may be reduced to:

$$\Phi = Ne^2\frac{\nu^2 j}{L_0} = 3.300 \times 10^{-6}\frac{\nu^2 j}{L_0}\,\text{k cal.} \quad (6)$$

The numerical factor is computed, using the value of 6.061×10^{23} for AVOGADRO's number N, and 4.774×10^{-10} e. s. u. for the electronic charge e; furthermore, the conversion factor 4.185×10^{10} is employed in order to express the energy in kcal. Experimental and calculated data are given in table 4.

Table 4. The Electrostatic Lattice Energy pro Grammolecule
of compounds crystallizing in the calcite or the $NaHF_2$ lattice.

	ν	a_h Å	c_h Å	L_0 Å	p	j	Φ kcal.
$NaNO_3$........	1	4.98	16.56	1.380	2.05	0.756	180
$MgCO_3$........	2	4.60[1]	15.21[1]	1.268	2.10	0.741	772
$CaCO_3$........	2	4.98[1]	17.04[1]	1.421	2.01	0.769	714
$ZnCO_3$........	2	4.65[1]	14.98[1]	1.249	2.14	0.729	771
$CdCO_3$........	2	4.91[1]	16.25[1]	1.355	2.09	0.743	724
$MnCO_3$........	2	4.85[1]	15.52[1]	1.294	2.16	0.724	739
$FeCO_3$........	2	4.67[1]	15.25[1]	1.272	2.12	0.735	762
$ScBO_3$........	3	4.75[1]	15.27[1]	1.274	2.15	0.727	1690
$InBO_3$........	3	4.77[1]	15.46[1]	1.289	2.13	0.724	1670
YBO_3.........	3	5.06[1]	17.21[1]	1.435	2.03	0.762	1580
$NaHF_2$........	1		13.84[3]	2.305	0.855	1.155	165
NaN_3.........	1	3.64[2]	15.20[2]	2.533	0.830	1.145	149

[1] Goldschmidt V. M. and Hauptmann H.: Nachr. Göttingen. III. **16**. (1932).
[2] Hendricks S. B. and Pauling L.: Journ. Amer. Chem. Soc. **47**, 2906 (1925).
[3] Andersen C. C. and Hassel O.: Z. physik. Chem. **123**, 151 (1926).

ν is the valency; a_h is the translation in the direction of the secondary axis, and c_h the translation in the direction of the principal axis (the hexagonal axes). The standard distance L_0 is the distance between ionic layers perpendicular to the principal axis, hence in the case of the calcite lattice it is ${}^{c_h}\!/_{12}$ and in the case of the $NaHF_2$ lattice it is ${}^{c_h}\!/_{6}$. The parameter p was defined as $\frac{L_1}{L_0}$ where L_1 is equal to ${}^{a_h}\!/_{\sqrt{3}}$.

The electrostatic lattice energies of the above carbonates and borates are considerable and these compounds are consequently insoluble in water. Goldschmidt and Hauptmann were aware of this and remarked furthermore that $ScBO_3$ and $InBO_3$ are resistant even against strong acids. It is likely that future methods of isolating scandium will be based on the stability of scandium borate. GOLDSCHMIDT and HAUPTMANN also determined the hardness which increases in the sequence $LiNO_3$, $MgCO_3$ and $ScBO_3$.

After the above paper had been written I perceived that EVJEN[1] had already proposed a similar method of determining MADELUNG's constant. In order to demonstrate the similarity and the difference between EVJEN's method and the present one it is found appropriate, verbatim, to quote the following sentences from EVJEN's paper:

"This immediately suggests a simple method of calculating the MADELUNG constant: Sum directly the potentials of the ions over a cube of side *nd* around the origin. The potentials of the ions inside the cube are summed in the ordinary manner each being given unit weight; the potentials of the ions forming the surface of the cube, however, are given the weights $^1/_2$, $^1/_4$ or $^1/_8$ according as they are situated on a face, an edge or a corner of the cube. This procedure, of course, is equivalent to summing by cells rather than by ions."

The last sentence quoted expresses the essential difference between EVJEN's method and the present one.

EVJEN has furthermore calculated MADELUNG's constant for the idealized calcite lattice. He used MADELUNG's method, and gives his results as a curve in a diagram on rather too small a scale. In order to compare his results with mine I have transferred my data to his standard distance, which is always the smallest distance between neighbour ions; and to his parameter, an angle φ the tan of which is $\frac{p}{4}$. The data thus transformed have been plotted as points (crosses)

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[1] EVJEN H. M.: Physical Review. **39**, 680 (1932).

into the diagram, Fig. 3. It will be observed that, especially in a region about $\varphi = 25°$, the agreement is not particularly good, the deviation amounting to about 1.3 per cent. Now one might raise the objection to my calculation that perhaps this deviation arises from the neglection of ions outside the rhombohedron of 512 ions. In view of this I have calculated the contribution of one more shell of ions, i. e. a 5th division, for the case of $p = \sqrt{4}$ or $\varphi = 26.56°$. I found a value of —0,0028 for this contribution. Using this, together with the other contributions for the case of the parameter $\sqrt{4}$ in table 3, for an extrapolation similar to that shown in Fig. 2, I found a value of 0.7699 for Madelung's factor. This is all on the basis of the old standard distance; transferring that to the present standard distance, i. e. the smallest distance between neighbour ions, I got a value of 1.722.

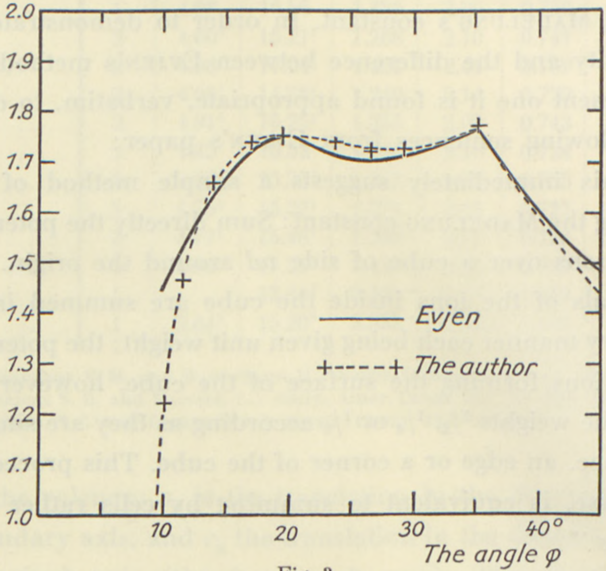

Fig. 3.

This most accurate value, which is probably no more than 1 per mille in error, is 2 per mille below my former value, but more than 10 per mille above Evjen's curve. Hence we are probably allowed to conclude that our calculations are the more accurate.

Summary.

The electrostatic lattice energy of a salt crystal cannot be evaluated by an uncritical summation, because the electrostatic force is a long range force, and the number of ions increases considerably with the distance. MADELUNG therefore applied a mathematical artifice in order to carry out the calculation. It is, however, found that a direct summation is feasible provided that it proceeds on a definite plan; this plan being founded on the experience that crystals of a nearly perfect shape can be obtained by crystallization. Perfect electro-neutral crystals were therefore used as stages in the calculation, and it was found that the lattice energy of even a small but perfect crystal comes close to that of an infinite crystal. Thus the electrostatic energy of an inner ion in a NaCl cube of 64 ions is no more than three per mille different from the lattice energy of an infinite NaCl lattice. By means of crystal cubes containing up to 1000 ions a value of 1.747558 has been extrapolated for MADELUNG's constant of the NaCl lattice in perfect agreement with EMERSLEBEN.

If the electric charge of the anion is assumed to be located at the centre, the calcite and $NaHF_2$ lattices may be described as a NaCl lattice deformed by being compressed or expanded along a trigonal axis. By the deformation a cube becomes a rhombohedron, and the lattice acquires a parameter determining the relative dimensions of the rhombohedron. The electrostatic energy of an inner ion with respect to all other ions in a rhombohedric crystal of 512 ions has been calculated in the case of nine values of the parameter, and an empiric formula for the variation of Madelung's factor with the parameter has been derived. The value of the electrostatic part of the lattice energy has been calculated in kcal, for $NaNO_3$, $MgCO_3$, $CaCO_3$, $ZnCO_3$, $CdCO_3$, $MnCO_3$, $FeCO_3$, $ScBO_3$, $InBO_3$, YBO_3, $NaHF_2$ and NaN_3. Evjen has earlier calculated Madelung's factor for the idealized calcite lattice, and in a diagram his data are compared with mine.

This work was carried out in "Den kongelige Veterinær- og Landbohøjskoles kemiske Laboratorium". I thank the head of the Laboratory, Professor Dr. phil. N. Bjerrum for his interest and for the readiness with which apparatus and materials were procured.

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MENGENFUNKTIONEN UND KONVEXE KÖRPER

VON

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§ 1. Einleitung.

Der formale Apparat der Brunn-Minkowskischen Theorie der konvexen Körper ist bisher nur für Polyeder und für Körper mit hinreichend glatter Berandung entwickelt worden; insbesondere liegen Formeln für die gemischten Volumina, auf denen die Beweise mehrerer wichtigen Sätze beruhen, nur für solche Körper vor. In vielen Fällen kann man mit Hilfe dieses Apparates Sätze für beliebige konvexe Körper beweisen, indem man durch Polyeder oder glatte Körper approximiert. In anderen Fällen hat dies aber zur Folge, dass bereits die allgemeine Formulierung der betreffenden Sätze unmöglich ist. Nun liegt es nahe zu vermuten, dass die in Ausdrücken für die gemischten Volumina von Polyedern bzw. glatten Körpern auftretenden Summen bzw. Integrale als Spezialfälle von Stieltjes-Integralen in Bezug auf total additive Mengenfunktionen auf der Oberfläche der Einheitskugel aufgefasst werden können. In der vorliegenden Arbeit zeigen wir, dass dies in der Tat der Fall ist und verwenden den so erweiterten Apparat, um einige Sätze der Theorie von bisher gemachten unnötigen Einschränkungen zu befreien.

Der entscheidende Begriff ist der der Oberflächenfunktion eines beliebigen konvexen Körpers. Es ist dies diejenige Mengenfunktion auf der Einheitskugel Ω, deren Wert für eine vorgeschriebene Menge ω von Ω gleich dem Flächeninhalt der Menge derjenigen Randpunkte des Körpers ist, durch die eine Stützebene mit zu ω gehöriger Normalenrichtung geht. Die dabei zur Verwendung kommende Flächeninhaltsdefinition ist eine dem vorliegenden Zweck angepasste Modifikation der Minkowskischen und führt ähnlich wie diese die Flächeninhaltsbestimmung auf Volumenbestimmung von Normalenmengen zurück. Für hinreichend glatte Körper ist diese Oberflächenfunktion das unbestimmte Integral der reziproken Gaußschen Krümmung der Randfläche als Funktion der Normalenrichtung.

Als ein Hauptresultat ergibt sich die vollständige Charakterisierung derjenigen Mengenfunktionen, die als Oberflächenfunktionen konvexer Körper auftreten können. Für Körper mit inneren Punkten zeigen wir: Zu jeder nicht negativen, total additiven Mengenfunktion auf der Kugel, die gewissen, trivialerweise notwendigen Bedingungen genügt, gibt es einen bis auf Translationen eindeutig bestimmten konvexen Körper, dessen Oberflächenfunktion sie ist.

Dieser Satz ist die natürliche Verallgemeinerung des Satzes von Minkowski, dass es ein, und bis auf Translationen nur ein konvexes Polyeder gibt, dessen Normalenrichtungen und Flächeninhalte der Seitenflächen mit gewissen trivialerweise notwendigen Einschränkungen willkürlich vorgeschrieben sind.

Durch Grenzübergang gewinnt Minkowski aus diesem Satz einen entsprechenden Satz für eine Klasse konvexer Körper, die er als stetig gekrümmt bezeichnet. Von einem solchen Körper $\mathfrak{K}$ wird verlangt, dass es eine positive stetige Funktion $F(\xi)$ auf der Einheitskugel derart gibt, dass für jeden konvexen Körper $\mathfrak{H}$ mit der Stützfunktion $H(\xi)$ das gemischte Volumen

$$V(\mathfrak{H},\mathfrak{K},\mathfrak{K}) = \frac{1}{3}\int_{\Omega} H(\xi)\, F(\xi)\, M(d\Omega)$$

ist, wo $M(d\Omega)$ das Mass des Flächenelementes $d\Omega$ der Einheitskugel Ω bedeutet. Diese sogenannte Krümmungsfunktion $F(\xi)$, die für hinreichend glatte Körper die reziproke Gaußsche Krümmung ist, wird also nicht differentialgeometrisch definiert, sondern durch unendlich viele Integralbedingungen festgelegt, und es bleibt bei Minkowski unentschieden, ob bei einem in diesem Sinne stetig gekrümmten Körper $\mathfrak{K}$ die Funktion $F(\xi)$ die übliche differentialgeometrische Deutung zulässt. Im Folgenden wird gezeigt, dass die Oberflächenfunktion eines beliebigen konvexen Körpers den obigen analogen Integralrelationen genügt und durch diese eindeutig bestimmt ist. Für einen im Minkowskischen Sinne stetig gekrümmten Körper mit der Krümmungsfunktion $F(\xi)$ folgt hieraus, dass seine Oberflächenfunktion gleich dem unbestimmten Integral von $F(\xi)$ ist, und damit, dass $F(\xi)$ die Ableitung der Oberflächenfunktion, also der Grenzwert des Quotienten entsprechender Flächeninhalte auf der Körperberandung und der Einheitskugel ist.

Für die Theorie der konvexen Körper verweisen wir, was Bezeichnungen, Resultate und Hinweise auf Originalliteratur betrifft, stets auf T. Bonnesen und W. Fenchel: »Theorie der konvexen Körper«[1]. Ebenso wie dort wird im Folgenden der n-dimensionale euklidische Raum zugrunde gelegt.

In § 2 stellen wir die erforderlichen Hilfsmittel aus der Theorie der total additiven Mengenfunktionen auf der Einheitskugel zusammen.

In § 3 führen wir die Oberflächenfunktion eines konvexen Körpers zunächst als Grenzfunktion von (in naheliegender Weise zu definierenden) Oberflächenfunktionen

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[1] Ergebnisse der Mathematik, Bd. 3, Heft 1, Berlin 1934; im folgenden kurz als »Bericht« zitiert.

konvexer Polyeder ein und zeigen, dass sie sich durch Integralrelationen der oben erwähnten Art charakterisieren lässt.

In § 4 beweisen wir dann den genannten Hauptsatz über die Bestimmung eines konvexen Körpers durch die Oberflächenfunktion. Wir gehen dabei wie Minkowski vom entsprechenden Polyedersatz aus und folgen überhaupt dem Minkowskischen Gedankengang.

In § 5 führen wir für $n-1$ beliebige konvexe Körper eine gemischte Oberflächenfunktion ein, die mit den gemischten Volumina durch gewisse Integralrelationen verknüpft und durch diese Relationen charakterisiert ist.

Als Spezialfälle hiervon betrachten wir in § 6 die gemischten Oberflächenfunktionen eines Körpers mit der Einheitskugel und zeigen, dass ein konvexer Körper auch durch jede dieser Funktionen bis auf Translationen eindeutig bestimmt ist. Für hinreichend glatte Körper sind diese Mengenfunktionen bis auf konstante Faktoren die unbestimmten Integrale der Krümmungsfunktionen des Körpers, d. h. der elementarsymmetrischen Funktionen der Hauptkrümmungsradien der Randfläche als Funktionen der Normalenrichtung.

Schliesslich kommen wir in § 7 auf die Definition der Oberflächenfunktion eines konvexen Körpers zurück und zeigen, dass man zu diesem Begriff statt wie in § 3 durch Polyederapproximation auch dadurch gelangt, dass man die Minkowskische Flächeninhaltsdefinition in der oben angedeuteten Weise auf beliebige Teilmengen der Körperberandung überträgt.[1]

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[1] Während der Ausarbeitung dieser Untersuchung erschien eine Arbeit von A. Alexandroff: Zur Theorie der gemischten Volumina von konvexen Körpern. I. Verallgemeinerung einiger Begriffe der Theorie von konvexen Körpern. [Rec. math. Moscou **44**, 947—970 u. deutsche Zusammen-

§ 2. Über nicht negative, total additive Mengenfunktionen auf der Kugel.

Es sei Ω die Oberfläche $|\xi| = 1$ der Einheitskugel des n-dimensionalen Raumes. Wir betrachten total additive, nicht negative Mengenfunktionen $\Phi(\omega)$, die für alle Borel-Mengen ω von Ω definiert sind. Wenn im folgenden von Mengenfunktionen die Rede ist, sind stets Funktionen mit diesen Eigenschaften gemeint. Wir werden vielfach eine Mengenfunktion $\Phi(\omega)$ als Massenbelegung von Ω auffassen und die entsprechende massengeometrische Terminologie verwenden. Das Integral[1] einer Funktion $G(\xi)$ über eine Borel-Menge ω von Ω mit Bezug auf eine Mengenfunktion $\Phi(\omega)$ schreiben wir

$$\int_{\omega} G(\xi)\, \Phi(d\Omega).$$

Das Mass auf Ω bezeichnen wir mit $M(\omega)$.

I. *Zwei Mengenfunktionen Φ und Ψ mit der Eigenschaft, dass für jede auf Ω stetige Funktion $G(\xi)$*

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fassung 970—972 (1937)] (Russisch). Wie wir aus dem deutschen Auszug entnehmen, verfolgt Alexandroff dieselben Ziele und führt in dem vorliegenden ersten Teil seiner Arbeit die Oberflächenfunktionen und gemischten Oberflächenfunktionen ein, und zwar, wie uns scheint, auf einem anderen Wege.

[1] Vgl. J. Radon: Theorie und Anwendungen der absolut additiven Mengenfunktionen. [S.—B. Akad. Wiss. Wien Abt. IIa, **122**, 1295—1438 (1913)]. Die im Folgenden vorkommenden Integrale existieren im allgemeinen im Sinne der ersten, der Riemannschen analogen Definition von Radon (S. 1322—1324). Für die Beweise der anzuführenden Sätze ist jedoch die systematische Verwendung der zweiten, allgemeineren, der Lebesgueschen analogen Definition (S. 1324—1328) zweckmässig. Zum Teil finden sich diese Sätze explizit bei Radon. Die übrigen Behauptungen können bekanntlich mit den von Radon entwickelten Hilfsmitteln bewiesen werden.

$$\int_{\Omega} G(\xi)\, \Phi(d\Omega) = \int_{\Omega} G(\xi)\, \Psi(d\Omega)$$

gilt, sind identisch.

Eine Borel-Menge ω von Ω heisst Stetigkeitsmenge der Mengenfunktion $\Phi(\omega)$, falls

$$\Phi(\overline{\omega}) = \Phi(\tilde{\omega})$$

ist, wo $\overline{\omega}$ die abgeschlossene Hülle und $\tilde{\omega}$ den offenen Kern (in Bezug auf Ω) von ω bedeuten. Ω selbst ist offenbar immer Stetigkeitsmenge. Gilt für zwei Mengenfunktionen Φ und Ψ die Ungleichung

$$\Phi(\omega) \leqq \Psi(\omega)$$

für alle gemeinsamen Stetigkeitsmengen von Φ und Ψ, so gilt sie für alle Borel-Mengen. Zwei Mengenfunktionen, die für alle gemeinsamen Stetigkeitsmengen denselben Wert haben, sind identisch.

Eine Folge von Mengenfunktionen $\Phi_1, \Phi_2, \ldots$ heisst konvergent, wenn es eine Mengenfunktion Φ derart gibt, dass

$$\Phi_\nu(\omega) \to \Phi(\omega)$$

für jede Stetigkeitsmenge ω von Φ. Die Mengenfunktion Φ ist dann eindeutig bestimmt und heisst die Grenzfunktion der Folge. Wir schreiben

$$\Phi_\nu \to \Phi.$$

Notwendig und hinreichend hierfür ist, dass

$$\Phi_\nu(\Omega) \to \Phi(\Omega)$$

und

$$\varliminf_{\nu \to \infty} \Phi_\nu(\omega) \geqq \Phi(\omega)$$

für jedes offene ω gilt.

II. *Eine Folge* $\Phi_1, \Phi_2, \dots$ *von Mengenfunktionen ist dann und nur dann konvergent, wenn*

$$\lim_{\nu \to \infty} \int_{\Omega} G(\xi)\, \Phi_\nu(d\Omega)$$

bei jedem stetigen $G(\xi)$ *auf* Ω *existiert. Ist* Φ *die Grenzfunktion der Folge, so gilt bei jedem stetigen* $G(\xi)$

$$\lim_{\nu \to \infty} \int_{\Omega} G(\xi)\, \Phi_\nu(d\Omega) = \int_{\Omega} G(\xi)\, \Phi(d\Omega),$$

und sogar gleichmässig in jeder Menge von gleichartig gleichmässig stetigen Funktionen $G(\xi)$.

Ausschlaggebend für das Folgende ist, dass man in den Sätzen I und II nicht beliebige stetige Funktionen $G(\xi)$ zu betrachten braucht, sondern sich auf Stützfunktionen konvexer Körper beschränken darf. Es gelten mit anderen Worten die Sätze:

III. *Zwei Mengenfunktionen* Φ *und* Ψ *mit der Eigenschaft, dass für jede Stützfunktion* $H(\xi)$

$$\int_{\Omega} H(\xi)\, \Phi(d\Omega) = \int_{\Omega} H(\xi)\, \Psi(d\Omega)$$

gilt, sind identisch.

IV. *Eine Folge* $\Phi_1, \Phi_2, \dots$ *von Mengenfunktionen ist dann und nur dann konvergent, wenn*

$$\lim_{\nu \to \infty} \int_{\Omega} H(\xi)\, \Phi_\nu(d\Omega)$$

bei jeder Stützfunktion $H(\xi)$ *existiert. Ist* Φ *die Grenzfunktion der Folge, so gilt für jede Stützfunktion* $H(\xi)$

$$\lim_{\nu \to \infty} \int_{\Omega} H(\xi)\, \Phi_\nu(d\Omega) = \int_{\Omega} H(\xi)\, \Phi(d\Omega),$$

und sogar gleichmässig in jeder Menge von gleichartig gleichmässig stetigen Funktionen $H(\xi)$.[1]

Um diese Sätze aus den Sätzen I und II abzuleiten, genügt es offenbar zu zeigen, dass die Stützfunktionen in dem Sinne eine Basis aller stetigen Funktionen bilden, dass jede stetige Funktion durch Linearkombinationen von Stützfunktionen gleichmässig approximiert werden kann.

Es sei $H_{\eta, r}(\xi)$ für $r > 1$ die Stützfunktion der konvexen Hülle der Einheitskugel und des Punktes $r\eta$, wo η ein beliebiger Punkt von Ω ist. Dann ist offenbar

$$H_{\eta, r}(\xi) - 1 \geqq 0$$

für alle ξ und zwar positiv im sphärischen Abstand kleiner als $\operatorname{arc}\cos\frac{1}{r}$ von η und sonst Null. Es sei

$$I_r = \int_{\Omega} \left[H_{\eta, r}(\xi) - 1\right] M(d\Omega)$$

das offenbar von η unabhängige Integral dieser Funktion über Ω, ferner $G(\xi)$ die zu approximierende stetige Funktion. Dann ist

$$F_r(\eta) = \int_{\Omega} G(\xi) \frac{H_{\eta, r}(\xi) - 1}{I_r} M(d\Omega)$$

eine stetige Funktion von η und strebt für $r \to 1$ gleichmässig gegen $G(\eta)$. Andererseits ist $F_r(\eta)$ für jedes r Differenz zweier Stützfunktionen. Für nicht negatives $G(\xi)$ ist dies unmittelbar ersichtlich[2], und im allgemeinen Fall schreibe man $G(\xi)$ als Differenz zweier nicht negativen Funktionen.

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[1] Selbstverständlich ist nur ein Teil dieses Satzes eine Verschärfung von II.

[2] Bericht, **19**, S. 28.

§ 3. Die Oberflächenfunktion eines konvexen Körpers.

Es sei $\mathfrak{P}$ ein konvexes Polyeder, $\mathfrak{x}^{(1)}, \mathfrak{x}^{(2)}, \ldots, \mathfrak{x}^{(N)}$ die Normaleneinheitsvektoren seiner $(n-1)$-dimensionalen Seiten und $v_1, v_2, \ldots, v_N$ deren $(n-1)$-dimensionale Volumina. Als Oberflächenfunktion $S(\mathfrak{P}; \omega)$ von $\mathfrak{P}$ bezeichnen wir die Mengenfunktion auf der Einheitskugel Ω, deren Wert für die Borel-Menge ω gleich der Summe derjenigen v_ν ist, für welche $\mathfrak{x}^{(\nu)}$ zu ω gehört. Man hat dann für jeden konvexen Körper $\mathfrak{H}$ mit der Stützfunktion $H(\mathfrak{x})$[1]

$$V(\mathfrak{H}, \mathfrak{P}, \ldots, \mathfrak{P}) = \frac{1}{n} \sum_{\nu=1}^{N} H(\mathfrak{x}^{(\nu)})\, v_\nu = \frac{1}{n} \int_{\Omega} H(\mathfrak{x})\, S(\mathfrak{P}; d\Omega).$$

Es sei nun $\mathfrak{K}$ ein beliebiger konvexer Körper und $\mathfrak{P}^1$, $\mathfrak{P}^2, \ldots$ eine Folge konvexer Polyeder, die gegen $\mathfrak{K}$ konvergieren. Dann gilt wegen der Stetigkeit der gemischten Volumina[2] für jeden konvexen Körper $\mathfrak{H}$

$$\lim_{\nu \to \infty} V(\mathfrak{H}, \mathfrak{P}^\nu, \ldots, \mathfrak{P}^\nu) = V(\mathfrak{H}, \mathfrak{K}, \ldots, \mathfrak{K}).$$

Nach IV und III gibt es also eine und nur eine Mengenfunktion $S(\mathfrak{K}; \omega)$, die wir als Oberflächenfunktion von $\mathfrak{K}$ bezeichnen, derart dass für jeden konvexen Körper $\mathfrak{H}$ mit der Stützfunktion $H(\mathfrak{x})$

$$V(\mathfrak{H}, \mathfrak{K}, \ldots, \mathfrak{K}) = \frac{1}{n} \int_{\Omega} H(\mathfrak{x})\, S(\mathfrak{K}; d\Omega)$$

ist. Wählt man insbesondere für $\mathfrak{H}$ die Einheitskugel, so erhält man[3] für die Oberfläche $S(\mathfrak{K})$ von $\mathfrak{K}$

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[1] Bericht, S. 41.

[2] Bericht, S. 40.

[3] Bericht, S. 47.

$$S(\mathfrak{K}) = S(\mathfrak{K}; \Omega).$$

Ist ferner $\mathfrak{K}^1, \mathfrak{K}^2, \ldots$ eine Folge beliebiger konvexer Körper, die gegen den Körper $\mathfrak{K}$ konvergieren, so folgt nach IV, dass die zugehörigen Oberflächenfunktionen $S(\mathfrak{K}^\nu; \omega)$ gegen eine Mengenfunktion $\Phi(\omega)$ konvergieren, die für jeden Körper $\mathfrak{H}$ mit der Stützfunktion $H(\xi)$ der Relation

$$V(\mathfrak{H}, \mathfrak{K}, \ldots, \mathfrak{K}) = \frac{1}{n}\int_\Omega H(\xi)\, \Phi(d\Omega)$$

genügt und daher nach III mit $S(\mathfrak{K}; \omega)$ übereinstimmt. Damit haben wir:

V. *Zu jedem konvexen Körper $\mathfrak{K}$ gibt es eine und nur eine Mengenfunktion $S(\mathfrak{K}; \omega)$, die Oberflächenfunktion von $\mathfrak{K}$, mit der Eigenschaft, dass für jeden konvexen Körper $\mathfrak{H}$ mit der Stützfunktion $H(\xi)$*

$$V(\mathfrak{H}, \mathfrak{K}, \ldots, \mathfrak{K}) = \frac{1}{n}\int_\Omega H(\xi)\, S(\mathfrak{K}; d\Omega) \tag{1}$$

ist, und diese Mengenfunktion hängt im Sinne der Konvergenz von Mengenfunktionen stetig von $\mathfrak{K}$ ab. Die gesamte Oberfläche $S(\mathfrak{K})$ von $\mathfrak{K}$ ist gleich $S(\mathfrak{K}; \Omega)$.

Ist $\mathfrak{K}$ speziell ein Polyeder, so ist $S(\mathfrak{K}; \omega)$ gleich der Summe der Inhalte der $(n-1)$-dimensionalen Seiten von $\mathfrak{K}$, deren Normaleneinheitsvektoren zur Menge ω gehören.

Hieraus geht speziell hervor, dass für einen hinreichend glatten Körper die Oberflächenfunktion $S(\mathfrak{K}; \omega)$ gleich dem unbestimmten Integral des Produktes der Hauptkrümmungsradien ist; denn dieses unbestimmte Integral genügt den Relationen (1)[1].

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[1] Dies entnimmt man aus den Formeln (5), S. 59 und (4), S. 62 des Berichtes.

Da $V(\mathfrak{H}, \mathfrak{K}, \ldots, \mathfrak{K})$ bei Translationen von $\mathfrak{K}$ ungeändert bleibt, gilt wegen der eindeutigen Bestimmtheit von $S(\mathfrak{K}; \omega)$, dass auch $S(\mathfrak{K}; \omega)$ translationsinvariant ist.

Wählt man für $\mathfrak{H}$ einen beliebigen Punkt a, so wird

$$H(\xi) = \Sigma a \xi$$

und

$$V(\mathfrak{H}, \mathfrak{K}, \ldots, \mathfrak{K}) = 0,$$

also

$$\int_{\Omega} \Sigma a \xi \, S(\mathfrak{K}; d\Omega) = 0.$$

Da dies für alle a gilt, hat man

$$\int_{\Omega} \xi \, S(\mathfrak{K}; d\Omega) = 0, \tag{2}$$

d. h. der Schwerpunkt der Massenbelegung $S(\mathfrak{K}; \omega)$ von Ω fällt in den Kugelmittelpunkt.

Ein konvexer Körper $\mathfrak{K}$ ist dann und nur dann höchstens $(n-2)$-dimensional, wenn $S(\mathfrak{K}) = S(\mathfrak{K}; \Omega) = 0$ ist, wenn also $S(\mathfrak{K}; \omega)$ identisch verschwindet.

Ist $\mathfrak{K}$ $(n-1)$-dimensional, und sind $\xi^{(0)}$ und $-\xi^{(0)}$ die Normaleneinheitsvektoren der Ebene, in der $\mathfrak{K}$ enthalten ist, so ist

$$S(\mathfrak{K}; \omega) = \begin{cases} 0 \\ \frac{1}{2} S(\mathfrak{K}) \\ S(\mathfrak{K}) \end{cases} \tag{3}$$

je nachdem ω keinen, einen oder beide Punkte $\xi^{(0)}$ und $-\xi^{(0)}$ enthält. Dies ist klar für $(n-1)$-dimensionale Polyeder und folgt allgemein durch Approximation durch solche.

Ist $\mathfrak{K}$ n-dimensional, d. h. hat $\mathfrak{K}$ innere Punkte, so ist für jeden Einheitsvektor η

$$S(\mathfrak{K};\,\omega_\eta) < S(\mathfrak{K};\,\Omega),$$

wo ω_η die Grosskugel mit dem Pol η, d. h. den Durchschnitt von Ω mit der zu η senkrechten Ebene durch den Nullpunkt bezeichnet. Auf keiner Grosskugel liegt also die gesamte Masse der Massenbelegung $S(\mathfrak{K};\,\omega)$. Wäre nämlich für ein η

$$S(\mathfrak{K};\,\omega_\eta) = S(\mathfrak{K};\,\Omega),$$

also

$$S(\mathfrak{K};\,\omega) = 0$$

für jede zu ω_η punktfremde Menge ω, so hätte man

$$V(\mathfrak{H}, \mathfrak{K}, \ldots, \mathfrak{K}) = \frac{1}{n}\int\limits_{\Omega} H(\xi)\, S(\mathfrak{K};\, d\Omega) = 0,$$

wenn $\mathfrak{H}$ die Einheitsstrecke $0, \eta$ bedeutet, weil deren Stützfunktion auf ω_η verschwindet. Andererseits ist das n-fache dieses gemischten Volumens gleich dem Inhalt der Projektion von $\mathfrak{K}$ auf eine zu η senkrechte Ebene[1], also von Null verschieden, weil $\mathfrak{K}$ innere Punkte besitzt.

Hieraus geht hervor: Wenn die Oberflächenfunktion $S(\mathfrak{K};\,\omega)$ eines Körpers $\mathfrak{K}$ nicht identisch verschwindet und für ein passendes η der Bedingung

$$S(\mathfrak{K};\,\omega_\eta) = S(\mathfrak{K};\,\Omega),$$

genügt, d. h. wenn die gesamte Masse der Massenbelegung $S(\mathfrak{K};\,\omega)$ auf einer Grosskugel liegt, so ist $\mathfrak{K}$ $(n-1)$-dimensional und $S(\mathfrak{K};\,\omega)$ ist von der Form (3). Ist umgekehrt $\xi^{(0)}$ ein beliebiger Einheitsvektor und S eine positive Zahl, so ist die Mengenfunktion

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[1] Bericht, S. 45.

$$\Phi(\omega) = \begin{cases} 0 \\ \frac{1}{2} S, \\ S \end{cases}$$

je nachdem ω keinen, einen oder beide Punkte $\mathfrak{x}^{(0)}$ und $-\mathfrak{x}^{(0)}$ enthält, eine Oberflächenfunktion, nämlich für die (unendlich vielen) $(n-1)$-dimensionalen Körper der Oberfläche S, die in einer zu $\mathfrak{x}^{(0)}$ senkrechten Ebene enthalten sind.

§ 4. Bestimmung eines konvexen Körpers durch die Oberflächenfunktion.

VI. *Zwei konvexe Körper mit inneren Punkten haben dann und nur dann dieselbe Oberflächenfunktion, wenn sie durch Translation ineinander übergeführt werden können.*

Der eine Teil des Satzes, nämlich die Translationsinvarianz der Oberflächenfunktion, ist bereits in § 3 gezeigt worden.

Es seien also $\mathfrak{H}$ und $\mathfrak{K}$ zwei konvexe Körper mit inneren Punkten, den Stützfunktionen $H(\mathfrak{x})$ bzw. $K(\mathfrak{x})$ und derselben Oberflächenfunktion

$$S(\omega) = S(\mathfrak{H}; \omega) = S(\mathfrak{K}; \omega).$$

Dann ist nach (1)

$$V(\mathfrak{H}, \mathfrak{K}, \ldots, \mathfrak{K}) = \frac{1}{n} \int_{\Omega} H(\mathfrak{x})\, S(d\Omega) = V(\mathfrak{H}, \mathfrak{H}, \ldots, \mathfrak{H}) = V(\mathfrak{H})$$

und

$$V(\mathfrak{K}, \mathfrak{H}, \ldots, \mathfrak{H}) = \frac{1}{n} \int_{\Omega} K(\mathfrak{x})\, S(d\Omega) = V(\mathfrak{K}, \mathfrak{K}, \ldots, \mathfrak{K}) = V(\mathfrak{K}),$$

wo $V(\mathfrak{H})$ und $V(\mathfrak{K})$ die Volumina von $\mathfrak{H}$ und $\mathfrak{K}$ und daher positiv sind. Folglich gehen die Minkowskischen Ungleichungen[1]

$$V(\mathfrak{H}, \mathfrak{K}, \ldots, \mathfrak{K})^n \geqq V(\mathfrak{H})\, V(\mathfrak{K})^{n-1}$$

und

$$V(\mathfrak{K}, \mathfrak{H}, \ldots, \mathfrak{H})^n \geqq V(\mathfrak{K})\, V(\mathfrak{H})^{n-1}$$

in

$$V(\mathfrak{H}) \geqq V(\mathfrak{K})$$

und

$$V(\mathfrak{K}) \geqq V(\mathfrak{H})$$

über. Also ist

$$V(\mathfrak{H}) = V(\mathfrak{K})$$

und in den Ungleichungen gilt das Gleichheitszeichen. Dies hat zur Folge, dass die Körper $\mathfrak{H}$ und $\mathfrak{K}$ homothetisch sind[1] und daher, da sie dasselbe Volumen haben, durch Translation auseinander hervorgehen.

VII. *Eine Mengenfunktion $\Phi(\omega)$ ist dann und nur dann Oberflächenfunktion eines konvexen Körpers $\mathfrak{K}$ mit inneren Punkten, wenn sie den folgenden beiden Bedingungen genügt:*

1) *Der Schwerpunkt der Massenbelegung $\Phi(\omega)$ fällt in den Nullpunkt, d. h.*

$$\int_{\Omega} \xi\, \Phi(d\Omega) = 0.$$

2) *Auf keiner Grosskugel liegt die gesamte Masse, d. h. für jeden Einheitsvektor η gilt für die Grosskugel ω_η mit dem Pol η*

$$\Phi(\omega_\eta) < \Phi(\Omega).$$

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[1] Bericht, S. 91.

Dann und nur dann, wenn für eine endliche Menge ω

$$\Phi(\omega) = \Phi(\Omega)$$

ist, ist $\mathfrak{K}$ *ein Polyeder.*

Wir betrachten zunächst den Fall, wo für eine endliche Menge ω

$$\Phi(\omega) = \Phi(\Omega)$$

ist. Es seien $\mathfrak{x}^{(1)}, \mathfrak{x}^{(2)}, \ldots, \mathfrak{x}^{(N)}$ die Punkte von ω und

$$v_\nu = \Phi(\mathfrak{x}^{(\nu)}), \qquad \nu = 1, 2, \ldots, N,$$

die entsprechenden Werte der Mengenfunktion, die wir ohne Beschränkung der Allgemeinheit positiv annehmen können. Infolge der Bedingungen 1) und 2) ist

$$\sum_{\nu=1}^{N} \mathfrak{x}^{(\nu)} v_\nu = 0,$$

und unter den Vektoren $\mathfrak{x}^{(1)}, \mathfrak{x}^{(2)}, \ldots, \mathfrak{x}^{(N)}$ gibt es n linear unabhängige.

Nach Minkowski[1] gibt es also ein konvexes Polyeder, dessen Oberflächenfunktion die gegebene Mengenfunktion $\Phi(\omega)$ ist.

Es sei nun $\Phi(\omega)$ eine beliebige den obigen Bedingungen 1) und 2) genügende Mengenfunktion. Für jede natürliche Zahl $\varkappa$ zerlegen wir die Kugel Ω in endlich viele (disjunkte) Borel-Mengen vom sphärischen Durchmesser kleiner als $\frac{1}{\varkappa}$. Diejenigen dieser Mengen, für welche Φ einen positiven Wert hat, seien $\Omega_1, \Omega_2, \ldots, \Omega_N$. Wir bezeichnen mit $\varrho_\nu \mathfrak{x}^{(\nu)}$, $\varrho_\nu > 0$, $|\mathfrak{x}^{(\nu)}| = 1$, den offenbar vom Nullpunkt verschiedenen

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[1] Bericht, **60**, S. 118.

Schwerpunkt der durch $\Phi(\omega)$ definierten Massenbelegung von Ω_ν, setzen also

$$(4)\qquad \int\limits_{\Omega_\nu} \xi\, \Phi(d\Omega) = \Phi(\Omega_\nu)\, \varrho_\nu\, \xi^{(\nu)}.$$

Dann ist $\arc\cos \frac{1}{\varkappa} < \varrho_\nu \leqq 1$, $\nu = 1, 2, \ldots, N$, sodass die ϱ_ν mit $\varkappa \to \infty$ gleichmässig gegen 1 konvergieren. Unter $\Phi_\varkappa(\omega)$ verstehen wir dann diejenige Mengenfunktion, deren Wert für die Borel-Menge ω gleich der Summe derjenigen Werte $\Phi(\Omega_\nu)\,\varrho_\nu$ ist, für welche $\xi^{(\nu)}$ zu ω gehört. Dann genügt $\Phi_\varkappa(\omega)$ nach (4) offenbar der Bedingung 1).

Für jede stetige Funktion $G(\xi)$ gilt ferner

$$\lim_{\varkappa \to \infty} \int\limits_{\Omega} G(\xi)\, \Phi_\varkappa(d\Omega) = \int\limits_{\Omega} G(\xi)\, \Phi(d\Omega);$$

denn für jedes $\varkappa$ ist

$$\int\limits_{\Omega} G(\xi)\, \Phi_\varkappa(d\Omega) = \int\limits_{\Omega} G_\varkappa(\xi)\, \Phi(d\Omega),$$

wo $G_\varkappa(\xi)$ in jeder Menge Ω_ν den konstanten Wert $G(\xi^{(\nu)})\,\varrho_\nu$ hat und sonst gleich $G(\xi)$ ist, und diese Funktionen konvergieren gleichmässig gegen $G(\xi)$. Also konvergiert nach II die Folge der Mengenfunktionen $\Phi_1, \Phi_2, \ldots$ gegen Φ.

Es sei $H_\eta(\xi)$ für einen beliebigen Einheitsvektor η die Stützfunktion der Strecke $0, \eta$. Diese Funktion $H_\eta(\xi)$ ist positiv in der offenen Halbkugel Ω_η^* mit dem (sphärischen) Mittelpunkt η und sonst 0. Also ist wegen der Bedingungen 1) und 2) das Integral

$$\int\limits_{\Omega} H_\eta(\xi)\, \Phi(d\Omega)$$

für jedes η positiv; denn anderenfalls wäre $\Phi(\Omega_\eta) = 0$, und es müsste wegen 1) die gesamte Masse der Massenbelegung $\Phi(\omega)$ auf der Ω_η berandenden Grosskugel ω_η liegen, was 2) widerspricht. Dieses Integral ist eine stetige Funktion von η; folglich ist für eine passende Konstante $c > 0$

$$\int_\Omega H_\eta(\xi)\,\Phi(d\Omega) \geqq c$$

für alle η. Nun gilt für jedes η

$$\lim_{\varkappa \to \infty} \int_\Omega H_\eta(\xi)\,\Phi_\varkappa(d\Omega) = \int_\Omega H_\eta(\xi)\,\Phi(d\Omega),$$

und zwar nach IV gleichmässig in η. Also gibt es ein $\varkappa_0$ derart, dass

$$\int_\Omega H_\eta(\xi)\,\Phi_\varkappa(d\Omega) > \frac{c}{2} \tag{5}$$

für $\varkappa \geqq \varkappa_0$ und alle η.

Hieraus entnehmen wir zunächst, dass die Mengenfunktionen $\Phi_\varkappa(\omega)$ für $\varkappa \geqq \varkappa_0$ der Bedingung 2) genügen; denn aus $\Phi_\varkappa(\omega_\eta) = \Phi_\varkappa(\Omega)$, also speziell $\Phi_\varkappa(\Omega_\eta) = 0$ würde ja das Verschwinden des Integrals (5) folgen.

Nach dem am Anfang des Beweises Gesagten gibt es also zu jedem $\varkappa \geqq \varkappa_0$ ein konvexes Polyeder $\mathfrak{P}^\varkappa$ mit $\Phi_\varkappa(\omega)$ als Oberflächenfunktion. Von diesen Polyedern können wir wegen der Translationsinvarianz der Oberflächenfunktion annehmen, dass sie alle den Nullpunkt enthalten, und wollen zeigen, dass sie dann in einer festen Kugel enthalten sind.

Hierzu bemerken wir, dass wegen

$$\Phi_\varkappa(\Omega) \leqq \Phi(\Omega)$$

die Oberflächen $S(\mathfrak{P}_\varkappa) = \Phi_\varkappa(\Omega)$ der Polyeder $\mathfrak{P}^\varkappa$ und damit nach der isoperimetrischen Ungleichung auch ihre Volumina $V(\mathfrak{P}^\varkappa)$ beschränkt sind. Ist nun die Strecke $0, r\eta$, wo $r > 0$ und η ein Einheitsvektor ist, in einem Polyeder $\mathfrak{P}^\varkappa$ enthalten, so ist die Stützfunktion von $\mathfrak{P}^\varkappa$ grösser oder gleich $r H_\eta(\xi)$, also

$$V(\mathfrak{P}^\varkappa) = V(\mathfrak{P}^\varkappa, \mathfrak{P}^\varkappa, \ldots, \mathfrak{P}^\varkappa) \geqq \frac{r}{n} \int_\Omega H_\eta(\xi)\, \Phi_\varkappa(d\Omega).$$

Folglich liegt r nach (5) unter einer von $\varkappa$ und η unabhängigen Schranke.

Nach dem Auswahlsatz von Blaschke gibt es daher eine konvergente Teilfolge $\mathfrak{P}^{\varkappa_1}, \mathfrak{P}^{\varkappa_2}, \ldots$ der Folge $\mathfrak{P}^\varkappa, \varkappa \geqq \varkappa_0$. Ist $\mathfrak{K}$ der Grenzkörper, so ist seine Oberflächenfunktion $S(\mathfrak{K}; \omega)$ wegen der stetigen Abhängigkeit der Oberflächenfunktion vom Körper die Grenzfunktion der Folge $\Phi_{\varkappa_1}, \Phi_{\varkappa_2}, \ldots$, also wegen $\Phi_\varkappa \rightarrow \Phi$

$$S(\mathfrak{K}; \omega) = \Phi(\omega).$$

Der Körper $\mathfrak{K}$ hat also die gewünschten Eigenschaften und ist nach VI bis auf Translationen eindeutig bestimmt.

Dass $\mathfrak{K}$ dann und nur dann ein Polyeder ist, wenn $\Phi(\omega) = \Phi(\Omega)$ ist für eine endliche Menge ω, hat sich zugleich ergeben.

Die festgestellte Beziehung zwischen konvexen Körpern mit inneren Punkten einerseits und Mengenfunktionen mit den Eigenschaften 1) und 2) andererseits kann offenbar dadurch eineindeutig gemacht werden, dass man nur Körper mit dem Schwerpunkt im Nullpunkt in Betracht zieht. Diese Beziehung, die nach V in der einen Richtung stetig ist, ist dann auch in der anderen stetig, d. h. es gilt:

VIII. *Eine Folge konvexer Körper* $\mathfrak{K}^1, \mathfrak{K}^2, \ldots$ *mit inneren Punkten und demselben Schwerpunkt konvergiert dann und nur dann gegen einen Körper* $\mathfrak{K}$ *mit inneren Punkten, wenn die Folge ihrer Oberflächenfunktionen* $S(\mathfrak{K}^\nu; \omega)$ *gegen die Oberflächenfunktion* $S(\mathfrak{K}; \omega)$ *von* $\mathfrak{K}$ *konvergiert.*

Die eine Hälfte dieser Behauptung ist in V enthalten. Zum Beweis der anderen genügt es, aus der Konvergenz der Folge $S(\mathfrak{K}^\nu; \omega)$ gegen $S(\mathfrak{K}; \omega)$ die gleichartige Beschränktheit der Körper $\mathfrak{K}^\nu$ zu folgern; denn jeder Grenzkörper einer Teilfolge von $\mathfrak{K}^\nu$ hat die Oberflächenfunktion $S(\mathfrak{K}; \omega)$, muss also mit $\mathfrak{K}$ identisch sein, und wenn alle konvergenten Teilfolgen einer gleichartig beschränkten Folge konvexer Körper denselben Grenzkörper haben, so ist die Folge selbst konvergent. Die Beschränktheit der Körper $\mathfrak{K}^\nu$ schliesst man wie im Beweis von VII die Beschränktheit der Polyeder $\mathfrak{P}^\varkappa$, wenn man beachtet, dass wegen der Konvergenz von $S(\mathfrak{K}^\nu; \omega)$ die Oberflächen $S(\mathfrak{K}^\nu) = S(\mathfrak{K}^\nu; \Omega)$ beschränkt sind.

§ 5. **Gemischte Oberflächenfunktionen.**

IX. *Zu* $n-1$ *konvexen Körpern* $\mathfrak{K}_1, \mathfrak{K}_2, \ldots, \mathfrak{K}_{n-1}$ *gibt es eine und nur eine Mengenfunktion* $S(\mathfrak{K}_1, \ldots, \mathfrak{K}_{n-1}; \omega)$, *die gemischte Oberflächenfunktion von* $\mathfrak{K}_1, \mathfrak{K}_2, \ldots, \mathfrak{K}_{n-1}$, *mit der Eigenschaft, dass für jeden konvexen Körper* $\mathfrak{H}$ *mit der Stützfunktion* $H(\xi)$

$$(6)\quad V(\mathfrak{H}, \mathfrak{K}_1, \ldots, \mathfrak{K}_{n-1}) = \frac{1}{n}\int_{\Omega} H(\xi)\, S(\mathfrak{K}_1, \ldots, \mathfrak{K}_{n-1}; d\Omega)$$

ist, und diese Mengenfunktion hängt im Sinne der Konvergenz von Mengenfunktionen stetig von den Körpern $\mathfrak{K}_1, \mathfrak{K}_2, \ldots, \mathfrak{K}_{n-1}$ *ab. Es ist*

$$S(\mathfrak{K}, \ldots, \mathfrak{K}; \omega) = S(\mathfrak{K}; \omega).$$

Wir betrachten zunächst konvexe Polyeder $\mathfrak{P}_1, \mathfrak{P}_2, \ldots, \mathfrak{P}_{n-1}$. Es seien $\mathfrak{p}_1(\xi), \mathfrak{p}_2(\xi), \ldots, \mathfrak{p}_{n-1}(\xi)$ die höchstens $(n-1)$-dimensionalen Polyeder, die die Polyeder $\mathfrak{P}_1, \mathfrak{P}_2, \ldots$, bzw. $\mathfrak{P}_{n-1}$ mit ihren Stützebenen der Richtung ξ gemeinsam haben. Das $(n-1)$-dimensionale gemischte Volumen

$$v\left(\mathfrak{p}_1(\xi), \ldots, \mathfrak{p}_{n-1}(\xi)\right) \geqq 0$$

ist nur für endlich viele Richtungen $\xi^{(1)}, \xi^{(2)}, \ldots, \xi^{(N)}$ positiv[1]. Wir setzen

$$v\left(\mathfrak{p}_1(\xi^{(\nu)}), \ldots, \mathfrak{p}_{n-1}(\xi^{(\nu)})\right) = v_\nu$$

und definieren als gemischte Oberflächenfunktion $S(\mathfrak{P}_1, \ldots, \mathfrak{P}_{n-1}; \omega)$ diejenige Mengenfunktion, deren Wert für die Borel-Menge ω gleich der Summe derjenigen v_ν ist, für welche $\xi^{(\nu)}$ zu ω gehört. Dann gilt für jeden konvexen Körper $\mathfrak{H}$ mit der Stützfunktion $H(\xi)$[2]

$$V(\mathfrak{H}, \mathfrak{P}_1, \ldots, \mathfrak{P}_{n-1}) = \frac{1}{n} \sum_{\nu=1}^{N} H(\xi^{(\nu)})\, v_\nu$$

$$= \frac{1}{n} \int_{\Omega} H(\xi)\, S(\mathfrak{P}_1, \ldots, \mathfrak{P}_{n-1}; d\Omega).$$

Hieraus folgert man den obigen Satz durch Schlüsse, die den Schlüssen in § 3 vollständig analog sind.

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[1] Diese Richtungen $\xi^{(\nu)}$ sind genau die Normalenrichtungen der $(n-1)$-dimensionalen Seiten des Polyeders

$$\lambda_1 \mathfrak{P}_1 + \cdots + \lambda_{n-1} \mathfrak{P}_{n-1}$$

für beliebige positive $\lambda_1, \lambda_2, \cdots, \lambda_{n-1}$. Vgl. Bericht, S. 42, ferner H. Weyl: Elementare Theorie der konvexen Polyeder. [Comment. math. helv., 7, 290—306 (1935), insbes. S. 306.]

[2] Bericht, S. 42.

Aus dem Satz IX und bekannten Integraldarstellungen der gemischten Volumina[1] geht hervor, dass für hinreichend glatte Körper

$$S(\mathfrak{K}_1, \ldots, \mathfrak{K}_{n-1}; \omega) = \int\limits_{\omega} D(H^{(1)}, \ldots, H^{(n-1)})\, M(d\Omega)$$

ist, wobei D ein gewisser Differentialausdruck zweiter Ordnung in den Stützfunktionen $H^{(1)}(\xi), H^{(2)}(\xi), \ldots, H^{(n-1)}(\xi)$ von $\mathfrak{K}_1, \mathfrak{K}_2, \ldots, \mathfrak{K}_{n-1}$ ist.

X. *Es seien* $\mathfrak{K}^{(1)}, \ldots, \mathfrak{K}^{(s)}, \mathfrak{K}_1, \ldots, \mathfrak{K}_{n-p-1}, 0 < p \leq n-1$, *beliebige konvexe Körper und* $\mu_1, \mu_2, \ldots, \mu_s$ *nicht negative Zahlen. Wird dann*

$$\mu_1 \mathfrak{K}^{(1)} + \ldots + \mu_s \mathfrak{K}^{(s)} = \mathfrak{K}$$

gesetzt, so ist

$$S(\underbrace{\mathfrak{K}, \ldots, \mathfrak{K}}_{p}, \mathfrak{K}_1, \ldots, \mathfrak{K}_{n-p-1}; \omega)$$

$$= \sum_{\sigma_1, \ldots, \sigma_p} \mu_{\sigma_1} \ldots \mu_{\sigma_p} S(\mathfrak{K}^{(\sigma_1)}, \ldots, \mathfrak{K}^{(\sigma_p)}, \mathfrak{K}_1, \ldots, \mathfrak{K}_{n-p-1}; \omega),$$

wo über jedes σ *von* 1 *bis* s *zu summieren ist.*

Für jeden konvexen Körper $\mathfrak{H}$ mit der Stützfunktion $H(\xi)$ gilt nämlich[2]

$$\frac{1}{n} \int\limits_{\Omega} H(\xi)\, S(\underbrace{\mathfrak{K}, \ldots, \mathfrak{K}}_{p}, \mathfrak{K}_1, \ldots, \mathfrak{K}_{n-p-1}; d\Omega)$$

$$= V(\mathfrak{H}, \underbrace{\mathfrak{K}, \ldots, \mathfrak{K}}_{p}, \mathfrak{K}_1, \ldots, \mathfrak{K}_{n-p-1})$$

$$= \sum_{\sigma_1, \ldots, \sigma_p} \mu_{\sigma_1} \ldots \mu_{\sigma_p} V(\mathfrak{H}, \mathfrak{K}^{(\sigma_1)}, \ldots, \mathfrak{K}^{(\sigma_p)}, \mathfrak{K}_1, \ldots, \mathfrak{K}_{n-p-1})$$

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[1] Bericht, S. 59, Formel (5).

[2] Bericht, S. 40.

$$= \frac{1}{n}\int_{\Omega} H(\xi) \sum_{\sigma_1,\dots,\sigma_p}{}' \mu_{\sigma_1}\dots\mu_{\sigma_p} S(\mathfrak{K}^{(\sigma_1)},\dots,\mathfrak{K}^{(\sigma_p)},\mathfrak{K}_1,\dots,\mathfrak{K}_{n-p-1}; d\Omega),$$

woraus nach III die Behauptung folgt.

Ebenso wie für die Oberflächenfunktion sieht man, dass jede gemischte Oberflächenfunktion $S(\mathfrak{K}_1,\dots,\mathfrak{K}_{n-1};\omega)$ der zu (2) analogen Relation

$$\int_{\Omega} \xi\, S(\mathfrak{K}_1,\dots,\mathfrak{K}_{n-1}; d\Omega) = 0$$

genügt und bei Translationen der Körper $\mathfrak{K}_1,\mathfrak{K}_2,\dots,\mathfrak{K}_{n-1}$ ungeändert bleibt.

Ist umgekehrt $\Phi(\omega)$ eine beliebige Mengenfunktion, die der Bedingung

$$\int_{\Omega} \xi\, \Phi(d\Omega) = 0$$

genügt, so gibt es konvexe Körper $\mathfrak{K}_1,\mathfrak{K}_2,\dots,\mathfrak{K}_{n-1}$ mit

$$S(\mathfrak{K}_1,\dots,\mathfrak{K}_{n-1};\omega) = \Phi(\omega). \tag{7}$$

Ist nämlich Ω^* die (immer vorhandene) Grosskugel kleinster Dimension, für welche

$$\Phi(\Omega^*) = \Phi(\Omega)$$

ist, p die Dimension des durch Ω^* bestimmten Unterraumes R^*, ferner $\eta^{(1)},\eta^{(2)},\dots,\eta^{(n-p)}$ paarweise orthogonale Normalenrichtungen dieses Unterraums und $\mathfrak{k}$ der nach VII vorhandene konvexe Körper in R^*, dessen Oberflächenfunktion in R^* die Mengenfunktion $\Phi(\omega)$ auf Ω^* ist, so gilt (7), wenn $\mathfrak{K}_1,\mathfrak{K}_2,\dots,\mathfrak{K}_{n-p}$ Einheitsstrecken der Richtungen $\eta^{(1)},\eta^{(2)},\dots,\eta^{(n-p)}$ und

$$\mathfrak{K}_{n-p+1} = \mathfrak{K}_{n-p+2} = \dots = \mathfrak{K}_{n-1} = \mathfrak{k}$$

sind.

Zwischen den gemischten Volumina beliebiger konvexer Körper besteht die Ungleichung[1]

$$V(\mathfrak{K}_1,\mathfrak{K}_2,\mathfrak{K}_3,\ldots,\mathfrak{K}_n)^2 \geqq V(\mathfrak{K}_1,\mathfrak{K}_1,\mathfrak{K}_3,\ldots,\mathfrak{K}_n)\cdot V(\mathfrak{K}_2,\mathfrak{K}_2,\mathfrak{K}_3,\ldots,\mathfrak{K}_n),$$

worin, falls die rechte Seite positiv ist, das Gleichheitszeichen dann und nur dann gilt, wenn für jeden konvexen Körper $\mathfrak{H}$

$$\frac{V(\mathfrak{K}_1,\mathfrak{K}_1,\mathfrak{K}_3,\ldots,\mathfrak{K}_n)}{V(\mathfrak{K}_2,\mathfrak{K}_2,\mathfrak{K}_3,\ldots,\mathfrak{K}_n)} = \frac{V(\mathfrak{H},\mathfrak{K}_1,\mathfrak{K}_3,\ldots,\mathfrak{K}_n)^2}{V(\mathfrak{H},\mathfrak{K}_2,\mathfrak{K}_3,\ldots,\mathfrak{K}_n)^2}$$

ist[2]. Nach IX ist dieses damit gleichwertig, dass die gemischten Oberflächenfunktionen $S(\mathfrak{K}_1,\mathfrak{K}_3,\ldots,\mathfrak{K}_n;\omega)$ und $S(\mathfrak{K}_2,\mathfrak{K}_3,\ldots,\mathfrak{K}_n;\omega)$ proportional sind.

Die bisher nur in Spezialfällen bewiesene Kappenkörperbehauptung Minkowskis[3] besagt hiernach, dass von zwei konvexen Körpern $\mathfrak{K}_1$ und $\mathfrak{K}_2$ des dreidimensionalen Raumes $\mathfrak{K}_1$ dann und nur dann mit $\mathfrak{K}_2$ oder einem Kappenkörper von $\mathfrak{K}_2$ homothetisch ist, wenn die gemischte Oberflächenfunktion $S(\mathfrak{K}_1,\mathfrak{K}_2;\omega)$ der Oberflächenfunktion $S(\mathfrak{K}_1;\omega)$ von $\mathfrak{K}_1$ proportional ist.

§ 6. Die Oberflächenfunktionen niedrigerer Ordnung eines konvexen Körpers.

Die gemischte Oberflächenfunktion

$$S_p(\mathfrak{K};\omega) = S(\underbrace{\mathfrak{K},\ldots,\mathfrak{K}}_{p},\underbrace{\mathfrak{S},\ldots,\mathfrak{S}}_{n-p-1};\omega), \tag{8}$$

---

[1] Vgl. W. Fenchel: Inégalités quadratiques entre les volumes mixtes des corps convexes. [C. R. Acad. Sci., Paris **203**, 647—650 (1936)] und A. Alexandroff: Neue Ungleichungen für die Mischvolumen konvexer Körper. [C. R. Acad. Sci. URSS, N. s. **14**, 155—157 (1937)].

[2] Vgl. W. Fenchel: Généralisation du théorème de Brunn et Minkowski concernant les corps convexes. [C. R. Acad. Sci., Paris **203**, 764—766 (1936)].

[3] Bericht, S. 92 u. 101.

wo $\mathfrak{S}$ die Einheitskugel ist, bezeichnen wir als p-te Oberflächenfunktion von $\mathfrak{K}$. Insbesondere ist dann

$$S_{n-1}(\mathfrak{K};\omega) = S(\mathfrak{K};\omega)$$

die Oberflächenfunktion im Sinne von § 3 und

$$S_0(\mathfrak{K};\omega) = M(\omega)$$

das Mass auf Ω.

Für hinreichend glatte Körper $\mathfrak{K}$ gilt

$$S_p(\mathfrak{K};\omega) = \frac{1}{\binom{n-1}{p}}\int\limits_{\Omega}\{R_1\ldots R_p\}\,M(d\Omega),$$

wo $\{R_1\ldots R_p\}$ die p-te elementarsymmetrische Funktion der Hauptkrümmungsradien der Randfläche von $\mathfrak{K}$ ist[1].

Ein konvexer Körper $\mathfrak{K}$ ist dann und nur dann höchstens $(p-1)$-dimensional, wenn

$$n\,W_p(\mathfrak{K}) = n\,V(\underbrace{\mathfrak{K},\ldots,\mathfrak{K}}_{p},\underbrace{\mathfrak{S},\ldots,\mathfrak{S}}_{n-p}) = S_p(\mathfrak{K};\Omega) = 0$$

ist. Dies folgt unmittelbar aus der Bedingung für das Verschwinden eines gemischten Volumens[2].

XI. *Zwei mindestens $(p+1)$-dimensionale konvexe Körper, wo $p>0$ ist, haben dann und nur dann dieselbe p-te Oberflächenfunktion, wenn sie durch Translation in einander übergeführt werden können.*

Die Translationsinvarianz der gemischten Oberflächenfunktionen ist bereits in § 5 bemerkt worden.

Sind $\mathfrak{H}$ und $\mathfrak{K}$ zwei mindestens $(p+1)$-dimensionale

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[1] Man entnimmt dies nach IX aus den Formeln (5), S. 59 und (7), S. 63 des Berichtes.

[2] Bericht, S. 41.

konvexe Körper mit den Stützfunktionen $H(\xi)$ bzw. $K(\xi)$ und derselben p-ten Oberflächenfunktion

$$S_p(\omega) = S_p(\mathfrak{H};\omega) = S_p(\mathfrak{K};\omega),$$

so gilt nach (6)

$$V(\mathfrak{H},\underbrace{\mathfrak{K},\ldots,\mathfrak{K}}_{p},\underbrace{\mathfrak{S},\ldots,\mathfrak{S}}_{n-p-1}) = \frac{1}{n}\int\limits_{\Omega} H(\xi)\,S_p(d\Omega)$$

$$= V(\underbrace{\mathfrak{H},\ldots,\mathfrak{H}}_{p+1},\underbrace{\mathfrak{S},\ldots,\mathfrak{S}}_{n-p-1})$$

und

$$V(\mathfrak{K},\underbrace{\mathfrak{H},\ldots\mathfrak{H}}_{p},\underbrace{\mathfrak{S},\ldots,\mathfrak{S}}_{n-p-1}) = \frac{1}{n}\int\limits_{\Omega} K(\xi)\,S_p(d\Omega)$$

$$= V(\underbrace{\mathfrak{K},\ldots,\mathfrak{K}}_{p+1},\underbrace{\mathfrak{S},\ldots,\mathfrak{S}}_{n-p-1}),$$

und nach einer oben gemachten Bemerkung sind diese beiden Grössen positiv. Hiernach schliesst man mit Hilfe der Ungleichung

$$V(\mathfrak{H},\underbrace{\mathfrak{K},\ldots,\mathfrak{K}}_{p},\underbrace{\mathfrak{S},\ldots,\mathfrak{S}}_{n-p-1})^{p+1}$$

$$\geqq V(\underbrace{\mathfrak{H},\ldots,\mathfrak{H}}_{p+1},\underbrace{\mathfrak{S},\ldots,\mathfrak{S}}_{n-p-1})\cdot V(\underbrace{\mathfrak{K},\ldots,\mathfrak{K}}_{p+1},\underbrace{\mathfrak{S},\ldots,\mathfrak{S}}_{n-p-1})^{p},$$

in der das Gleichheitszeichen nur für homothetische $\mathfrak{H}$ und $\mathfrak{K}$ gilt[1], ebenso wie beim Beweis von VI.

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[1] Man folgert diese Ungleichung und die Bedingung für Gleichheit aus dem Satz der in Fussnote 2 Seite 25 zitierten Note in derselben Weise wie man die in § 4 angegebene Minkowskische Ungleichung aus dem Brunn-Minkowskischen Satz herleitet (Bericht, S. 91). Beim Beweis der Bedingung für Gleichheit wird in der genannten Note benutzt, dass die gemischten Volumina

$$V(\mathfrak{H},\ldots,\mathfrak{H},\mathfrak{K},\ldots,\mathfrak{K},\underbrace{\mathfrak{S},\ldots,\mathfrak{S}}_{n-p-1})$$

von Null verschieden sind, was unter der obigen Voraussetzung, dass $\mathfrak{H}$ und $\mathfrak{K}$ mindestens $(p+1)$-dimensional sind, stets der Fall ist.

Während im Falle $p = n - 1$ die genaue Charakterisierung derjenigen Mengenfunktionen $\Phi(\omega)$ gelang, die als Oberflächenfunktionen konvexer Körper auftreten können, scheint das entsprechende Problem bei den Oberflächenfunktionen p-ter Ordnung für $p < n - 1$ schwierig zu sein. Dass die Mengenfunktionen $S_p(\mathfrak{K}; \omega)$ für $0 < p < n - 1$ starken nicht trivialen Einschränkungen unterliegen, sieht man leicht an Beispielen[1].

§ 7. Direkte Definition der Oberflächenfunktion.

Es sei $\mathfrak{K}$ ein beliebiger konvexer Körper und ω eine Borel-Menge von Ω, ferner t eine beliebige positive Zahl. Zu jeder Stützebene von $\mathfrak{K}$, deren Normaleneinheitsvektor ξ zu ω gehört, betrachten wir die Punkte a von $\mathfrak{K}$, die in dieser Ebene liegen. Von jedem dieser Punkte a tragen wir die Strecke

$$a + \tau \xi, \qquad 0 < \tau \leqq t,$$

ab. Die Vereinigungsmenge aller dieser Strecken ist dann eine Borel-Menge $B_t(\mathfrak{K}; \omega)$ des Raumes, die wir die zu ω und t gehörige Bürstenmenge von $\mathfrak{K}$ nennen. Offenbar ist $B_t(\mathfrak{K}; \Omega)$ die mengentheoretische Differenz des Parallelkörpers $\mathfrak{K} + t\mathfrak{S}$ von $\mathfrak{K}$ und $\mathfrak{K}$ selbst. Bezeichnet man für einen Punkt p ausserhalb $\mathfrak{K}$ mit p^* den (bekanntlich eindeutig bestimmten) Punkt von $\mathfrak{K}$, der von p minimalen Abstand hat, so besteht $B_t(\mathfrak{K}; \omega)$ genau aus den Punkten p, für welche die Strecke p^*p höchstens die Länge t und eine Richtung aus ω hat. Das n-dimensionale Mass $V_t(\mathfrak{K}; \omega)$

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[1] Vgl. z. B. A. Alexandroff: Über die Frage nach der Existenz eines konvexen Körpers bei dem die Summe der Hauptkrümmungsradien eine gegebene positive Funktion ist, welche den Bedingungen der Geschlossenheit genügt. [C. R. Acad. Sci. URSS, N. s. **14**, 59—60 (1937)].

von $B_t(\mathfrak{K};\omega)$ ist eine Mengenfunktion auf Ω, und es gilt

$$V_t(\mathfrak{K};\Omega) = V(\mathfrak{K}+t\mathfrak{S}) - V(\mathfrak{K}). \tag{9}$$

XII. *Für jede Borel-Menge ω von Ω gilt*

$$S(\mathfrak{K};\omega) = \lim_{t\to 0} \frac{V_t(\mathfrak{K};\omega)}{t}.$$

In diesem Satz ist natürlich enthalten, dass die Mengenfunktion $\frac{V_t(\mathfrak{K};\omega)}{t}$ für $t\to 0$ gegen die Oberflächenfunktion im Sinne von § 2 konvergiert; er besagt aber mehr, nämlich nicht nur die Konvergenz der Funktionswerte für die Stetigkeitsmengen von $S(\mathfrak{K};\omega)$, sondern für alle Borel-Mengen von Ω.

Wir zeigen zunächst, dass $V_t(\mathfrak{K};\omega)$ bei festem t im Sinne der Konvergenz von Mengenfunktionen stetig von $\mathfrak{K}$ abhängt. Hierzu haben wir nach § 2 zu zeigen: Konvergiert die Folge $\mathfrak{K}^1, \mathfrak{K}^2, \ldots$ konvexer Körper gegen den Körper $\mathfrak{K}$, so gilt

$$V_t(\mathfrak{K}^\nu;\Omega) \to V_t(\mathfrak{K};\Omega)$$

und für jedes offene ω

$$\varliminf_{\nu\to\infty} V_t(\mathfrak{K}^\nu;\omega) \geqq V_t(\mathfrak{K};\omega). \tag{10}$$

Die erste Behauptung folgt wegen (9) aus der Stetigkeit des Volumens. Es sei nun ω eine offene Menge von Ω. Dann ist die Bürstenmenge $B_t(\mathfrak{K};\omega)$ relativ zu $B_t(\mathfrak{K};\Omega)$ offen, und ihr offener Kern $\tilde{B}_t(\mathfrak{K};\omega)$, der durch Weglassen der zur Berandung von $\mathfrak{K}+t\mathfrak{S}$ gehörigen Punkte entsteht, hat ebenfalls das Mass $V_t(\mathfrak{K};\omega)$. Ist nun p ein Punkt von $\tilde{B}_t(\mathfrak{K};\omega)$ und p^* bzw. p^*_ν der Punkt von $\mathfrak{K}$ bzw. $\mathfrak{K}^\nu$, der von p minimalen Abstand hat, so konvergiert p_ν^* gegen p^*, also die Strecke $p_\nu^* p$ gegen $p^* p$. Da ω offen ist, liegt also p für alle hinreichend grossen ν in $B_t(\mathfrak{K}^\nu; \omega)$; d. h. $B_t(\mathfrak{K}; \omega)$ ist im Limes inferior der Mengenfolge $B_t(\mathfrak{K}^\nu; \omega)$ enthalten, und es gilt daher (10).

Wir betrachten nun die beiden Mengenfunktionen $S(\mathfrak{K}, \omega)$ und $\frac{V_t(\mathfrak{K}; \omega)}{t}$. Ist $\mathfrak{K}$ ein Polyeder, so gilt offenbar für jede Borel-Menge ω die Ungleichung

$$S(\mathfrak{K}; \omega) \leqq \frac{V_t(\mathfrak{K}; \omega)}{t};$$

denn die Bürstenmenge $B_t(\mathfrak{K}; \omega)$ enthält diejenigen Prismen der Höhe t, deren Grundflächen die $(n-1)$-dimensionalen Seiten von $\mathfrak{K}$ mit Normalenrichtungen aus ω sind. Ist $\mathfrak{K}$ ein beliebiger konvexer Körper, so folgt hieraus durch Polyederapproximation wegen der stetigen Abhängigkeit der beiden Mengenfunktionen vom Körper dieselbe Ungleichung für alle gemeinsamen Stetigkeitsmengen der beiden Mengenfunktionen, also nach § 2 ebenfalls für alle Borel-Mengen. Es gilt also

$$0 \leqq \frac{V_t(\mathfrak{K}; \omega)}{t} - S(\mathfrak{K}; \omega) \leqq \frac{V_t(\mathfrak{K}; \Omega)}{t} - S(\mathfrak{K}; \Omega),$$

letzteres wegen der Additivität von $\frac{V_t(\mathfrak{K}; \omega)}{t} - S(\mathfrak{K}; \omega)$. Nach Minkowski konvergiert aber die rechte Seite mit t gegen Null, womit der Satz bewiesen ist.

Aus der Definition der Bürstenmenge entnimmt man für beliebiges positives Δt die Relation

$$V_{t+\Delta t}(\mathfrak{K}; \omega) = V_t(\mathfrak{K}; \omega) + V_{\Delta t}(\mathfrak{K} + t\mathfrak{S}; \omega).$$

Nach XII gilt also für jede Borel-Menge ω

$$(11)\qquad \lim_{\Delta t \to 0} \frac{V_{t+\Delta t}(\mathfrak{K};\omega) - V_t(\mathfrak{K};\omega)}{\Delta t} = S(\mathfrak{K} + t\mathfrak{S};\omega).$$

Nun ist nach X und (8)

$$S(\mathfrak{K} + t\mathfrak{S};\omega) = \sum_{\nu=1}^{n} \binom{n-1}{\nu-1} t^{\nu-1} S_{n-\nu}(\mathfrak{K};\omega).$$

Durch Integration von (11) nach t ergibt sich also der Ausdruck

$$V_t(\mathfrak{K};\omega) = \frac{1}{n} \sum_{\nu=1}^{n} \binom{n}{\nu} t^{\nu} S_{n-\nu}(\mathfrak{K};\omega)$$

für das Volumen der Bürstenmenge, der für $\omega = \Omega$ in die Steinersche Formel für das Volumen eines Parallelkörpers übergeht.

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ÜBER DIE NULLSTELLENVERTEILUNG EINER ANALYTISCHEN GRENZPERIODISCHEN FUNKTION

VON

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§ 1.

Einleitung. Formulierung des Hauptsatzes.

Bevor wir unsere Aufgabe formulieren, wollen wir kurz einige der wichtigsten Eigenschaften der analytischen fastperiodischen Funktionen zusammenstellen[1].

Eine in einem vertikalen Streifen $\alpha < \sigma < \beta \, (-\infty \leqq \alpha < \beta \leqq +\infty)$ der komplexen $s = \sigma + it$— Ebene reguläre Funktion heisst fastperiodisch in (α, β), falls zu jedem $\varepsilon > o$ eine relativ dichte Menge von Verschiebungszahlen $\tau = \tau(\varepsilon) = \tau_f(\varepsilon)$ existiert, d. h. es gibt eine Länge $l = l(\varepsilon)$, so dass in jedem Intervall der Länge l auf der reellen Zahlenachse mindestens ein Punkt τ existiert, für welchen die Ungleichung

$$|f(s + i\tau) - f(s)| \leqq \varepsilon$$

für alle s des Streifens gilt. Ferner heisst eine reguläre Funktion fastperiodisch in $[\alpha, \beta]$, falls sie in jedem »beschnittenen« Streifen $(\alpha <) \, \alpha_1 < \sigma < \beta_1 \, (< \beta)$ fastperiodisch ist. Überall werden eckige Klammern in diesem Sinne gebraucht. Es gilt der Satz, dass jede in $[\alpha, \beta]$ fastperiodische Funktion in $[\alpha, \beta]$ beschränkt und gleichmässig stetig ist.

Zu jeder in $[\alpha, \beta]$ fastperiodischen Funktion $f(s)$ gehört eine Dirichletentwicklung

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[1] Die Theorie der analytischen fastperiodischen Funktionen findet man in H. Bohr [1].

$$f(s) \sim \sum_n A_n e^{\Lambda_n \cdot s}$$

mit reellen Exponenten Λ_n und komplexen Koefficienten $A_n \neq 0$, welche ihrerseits die Funktion eindeutig bestimmt.

Die Eigenschaft der Fastperiodizität ist invariant bei Addition, Multiplikation und gleichmässigem Grenzübergang, und die Rechnungen spiegeln sich in den entsprechenden formalen Rechnungen mit den Dirichletentwicklungen wieder.

Über den Quotienten zweier fastperiodischen Funktionen hat H. Bohr den folgenden Satz bewiesen[1]:

Es sei $-\infty \leqq \alpha < \beta \leqq +\infty$, und es seien $f(s)$ und $g(s)$ zwei in $[\alpha, \beta]$ reguläre fastperiodische Funktionen, von denen $g(s)$ nicht identisch verschwindet. Ferner sei der Quotient $h(s) = \frac{f(s)}{g(s)}$ im ganzen Streifen (α, β) regulär, d. h. jede im Streifen (α, β) gelegene Nullstelle von $g(s)$ sei zugleich Nullstelle von $f(s)$, und zwar von mindestens eben so hoher Multiplizität. Dann ist dieser Quotient wiederum eine in $[\alpha, \beta]$ fastperiodische Funktion.

Eine notwendige und hinreichende Bedingung für die Fastperiodizität in $[\alpha, \beta]$ ist, dass $f(s)$ Grenzfunktion einer in $[\alpha, \beta]$ gleichmässig konvergierenden Folge von Exponentialpolynomen $p(s) = \sum_n a_n e^{\lambda_n \cdot s}$ mit reellen Exponenten λ_n und komplexen Koeffizienten a_n ist. Die Dirichletentwicklung entsteht aus diesen Polynomen durch formalen Grenzübergang.

Zu einer in $[\alpha, \beta]$ fastperiodischen Funktion

$$f(s) \sim \sum_n A_n e^{\Lambda_n \cdot s}$$

---

[1] H. Bohr [2].

gibt es immer eine Folge von Exponentialpolynomen

$$f_p(s) = \sum_{n=1}^{N_p} A_n^{(p)} e^{\Lambda_n^{(p)} s},$$

in welchen jeder Exponent $\Lambda_n^{(p)}$ einer der Exponenten Λ_n ist und welche gleichmässig in $[\alpha, \beta]$ gegen $f(s)$ konvergiert.

Unter dem Modul M_f einer fastperiodischen Funktion $f(s)$ versteht man den kleinsten Zahlenmodul, welcher die Exponenten der Funktion enthält, also die Gesamtheit aller Zahlen, welche auf mindestens eine Weise durch eine Linearkombination

$$h_1 \Lambda_{n_1} + \cdots + h_p \Lambda_{n_p}$$

mit ganzzahligen Koeffizienten $h_1, \cdots, h_p$ darstellbar sind.

Periodische Funktionen der Periode ip sind dadurch charakterisiert, dass die Exponenten ganzzahlige Vielfache der Zahl $\frac{2\pi}{p}$ sind; d. h. der Modul einer solchen Funktion ist in dem Modul aller ganzzahligen Vielfachen der Zahl $\frac{2\pi}{p}$ enthalten.

Grenzperiodische Funktionen der Grenzperiode ip sind dadurch charakterisiert, dass die Exponenten rationale Vielfache der Zahl $\frac{2\pi}{p}$ sind; d. h. der Modul einer solchen Funktion ist in dem Modul aller rationalen Vielfachen der Zahl $\frac{2\pi}{p}$ enthalten. Dabei ist zugleich jedes rationale Vielfache von ip eine Grenzperiode der Funktion. Die Eigenschaft der Grenzperiodizität mit der Grenzperiode ip ist offenbar bei Addition, Multiplikation und gleichmässigem Grenzübergang invariant.

Damit eine Funktion $f(s)$ in $[\alpha, \beta]$ grenzperiodisch der Grenzperiode ip ist, ist notwendig und hinreichend, dass man zu $\varepsilon > 0$ und jedem beschnittenen Streifen $(\alpha <)\, \alpha_1 < \sigma < \beta_1\, (< \beta)$ eine rationale Zahl r mit der Eigenschaft finden kann, dass jedes ganzzahlige Vielfache der Zahl irp eine zu ε gehörige Verschiebungszahl der Funktion $f(s)$ im Streifen $[\alpha_1, \beta_1]$ ist. Aus dieser Charakterisierung folgt leicht durch Betrachtung des Bohrschen Beweises über den Quotienten, dass die Funktion $h(s)$ grenzperiodisch der Grenzperiode ip ist, wenn die Funktionen $f(s)$ und $g(s)$ beide grenzperiodische Funktionen der Grenzperiode ip sind[1].

Die Frage der Nullstellenverteilung einer analytischen fastperiodischen Funktion ist früher von B. Jessen[2] behandelt worden, wobei er die folgenden beiden Sätze bewiesen hat:

Satz A. Es sei $-\infty \leqq \alpha < \beta \leqq +\infty$ und $f(s) = f(\sigma + it)$ eine in $[\alpha, \beta]$ reguläre fastperiodische Funktion, die nicht identisch verschwindet. Dann ist für beliebiges positives T die Funktion

$$\varphi_f(\sigma; T) = \frac{1}{2T}\int_{-T}^{+T} \log|f(\sigma + it)|\,dt$$

eine im Intervall $\alpha < \sigma < \beta$ stetige Funktion von σ. Für $T \to \infty$ strebt diese Funktion gleichmässig in jedem abgeschlossenen Teilintervall von $\alpha < \sigma < \beta$ gegen eine stetige Grenzfunktion

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[1] Der Beweis beruht nämlich darauf dass es zu jedem $\varepsilon > 0$ und jedem beschnittenen Streifen $(\alpha <)\, \alpha_1 < \sigma < \beta_1\, (< \beta)$ ein $\eta > 0$ und einen beschnittenen Streifen $(\alpha <)\, \alpha_2 < \sigma < \beta_2\, (< \beta)$ derart gibt, dass jede zu η gehörige gemeinsame Verschiebungszahl von $f(s)$ und $g(s)$ im Streifen (α_2, β_2) eine zu ϵ gehörige Verschiebungszahl von $h(s)$ im Streifen (α_1, β_1) ist.

[2] B. Jessen [1]. Jessen beweist auch (was wir jedoch nicht benutzen werden), dass die Fuktion

$$\varphi_f(\sigma; \gamma, \delta) = \frac{1}{\delta - \gamma}\int_{\gamma}^{\delta} \log|f(\sigma + it)|\,dt$$

für $\delta - \gamma \to \infty$ gleichmässig in jedem abgeschlossenen Teilintervall von $\alpha < \sigma < \beta$ gegen eine stetige Grenzfunktion $\varphi_f(\sigma) = \lim_{(\delta - \gamma) \to \infty} \varphi_f(\sigma; \gamma, \delta)$ strebt.
Für unsere Anwendungen wählen wir $\gamma = -T$ und $\delta = +T$.

$$\varphi_f(\sigma) = \lim_{T\to\infty} \varphi_f(\sigma; T).$$

$\varphi_f(\sigma)$ heisst die zur Funktion $f(s)$ gehörige Jensensche Funktion; sie ist eine konvexe Funktion von σ und bestimmt in der folgenden Weise die Verteilung der Nullstellen von $f(s)$: Ist $\alpha < \alpha' < \beta' < \beta$, und bezeichnen wir mit $N(\alpha', \beta'; T)$ die Anzahl der Nullstellen von $f(s)$ im Rechteck $\alpha' < \sigma < \beta', -T < t < +T$, so existiert für $T \to \infty$, falls nur $\varphi_f(\sigma)$ in den Punkten α' und β' differenzierbar ist, der Grenzwert

$$H(\alpha', \beta') = \lim_{T\to\infty} \frac{N(\alpha', \beta'; T)}{2T},$$

und es gilt die Jensensche Formel

$$H(\alpha', \beta') = \frac{1}{2\pi}\bigl(\varphi'(\beta') - \varphi'(\alpha')\bigr).$$

Die Grösse $H(\alpha', \beta')$ wird als Häufigkeit der Nullstellen von $f(s)$ im Streifen $\alpha' < \sigma < \beta'$ bezeichnet. Für beliebige Werte von α' und β' treten an Stelle dieser Formel die allgemeineren Relationen

$$\frac{1}{2\pi}\bigl(\varphi'(\beta'-0) - \varphi'(\alpha'+0)\bigr) \leqq \underline{\lim}_{T\to\infty} \frac{N(\alpha', \beta'; T)}{2T} \leqq$$

$$\overline{\lim}_{T\to\infty} \frac{N(\alpha', \beta'; T)}{2T} \leqq \frac{1}{2\pi}\bigl(\varphi'(\beta'+0) - \varphi'(\alpha'-0)\bigr).$$

Satz B. Die in $[\alpha, \beta]$ fastperiodische Funktion $f(s)$ ist dann und nur dann im Streifen $(\alpha \leqq)\, \alpha_0 < \sigma < \beta_0\, (\leqq \beta)$ von Null verschieden, wenn ihre zugehörige Jensensche Funktion $\varphi_f(\sigma)$ in $\alpha_0 < \sigma < \beta_0$ linear ist. Ist dies der Fall, und ist $\varphi_f(\sigma) = \varkappa + \lambda\sigma$, so ist $f(s)$ eindeutig in der Form

$$f(s) = \varepsilon \cdot e^{\varkappa + \lambda s + g(s)}$$

darstellbar, wobei $|\varepsilon| = 1$ ist und $g(s)$ eine in $[\alpha_0, \beta_0]$ fastperiodische Funktion ohne konstantes Glied in der Dirichletentwicklung bedeutet. Ferner enthält der Modul M_f der Dirichletexponenten von $f(s)$ sowohl die Zahl λ als auch den Modul M_g der Dirichletexponenten von $g(s)$.

Im Anschluss an diese Sätze liegt es nahe zu fragen: Welche konvexen Funktionen $\varphi(\sigma), \alpha < \sigma < \beta$ können als Jensensche Funktion einer in $[\alpha, \beta]$ fastperiodischen Funktion vorkommen? Diese Frage können wir indessen nicht beantworten; aber die Vermutung ist naheliegend, dass jede konvexe Funktion diese Eigenschaft hat. Wir können auch die Frage etwas allgemeiner stellen, nämlich wie folgt: Gegeben sei ein beliebiger Zahlenmodul M; welche Bedingungen muss dann eine in $\alpha < \sigma < \beta$ konvexe Funktion $\varphi(\sigma)$ erfüllen, damit es eine in $[\alpha, \beta]$ fastperiodische Funktion $f(s)$ gibt, für welche $\varphi_f(\sigma) = \varphi(\sigma)$ ist, wenn noch verlangt wird, dass der Modul M_f der Dirichletexponenten von $f(s)$ gleich M oder in M enthalten ist?

Auf Grund des oben erwähnten Satzes B haben wir sofort die notwendige Bedingung, dass $\varphi'(\sigma)$ in den eventuellen Konstanzintervallen nur Werte aus M annimmt. Hinreichend ist aber diese Bedingung nicht in allen Fällen; besteht z. B. der Modul M aus allen ganzzahligen Vielfachen der Zahl $\frac{2\pi}{p}$, d. h. handelt es sich um die Charakterisierung derjenigen konvexen Funktionen $\varphi(\sigma)$, die als Jensensche Funktion einer periodischen Funktion $f(s)$ der Periode ip vorkommen können, so findet man als weitere notwendige Bedingung, dass $\varphi(\sigma)$ stückweise linear ist. Beide Bedingungen zusammen sind in diesem Falle hinreichend. Für beliebige Modulen M scheint die Frage sehr schwierig zu sein; dagegen wollen wir sie in dem speziellen Falle, wo der Modul M aus allen rationalen Vielfachen der Zahl $\frac{2\pi}{p}$ besteht, beantworten, d. h. wo es sich um die Charakterisierung derjenigen konvexen Funktionen $\varphi(\sigma)$ handelt, die als Jensensche Funktion einer grenzperiodischen Funktion $f(s)$ der Grenzperiode ip vorkommen können. Das Ziel der vorliegenden Arbeit ist zu zeigen, dass die oben gefundene notwendige Bedingung zugleich hinreichend ist; es gilt nämlich der folgende Hauptsatz.

Satz 1. Es seien gegeben der Modul M, der aus allen rationalen Vielfachen der Zahl $\frac{2\pi}{p}$ besteht, sowie eine konvexe Funktion $\varphi(\sigma)$, $\alpha < \sigma < \beta$, für welche $\varphi'(\sigma)$ in den eventuellen Konstanzintervallen nur Werte aus M annimmt. Dann ist es möglich eine in $[\alpha, \beta]$ analytische grenzperiodische Funktion $f(s)$ der Grenzperiode ip zu bestimmen, deren Jensensche Funktion gleich der gegebenen konvexen Funktion ist; d. h. es gilt $\varphi_f(\sigma) = \varphi(\sigma)$.

Für Ratschläge bei der Ausarbeitung der vorliegenden Untersuchung bin ich Prof. B. Jessen zu grossem Dank verpflichtet.

§ 2,

Zurückführung des Hauptsatzes auf einen Spezialfall.

In diesen Paragraphen wollen wir den in der Einleitung formulierten Satz 1 auf den folgenden Spezialfall zurückführen:

Satz 2. Es seien gegeben der Modul M, der aus allen rationalen Vielfachen der Zahl $\frac{2\pi}{p}$ besteht, sowie eine konvexe Funktion $\varphi(\sigma), -\infty < \sigma < +\infty$, für welche $\varphi'(\sigma)$ in den eventuellen Konstanzintervallen nur Werte aus M annimmt. Es gebe ferner zwei Zahlen γ und δ, $\gamma < \delta$ mit der Eigenschaft, dass $\varphi(\sigma)$ auf jeder der beiden Halbgeraden $\sigma \leqq \gamma$ und $\sigma \geqq \delta$ linear ist. Dann ist es möglich eine in $[-\infty, \infty]$ analytische grenzperiodische Funktion $f(s)$ der Grenzperiode ip zu bestimmen, deren Jensensche Funktion gleich der gegebenen konvexen Funktion ist; d. h. es gilt $\varphi_f(\sigma) = \varphi(\sigma)$.

Um aus diesem Satz den Satz 1 zu folgern, verfahren wir ähnlich wie beim Beweis des Weierstrassschen Produktsatzes folgendermassen:

Sei $\varphi(\sigma)$, $\alpha < \sigma < \beta$, die gegebene konvexe Funktion. Mit A bezeichnen wir die Menge der Punkte der σ-Achse, in welchen $\varphi(\sigma)$ eine der folgenden zwei Eigenschaften hat

1) $\varphi(\sigma)$ differenzierbar mit $\varphi'(\sigma)$ in M,

2) $\varphi(\sigma)$ nicht differenzierbar.

Es ist klar, dass die Punktmenge A überall dicht auf der σ-Achse liegt.

In der Punktmenge A definieren wir jetzt eine Funktion $\varrho(\sigma)$ folgendermassen

$$\varrho(\sigma) = \begin{cases} \varphi'(\sigma), \text{ wenn } \varphi(\sigma) \text{ differenzierbar ist,} \\ r \cdot \dfrac{2\pi}{p}, \text{ wo } r \text{ rational ist und der Ungleichung} \\ \varphi'(\sigma - 0) < r \cdot \dfrac{2\pi}{p} < \varphi'(\sigma + 0) \text{ genügt, wenn } \varphi(\sigma) \\ \quad \text{nicht differenzierbar ist.} \end{cases}$$

Die Werte der Funktion $\varrho(\sigma)$ gehören dann alle dem Modul M an.

Wir wählen jetzt aus der Menge A zwei Folgen von Zahlen $\gamma_1, \gamma_2, \gamma_3, \ldots$ und $\delta_1, \delta_2, \delta_3, \ldots$, derart dass

$$\alpha < \ldots < \gamma_3 < \gamma_2 < \gamma_1 < \delta_1 < \delta_2 < \delta_3 < \ldots < \beta,$$

und $\delta_n \to \beta$ und $\gamma_n \to \alpha$ für $n \to \infty$. Für jeden Wert von n definieren wir eine konvexe Funktion $\psi_n(\sigma), -\infty < \sigma < +\infty$, in der folgenden Weise

$$\psi_n(\sigma) = \begin{cases} \varrho(\gamma_n)(\sigma - \gamma_n) + \varphi(\gamma_n) & \text{für } \sigma \leqq \gamma_n, \\ \varphi(\sigma) & \text{für } \gamma_n < \sigma < \delta_n, \\ \varrho(\delta_n)(\sigma - \delta_n) + \varphi(\delta_n) & \text{für } \sigma \geqq \delta_n. \end{cases}$$

Nun gilt

$$\psi_1(\sigma) \leqq \psi_2(\sigma) \leqq \dots,$$

und ferner ist klar, dass $\psi_n(\sigma)$ im Intervalle $\alpha < \sigma < \beta$ gegen $\varphi(\sigma)$ strebt. Definieren wir jetzt eine andere Folge von Funktionen,

$$\varphi_1(\sigma) = \psi_1(\sigma),$$

und für $n \geqq 2$

$$\varphi_n(\sigma) = \psi_n(\sigma) - \psi_{n-1}(\sigma),$$

so gilt offenbar in $\alpha < \sigma < \beta$

$$\varphi(\sigma) = \sum_{n=1}^{\infty} \varphi_n(\sigma).$$

Jede der Funktionen $\varphi_n(\sigma)$ genügt den Bedingungen des Satzes 2; $\varphi_n(\sigma)$ ist nämlich eine für $-\infty < \sigma < +\infty$ konvexe Funktion, welche für $\sigma \leqq \gamma_n$ und $\sigma \geqq \delta_n$ linear mit $\varphi_n'(\sigma)$ in M ist. Es gibt also eine in $[-\infty, \infty]$ analytische grenzperiodische Funktion $f_n(s)$, für welche $\varphi_{f_n}(\sigma) = \varphi_n(\sigma)$ ist.

Für $n \geqq 2$ ist die Funktion $\varphi_n(\sigma)$ im Intervalle $\gamma_{n-1} < \sigma < \delta_{n-1}$ gleich Null; nach dem Satze B der Einleitung ist also $f_n(s)$ für $\gamma_{n-1} < \sigma < \delta_{n-1}$ eindeutig in der Form

$$f_n(s) = \varepsilon_n e^{g_n(s)}$$

darstellbar; wobei $|\varepsilon_n| = 1$ und $g_n(s)$ eine in $[\gamma_{n-1}, \delta_{n-1}]$ grenzperiodische Funktion der Grenzperiode ip ohne konstantes Glied in der Dirichletentwicklung ist.

Es sei jetzt $n \geqq 3$. Dann ist es möglich ein Exponentialpolynom $g_n^*(s)$ ohne konstantes Glied und mit Exponenten aus M, also eine analytische grenzperiodische Funktion der Grenzperiode ip zu bestimmen, für welche

$$|g_n(s) - g_n^*(s)| < \frac{1}{2^n}$$

für $\gamma_{n-2} < \sigma < \delta_{n-2}$.

Die Funktion $\frac{1}{\varepsilon_n} e^{-g_n^*(s)}$ ist dann eine in $[-\infty, \infty]$ analytische grenzperiodische Funktion der Grenzperiode ip, deren Jensensche Funktion nach dem Satze B identisch gleich Null ist. Wählen wir also

$$f_n^*(s) = f_n(s) \frac{1}{\varepsilon_n} e^{-g_n^*(s)} = e^{g_n(s) - g_n^*(s)},$$

dann ist $f_n^*(s)$ eine in $[-\infty, \infty]$ analytische grenzperiodische Funktion der Grenzperiode ip, für welche

$$\varphi_{f_n^*}(\sigma) = \varphi_{f_n}(\sigma) = \varphi_n(\sigma)$$

in $-\infty < \sigma < \infty$ gilt. Ferner ist für $\gamma_{n-2} < \sigma < \delta_{n-2}$

$$e^{-\frac{1}{2^n}} < |f_n^*(s)| < e^{\frac{1}{2^n}}.$$

Hieraus folgt, dass das unendliche Produkt

$$f(s) = f_1(s) \cdot f_2(s) \prod_{n=3}^{\infty} f_n^*(s)$$

in $[\alpha, \beta]$ gleichmässig konvergent ist. Da jeder Faktor des Produktes eine in $[\alpha, \beta]$ grenzperiodische Funktion der Grenzperiode ip ist, ist auch $f(s)$ eine solche Funktion. Die dieser Funktion entsprechende Jensensche Funktion ist nun gleich der gegebenen konvexen Funktion $\varphi(\sigma)$; denn für jedes $n \geqq 3$ gilt im Streifen $\gamma_{n-2} < \sigma < \delta_{n-2}$

$$f(s) = f_1(s) f_2(s) \ldots f^*_{n-1}(s) \prod_{\nu=n}^{\infty} f^*_\nu(s),$$

wo

$$e^{-\frac{1}{2^\nu}} < |f^*_\nu(s)| < e^{\frac{1}{2^\nu}} \text{ für jedes } \nu \geqq n;$$

also ist

$$\log|f(s)| = \log|f_1(s)| + \log|f_2(s)| + \cdots + \log|f^*_{n-1}(s)| + \sum_{\nu=n}^{\infty} \log|f^*_\nu(s)|,$$

wo die letzte Reihe durch die Reihe $\sum_{\nu=n}^{\infty} \frac{1}{2^\nu}$ majorisiert wird, und hieraus folgt sofort

$$\varphi_f(\sigma) = \varphi_{f_1}(\sigma) + \varphi_{f_2}(\sigma) + \cdots + \varphi_{f_{n-1}}(\sigma) + \sum_{\nu=n}^{\infty} \varphi_{f_\nu}(\sigma) = \varphi(\sigma).$$

§ 3.

Einleitende Konstruktionen zum Beweis des Hauptsatzes. Konstruktion einer brauchbaren Nullstellenmenge.

In den folgenden beiden Paragraphen wollen wir den Satz 2 beweisen.

Sei $\varphi(\sigma), -\infty < \sigma < +\infty$, die gegebene konvexe Funktion, $\varphi'(\sigma) = r_1 \cdot \frac{2\pi}{p}$ für $\sigma < \gamma$ und $= r_2 \frac{2\pi}{p}$ für $\sigma > \delta$. Wir bemerken, dass der Satz im Fall $r_1 = r_2$ trivial ist; in diesem Fall gilt ja $\varphi(\sigma) = \varkappa + \lambda\sigma, -\infty < \sigma < +\infty$, wo λ in M liegt, also ist die Funktion $f(s) = e^{\varkappa + \lambda s}$ grenzperiodisch der Grenzperiode ip, und es gilt offenbar $\varphi_f(\sigma) = \varkappa + \lambda\sigma$. Wir können deshalb im folgenden $r_1 < r_2$ annehmen.

In diesem Paragraphen werden wir, von der gegebenen konvexen Funktion $\varphi(\sigma)$ ausgehend, eine Punktmenge S konstruieren, die dann in § 4 als Nullstellenmenge der Funktion $f(s)$ benutzt werden soll. Die Punktmenge S muss deshalb im Streifen $\gamma \leqq \sigma \leqq \delta$ gelegen sein. Jeder Punkt von S soll eine zweifache Nullstelle von $f(s)$ sein. Da für $\alpha' < \gamma$ und $\beta' > \delta$

$$\frac{1}{2\pi}\left(\varphi'(\beta') - \varphi'(\alpha')\right) = \frac{r_2 - r_1}{p}$$

ist, muss also, wenn mit $N(T)$ die doppelte Anzahl der Punkte von S im Streifen $-T < t < +T$ bezeichnet wird, die Relation

$$\lim_{T \to \infty} \frac{N(T)}{2T} = \frac{r_2 - r_1}{p}$$

erfüllt sein.

Wir wollen es so einrichten, dass S aus je einem Punkt der Geraden

$$t = k \cdot q, q = \frac{2p}{r_2 - r_1}, k = 0, \pm 1, \pm 2, \ldots$$

besteht. Dabei ist natürlich die Wahl von q mit Rücksicht auf die obige Limesrelation getroffen worden. Den auf der Geraden $t = k \cdot q$ liegenden Punkt von S bezeichnen wir mit $\sigma(k) + ikq$; die Menge S wird dann durch die Funktion

$$\sigma = \sigma(k)$$

angegeben.

Die Konstruktion von S, d. h. von $\sigma(k)$, beruht nun darauf, dass wir eine Folge von stückweise linearen konvexen Funktionen $\varphi_n(\sigma)$ konstruieren, die gegen $\varphi(\sigma)$ strebt. Die rationalen Zahlen zwischen r_1 und r_2 werden in eine Folge

$$r_1, r_2, r_3, \ldots, r_n, \ldots$$

geordnet, und für jedes n bezeichnen wir mit $\psi_n(\sigma)$ diejenige lineare Funktion, deren Bild die Stützgerade der Neigung $r_n \cdot \frac{2\pi}{p}$ der Kurve $\varphi(\sigma)$ ist. Setzen wir dann

$$\varphi_n(\sigma) = \operatorname{Max}\{\psi_1(\sigma), \psi_2(\sigma), \ldots, \psi_{n+1}(\sigma)\},$$

so gilt offenbar $\varphi_n(\sigma) \to \varphi(\sigma)$, sogar gleichmässig für alle σ.

Für jedes n bezeichnen wir mit $r_1^n, r_2^n, \ldots, r_{n+1}^n$ diejenige Permutation der Zahlen $r_1, r_2, \ldots, r_{n+1}$, für welche $r_1^n < r_2^n < \ldots < r_{n+1}^n$ ist, und mit $\psi_1^n(\sigma), \psi_2^n(\sigma), \ldots, \psi_{n+1}^n(\sigma)$ die entsprechende Permutation von $\psi_1(\sigma), \psi_2(\sigma), \ldots, \psi_{n+1}(\sigma)$[1]. Dann ist auch

$$\varphi_n(\sigma) = \operatorname{Max}\{\psi_1^n(\sigma), \psi_2^n(\sigma), \ldots, \psi_{n+1}^n(\sigma)\}.$$

Es sei σ_j^n die Abszisse des Schnittpunktes der Kurven $\psi_j^n(\sigma)$ und $\psi_{j+1}^n(\sigma)$; dann ist offenbar $\sigma_1^n \leqq \sigma_2^n \leqq \ldots \leqq \sigma_n^n$. Jedem σ_j^n ordnen wir die Differenz $p_j^n = (r_{j+1}^n - r_j^n)\frac{2\pi}{p}$ zwischen den Neigungen von $\psi_{j+1}^n(\sigma)$ und $\psi_j^n(\sigma)$ zu. Für jedes n verhalten sich die Zahlen $p_1^n, p_2^n, \ldots, p_n^n$ zu einander wie ein System von teilerfremden natürlichen Zahlen $P_1^n, P_2^n, \ldots, P_n^n$, deren Summe wir mit Q_n bezeichnen.

Der Übergang von $\varphi_n(\sigma)$ zu $\varphi_{n+1}(\sigma)$ geschieht durch Hinzunahme einer weiteren Stützgeraden, nämlich der Geraden $\psi_{n+2}(\sigma)$. Das $(n+2)$-Tupel $r_1^{n+1}, r_2^{n+1}, \ldots, r_{n+2}^{n+1}$ entsteht also aus dem $(n+1)$-Tupel $r_1^n, r_2^n, \ldots, r_{n+1}^n$ durch Einschiebung der Zahl r_{n+2}; es sei etwa

$$r_{j_n}^n < r_{n+2} < r_{j_n+1}^n.$$

Dann unterscheidet sich das zu $\varphi_{n+1}(\sigma)$ gehörige $(n+1)$-

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[1] Für jedes n gilt offenbar $r_1^n = r_1$, $r_{n+1}^n = r_2$.

Tupel $\sigma_1^{n+1}, \sigma_2^{n+1}, \ldots, \sigma_{n+1}^{n+1}$ von dem zu $\varphi_n(\sigma)$ gehörigen n-Tupel $\sigma_1^n, \sigma_2^n, \ldots, \sigma_n^n$ dadurch, dass an Stelle von $\sigma_{j_n}^n$ die beiden Zahlen $\sigma_{j_n}^{n+1}$ und $\sigma_{j_n+1}^{n+1}$ getreten sind; für $j < j_n$ gilt $\sigma_j^n = \sigma_j^{n+1}$, und für $j > j_n$ gilt $\sigma_j^n = \sigma_{j+1}^{n+1}$. Für die zugeordneten Zahlen p_j^n hat man

$$p_j^n = \begin{cases} p_j^{n+1} & \text{für } j < j_n, \\ p_j^{n+1} + p_{j+1}^{n+1} & \text{für } j = j_n, \\ p_{j+1}^{n+1} & \text{für } j > j_n. \end{cases}$$

Hieraus folgt sofort, dass Q_n ein Teiler von Q_{n+1} ist, und

$$\frac{Q_{n+1}}{Q_n} \cdot P_j^n = \begin{cases} P_j^{n+1} & \text{für } j < j_n, \\ P_j^{n+1} + P_{j+1}^{n+1} & \text{für } j = j_n, \\ P_{j+1}^{n+1} & \text{für } j > j_n. \end{cases}$$

Zu jeder der Funktionen $\varphi_n(\sigma)$ definieren wir jetzt eine Punktmenge S_n, welche aus je einem Punkt der Geraden $t = k \cdot q$, $k = 0, \pm 1, \pm 2, \ldots$ besteht. Bezeichnen wir den auf der Geraden $t = k \cdot q$ liegenden Punkt von S_n mit $\sigma_n(k) + ikq$, so wird die Punktmenge S_n durch die Funktion

$$\sigma = \sigma_n(k)$$

gegeben. Es handelt sich also darum diese Funktion $\sigma_n(k)$ zu definieren.

Auf Grund der obigen Relationen können wir offenbar für jedes n die Menge K aller ganzen Zahlen k derart in n disjunkte Mengen $K_1^n, K_2^n, \ldots, K_n^n$ zerlegen, dass folgende Bedingungen erfüllt sind:

1) Die Menge K_j^n besteht aus P_j^n Restklassen mod. Q_n.

2) Für jedes n gilt

$$K_j^n = \begin{cases} K_j^{n+1} & \text{für } j < j_n, \\ K_j^{n+1} + K_{j+1}^{n+1} & \text{für } j = j_n, \\ K_{j+1}^{n+1} & \text{für } j > j_n. \end{cases}$$

Es sei eine Folge von derartigen Zerlegungen von K fest gewählt; wir definieren dann die Funktion $\sigma_n(k)$ und damit die Menge S_n dadurch, dass wir $\sigma_n(k) = \sigma_j^n$ für alle k der Menge K_j^n setzen. Jede dieser Mengen S_n erfüllt dann die folgenden Bedingungen:

1) S_n gehört dem Streifen $\gamma \leqq \sigma \leqq \delta$ an und ist periodisch mit der Periode $iQ_n q$.

2) Die Punkte von S_n liegen alle auf den durch die Nichtdifferenzierbarkeitspunkte von $\varphi_n(\sigma)$ gehenden Geraden, und zwar ist die Anzahl der einer Periode von S_n angehörigen Punkte auf einer dieser Geraden $\sigma = \sigma_0$ dem zugehörigen Sprung $\varphi_n'(\sigma_0+0) - \varphi_n'(\sigma_0-0)$ proportional. Also gilt, wenn $N_n(\alpha', \beta'; T)$ die doppelte Anzahl der im Rechteck $\alpha' < \sigma < \beta', -T < t < T$ liegenden Punkte von S_n bedeutet, für beliebige Punkte α' und β' eine Relation

$$\lim_{T \to \infty} \frac{N_n(\alpha', \beta'; T)}{2T} = c_n \cdot \left(\varphi_n'(\beta'-0) - \varphi_n'(\alpha'+0)\right),$$

wo c_n eine von α' und β' unabhängige Konstante ist. Wählen wir insbesondere $\alpha' < \gamma$ und $\beta' > \delta$, so erhalten wir

$$\lim_{T \to \infty} \frac{N_n(\alpha', \beta'; T)}{2T} = \frac{2}{q} = \frac{r_2 - r_1}{p}, \; \varphi_n'(\beta') - \varphi_n'(\alpha') = \frac{2\pi}{p}(r_2 - r_1),$$

also

$$c_n = \frac{1}{2\pi}.$$

Für beliebige α' und β' gilt also

$$\lim_{T\to\infty}\frac{N_n(\alpha',\beta';T)}{2T}=\frac{1}{2\pi}\left(\varphi_n'(\beta'-0)-\varphi_n'(\alpha'+0)\right).$$

Die gewünschte Menge S entsteht nun durch einen Grenzübergang. Wir wollen zeigen dass die Funktionenfolge

$$\sigma_1(k),\sigma_2(k),\ldots,\sigma_n(k),\ldots$$

für $n\to\infty$ gleichmässig in k gegen eine Funktion $\sigma(k)$ strebt; diese Funktion $\sigma(k)$ definiert dann die gewünschte Menge S. Zum Beweis werde das Intervall $\gamma\leqq\sigma\leqq\delta$ in endlich viele Teilintervalle der Länge $\leqq\frac{\varepsilon}{2}$ zerlegt und in jedem Teilintervall ein Punkt der Menge A gewählt. Der Abstand zwischen zwei aufeinander folgenden dieser Punkte ist $\leqq\varepsilon$. Es seien

$$r_{n_1}\frac{2\pi}{p},r_{n_2}\frac{2\pi}{p},\ldots,r_{n_m}\frac{2\pi}{p}$$

die Werte der Funktion $\varrho(\sigma)$ in diesen Punkten und $N=N(\varepsilon)=\operatorname{Max}\{n_1,n_2,\ldots,n_m\}$. Dann gilt offenbar

$$|\sigma_n(k)-\sigma_{n+p}(k)|\leqq\varepsilon \text{ für alle } n>N(\varepsilon) \text{ und alle } p\geqq 0.$$

In diesem Paragraphen wollen wir noch beweisen, dass für beliebige Punkte α' und β' die Relationen

$$\frac{1}{2\pi}\left(\varphi'(\beta'-0)-\varphi'(\alpha'+0)\right)\leqq\varliminf_{T\to\infty}\frac{N(\alpha',\beta';T)}{2T}$$
$$\leqq\varlimsup_{T\to\infty}\frac{N(\alpha',\beta';T)}{2T}\leqq\frac{1}{2\pi}\left(\varphi'(\beta'+0)-\varphi'(\alpha'-0)\right)$$

gelten, wenn mit $N(\alpha',\beta';T)$ die doppelte Anzahl der im Rechteck $\alpha'<\sigma<\beta', -T<t<T$ liegenden Punkte von S bezeichnet wird.

Für ein beliebiges $\varepsilon < \frac{\beta' - \alpha'}{2}$ gilt

$$\frac{N(\alpha', \beta'; T)}{2T} \geqq \frac{N_n(\alpha' + \varepsilon, \beta' - \varepsilon; T)}{2T} \quad \text{für } n > N(\varepsilon).$$

Hieraus folgt

$$\underline{\lim}_{T \to \infty} \frac{N(\alpha', \beta'; T)}{2T} \geqq \lim_{T \to \infty} \frac{N_n(\alpha' + \varepsilon, \beta' - \varepsilon; T)}{2T} = \frac{1}{2\pi}\left(\varphi_n'(\beta' - \varepsilon - 0) - \varphi_n'(\alpha' + \varepsilon + 0)\right)$$

für $n > N$, und hieraus für $n \to \infty$[1]

$$\underline{\lim}_{T \to \infty} \frac{N(\alpha', \beta'; T)}{2T} \geqq \frac{1}{2\pi}\left(\varphi'(\beta' - \varepsilon - 0) - \varphi'(\alpha' + \varepsilon + 0)\right)$$

für jedes ε, also für $\varepsilon \to 0$

$$\underline{\lim}_{T \to \infty} \frac{N(\alpha', \beta'; T)}{2T} \geqq \frac{1}{2\pi}\left(\varphi'(\beta' - 0) - \varphi'(\alpha' + 0)\right).$$

Durch Approximation von aussen ergibt sich analog

$$\overline{\lim}_{T \to \infty} \frac{N(\alpha', \beta'; T)}{2T} \leqq \frac{1}{2\pi}\left(\varphi'(\beta' + 0) - \varphi'(\alpha' - 0)\right).$$

Wenn α' und β' Differenzierbarkeitspunkte von $\varphi(\sigma)$ sind, gilt also insbesondere

$$\lim_{T \to \infty} \frac{N(\alpha', \beta'; T)}{2T} = \frac{1}{2\pi}\left(\varphi'(\beta') - \varphi'(\alpha')\right).$$

Wenn es also eine in $[-\infty, \infty]$ grenzperiodische Funktion

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[1] Hierbei benutzen wir, dass für jedes σ

$$\underline{\lim}_{n \to \infty} \varphi_n'(\sigma - 0) \geqq \varphi'(\sigma - 0), \quad \overline{\lim}_{n \to \infty} \varphi_n'(\sigma + 0) \leqq \varphi'(\sigma + 0),$$

was man aus der Konvexität leicht entnimmt.

$f(s)$ der Grenzperiode ip gibt, die in jedem Punkt von S eine zweifache Nullstelle hat und sonst von Null verschieden ist, muss nach Satz A für beliebige gemeinsame Differenzierbarkeitspunkte von $\varphi(\sigma)$ und $\varphi_f(\sigma)$ die Relation

$$\frac{1}{2\pi}\left(\varphi'(\beta')-\varphi'(\alpha')\right)=\frac{1}{2\pi}\left(\varphi_f'(\beta')-\varphi_f'(\alpha')\right)$$

erfüllt sein, woraus folgt, dass $\varphi(\sigma)-\varphi_f(\sigma)$ linear sein muss, etwa $=\varkappa+\lambda\sigma$. Dabei muss offenbar λ zum Modul M gehören; denn nach Satz B liegt der konstante Wert von $\varphi_f'(\sigma)$ für $\sigma<\gamma$ in M. Setzen wir dann $g(s)=f(s)\,e^{\varkappa+\lambda s}$, so ist $g(s)$ offenbar grenzperiodisch der Grenzperiode ip, und es gilt $\varphi_g(\sigma)=\varphi_f(\sigma)+\varkappa+\lambda\sigma=\varphi(\sigma)$. Zum Beweis des Satzes 2 genügt es also, eine grenzperiodische Funktion $f(s)$ der Grenzperiode ip zu konstruieren, welche in jedem Punkt von S eine zweifache Nullstelle hat und sonst von Null verschieden ist.

§ 4.

Konstruktion einer zugehörigen Funktion.

In diesem Paragraphen beschäftigen wir uns mit der Funktion

$$1-e^{as^2},$$

wo a eine Konstante >0 ist. Diese Funktion hat für $s=0$ eine doppelte Nullstelle und für $s=\sqrt{\frac{2g\pi i}{a}}$, g ganz $\neq 0$, einfache Nullstellen.

Sei im Streifen $\gamma\leqq\sigma\leqq\delta$ eine Punktmenge $\{s_k\}$ mit $s_k=\sigma_k+ikq$ $\gamma\leqq\sigma_k\leqq\delta$, $k=0,\pm1,\pm2,\ldots$ gegeben. Dann ist das unendliche Produkt

$$\prod_{k=-\infty}^{\infty}\left(1-e^{a(s-s_k)^2}\right)$$

in jeder beschränkten Punktmenge der Ebene gleichmässig konvergent. Die Reihe

$$\sum_{k=-\infty}^{\infty} \left| e^{a(s-s_k)^2} \right|$$

ist nämlich in jeder beschränkten Punktmenge der Ebene gleichmässig konvergent, was daraus folgt, dass gleichmässig in jeder beschränkten Punktmenge der Ebene

$$\left| e^{a(s-s_k)^2} \right| = e^{a(\sigma-\sigma_k)^2} e^{-a(t-kq)^2} = O\left(\frac{1}{k^2}\right)$$

ist.

Ferner gilt, dass zu jedem Streifen $\gamma^* \leqq \sigma \leqq \delta^*$ eine von der Menge $\{s_k\}$ unabhängige Konstante K mit der Eigenschaft existiert, dass der absolute Betrag des Produktes in $\gamma^* \leqq \sigma \leqq \delta^*$ diese Konstante K nicht übersteigt. Dies folgt sofort daraus, dass jeder Wert, den ein Produkt annimmt, von einem anderen (oder vielleicht demselben) im Rechteck $\gamma^* \leqq \sigma \leqq \delta^*, 0 \leqq t \leqq q$ angenommen wird. Ferner bemerken wir, dass diese Überlegungen auch Gültigkeit behalten, wenn man einen oder mehrere Faktoren weglässt.

Wir betrachten ein bestimmtes dieser Produkte

$$p(s) = \prod_{k=-\infty}^{\infty} \left(1 - e^{a(s-s_k)^2}\right), \; s_k = \sigma_k + ikq\,.$$

Wir wollen zeigen, dass man zu beliebigem $\varepsilon > 0$ und einem vorgegebenen Streifen $\gamma^* \leqq \sigma \leqq \delta^*$ ein $\eta > 0$ so finden kann, dass jedes Produkt

$$p^*(s) = \prod_{k=-\infty}^{\infty} \left(1 - e^{a(s-s'_k)^2}\right),$$

wo man jedes σ_k um weniger als η geändert hat, wo also

$|\sigma_k' - \sigma_k| = \eta(k) < \eta$, im Streifen $\gamma^* \leqq \sigma \leqq \delta^*$ von dem ursprünglichen um weniger als ε abweicht.

Es gilt nämlich

$$\left| p(s) - p^*(s) \right| < K \sideset{}{'}\sum_{-\infty}^{\infty} \left| e^{a(s-s_k)^2} - e^{a(s-s_k')^2} \right|$$

$$\leqq K\eta \sideset{}{'}\sum_{-\infty}^{\infty} \left| 2\,a\,(s-s_k'')\,e^{a(s-s_k'')^2} \right|$$

mit $s_k'' = \sigma_k'' + ikq$, $\sigma_k'' = \sigma_k + \theta(\sigma_k' - \sigma_k)$ $0 < \theta < 1$[1].

Hieraus folgt sofort, dass die Funktion

$$f_a(s) = \prod_{-\infty}^{\infty} \left(1 - e^{a(s-s_k)^2}\right),$$

wo die s_k die Werte der Menge S (§ 3) sind, in $[-\infty, \infty]$ grenzperiodisch der Grenzperiode ip ist; denn diese Funktion lässt sich ja beliebig gut durch periodische Funktionen annähern, deren Perioden sämtlich rationale Vielfache der Zahl ip sind. Diese approximierenden Funktionen sind die Produkte, die entstehen, wenn man die s_k die Punkte der Mengen S_n (§ 3) durchlaufen lässt. Die Menge S_n hat ja die Periode iQ_nq, die gerade ein rationales Vielfaches von ip ist.

Die gewünschte Funktion entsteht nun durch einen Grenzübergang. Wir wählen zwei Folgen von Zahlen

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[1] Dies folgt mit Hilfe der Umformung

$$\prod_{\nu=0}^{\infty} a_\nu - \prod_{\nu=0}^{\infty} b_\nu = (a_0 - b_0)\prod_{\nu=1}^{\infty} a_\nu + b_0\left(\prod_{\nu=1}^{\infty} a_\nu - \prod_{\nu=1}^{\infty} b_\nu\right) =$$

$$(a_0 - b_0)\prod_{\nu=1}^{\infty} a_\nu + b_0\left((a_1 - b_1)\prod_{\nu=2}^{\infty} a_\nu + b_1\left(\prod_{\nu=2}^{\infty} a_\nu - \prod_{\nu=2}^{\infty} b_\nu\right)\right) =$$

$$(a_0 - b_0)\prod_{\nu=1}^{\infty} a_\nu + (a_1 - b_1)\,b_0\prod_{\nu=2}^{\infty} a_\nu + \cdots.$$

$$\delta < \delta_1 < \delta_2 < \cdots \quad \text{und} \quad \cdots < \gamma_2 < \gamma_1 < \gamma$$

mit $\delta_n \to \infty$ und $\gamma_n \to -\infty$. Die Zahl a wird so klein gewählt, dass die Funktion

$$F_0(s) = f_a(s) = \prod_{\nu=-\infty}^{\infty} \left(1 - e^{a(s-s_\nu)^2}\right), \; s_\nu \varepsilon S$$

in $\gamma \leqq \sigma \leqq \delta$ doppelte Nullstellen in den Punkten von S hat und sonst in $\gamma_1 \leqq \sigma \leqq \delta_1$ nullstellenfrei ist. Analog werde a_n für jedes n so klein gewählt, dass die Funktion $f_{a_n}(s)$ in $\gamma \leqq \sigma \leqq \delta$ Nullstellen in den Punkten von S hat und sonst in $\gamma_{n+1} \leqq \sigma \leqq \delta_{n+1}$ nullstellenfrei ist. Bilden wir nun

$$\frac{f_a(s)}{f_{a_1}(s)},$$

so ist diese Funktion grenzperiodisch der Grenzperiode ip in $[\gamma_2, \delta_2]$ und nullstellenfrei in $\gamma_1 \leqq \sigma \leqq \delta_1$. Nach Satz B gilt also für $\gamma_1 < \sigma < \delta_1$

$$\frac{f_a(s)}{f_{a_1}(s)} = e^{\lambda_1 s + h_1(s)},$$

wo λ_1 im Modul M liegt und $h_1(s)$ grenzperiodisch der Grenzperiode ip ist. Es ist daher möglich ein Exponentialpolynom $h_1^*(s)$ mit Exponenten aus M, also eine analytische grenzperiodische Funktion der Grenzperiode ip zu bestimmen, für welche

$$\left| h_1(s) - h_1^*(s) \right| < \frac{1}{2}$$

für $\gamma < \sigma < \delta$ gilt. Setzen wir nun

$$F_1(s) = f_{a_1}(s)\, e^{\lambda_1 s + h_1^*(s)},$$

so ist diese Funktion eine in $[-\infty, \infty]$ analytische grenzperiodische Funktion der Grenzperiode ip, die in $\gamma_2 \leqq \sigma < \gamma$, $\delta < \sigma \leqq \delta_2$ nullstellenfrei ist.

Bilden wir

$$\frac{F_1(s)}{f_{a_2}(s)},$$

so ist diese Funktion grenzperiodisch der Grenzperiode ip in $[\gamma_3, \delta_3]$ und nullstellenfrei in $\gamma_2 \leqq \sigma \leqq \delta_2$. Dann gilt für $\gamma_2 < \sigma < \delta_2$

$$\frac{F_1(s)}{f_{a_2}(s)} = e^{\lambda_2 s + h_2(s)},$$

und wir wählen $h_2^*(s)$ derart, dass

$$\left| h_2(s) - h_2^*(s) \right| < \frac{1}{2^2}$$

für $\gamma_1 < \sigma < \delta_1$ gilt. Setzen wir nun

$$F_2(s) = f_{a_2}(s)\, e^{\lambda_2 s + h_2^*(s)},$$

so ist diese Funktion eine in $[-\infty, \infty]$ analytische grenzperiodische Funktion der Grenzperiode ip, die in $\gamma_3 \leqq \sigma < \gamma$, $\delta < \sigma \leqq \delta_3$ nullstellenfrei ist.

Indem man auf diese Weise fortfährt, erhält man eine Folge von Funktionen

$$F_0(s), F_1(s), \ldots, F_n(s), \ldots,$$

die alle in $[-\infty, \infty]$ grenzperiodisch sind und für welche $F_n(s)$ in $\gamma_{n+1} \leqq \sigma < \gamma$, $\delta < \sigma \leqq \delta_{n+1}$ nullstellenfrei ist. Ferner gilt

$$F_{n+1}(s) = F_n(s)\, e^{h_{n+1}^*(s) - h_{n+1}(s)}$$

für $\gamma_{n+1} < \sigma < \delta_{n+1}$, wobei

$$\left| h_{n+1}(s) - h_{n+1}^*(s) \right| < \frac{1}{2^{n+1}}$$

für $\gamma_n < \sigma < \delta_n$ ist. Diese Folge strebt nun offenbar gleichmässig in $[-\infty, \infty]$ gegen eine Grenzfunktion

$$F(s);$$

denn für beliebige γ' und δ' gilt ja $\gamma_n < \gamma'$ und $\delta_n > \delta'$ für $n \geqq N$, und man hat

$$F_{n+p}(s) = F_n(s)\, e^{(h_{n+p}^*(s) - h_{n+p}(s)) + \cdots + (h_{n+1}^*(s) - h_{n+1}(s))}$$

für $\gamma_n < \sigma < \delta_n$.

Diese Funktion $F(s)$ ist also eine in $[-\infty, \infty]$ grenzperiodische Funktion der Grenzperiode ip, die in jedem Punkt von S eine zweifache Nullstelle besitzt und sonst von Null verschieden ist. Hiermit ist der Beweis des Satzes 2 vollendet.

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METHODEN ZUR NACHFORSCHUNG DES ELEMENTES 85

VON

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VERÖFFENTLICHT VON
ULRIK KEEL

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Vorwort.

Beim Tode des Professors Dr. phil. Erik Buch Andersen im November 1937 lagen zwei angefangene Arbeiten vor, und zwar Studien über anorganische Schwefelverbindungen mit Anwendung von aktivem Schwefel und eine Arbeit über Methoden zur Nachforschung des Elementes 85 (Ekajod). Ein grosser Teil der Versuche war in Zusammenarbeit mit Dipl.-Ing. Ulrik Keel ausgeführt, der auf Grund der hinterlassenen Journale die folgende Abhandlung verfasst hat. Von den beiden angefangenen Arbeiten war nur die Arbeit über das Element 85 so weit geführt, dass an eine Veröffentlichung zu denken war. Buch Andersen hat in derselben Methoden zur Isolierung dieses Elementes gegeben und ihre Anwendung versucht, und diese von ihm ausgearbeiteten Methoden dürften auch für andere Forscher von Interesse und Nutzen sein. U. Keel hat im folgenden eine Übersicht über die erzielten Resultate gegeben. Eine Diskussion der Ergebnisse der Messungen ist nicht versucht worden, da diese Arbeit infolge ihrer Natur für unabgeschlossen betrachtet werden muss. Wir haben es für eine selbstverständliche Pflicht Buch Andersens Andenken gegenüber gehalten, möglichst viel aus seinen hinterlassenen Journalen zu veröffentlichen.

Aarhus Universitet, Det fysiske Institut. Sven Werner.
Februar 1938.

Laut den geltenden Anschauungen über Kernstruktur und Kernstabilität sollte ein dualer, radioaktiver Zerfall, so wie er bisher nur bei den C-Gliedern der natürlichen, radioaktiven Serien bemerkt worden ist, die Möglichkeit haben, häufiger in Erscheinung zu treten. Ein dualer Zerfall an ähnlichen Stellen der anderen natürlichen, radioaktiven, Serien, könnte dann möglicherweise zur Bildung von Isotopen der bisher unbekannten Elemente 85 und 87 Anlass geben; selbstverständlich könnten dann auch neue Isotopen der schon bekannten Elemente gebildet werden.

Da die Isotopen von 85 und 87 wahrscheinlich instabil sind, und somit durch ihre Radioaktivität nachweisbar sein sollten, scheint es angeraten eine chemische Isolierung zu versuchen, und das isolierte Produkt mit einer empfindlichen Zählrohr-Anordnung auf Aktivität zu prüfen. Um von jeder Hypothese, wo etwa eine solche Abzweigung stattfindet, unabhängig zu sein, werden Mineralien verwendet, die Zersetzungsprodukte in radioaktivem Gleichgewicht enthalten. Aus früheren Untersuchungen[1] ist bekannt, dass die Konzentration dieser Elemente jedenfalls sehr gering sein muss; es werden deshalb sehr grosse Anforderungen an die chemische Trennung gestellt, da das Auftreten auch nur von geringsten Mengen anderer radioaktiver Elemente vermieden werden muss. Da 85 die günstigsten Bedingungen in chemischer Hinsicht zu bieten

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[1] G. Hevesy und R. Hobbie, Zs. f. anorg. Ch. 208, 107, 1932.

scheint, wurde zuerst eine Nachforschung dieses Elementes versucht.

Alle Messungen der Aktivität wurden durch eine früher geschilderte Zählrohr-Anordnung vorgenommen[1]. Eigenartig hierbei ist, dass der untersuchte Stoff durch Natronwasserglas an der Innenwand des Zählrohres (das auswechselbar ist) angebracht wird, sodass die ausgesandten Partikel nicht erst durch eine Membran gehen müssen; dadurch wird gleichzeitig eine grössere Zählerfläche und eine bessere Geometrie für die Registrierung der ausgesandten Partikeln erzielt. Ferner ist der natürliche Effekt, der von kosmischer Strahlung und fremder Radioaktivität herrührt, durch Bleischützung und teilweise Kompensation der Wirkung der durchdringenden kosmischen Strahlung auf einen niedrigen Wert herabgedrückt, wodurch grosse Empfindlichkeit für schwache Aktivitäten erreicht wird. Als Beispiel kann erwähnt werden, dass 47 mg KCl 21 Nettostösse/min gibt. Die Dimensionen von Rohr und Draht sind dieselben wie in der erwähnten Arbeit angeführt. Die wirksame Zählerfläche ist 45 cm^2; der natürliche Effekt etwa 8—9 Stösse/min; natürlicher Effekt pr. cm^2 wirksame Zählerfläche also etwa 0,20 Stösse/min. Durch Anordnung eines Kondensators von 100 cm parallel mit der Ableitung des Kompensationszählers, die von C. B. Madsen angegeben ist[2], ist die Kompensation der Wirkung der kosmischen Strahlung weiter gesteigert.

Der Messungsvorgang ist übrigens folgender: Eine Reihe Messingrohre der richtigen Dimensionen werden an der Innenwand mit Natronwasserglas überzogen und getrocknet. Vor dem Gebrauch eines solchen Rohres wird ihr natür-

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[1] E. Buch Andersen, Zs. f. Phys. 98, 597, 1936.

[2] C. B. Madsen, Zs. f. Phys. 101, 72, 1936.

licher Effekt, der bei den verschiedenen Rohren verschieden ist, und bisweilen wegen zufälliger radioaktiver Verunreinigung ziemlich hoch sein kann, gemessen. Der natürliche Effekt ist gewöhnlich 5—10 Stösse/min. Beträgt der natürliche Effekt über 12—15 Stösse/min, wird das Rohr als unbrauchbar verworfen. Zählrohre mit kleinem natürlichen Effekt werden vorzugsweise bei den Messungen verwendet, wo geringe oder keine Aktivität zu erwarten ist. Wenn der Stoff angebracht werden soll, werden die mittleren Teile der Innenwand des Rohres wieder mit einer Lösung von Natronwasserglas angefeuchtet, und eine abgewogene Menge des fein pulverisierten Stoffes wird durch das Rohr geschüttet, wodurch ein grösserer oder kleinerer Teil davon hängen bleibt. Der Rest des Stoffes wird wieder gewogen, sodass die Menge des Stoffes in dem Rohre festgestellt ist. Nach dem Trocknen im Wärmeschrank bei etwa 80° C oder im Luftstrom kann das Rohr verwendet werden. Kontrolversuche ergaben, dass diese Behandlung mit Natronwasserglas den natürlichen Effekt der Zählrohre nicht ändert.

I. Versuch mit Mineralien.

Für die erste Versuchsreihe wurden Pechblende und Thorit verwendet. Von den benutzten Methoden soll nur die am häufigsten angewandte erwähnt werden. Eine Probe fein pulverisiertes Thorit wird mit entweder $NaKCO_3$ oder $NaOH$ alkalisch geschmolzen, die Schmelzmasse wird mit Wasser, dem ein wenig KJO_3 zugesetzt wird, extrahiert, die Flüssigkeit mit H_2SO_4 sauer gemacht, mit SO_2 reduziert, und es wird mit Silbernitrat gefällt. Das Silberjodid wird sorgfältig mit grossen Wassermengen ausgewaschen, danach mit Zink und verdünnter Schwefelsäure behandelt, wobei schwere metallene Komponenten in dem Niederschlag verbleiben, während die Lösung von HJ wieder mit Rücksicht auf den Sauerstoff der Luft mit SO_2 reduziert und mit Silbernitrat gefällt wird. Dieses Silberjodid wird noch einmal in derselben Weise mit Zink und Schwefelsäure behandelt. Der Lösung von HJ, die die Ekajodverbindung enthalten sollte, wird eine gesättigte Lösung von Jod in Wasser zugesetzt (zur Befreiung von Ekajod), und die Flüssigkeit wird mit Äther oder Chloroform extrahiert. Der Äther (oder das Chloroform) wird von der Wasserfraktion geschieden, das Lösungsmittel wird abgedampft, und der Abdampfrest bei 120° C. sublimiert. Das Sublimat wird zuerst mit NaOH, danach mit verdünnter Schwefelsäure extrahiert. Diese Lösungen werden vereinigt, ein wenig NaJ wird zugesetzt, mit SO_2 reduziert und mit Silbernitrat gefällt. Der letzte Niederschlag von Silberjodid wird — eventuell nach noch einer Behandlung mit Zink und Schwefelsäure — auf Radioaktivität untersucht.

In vielen Fällen konnte in dieser Weise aus Thorit ein aktives Produkt gewonnen werden, und Blindproben zeigten, dass diese Aktivität nicht von den angewendeten Chemikalien herrührte. Ebenfalls wurde genau überwacht, dass ganz bestimmte Gläser bei den verschiedenen Stufen des Fraktionierungsprozesses benutzt wurden, sodass die für die späteren Stufen benutzten Gläser mit keinen stark aktiven Stoffen in Berührung kamen (auch nicht während der Reinigung der Gläser). Die gefundene Aktivität hat im Laufe eines Monats nicht abgenommen. Die positiven Versuche waren jedoch nicht reproduzierbar, indem eine andere Serie Thoritproben ganz negative Resultate gaben (was die Effektivität der Fraktionierung zeigt). Es ergab sich danach, dass die Mineralien, die positive Resultate gegeben hatten, alle in einem Achatmörser pulverisiert worden waren, der ein Jahr zuvor zur Zermalmung von alten Emanationsrohren verwendet wurde, während die übrigen Mineralproben in anderer Weise zermalmt worden sind. Dadurch wurde die Aufmerksamkeit auf RaD als Ausgangsmaterial gelenkt.

II. Versuche mit RaD.

Die Versuche wurden dann mit RaD-Lösungen, fortgesetzt. Es wurden zwei verschiedene Lösungen, je etwa 1 Jahr alt, verwendet, und eine Reihe Versuche wurden mit denselben durchgeführt; wie die Mineralversuche, waren die Versuche auf die vermuteten Halogeneigenschaften des Elementes 85 gegründet.

Die erste Versuchsreihe wurde mit einer RaD-Nitratlösung vorgenommen, die etwa ein Jahr vor dem Beginn der Versuche durch Extrahierung von alten Emanationsrohren hergestellt war. Zur Herstellung der Lösung wurde die von Bjerge angegebene Methode benutzt[1].

Die zuerst benutzte Methode war folgende: Einer bestimmten Menge der Lösung wird ein wenig verdünnte Schwefelsäure und Kaliumjodat zugesetzt, es wird mit Sulfit reduziert und mit Silbernitrat gefällt. Das Silberjodid wird dann durch Dekantierung ausgewaschen, danach mit Zink und verdünnter Schwefelsäure behandelt. Die Lösung von Jodwasserstoff wird mit Sulfit reduziert und mit Silbernitrat gefällt. Dieses Silberjodid wird noch einmal mit Zink und Schwefelsäure behandelt, und die Lösung (von HJ) in den Kolben eines Jodbestimmungsapparates (nach Julius Petersen), der Ferrisulfat enthält, filtriert. Das Kugelrohr des Destillationsapparates enthält ver-

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[1] Bjerge, Zs. f. Phys. 89, 277, 1934.

dünntes Natriumhydroxyd mit ein wenig Sulfit versetzt. Es wird ungefähr 40 Minuten lang bei Stickstoffdurchleitung destilliert. Das Destillat wird schwefelsauer gemacht und mit Silbernitrat gefällt. Das Silberjodid wird durch Dekantierung gewaschen und getrocknet. Die Remanenz wird ein paar Minuten lang mit Eisenpulver erwärmt, filtriert, es wird ein wenig Natriumjodid zugesetzt, mit Sulfit reduziert und mit Silbernitrat gefällt. Das Silberjodid wird durch Dekantierung gewaschen und getrocknet. Die beiden gewonnenen Silberjodide wurden auf Aktivität untersucht, und es zeigte sich, dass nur das aus dem Destillat gewonnene Jodid aktiv war. Eine Blindprobe, in denselben Gläsern ausgeführt, gab inaktives Jodid.

Danach folgte ein etwas geänderter Vorgang. Dieselbe Menge RaD-Lösung wird in derselben Weise wie oben zweimal mit Zink und Schwefelsäure behandelt. Der Lösung von Jodwasserstoff wird eine gesättigte Lösung von Jod in Wasser zugesetzt, um eventuelles Ekajod zu befreien. Diese Lösung wird mit Äther extrahiert, der sich nach halbstündigem Schütteln von der Wasserfraktion scheidet. Die Ätherfraktion wird im Luftstrom abgedampft, und der Abdampfrest eine Stunde lang bei 140° C. sublimiert. Das Sublimat wird mit Natriumhydroxyd extrahiert und ein wenig Sulfit und ein wenig Natriumjodid zugesetzt. Die Lösung wird mit verdünnter Schwefelsäure sauer gemacht, und mit Silbernitrat gefällt. Das gefällte Silberjodid wird durch Dekantierung gewaschen und getrocknet. Die Remanenz der Sublimation wird erst mit Natriumhydroxyd, dem Sulfit zugesetzt ist, dann mit verdünnter Schwefelsäure extrahiert. Die beiden Lösungen werden vereinigt, ein wenig Natriumjodid wird zugesetzt und die schwefelsaure Lösung mit Silbernitrat gefällt. Das Jodid wird gewaschen und getrocknet. Die beiden Jodide werden auf Aktivität untersucht. Nachstehend sind die Resultate von zwei gleichartigen Versuchen angegeben. Die Zahl der Stösse ist in Zählperioden von 30—80 Minuten Dauer, gewöhnlich 30—50 Minuten, bestimmt.

Versuch I.

0,089 g AgJ aus dem Sublimat der Ätherfraktion.

Natürlicher Effekt des Rohres: 9,3 Stösse/min

Stunden	Tage	Bruttostösse/min
0	0	27,6
17,9	0,75	19,5
24,7	1,03	17,4
39,7	1,65	19,8
72,1	3,00	18,3
114,0	4,75	18,3
141,6	5,90	21,8
233,7	9,74	25,1
354,6	14,8	20,9
620,4	25,8	21,1
1052,1	43,8	19,9

0,138 g AgJ aus der Remanenz des Sublimates.

Natürlicher Effekt des Rohres: 12,1 Stösse/min

Stunden	Tage	Bruttostösse/min
0	0	9,5
19,1	0,80	14,3
161,1	6,71	16,5

Versuch II.

0,157 g AgJ aus dem Sublimat der Ätherfraktion.

Natürlicher Effekt des Rohres: 9,0 Stösse/min

Stunden	Tage	Bruttostösse/min
0	0	18,6
1,9	0,08	21,6

Stunden	Tage	Bruttostösse/min
13,4	0,56	24,8
25,3	1,05	22,2
66,7	2,78	21,9
184,9	7,77	21,0
305,0	12,7	21,3
452,0	18,0	23,9
549,5	22,9	21,0

0,200 g AgJ aus der Remanenz des Sublimates.

Natürlicher Effekt des Rohres: 10,4 Stösse/min

Stunden	Tage	Bruttostösse/min
0	0	14,7
14,4	0,60	14,4

In beiden Fällen hat das aus der Sublimationsfraktion hergestellte Silberjodid eine deutliche Aktivität.

Die Wasserfraktionen der beiden Versuche wurden ebenfalls untersucht, indem ein wenig Sulfit zugesetzt und mit Silbernitrat gefällt wurde, nachdem der gelöste Äther abgedampft war. Das Jodid wurde in gewöhnlicher Weise gewaschen und getrocknet. Die Aktivitätsuntersuchung ergab:

Versuch I.

0,230 g AgJ aus der Wasserfraktion.

Natürlicher Effekt des Rohres: 10,3 Stösse/min

Stunden	Tage	Bruttostösse/min
0	0	32,0
17,2	0,72	32,7
182,3	7,60	27,1

Versuch II.

0,149 g AgJ aus der Wasserfraktion.

Natürlicher Effekt des Rohres: 9,4 Stösse/min

Stunden	Tage	Bruttostösse/min
0	0	21,9
13,8	0,58	17,3

Weiter wurde noch ein Versuch in gleicher Weise ausgeführt, und auch dieser hat ein ähnliches Resultat ergeben: die Nettostosszahl[1] des Sublimatsilberjodids war 8 pro Minute, die des Remanenzsilberjodids 5 pro Minute und die der Wasserfraktion 5 pro Minute.

Blindproben auf den Versuchsgang waren inaktiv.

Danach wurde die doppelte Menge derselben RaD-Lösung in Arbeit genommen. Diese wurde in derselben Weise wie in den obenerwähnten drei Versuchen behandelt, jedoch wurde allen Flüssigkeiten, aus denen Silberjodid gefällt worden war, Salzsäure zwecks Ausscheidung von Überschuss von Silber zugesetzt. Nach der Filtrierung wurde ein wenig Bleinitrat- und Wismutnitratlösung zugesetzt, dann mit Schwefelwasserstoff gefällt, um die freien Fraktionen auf RaD, RaE und RaF zu untersuchen. Der ausgeschiedene Schwefelwasserstoff-Niederschlag wurde durch Dekantierung gewaschen, getrocknet und wie die Jodide auf Aktivität untersucht.

Die gesamte Fraktionierung sieht dann aus, wie folgt:

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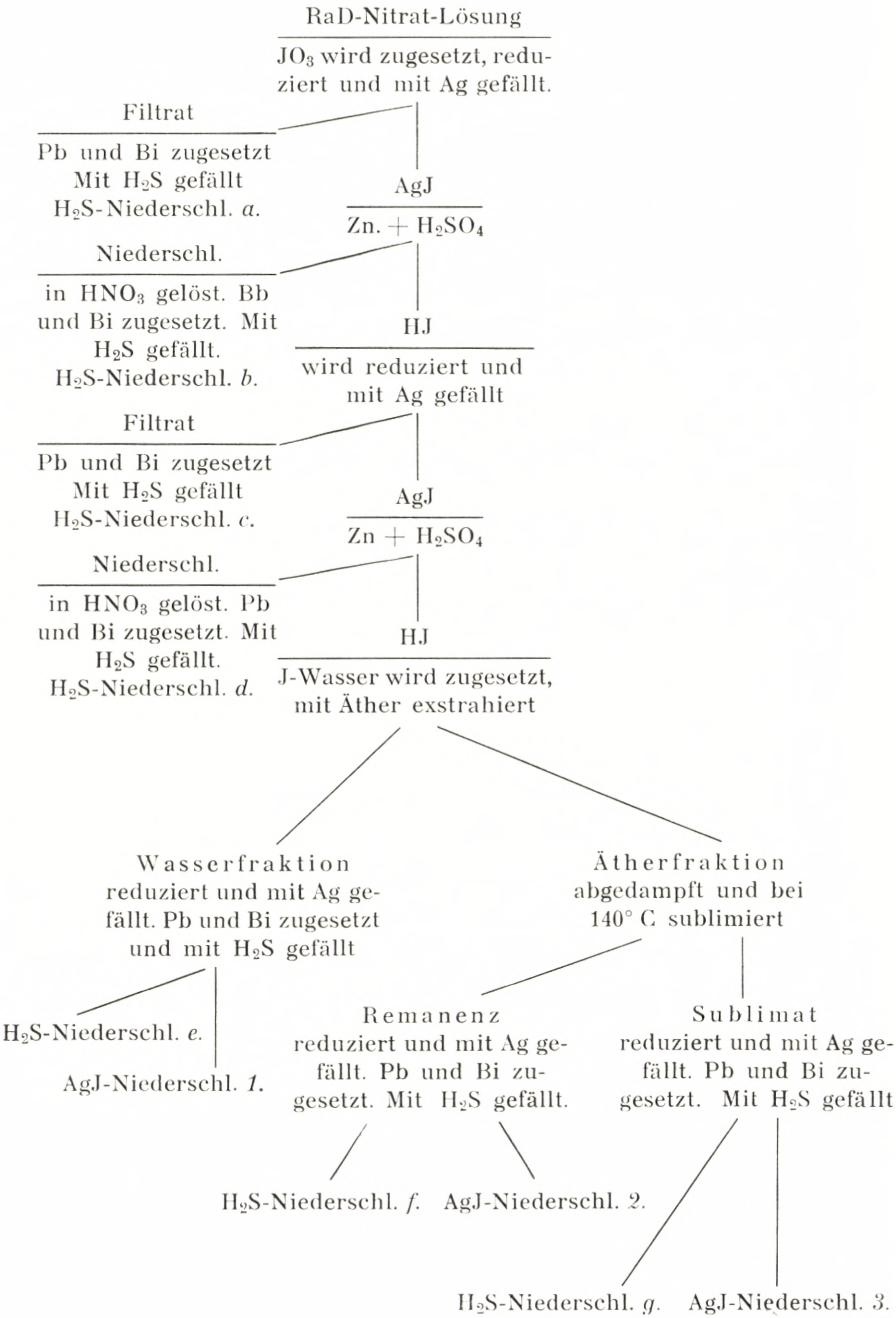
[1] Bruttostosszahl minus natürlicher Effekt.



RaD-Nitrat-Lösung

JO_3 wird zugesetzt, reduziert und mit Ag gefällt.

Filtrat

Pb und Bi zugesetzt
Mit H_2S gefällt
H_2S-Niederschl. *a.*

AgJ

Zn. + H_2SO_4

Niederschl.

in HNO_3 gelöst. Bb und Bi zugesetzt. Mit H_2S gefällt.
H_2S-Niederschl. *b.*

HJ

wird reduziert und mit Ag gefällt

Filtrat

Pb und Bi zugesetzt
Mit H_2S gefällt
H_2S-Niederschl. *c.*

AgJ

Zn + H_2SO_4

Niederschl.

in HNO_3 gelöst. Pb und Bi zugesetzt. Mit H_2S gefällt.
H_2S-Niederschl. *d.*

HJ

J-Wasser wird zugesetzt, mit Äther exstrahiert

Wasserfraktion
reduziert und mit Ag gefällt. Pb und Bi zugesetzt und mit H_2S gefällt

H_2S-Niederschl. *e.*

AgJ-Niederschl. *1.*

Ätherfraktion
abgedampft und bei 140° C sublimiert

Remanenz
reduziert und mit Ag gefällt. Pb und Bi zugesetzt. Mit H_2S gefällt.

H_2S-Niederschl. *f.*

AgJ-Niederschl. 2.

Sublimat
reduziert und mit Ag gefällt. Pb und Bi zugesetzt. Mit H_2S gefällt

H_2S-Niederschl. *g.*

AgJ-Niederschl. 3.

Die Aktivitätsuntersuchung der ersten H_2S-Niederschläge ergab:

Niederschlag	a	unmessbar stark
—	b	— —
—	c	— —
—	d	350 Bruttostösse/min

Die übrigen Resultate waren:

0,070 g AgJ *3.* Sublimat.

Natürlicher Effekt: 9,5 Stösse/min

Stunden	Tage	Bruttostösse/min
0	0	14,4
18,8	0,78	12,6
50,7	2,11	16,5
90,7	3,78	13,4
192,2	7,97	15,5
333,0	13,88	16,3
429,8	17,91	15,3

0,108 g H_2S-Niederschlag *g.* Sublimat.

Natürlicher Effekt: 9,7 Stösse/min

Stunden	Tage	Bruttostösse/min
0	0	21,4
20,4	0,85	22,2
46,0	1,92	21,6

0,110 g AgJ *2.* Remanenz.

Natürlicher Effekt: 8,9 Stösse/min

Stunden	Tage	Bruttostösse/min
0	0	17,3
19,1	0,80	13,5
92,8	3,87	14,0
215,2	8,97	19,8

0,079 g H_2S-Niederschlag *f.* Remanenz.

Natürlicher Effekt: 10,4 Stösse/min

Stunden	Tage	Bruttostösse/min
0	0	24,1
23,3	0,97	13,5
75,7	3,15	15,3

0,182 g AgJ *1.* Wasserfrakt.

Natürlicher Effekt: 10,3 Stösse/min

Stunden	Tage	Bruttostösse/min
0	0	11,8
71,7	2,98	12,8
172,0	7,17	16,9
194,7	8,11	16,7

0,102 g H_2S-Niederschlag *e.* Wasserfrakt.

Natürlicher Effekt: 8,9 Stösse/min

Stunden	Tage	Bruttostösse/min
0	0	21,3
21,8	0,91	20,1
214,7	8,95	21,0
284,4	11,85	20,5

Bei den Blindproben waren die Silberjodidfällungen inaktiv; dagegen war die Aktivität der H_2S-Niederschläge stark schwankend; es war ein Teil der Proben sowohl aktiv wie inaktiv, und die Inaktivität war nicht sicher reproduzierbar. Die Aktivität der Proben schwankt zwischen 0 und 30 Bruttostössen/min.

Eine Serie von Versuchen, die nach der gleichen Fraktionierungsmethode geplant war, gelangte nicht zur Ausführung. Vor allen Dingen war zu untersuchen, inwieweit Proportionalität zwischen den benutzten RaD-Mengen und der Aktivität des Sublimatsilberjodids bestand. Die Resultate des obenerwähnten Versuches ergaben jedoch keine Übereinstimmungen mit den vorausgehenden Versuchsergebnissen.

Der letzte Versuch, der mit dieser RaD-Lösung vorgenommen wurde, war ein Entleerungsversuch, durch welchen man prüfen wollte, ob die Aktivität dem Jod auch durch eine lange Reihe von Prozessen folgt. Die selbe Menge, die man bei den drei ersten Versuchen benutzte, wurde in Arbeit genommen. Der Lösung wurde, wie oben, ein wenig Schwefelsäure und Kaliumjodat zugesetzt, es wurde mit Sulfit reduziert und mit Silbernitrat gefällt. Das Jodid wurde ausgewaschen und mit Zink und verdünnter Schwefelsäure behandelt. Die Lösung von Jodwasserstoff wird mit Sulfit reduziert und mit Silbernitrat gefällt. Das Jodid wird mit Zink und verdünnter Schwefelsäure behandelt. Die Zink- und Schwefelsäurebehandlung wird insgesamt 6 mal vorgenommen. Das zuletzt gewonnene Silberjodid wurde auf Aktivität untersucht und erwies sich inaktiv.

Danach wurde die zweite RaD-Lösung in Arbeit genommen. Diese war, wie oben erwähnt, aus alten Emanationsrohren hergestellt. Der Vorgang folgt dem oben angegebenen Fraktionierungsschema, jedoch ohne Fällung der H_2S-Niederschläge. Mit derselben Menge Lösung wie bei den ersten drei Versuchen, und indem man auf Grund von Verdünnungsproben, Sulfidfällungen in denselben und darauffolgender Aktivitätsmessung annahm, dass die beiden Lösungen gleich stark waren, hat man folgende Aktivitäten gefunden:

0,122 g AgJ *3*. Sublimat.

Natürlicher Effekt: 9,5 Stösse/min

Stunden	Tage	Bruttostösse/min
0	0	17,2
16,3	0,68	17,4
68,5	2,85	14,4
88,8	3,70	15,9
330,5	13,77	13,4

0,111 g AgJ *2*. Remanenz.

Natürlicher Effekt: 10,1 Stösse/min

Stunden	Tage	Bruttostösse/min
0	0	25,3

0,155 g AgJ *1*. Wasserfrakt.

Natürlicher Effekt: 9,2 Stösse/min

Stunden	Tage	Bruttostösse/min
0	0	15,4

Der Versuch wurde wiederholt, jedoch mit geänderter Technik bei der Sublimation. In den vorhergehenden Versuchen wurde ein mit Filtrierpapir umwickeltes, wassergekühltes Reagenzglas benutzt, und dieses wurde im Halse eines Rundkolbes angebracht. Beim Hineinsetzen und Herausnehmen muss genau überwacht werden, dass das Filtrierpapier die Kolbenwände nicht berührt. Die Erwärmung geschah in einem Wärmeschrank. Die Sublimation und Kondensierung wurde mit Hilfe von zwei durch Rohre (Schliff) verbundenen U-Rohre vorgenommen. Das weite Rohr, mit dem Jod, wurde in einem Glyzerinbad erwärmt, während das zweite, enge Rohr in einem Dewargefäss mit flüssiger Luft abgekühlt worden war.

Durch dieses Verfahren kann man es vermeiden, dass eine eventuelle Aktivität im Sublimat von etwaigen Rückstossatomen herrührt. Weiterhin wurde dreimal mit Zink und verdünnter Schwefelsäure behandelt, statt zweimal bei den vorhergehenden Versuchen. Die Messung der Aktivität gab folgende Resultate:

0,154 g AgJ *3.* Sublimat. Fl. L.

Natürlicher Effekt: 11,5 Stösse/min

Stunden	Tage	Bruttostösse/min
0	0	23,9
22,1	0,92	12,3
24,1	1,00	15,0
44,8	1,87	15,2
356,3	14,85	10,9

0,178 g AgJ *2.* Remanenz.

Natürlicher Effekt: 10,0 Stösse/min

Stunden	Tage	Bruttostösse/min
0	0	13,5
72,0	3,00	17,0

0,217 g AgJ *1.* Wasserfraktion.

Natürlicher Effekt: 8,2 Stösse/min

Stunden	Tage	Bruttostösse/min
0	0	20,9

Ein Entleerungsversuch, ähnlich dem mit der zweiten RaD-Lösung vorgenommen, wurde ausgeführt. Das nach sechs Behandlungen mit Zink und Schwefelsäure gewonnene AgJ war inaktiv:

0,307 g AgJ. Sechs Zn-Behandlungen.

Natürlicher Effekt: 12,4 Stösse/min

Stunden	Tage	Bruttostösse/min
0	0	14,1
231,8	9,66	12,2

III. Versuch mit Sulfidmineralien.

Schliesslich sei noch eine dritte Versuchsserie erwähnt, wobei Ausgangsmaterialien und Voraussetzungen für die Anwendung derselben ganz andere waren als bei den vorigen Versuchen, wo sich der Versuchsgang auf die ausgeprägten Halogeneigenschaften stützte. Teils durch geochemische Erwägungen[1], die hier nicht näher zu behandeln sind, und teils durch Mutmassungen (vergl. die Zusammenstellung Seite 21) über die vermuteten physischen und chemischen Eigenschaften des Ekajods, kam Buch Andersen zu der Ansicht, dass 85 eventuell als trivalentes Ekajod existierte; als solches musste man es unter den Sulfidmineralien vom Typus X_2S_3, also im Spiessglanz, Wismutglanz und ähnlichen Mineralien, suchen.

Der Vorgang in grossen Zügen war folgender:

Das Mineral (1 kg) wird mit konzentrierter Salpetersäure oxydiert. Eventuelles Ekajod sollte dann zu Ekajodat oxydiert werden. Die oxydierte Masse wird durch kochendes Wasser ausgezogen. Nach Neutralisierung des Hauptteils der freien Säure, wird ein wenig Natriumjodat zugesetzt, mit Überschuss von Hydrazinsulfat reduziert und mit Silbernitrat gefällt. Das Jodid wurde in gewöhnlicher Weise gewaschen und getrocknet. Weiter wurden kleine Mengen

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[1] V. M. Goldschmidt, Geochemische Verteilungsgesetze der Elemente (Bd. II).

Zusammenstellung der Eigenschaften der Halogene und ihre Verbindungen.

	F	Cl	Br	J	85
Atomnummer	9	17	35	53	
Atomgewicht (1935)	19,000	35,457	79,916	126,92	
Isotopen stabile	19	35; 37	79; 81	127	
Elektronenkonfiguration	2,7	2, 8, 7	2, 8, 18,7	2,8, 18, 18,7	2,8,18,32,18,7
Häufigkeit, %	0,026	0,19	6 · $10^{\div 6}$	7 · $10^{\div 8}$	
Spez. Gew.	fl. 1,14	÷195°: 2,12	÷195°: 3,107	25°: 4,932	
Atomvolumen	fl. 16,7	÷195°: 16,7	÷195°: 19,46	25°: 25,74	
Atomradius ($cm^{\div 8}$)		1,07	1,19	1,36	
Scheinbarer Ionenradius ($cm^{\div 8}$)[1]		1,81 ($Cl^{\div}$)	1,96 ($Br^{\div}$)	2,20 ($J^{\div}$) 0,94 (J^{5+})	
Wirklicher Ionenradius ($cm^{\div 8}$)[1]		0,95 ($Cl^{\div}$)	1,02 ($Br^{\div}$)	1,12 ($J^{\div}$)	
Schmelzpunkt	÷ 233°	÷ 102°	÷ 7,3°	113°	
Siedepunkt	÷ 187°	÷ 33,7	58,6°	185°	
Normalpotential (Volt)[1]	+ 1,92	+ 1,36	+ 1,08	+ 0,54	
Bildungswärme, kcal. (HR gasf.)	35,8	22,0	8,5	÷ 6,2 festes Jod	
Schmelzpunkt HR	÷ 83°	÷ 111°	÷ 87°	÷ 52°	
Siedepunkt HR	+ 19,4°	÷ 83°	÷ 68°	÷ 36°	
Bildungswärme (kcal) AgR[1]	23,2	29,4	22,7	13,8	
Schmelzpunkt NaR	988°	800°	740°	660°	
Siedepunkt 760 mm, NaR	1695°	1441°	1393°	1300°	
Schmelzpunkt, KR	846°	768°	728°	693°	
Siedepunkt 760 mm, KR	1505°	1417°	1381°	1331°	
Löslichkeit AgR, gMol/l		1,5 · $10^{\div 5}$	7,15 $10^{\div 7}$	1,08 $10^{\div 8}$	
Löslichkeit, CuR, gMol/l		1,1 · $10^{\div 3}$	2,0 · $10^{\div 4}$	2,25 · $10^{\div 6}$	
Löslichkeit Hg_2R_2, gMol/l		5,5 · $10^{\div 14}$	6,5 · $10^{\div 18}$	2,9 · $10^{\div 24}$	
Löslichkeit, TlR gMol/l		1,61 · $10^{\div 2}$	1,64 · $10^{\div 3}$	1,92 · $10^{\div 4}$	
$R^{\div} + 3H_2O + 6\oplus = RO_3^{\div} + 6H^+$		1,45 Volt	1,41 Volt	1,08 Volt	
Löslichkeit 20° $NaRO_3$ g/100g H_2O		99	34,5	9,1	
Löslichkeit 100° $NaRO_3$ g/100g H_2O		204	90,9	33,9	
Löslichkeit 20° KRO_3 g/100g H_2O		7,2	6,9	8,1	
Löslichkeit 100° KRO_3 g/100g H_2O		55,5	49,8	32,1	
Löslichkeit[1]) 20° AgRO g/100g H_2O		9	0,16	0,044	

[1] Ephraim, Anorganische Chemie, 5. Aufl. 1934.

(etwa 200 mg) Bariumsulfat, Bleisulfat, Sulfide, Hydroxyde und Phosphate in die Flüssigkeit gefällt, um zu untersuchen, wie sich die in dem Mineral befindliche Aktivität verteilen würde.

Von der geplanten Versuchsserie teils mit 1 kg Spiessglanz, teils mit 300 g Wismutglanz als Ausgangsmaterial für jeden Versuch, wurden nur ein paar einzelne Versuche ausgeführt. Die gewonnene Halogenfraktion war nicht aktiv.

Zum Schluss möchten wir Herrn Hjalmar Nielsen, Aarhus Sten- og Gruskompagni und dem Carlsberg-Fond für Unterstützungen dieser Arbeit unseren besten Dank aussprechen.

Zusammenfassung.

In den von E. Buch Andersen hinterlassenen Journalen sind drei Versuchsreihen über chemische Methoden ausgearbeitet, die zur Isolierung des Elementes 85 führen sollen. Diese Methoden wurden teils bei der Aufarbeitung von bestimmten Mineralien und teils bei RaD in Anwendung gebracht. Man hat versucht das Element 85 durch seine vermutete Radioaktivität nachzuweisen. In keinem Fall konnte ein radioaktives Halogen mit Sicherheit nachgewiesen werden. Die in gewissen Fällen festgestellten Aktivitäten sind wahrscheinlich bekannten radioaktiven Elementen zuzuschreiben, die durch die Stufen der Trennungsprozesse mitgerissen worden sind. Die ausgearbeiteten Methoden dürften bei weiteren Versuchen, die das Auffinden des Elementes 85 bezwecken, von Wert sein.

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THE RAMAN SPECTRA OF THE DEUTERATED BENZENES

BY

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I. Introductory Remarks.

There exists today rather strong evidence of widely different sorts indicating that the benzene molecule has the symmetry of a plane hexagon (D_{6h} in standard symmetry notation). In particular the recent spectroscopic investigations of benzene and benzene-d_6 by Ingold and his associates have cleared up several confusing points which had hitherto stood in the way of a whole-hearted acceptance of the D_{6h} structure. The spectra of the partially deuterated benzenes should be expected to confirm this structure. Such a confirmation is highly desirable, however, because of the particular nature of the evidence for the D_{6h} structure furnished by the spectra of benzene and benzene-d_6. One may calculate in a perfectly general way that the D_{6h} model should have a certain number of mutually exclusive Raman and infrared active fundamentals, and when analysis of the data for benzene and benzene-d_6 shows that the proper number, and no more, are observed, one decides in favor of the D_{6h} structure. This argument is somewhat negative in character, and it is reassuring to have constructive evidence for the D_{6h} model from the spectra of a series of deuterium derivatives possessing a wide variety of selection rules. In the following paper this evidence is presented and discussed.

Stepwise substitution of deuterium for hydrogen in benzene gives a series of compounds which resemble one another quite closely in physical properties, but which cover a wide range of molecular symmetries. Since the selection rules governing the activity of internal vibrations in the Raman effect, and indeed in all types of molecular spectra, are derived from considerations of molecular symmetry, one should expect to find a great latitude in the selection rules for the eleven partially deuterated benzenes. This variation in selection restrictions has the valuable result that, on the basis of a D_{6h} structure for benzene and insofar as symmetry alone is concerned, all the fundamental frequencies become Raman-active in eight of the eleven compounds. We may therefore expect to obtain from the Raman spectra of the derivatives not only a confirmation of the D_{6h} structure but also much information about the internal frequencies which are spectroscopically latent in benzene. It was chiefly with this latter expectation in mind that the present investigation was undertaken.

II. Brief Survey of Theoretical Background.

The study and interpretation of the spectra of any molecule are greatly facilitated if the molecule possesses a high degree of symmetry, that is, if there are many symmetry operations which one can perform on the stationary molecule. In the first place, considerations of symmetry form the basis for a method of classifying internal vibrations which is of the greatest usefulness in understanding the nature of, and interrelations between, the vibrational degrees of freedom. The application of symmetry arguments to the classification of harmonic vibrations in molecules has been made by WIGNER[1] and by PLACZEK[2]. Secondly the problem of interpreting Raman and infra-red spectra is quite considerably simplified when the originating molecule is highly symmetrical, inasmuch as the presence of symmetry lays heavy restrictions on the spectroscopic activity of internal vibrations. The nature of these restrictions for the various symmetry classes of harmonic molecular vibrations has been formulated by PLACZEK[2]. Thirdly the simplification of the functional relationships among the several vibrational frequencies which is produced by the presence of molecular symmetry may be of great advantage in interpreting the spectra of various isotopic configurations of the same molecule. This simplification takes a most useful form in the product rule found by E. TELLER[3].

All of these generalizations which are so helpful in the study of molecular spectra have been discussed both in theoretical and practical detail several times. We give in the following paragraphs only such a brief resumé of them as will enable the reader to follow the ensuing applications without having to refer to the original articles.

To describe completely the symmetry of a given point group, there is required only a small number of essential

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[1] WIGNER, Gött. Nachrichten, **1930**, 133.

[2] G. PLACZEK, Handbuch der Radiologie, Bd. VI/2, p. 283. The treatments of PLACZEK and of WIGNER are fundamentally equivalent, but since WIGNER uses the formalism of the mathematical theory of groups, one must have a least a superficial knowledge of group theory to apply his results to concrete molecules. On the other hand the method of PLACZEK requires no specialized knowledge. For a lucid and detailed discussion of the application of PLACZEK's procedure to various reasonable structures for benzene, see ANGUS, BAILEY, HALE, INGOLD, LECKIE, THOMPSON, RAISIN, and WILSON, "Structure of Benzene VIII", J. Chem. Soc. (London) **1936**, p. 971.

[3] ANGUS et al. loc. cit. p. 978 state the product rule without proof. The rule was first published, with proof, by O. REDLICH, who found it independently: Z. phys. Chem. B, **28**, 371 (1935).

symmetry elements. The point group may, and frequently does, possess other elements of symmetry, but it is always possible to express the latter as the result of successive application of the essential symmetry operations. When the constituent atoms of a molecule whose symmetry is that of a given point group undergo vibratory motion, the configuration of the motion may or may not maintain the fundamental symmetry elements. Correspondingly we are able to classify the normal vibrations according to the kind of symmetry elements which they preserve. The two extreme classes are the one in which all symmetry elements are preserved — called the totally symmetrical class — and the one in which all are violated. It is obvious that all possible vibrations of the molecular system must be classifiable somewhere within the range of these two extremes. The procedure which we have used for finding the number of vibrations present in the several symmetry classes of each of the symmetry groups to which the various deuterated benzenes belong is that of Placzek[1]. The results are listed in the accompaning Tables I to VI.

In column 1 of the Tables we have listed the symbols[2] for the various symmetry classes. These symbols represent in shorthand fashion the symmetry properties of each class, which are described in full in column 2. The symbols + and — show respectively that a given symmetry class is symmetric or antisymmetric to the indicated symmetry element. In the Tables for D_{6h} and D_{3h}, the violation of the three-fold axis, which is not a simple antisymmetric violation, and which results in the presence of two vibrations of equal frequency, is indicated by $\varepsilon^{\pm 1}$*. Column 3 gives

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[1] Placzek loc. cit.

[2] Placzek's notation; cf. Tisza, Zeitschr. f. Phys. 82, 285 (1932).

* Cf. Placzek, loc. cit. p. p. 284—285, and Tables. p. 295.

the number of real frequencies, and in addition, the null-frequencies of translation and rotation in each class. Finally in Column 4 are found the Raman and infra-red selection principles for the vibrations of each class. Here the + sign indicates that the symmetry class is spectroscopically active and a — sign that it is inactive. We have not included the rules for the state of polarization of the Raman lines, because these can be summed up very briefly by saying that all Raman lines should have a depolarization factor of $^6/_7$ except those due to frequencies of the first class in each Table. For these latter, the depolarization is not determined by symmetry, and may lie between zero and $^6/_7$.

Table I.

$D_{6h}: C_6H_6,\ C_6D_6$.

Symmetry Class	Essential Elements of Symmetry				Number of Vibrations	Selection Rules	
	C_3^z	C_2^z	C_2^y	i		Raman	Infra-red
A_{1g}	+	+	+	+	2	+	—
A_{1u}	+	+	+	—	0	—	—
A_{2g}	+	+	—	+	1 R_z	—	—
A_{2u}	+	+	—	—	1 T_z	—	+
B_{1g}	+	—	+	+	0	—	—
B_{1u}	+	—	+	—	2	—	—
B_{2g}	+	—	—	+	2	—	—
B_{2u}	+	—	—	—	2	—	—
E_g^+	$\varepsilon^{\pm 1}$	+	±	+	4	+	—
E_u^+	$\varepsilon^{\pm 1}$	+	±	—	2	—	—
E_g^-	$\varepsilon^{\pm 1}$	—	±	+	1 $R_{x,y}$	+	—
E_u^-	$\varepsilon^{\pm 1}$	—	±	—	3 $T_{x,y}$	—	+

In Fig. 1 are reproduced schematically the modes of harmonic vibration, insofar as these are determined by

Table II.

D_{3h} : sym-$C_6H_3D_3$.

Symmetry Class	Essential Elements of Symmetry			Number of Vibrations	Selection Rules	
	C_3^z	C_2^y	σ_h		Raman	Infra-red
A_1'	+	+	+	4	+	−
A_1''	+	+	−	0	−	−
A_2'	+	−	+	3 R_z	−	−
A_2''	+	−	−	3 T_z	−	+
E'	$\varepsilon^{\pm 1}$	±	+	7 $T_{x,y}$	+	+
E''	$\varepsilon^{\pm 1}$	±	−	3 $R_{x,y}$	+	−

Table III.

V_h : para-$C_6H_4D_2$, para-$C_6H_2D_4$.

Symmetry Class	Essential Elements of Symmetry			Number of Vibrations	Selection Rules	
	C_2^y	C_2^z	i		Raman	Infra-red
A_{1g}	+	+	+	6	+	−
A_{1u}	+	+	−	2	−	−
B_{1g}	+	−	+	1 R_y	+	−
B_{1u}	+	−	−	5 T_y	−	+
B_{2g}	−	+	+	5 R_z	+	−
B_{2u}	−	+	−	3 T_z	−	+
B_{3g}	−	−	+	3 R_x	+	−
B_{3u}	−	−	−	5 T_x	−	+

Table IV.

C_{2v} : C_6H_5D, m-$C_6H_4D_2$, vic-$C_6H_3D_3$, m-$C_6H_2D_4$, C_6HD_5.

Symmetry Class	Essential Elements of Symmetry		Number of Vibrations	Selection Rules	
	C_2^y	σ_z		Raman	Infra-red
A_1	+	+	11 T_y	+	+
A_2	+	−	3 R_y	+	−
B_1	−	+	10 T_x R_z	+	+
B_2	−	−	6 T_z R_x	+	+

Table V.

C_{2v}^{*} : ortho-$C_6H_4D_2$, ortho-$C_6H_2D_4$.

Symmetry Class	Essential Elements of Symmetry		Number of Vibrations	Selection Rules	
	C_2^x	σ_z		Raman	Infra-red
A_1	+	+	11 T_x	+	+
A_2	+	—	5 R_x	+	—
B_1	—	+	10 T_y R_z	+	+
B_2	—	—	4 T_z R_y	+	+

Table VI.

C_s : unsym-$C_6H_3D_3$.

Symmetry Class	Essential Elements of Symmetry	Number of Vibrations	Selection Rules	
	σ_z		Raman	Infra-red
A′	+	21 T_xT_y R_z	+	+
A″	—	9 T_z R_xR_y	+	+

symmetry, for the thirty degrees of internal freedom in benzene. For convenience in discussing the frequencies in the deuterium derivatives, the vibrations have been numbered according to Wilson[1]. In all but one of the partially deuterated benzenes, the doubly-degenerate frequencies split up into their components. Therefore it becomes desirable to assign to the components a notation which distinguishes sharply between them and at the same time indicates their common ancestry. The following convention is adopted: That component of a degenerate benzene vibration which preserves a two-fold axis passing through para carbon atoms is denoted by "a", and the other com-

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[1] Wilson, Phys. Rev. **45**, 706 (1934).

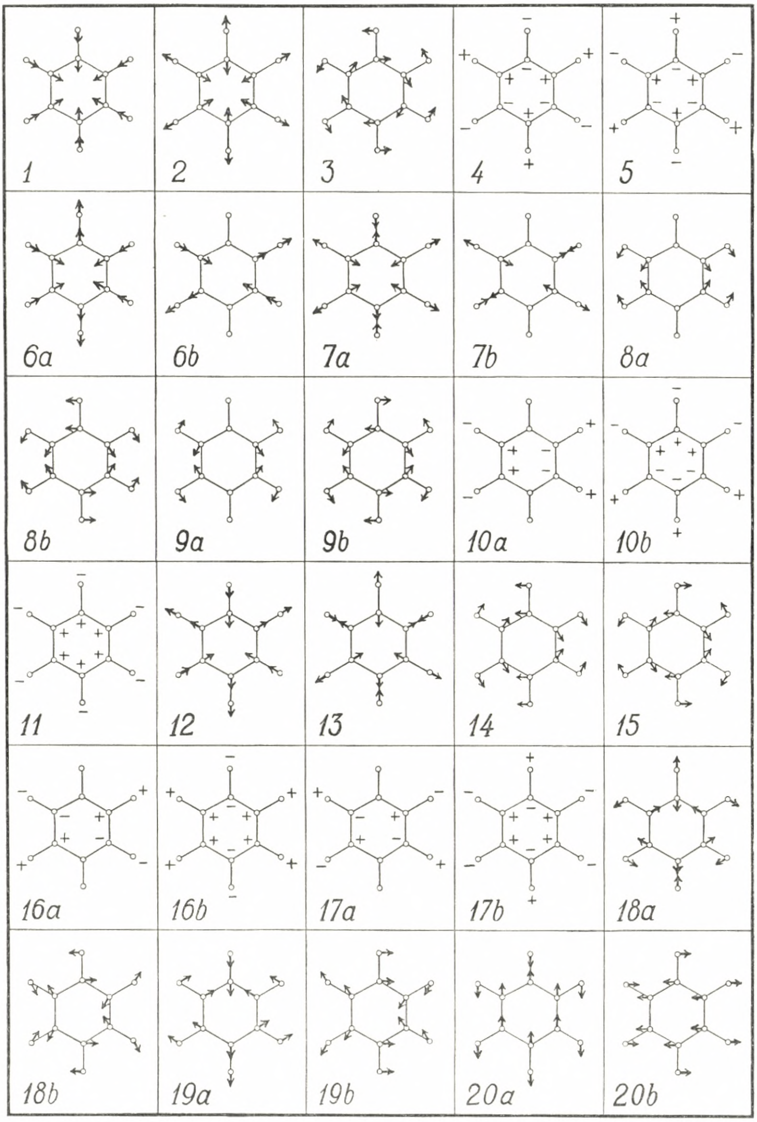
1
2
3
4
5
6a
6b
7a
7b
8a
8b
9a
9b
10a
10b
11
12
13
14
15
16a
16b
17a
17b
18a
18b
19a
19b
20a
20b

Fig. 1.

ponent by "b". The degenerate vibrations are labelled according to this convention in Fig. 1. One may readily classify each component of the degenerate vibrations in the derivatives with the help of Fig. 1 (cf. Fig. 2, below). Our convention agrees with the notation of WILSON except for the four frequencies of class E_g^+. We have taken the liberty of reversing WILSON's convention for these latter vibrations because his own notation is not entirely consistent and because the other notation is the more natural for the vibrations in substituted benzenes possessing lower symmetry than D_{6h}.

It should be remarked that the modes of vibration shown in Fig. 1 are specifically those for a D_{6h} structure only. From a formal standpoint, as soon the D_{6h} symmetry is destroyed by deuterium substitution, these modes lose their identity and others, determined by the new symmetry and by the appearance of additional constants in the force system, come into being. Of course substitution by deuterium changes the total mass of the molecule only slightly, and therefore vibrations which in D_{6h} may be regarded as essentially carbon vibrations (e.g., ν_1, ν_6, ν_8,) will have modes which are not greatly different in the substituted benzenes[1]. The modes which are essentially hydrogen vibrations, however, (ν_2, ν_3, ν_5 etc.) will be changed greatly due to the large percentage mass difference between hydrogen and deuterium. Consequently the enumeration of frequencies in the intermediate deuterium derivatives on the basis of the D_{6h} frequencies is to a considerable extent arbitrary. The actual modes in the various derivatives are to be ob-

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[1] Changes in the carbon vibrations may be regarded as approximately equivalent to those produced by a small isotopic mass shift. Such changes have been discussed by TELLER, Hand- u. Jahrb. der chem. Phys. Bd. 9, II, p. 141 ff.

tained by combination of the appropriate modes of D_{6h}. The exact nature of the superposition of the D_{6h} vibration forms depends on specific characteristics of the force system, and these characteristics are not determinable from symmetry considerations alone. We shall presently have occasion to discuss in some detail the remarkable effect on certain carbon modes of vibration which deuterium substitution produces because of the special nature of the potential function in benzene.

The modes in Fig. 1 are therefore to be regarded simply as a guide to the general nature of the vibrations in the derivatives. For this reason we have made no attempt to depict the D_{6h} vibrational amplitudes on the proper scale. The only conditions satisfied are those of symmetry.

The results of Tables I—VI are summarized pictorially in Fig. 2. By assembling in this fashion the features of the different symmetry groups, it is possible to get a somewhat clearer and more coherent idea of the interrelations among the frequencies, and of the effect of symmetry on spectroscopic activity, when one passes from one derivative to another.

There is no unique way of arranging the six symmetry groups. The one which we have adopted has been chosen arbitrarily with the idea of presenting most clearly the changes in selection principles and in frequency classification brought about by a step-wise removal of the fundamental elements of D_{6h} symmetry. The elements of the diagram are self-explanatory: each rectangular block represents one symmetry class belonging to the symmetry group whose symbol is listed at the extreme right and left sides of the Figure. Within each block are written the numbers of the real frequencies and the symbols of the rotational and translational null-frequencies which belong to that class. Above each block is placed the symbol for the symmetry class and an indication of its spectroscopic activity: R if Raman-active, I if infrared-active, a dash if inactive in one and two dashes if inactive in both.

The remaining advantage which molecular symmetry lends to spectroscopic interpretation is the ready calculation of various frequency relationships among the isotopic forms of the same molecule by means of the product rule of E. TELLER[1]. The product rule is a theorem which enables us to compute, independently of spectroscopic observation, the ratio (denoted by τ) between the product of a certain set of frequencies in one isotopic form of a molecule, and the product of the same set in another isotopic form. By a "set" we mean a collection of frequencies whose modes of vibration have a common symmetry. If the two isotopic forms under consideration belong to the same symmetry group, the sets to which the product rule is applicable are simply the symmetry classes of that group. For example if we wish to apply the product rule to the calculation of frequency product ratios for benzene and benzene-d_6, we may apply it individually to each of the ten blocks of frequencies shown in Fig. 2. If we wish to compare the frequencies of p-benzene-d_2 and p-benzene-d_4, we may utilize the product rule for the eight classes of V_h. On the other hand, if the isotopic forms belong to two different symmetry groups, the sets are the symmetry classes of a third group, namely the one which has as elements of symmetry the elements common to the two groups. Hence to compare the frequencies in benzene (D_{6h}) and p-benzene-d_2 (V_h), for example, it is necessary to classify them

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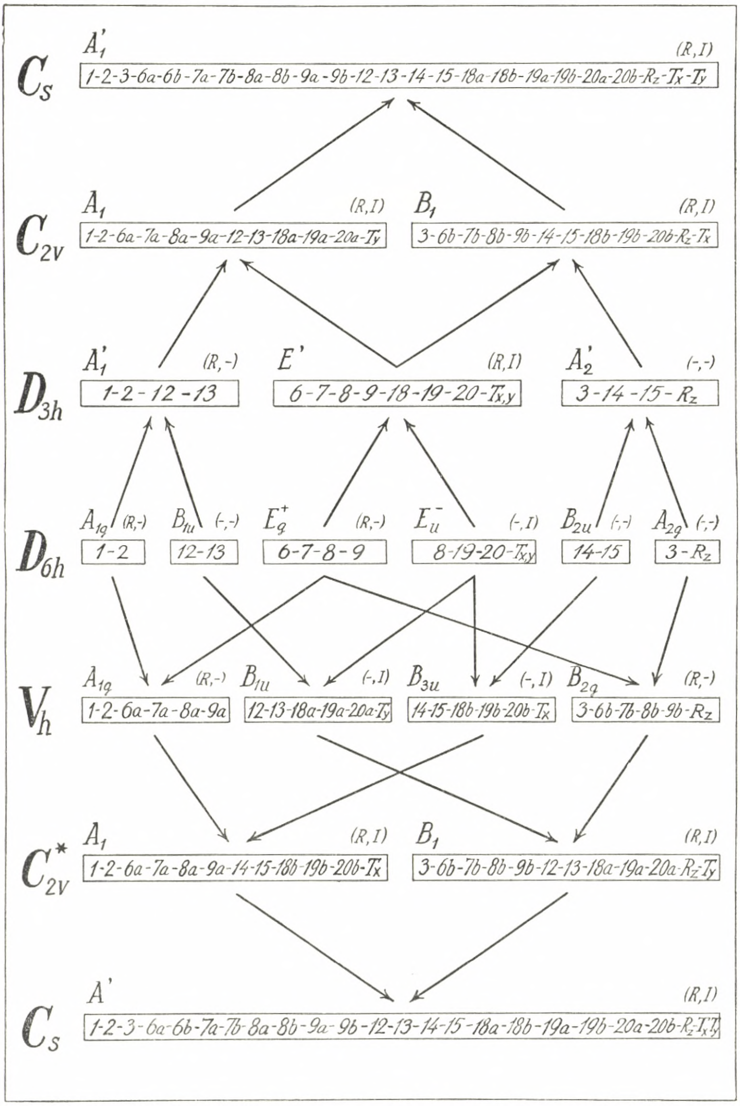
[1] ANGUS et al; REDLICH, loc. cit.



C_s
A_1' (R,I)
1-2-3-6a-6b-7a-7b-8a-8b-9a-9b-12-13-14-15-18a-18b-19a-19b-20a-20b-R_z-T_x-T_y
C_{2v}
A_1 (R,I)
1-2-6a-7a-8a-9a-12-13-18a-19a-20a-T_y
B_1 (R,I)
3-6b-7b-8b-9b-14-15-18b-19b-20b-R_z-T_x
D_{3h}
A_1' (R,-)
1-2-12-13
E' (R,I)
6-7-8-9-18-19-20-$T_{x,y}$
A_2' (-,-)
3-14-15-R_z
D_{6h}
A_{1g} (R,-)
1-2
B_{1u} (-,-)
12-13
E_g^+ (R,-)
6-7-8-9
E_u^- (-,I)
8-19-20-$T_{x,y}$
B_{2u} (-,-)
14-15
A_{2g} (-,-)
3-R_z
V_h
A_{1g} (R,-)
1-2-6a-7a-8a-9a
B_{1u} (-,I)
12-13-18a-19a-20a-T_y
B_{3u} (-,I)
14-15-18b-19b-20b-T_x
B_{2g} (R,-)
3-6b-7b-8b-9b-R_z
C_{2v}^*
A_1 (R,I)
1-2-6a-7a-8a-9a-14-15-18b-19b-20b-T_x
B_1 (R,I)
3-6b-7b-8b-9b-12-13-18a-19a-20a-R_z-T_y
C_s
A' (R,I)
1-2-3-6a-6b-7a-7b-8a-8b-9a-9b-12-13-14-15-18a-18b-19a-19b-20a-20b-R_z-$T_x$$T_y$

Fig. 2a.

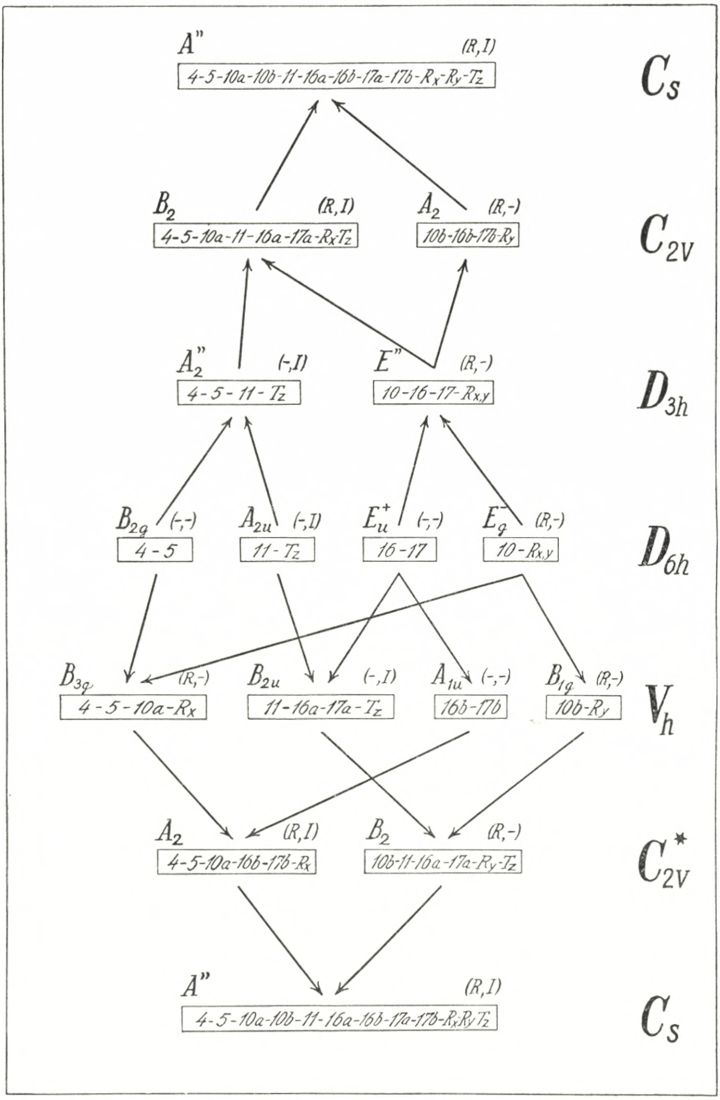

A'' (R,I)
4-5-10a-10b-11-16a-16b-17a-17b-Rx-Ry-Tz
Cs
B2 (R,I)
4-5-10a-11-16a-17a-Rx-Tz
A2 (R,-)
10b-16b-17b-Ry
C2V
A2'' (-,I)
4-5-11-Tz
E'' (R,-)
10-16-17-Rx,y
D3h
B2g (-,-)
4-5
A2u (-,I)
11-Tz
Eu+ (-,-)
16-17
Eg- (R,-)
10-Rx,y
D6h
B3g (R,-)
4-5-10a-Rx
B2u (-,I)
11-16a-17a-Tz
A1u (-,-)
16b-17b
B1g (R,-)
10b-Ry
Vh
A2 (R,I)
4-5-10a-16b-17b-Rx
B2 (R,-)
10b-11-16a-17a-Ry-Tz
C2V*
A'' (R,I)
4-5-10a-10b-11-16a-16b-17a-17b-Rx-Ry-Tz
Cs

Fig. 2b.

according to the eight blocks in V_h, because the common elements of D_{6h} and V_h are simply the elements of V_h.

In Tables VII—IX we reproduce the τ-ratios, calculated by TELLER's rule[1], for various important symmetry group relationships. The Tables are perhaps best explained by two simple examples:

In Table VII, column 2, row 1 we find that the τ-ratio of the product of frequencies in symmetry class A_{1g} in benzene to the product of the same frequencies in benzene-d_6 is 1.414. Reference to Fig. 2 shows that only the frequencies ν_1 and ν_2 are in this class. Hence we know that:

$$\tau = 1.414 = \frac{\nu_1 \cdot \nu_2 \text{ (in } C_6H_6)}{\nu_1 \cdot \nu_2 \text{ (in } C_6D_6)}$$

In Table VIII, column 5, row 2, τ is listed as 1.961. Hence we know from Fig. 2 that:

$$\tau = 1.961 = \frac{\nu_6 \cdot \nu_7 \cdot \nu_8 \cdot \nu_9 \cdot \nu_{18} \cdot \nu_{19} \cdot \nu_{20} \text{ (in sym-} C_6H_3D_3)}{\nu_6 \cdot \nu_7 \cdot \nu_8 \cdot \nu_9 \cdot \nu_{18} \cdot \nu_{19} \cdot \nu_{20} \text{ (in } C_6D_6)}$$

We have not given τ's for relations involving the isotopic derivatives for C_{2v} symmetry or less. For many of these relations we have no particular need, and application of most of the others to the spectra is either impossible, or of no assistance in making an assignment because several alternative assignments of lines satisfy the rule equally well.

The product rule can be used advantageously to calculate unobservable frequencies in benzene and benzene-d_6. For example we find in Fig. 2 that the frequencies ν_3 and

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[1] The necessary moments of inertia have been calculated by taking the C-C distance as 1.40 Å and the C-H distance as 1.08 Å.

ν_{6b} to ν_{9b} are in one Raman-active block in V_h. Since frequencies ν_6 to ν_9 are also observable in D_{6h}, we may calculate the remaining, unobservable ν_3 in both benzene and benzene-d_6 by utilizing τ-values from column 6,

Table VII.

D_{6h}	A_{1g}	A_{2g}	A_{2u}	B_{1u}	B_{2g}	B_{2u}	E_g^+	E_u^+	E_g^-	E_u^-
$C_6H_6 : C_6D_6$	1.414	1.286	1.362	1.414	1.414	1.414	2.000	1.414	1.286	1.925

Table VIII.

D_{6h}	$\underbrace{A_{1g}\ B_{1u}}$	$\underbrace{A_{2g}\ B_{2u}}$	$\underbrace{A_{2u}\ B_{2g}}$	$\underbrace{E_g^+\ E_u^-}$	$\underbrace{E_g^-\ E_u^+}$
D_{3h}	A_1'	A_2'	A_2''	E'	E''
C_6H_6 : sym-$C_6H_3D_3$	1.414	1.345	1.387	1.959	1.346
sym-$C_6H_3D_3$: C_6D_6	1.414	1.351	1.388	1.961	1.352

Table IX.

D_{6h}	$\underbrace{A_{1g}\ E_g^+}$	$\underbrace{E_u^+}$	$\underbrace{E_g^-}$	$\underbrace{B_{1u}\ E_u^-}$	$\underbrace{A_{2g}\ E_g^+}$	$\underbrace{A_{2u}\ E_u^+}$	$\underbrace{B_{2g}\ E_g^-}$	$\underbrace{B_{2u}\ E_u^-}$
V_h	A_{1g}	A_{1u}	B_{1g}	B_{1u}	B_{2g}	B_{2u}	B_{3g}	B_{3u}
C_6H_6 : p-$C_6H_4D_2$	1.414	1.000	1.000	1.396	1.367	1.396	1.324	1.396
p-$C_6H_4D_2$: p-$C_6H_2D_4$	1.414	1.414	1.286	1.396	1.370	0.988	1.030	1.396
p-$C_6H_2D_4$: C_6D_6	1.414	1.000	1.000	1.396	1.373	1.396	1.330	1.396

Table IX. There are other possibilities of calculating unobserved frequencies which will be considered in detail later. It should be remarked here that use of the product rule to compute unobservable frequencies is a perfectly valid procedure within the limits of the assumption of identical harmonic potential functions for isotopic molecules. It is of course necessary that the assignment of observed frequencies be made correctly, but no special knowledge of the potential system is assumed or required.

III. Experimental Procedure and Results.

Previous investigations of the Raman spectra of various deuterated benzenes have been made by Redlich and Stricks[1] and by Ingold and associates[2]. Redlich and Stricks prepared benzene-d_1 and the three benzene-d_2's by decomposing appropriate Grignard reagents with deuterium oxide. They attempted to prepare higher derivatives by the decarboxylation of calcium salts of benzene-carboxylic acids with $Ca(OD)_2$, but obtained only mixtures of the various derivatives. The Raman spectra of benzene-d_1 and the benzene-d_2's reported in their papers agree in general with those to be discussed here but are less complete. In addition they show very definite evidence that the compounds were not pure but contained rather considerable amounts of lower derivatives including benzene itself. Redlich and Stricks assign the six totally symmetrical vibrations as well as ν_{10a} in para-benzene-d_2 and para-benzene-d_4 to observed frequencies on the basis of calculations made from equations obtained from Wilson's potential system[3]. Since the assignment which we shall make later on agrees with theirs, we have no further reason for discussing their results.

Ingold and his associates have reported the preparation of benzene-d_1, para-benzene-d_2 and sym-benzene-d_3. They

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[1] Redlich and Stricks, Monatshefte f. Chem. **67**, 213; **68**, 47, 374 (1936).

[2] Ingold and associates, Nature **135**, 1033 (1935); **139**, 880 (1937).

[3] Wilson, loc. cit.

have given preliminary data on the Raman spectrum of benzene-d_1 which are incomplete but which are in agreement with those of Redlich and Stricks. They have also reported briefly on the Raman and infrared absorption spectra of sym-benzene-d_3. We agree with the frequencies and assignments of Raman lines which they have given, and will not discuss their report further. Part of the infrared frequencies are of value to us in deciding about certain doubtful assignments, and will be considered in some detail later on. Unfortunately no indications of relative intensities of the infrared bands are given in their brief note and our interpretations using the infrared data are for this reason somewhat insecure.

The spectrograph used in the present investigation was the four-prism instrument previously described[1]. Since the quantities of liquid being studied were not particularly small (6—10 cc.), no special microtechnique was necessary. The spectroscopic data obtained are correspondingly more reliable, particularly with regard to weak lines, than those obtained by investigators who have used very small amounts of liquid. The excitation source was unfiltered mercury radiation from arcs operated so as to give almost no continous background. The Raman lines obtained were due to excitation both by Hg-4358 and by Hg-4047. All lines in the spectra reported here have appeared from both excitation sources except for one or two isolated instances in which a strong line from one source coincided with a weak line from the other. In such cases the weak line has always been found on at least two plates.

The frequencies of the Raman lines were measured from photographic enlargements by interpolation between

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[1] Langseth, Zeitschr. f. Phys. **72**, 350 (1931).

Table X. Observed Fr

C_6H_6		C_6H_5D		$C_6H_4D_2$							
				ortho		meta		para		unsym.	
$\tilde{\nu}$	I	$\tilde{\nu}$	I	$\tilde{\nu}$	I	$\tilde{\nu}$	I	$\tilde{\nu}$	I	$\tilde{\nu}$	I
606.4	4	381	0 d	384	0 d	374	0 d	400	0 d	395	0
849.7	1	403	0 d	581.6	0	598.4	4	593.6	4	562	0
992.5	10	598.5	5	598.3	5	710.5	2	598.8	4	593.5	6
1177.9	5	602.0	5	658	0 d	818	½ d	634.0	2	635.0	2
1585.9	3	780	1	692	0 d	838.1	1	738.0	1	707	2
1604.2	2	851.7	2	773.8	0	855	0 d	850	1 d	772.2	1
3048.3	5	859.5	2	782.1	1	970.5	10	911.1	4	785	0
3061.5	8	980.9	10	825	0	1006.1	5	966	1 d	822.7	0
		1008.6	5	841.6	1	1030	0	978.5	10	841.1	3
		1032.4	1	856	0 d	1051	0	1166.6	2	915	1
		1077	1 d	976.0	10	1081.5	½ d	1175.4	4	927	1
		1158.2	2	992.8	3	1107.7	1	1273.4	0 d	966.4	10
		1176.5	4	1035	0 d	1143.9	0	1568.3	3	987.4	2
		1418	0 d	1055.4	1	1168.4	2	1589.2	5	996.0	2
		1575.7	3	1077	0 d	1177.2	1	2223	0 d	1054.7	0
		1593.8	5	1130.7	2	1397.2	1	2261	1 d	1070.2	0
		1610	0	1160.0	2	1418.8	0	2279.4	8	1128.3	1
		2269.8	3	1177.5	2	1563.0	1	3042.3	3	1139.1	3
		2313.0	1	1248	0 d	1583.1	3	3054 6	8	1270	1
		3040	3 d	1384.8	0	2249.2	1	3155.3	0	1366	0
		3055.5	8	1402.8	1	2264.9	1	3174.5	0	1390	1
		3064.2	6	1573	2 d	2272.1	2			1461	0
		3167.9	1	1588.0	4	2284.4	4			1556	2
				2257.9	1	2308.4	½			1578	5
C_6D_6				2273.3	3	2337	0 d			2207.2	0
				2280.8	5	2991.8	1			2234.2	0
$\tilde{\upsilon}$	I			2298	0	3047	4 d			2270	4
				2313.5	1	3058.8	8			2283.6	8
				2993	0	3153	0			2297.3	1
579.3	1			3001	0					3023.4	0
663.5	3			3035.3	3					3045.1	6
869.1	4			3053	8 d					3055.7	8
945.2	10			3064	8 d					3087	0
1553.2	3										
2265.7	6										
2293.2	8										

encies and Intensities.

$C_6H_3D_3$				$C_6H_2D_4$						C_6HD_5	
vic.		sym.		ortho		meta		para			
$\tilde{\nu}$	I	$\tilde{\nu}$	I	$\tilde{\nu}$	I	$\tilde{\nu}$	I	$\tilde{\nu}$	I	$\tilde{\nu}$	I
374	1 d	373	1	369	0 d	375	0 d	585.0	6	371	0 d
592	5	593.7	3	589.3	6	589.0	6	605.3	$^1/_2$	584.8	6
657	0 d	711.7	2	625.4	1 d	632.3	2	630.3	0	614	0
712.0	2	815	0 d	688.3	3	705.1	5	662.3	4	632	0
744	0 d	834.3	2	710	1	711.1	5	765.3	2	664.2	4
779.3	1	956.6	10	738.7	2	832.5	2	859.7	5	691.3	2
825	0 d	1003.9	6	778	0 d	847.0	3	927	1 d	711.6	5
838.7	4	1072	0 d	813.1	1	953.8	10	949.9	1	812.0	1
863.4	0	1101.7	2	842.2	5	986.4	4	959.6	10	836.4	4
920	0 d	1396.2	0	932.3	3	994.3	5	1051	$^1/_2$ d	847.9	2
965.3	10	1415.1	0	960.4	10	1057	0 d	1098	0 d	857.9	5
992.3	5	1575.9	3	974.0	2	1095.7	3	1137.4	1	950.9	10
031	0	2241	1 d	1004.1	0	1175.9	1	1253	1 d	977.1	4
055.6	1	2272	1 d	1057	0	1197.7	1	1541.5	1	1034.2	1
095.5	3	2283.8	3	1069	0	1209	1 d	1563.0	3	1098.9	1
131.0	1	2974.6	2	1099.4	1	1374	0 d	1571.7	5	1140.1	1
150.4	2	3055.1	4	1136.5	4	1409	0 d	2113	0 d	1173.5	2
363.2	0	3148	0 d	1170.0	2	1541	0 d	2158	0 d	1225	0 d
385.6	1			1252	0 d	1564.6	5	2219	0 d	1323	0 d
554.5	0			1289	1 d	1571.3	5	2245	0 d	1360	1 d
575.3	4			1348.5	0	2198.5	0	2265.0	6	1412	0 d
582.2	3			1372.3	2	2223.2	0	2283.0	8	1532	0 d
240.2	1			1478	1 d	2271.8	5	3042.9	8	1557.9	6
259.8	2			1547.7	1	2287.2	8			1570.4	6
280.8	4			1571.8	5	3051.4	8			2221	0
288.1	8			1578.1	2					2246	0
312	1 d			2160	0 d					2256	0
82	1 d			2187.0	0					2268.3	7
50.6	5			2208.9	0					2288.8	9
58.7	8			2251	1 d					3050.6	8
				2270.0	6						
				2289.9	8						
				2984	0 d						
				3046.2	3						
				3058.3	6						

standard lines of the iron arc. The frequencies of the very strong lines have been determined from at least two plates, and on each plate from three sources of excitation: Hg-4047, 4078 and 4358 Å. Since the lines excited by these three sources on any one plate vary greatly in intensity and breadth, measurements of one Raman frequency from the three different sources serve as valuable checks on one another. The positions of the strong highly polarized lines are the most easily measured, and may be considered accurate to ± 0.2 cm.$^{-1}$. The frequencies of the other lines may usually be trusted to ± 0.5 cm.$^{-1}$. Exceptions to this statement must be made for the very faint lines and for lines marked "d" in Table X, whose frequencies may be in error by 1—2 cm.$^{-1}$, or, in one or two instances, by somewhat more.

The deuterated benzenes were prepared by the modified Grignard process described by Langseth and Klit[1]. The method is quite satisfactory except for the great difficulty of removing the very last traces of water from the ether in which the Grignard reaction takes place. A trace of water leads to the presence in each deuterated benzene of small amounts of certain lower deuterated benzenes, but never of isomers of the particular compound under consideration. This is made abundantly clear by the method which has been used in analyzing the spectroscopic data.

Our procedure was as follows: First all lines in the spectrum of each derivative were measured, assigned to source of excitation and listed according to frequency and intensity. This was done for each derivative independently and without regard to the spectra of other derivatives. The sets of frequencies of the derivatives were next considered

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[1] Langseth and Klit, Kgl. Danske Vidsk. Selsk. math.-fys. Medd. **XV**, No. 13 (1938).

in the order of their deuterium content. The spectrum of benzene-d_1 was compared with that of benzene, and since the spectrum of benzene is accurately known, it was possible to decide which, if any, of the weak lines found in the benzene-d_1 spectrum might be attributed to strong lines in benzene. Having thus established the spectrum of benzene-d_1, the frequencies of the benzene-d_2 derivatives could be examined in the same way, comparing weak lines with the strong lines of benzene-d_1. The same procedure was repeated for all the derivatives. The criteria which were always satisfied before an observed line was rejected as belonging to a derivative of lower deuterium content were: 1) the frequency must coincide within $\pm$ 0.3 cm.$^{-1}$ with that of a strong line of a lower derivative; 2) the intensity of the line must have a reasonable ratio ($<1:20$) to that of the strong line in a lower derivative; 3) the lower derivative must be a proper isomer. By a "proper isomer" is meant an isomer which can be formed from the higher deuterium derivative by replacing one of the latter's deuterium atoms with hydrogen. Thus of the benzene-d_2's only meta-benzene-d_2 is to be expected as an impurity in sym-benzene-d_3, since the replacement of any one of the latter's three deuterium atoms by hydrogen gives only the meta derivative. Similarly unsym-benzene-d_3 will be the only benzene-d_3 derivative present in para-benzene-d_4, and so on.

In practice only the strong totally symmetrical lines in the regions about 990, 2290 and 3050 cm.$^{-1}$ are of sufficient intensity to appear as improper lines, and since those in the neighborhood of 990 cm.$^{-1}$ are extremely sharp, their identification by frequency measurement is quite secure. Except for these lines, only three other cases in all of spurious lines have been found.

The observed frequencies for each derivative are given in Table X. The intensities listed have been estimated visually on an arbitrary scale of 10. Particularly diffuse lines are marked "d" and particularly weak ones "0".

IV. Discussion of Observed Spectra.

The order of discussion of an interlacing series of spectra is necessarily arbitrary. In principle it must lie somewhere within the extremes of considering all the frequencies of each derivative separately, and of tracing the course of each individual frequency through the several derivatives in the series. The extreme procedures are neither possible nor desirable—the first because it rules out the very advantages which accrue from a knowledge of series variations; the second because the changes in symmetry properties of one frequency in the different members of the series cause it to lose, to a greater or lesser extent, the characteristics by which it may be singled out as a specific vibration. We therefore adopt the middle course of considering first those vibrations whose nature makes it likely that they will maintain their characteristic features throughout the series. When these frequencies have been properly catalogued, they will be eliminated from the spectra, and we will then take up the simplified spectra, singly or in appropriate groups, and will identify as many of the observed frequencies as possible.

1. The Totally Symmetrical Vibration ν_1.

It is clear that those vibrations which we have referred to as "essentially carbon vibrations" will vary least in frequency in the several deuterated benzenes. In particular, the one vibration which should preserve its identity throughout the series is the totally symmetrical carbon frequency ν_1. ν_1 has been identified unequivocally in benzene and benzene-d_6, in which it occurs respectively at 992.5 and 945.2 cm.$^{-1}$. Let us therefore consider this frequency in the intermediate derivatives[1].

a. Interpretation of Irregular Frequency Shifts.

If we assume that the substitution of each deuterium atom produces the same downward shift in ν_1, this shift should be one-sixth of the benzene—benzene-d_6 shift, namely 7.9 cm.$^{-1}$ per D-atom[2]. The value of ν_1 should therefore change in regular fashion, and should be a constant for the various isomers of a given isotopic species. These changes are shown by the lower dotted line in Fig. 3. When the spectra are examined, one finds that for four compounds (the ortho- and the para-substituted derivatives) the predicted shift is closely confirmed by the presence of a line whose great intensity leaves little room to doubt that it is ν_1.

In the other derivatives, ν_1 is found near enough to the predicted point to confirm its identity, but far enough away to show that something is disturbing the validity of the assumption on which the shifts were calculated. The nature of the disturbance is indicated by the existence in the spectra of these derivatives of a companion line close to, and on

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[1] Cf. the preliminary discussion by Klit and Langseth, J. Chem. Phys. **5**, 925 (1937).

[2] We know that the shift in ν_1 from benzene to benzene-d_6 (47 cm.$^{-1}$) is not much larger than that which would be produced by the substitution of six C^{13}-isotopes in the ring (38 cm.$^{-1}$). Hence the effect on ν_1 of substituting one D-atom should be about that of replacing one C^{12} by a C^{13} isotope. On the basis of the discussion by Teller, loc. cit., of frequency changes produced by small percentage mass increments, our assumption may be justified.

the high frequency side of, ν_1. To understand the presence of this line, which is of quite variable intensity and which appears to exert a pronounced influence on ν_1, we must recall that a frequency of very nearly 1000 cm.$^{-1}$ has been assigned to the trigonal vibration form ν_{12} in benzene (see Fig. 1) by KOHLRAUSCH[1].

The frequency ν_1 would be entirely unconcerned about the presence of a nearby fundamental such as ν_{12} if there were no dynamical relation between the two vibrations. The criterion[2] for dynamical connection between two harmonic vibrations is simply that the two frequencies occupy the same symmetry block. Therefore if the vibration form ν_{12} does indeed have a frequency of about 1000 cm.$^{-1}$, it can only interact with ν_1 in derivatives belonging to symmetry groups D_{3h}, C_{2v}, and C_s, as a glance at Fig. 2 quickly reveals. It is, however, just in the derivatives of these symmetry types that we find the striking disagreement between estimated and observed values of ν_1 and the presence of the unexpectedly strong companion line.

To obtain an understanding of the nature and extent of the interaction between ν_1 and ν_{12}, it is helpful to estimate the frequency changes of the latter in the various derivatives on the assumption that no interaction takes place. Interaction is forbidden by symmetry in the groups D_{6h}, V_h and C_{2v}^*, and accordingly ν_{12} should have its undisturbed position in compounds of these groups. The frequency is Raman-active only in C_{2v}^*, and in the spectra of ortho-benzene-d_2 and ortho-benzene-d_4 the separation, Δ, of ν_{12} from ν_1 is 16.8 cm.$^{-1}$ and 13.6 cm.$^{-1}$ respectively. We know from the

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[1] KOHLRAUSCH, Zeitschr. phys. Chem. B, **30**, 305 (1935). The arguments for his assignment have been reviewed by LORD and ANDREWS, Journ. Phys. Chem. **41**, 153 (1937).

[2] Cf. for example PLACZEK, loc. cit., p. 283 ff.

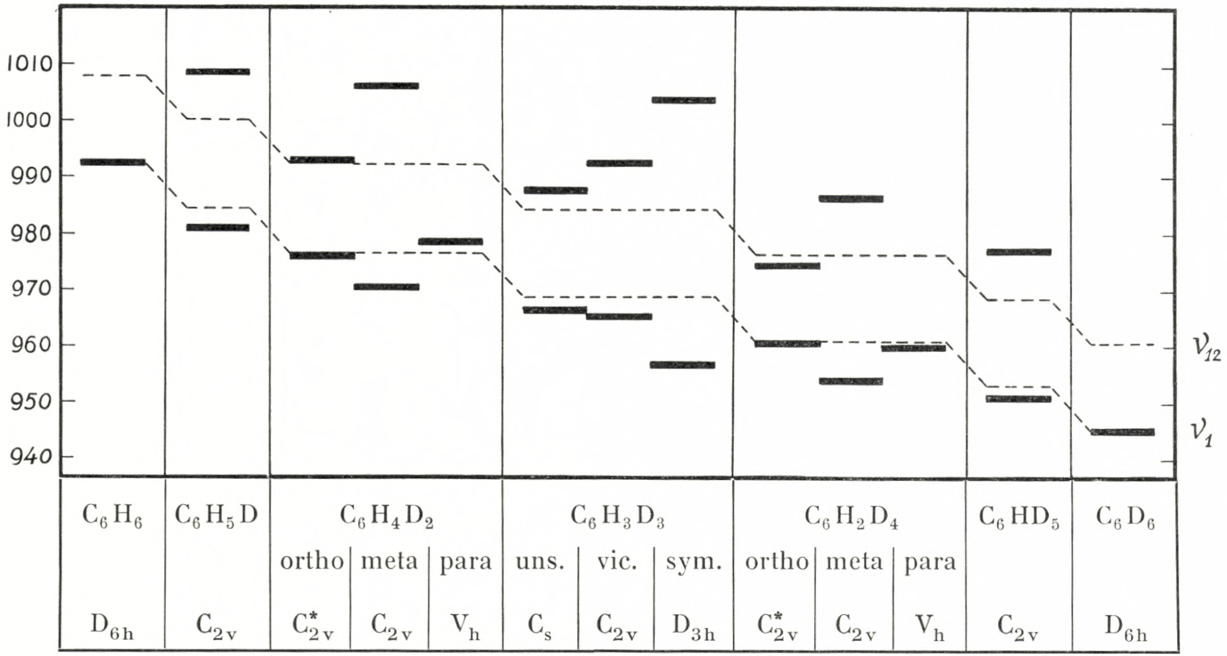

Fig. 3.

In all the deuterated benzenes with C_{2v} symmetry except the two ortho compounds, ν_{12} is symmetric to the two-fold axis, which passes through two para carbon atoms. In the ortho compounds the two-fold axis passes between the two ortho carbon atoms and thus ν_{12} violates the axis (see Fig. 1). To emphasize this distinction we have marked the compounds C^*_{2v}.

product rule that the shift in ν_{12} on passing from benzene to benzene-d_6 must be almost precisely the same as that for ν_1. This means that Δ should be about the same in all derivatives, and that any noticeably altered separation is to be ascribed to interaction between the two. In Fig. 3 the upper dotted line shows the calculated value of ν_{12} found by adding 15.5 cm.$^{-1}$, the mean of the observed Δ's, to the frequency of the lower dotted line[1]. The observed values of ν_1 and ν_{12} are shown by the solid lines in Fig. 3.

The formal mathematical procedure for computing precisely the positions and relative intensities of ν_1 and ν_{12} in the various derivatives offers no difficulties in principle. There is no way of evaluating all the necessary harmonic constants, however, and therefore in practice there exists no rigorously correct method of computing Δ and $\frac{I_{12}}{I_1}$, the intensity ratio of ν_{12} to ν_1, One must resort to some approximation procedure. For example, one may make simplifying assumptions about the molecular potential system so that the number of harmonic constants is reduced

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[1] We should remark that our use of the product rule in concluding that Δ is approximately the same for the two D_{6h} molecules requires the two quite reasonable assumptions that 1) the hydrogen stretching frequencies ν_2 and ν_{13} undergo the same percentage shift from benzene to benzene-d_6; 2) The anharmonicities of the carbon vibrations ν_1 and ν_{12} are about equal. On the basis of these assumptions Δ should differ in the two compounds by about 5 %, i. e. by less than 1 cm^{-1}. This is probably somewhat smaller than our error in estimating Δ.

In the preliminary note of KLIT and LANGSETH, the upper dotted line was calculated by assuming that the change in ν_{12} from ortho-benzene-d_2 to ortho-benzene-d_4 might be used to extrapolate ν_{12} in both directions. This procedure is quite heavily dependent on the accuracy which ν_{12} is observed in the ortho compounds, since small errors in either value of ν_{12} may lead to rather large differences between Δ in benzene and in benzene-d_6. The figure in their communication shows that the differences in these two Δ's are rather too large, i. e., that either ν_{12} is too far from ν_1 in benzene or too close in benzene-d_6.

sufficiently to evaluate all of them from available data. Such a potential system has been suggested by WILSON[1], who described the potential energy of the planar vibrations in terms of four constants only, namely those for the stretching and bending of the C-C and C-H bonds.

Even so simplified a potential system as this gives complicated secular determinants for the totally symmetrical frequencies in all the deuterated benzenes except sym-benzene-d_3. The determinant for the A_1' class in this compound, however, may be easily set up and solved. Only the three constants K (for C-C stretching), k (C-C-C bending) and q (C-H stretching) are involved, and the frequency equations are:

$$\left.\begin{aligned}
\sum^{4} \lambda_i &= \frac{m_H + m_D}{m_H m_D}\, q + \frac{1}{M}(K + 12k + 2q) \\
\sum^{6} \lambda_i \lambda_j &= \frac{M(m_H + m_D) + m_H m_D}{M^2 m_H m_D} \cdot (K + 12k + q)q + \frac{12}{M^2} \cdot Kk + \frac{1}{m_H m_D} \cdot q^2 \\
\sum^{4} \lambda_i \lambda_j \lambda_k &= \frac{2M + m_H + m_D}{2M^2 m_H m_D} \cdot (K + 12k)q^2 + \frac{m_H + m_D}{M^2 m_H m_D} \cdot 12\,Kkq \\
\prod^{4} \lambda_i &= \frac{12}{M^2 m_H m_D} \cdot Kkq^2
\end{aligned}\right\} (1)$$

where $\lambda_i = 4\pi^2 \nu_i^2$.

The force constants may be evaluated from the observed benzene spectrum. The mean values[2] from benzene and benzene-d_6 are: $K = 7.595$; $k = 0.656$; $q = 5.079$, all in units of 10^5 dynes per cm. With the aid of this single set

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[1] WILSON, loc. cit.

[2] Cf. LORD and ANDREWS, loc. cit.

of constants we may calculate the accompanying frequency table:

Table XI.

Compound	Frequency in cm.$^{-1}$				
		ν_1	ν_{12}	ν_2	ν_{13}
C_6H_6	obs. calc.	992.5 993.8	— 1011.8	3061.5 3070.3	— 3071.0
sym-$C_6H_3D_3$	obs. calc.	956.6 951.2	1003.9 1004.5	3055.1 3070.7	2283.8 2285.8
C_6D_6	obs. calc.	945.2 944.6	— 961.2	2293.2 2284.8	— 2286.7

It will be seen that the agreement with observation is good; in particular the wide separation of ν_1 and ν_{12} in sym-benzene-d_3 is rather well calculated. The fact that we are able to compute so closely the positions of the components of the doublet supports the assignment of the upper component to ν_{12}. The discrepancies between observation and calculation of ν_2 and ν_{13} may be ascribed chiefly to anharmonicity, the mean value of the constant q being too large for benzene and too small for benzene-d_6.

The agreement is close enough to warrant a computation of the amplitudes for the four A_1' frequencies. The amplitudes implicit in Equations (1) for vibrational quantum number $\frac{3}{2}$ are listed in Table XII, Column 2. It will be seen immediately from the numerical values of the amplitudes that the four A_1' vibrations may be regarded as essentially the totally symmetrical vibrations of two superposed but independent triangular molecules. In ν_1 and ν_{13} the amplitudes of the hydrogen atoms and of their parent carbon atoms are small compared with those of the deuteriums and of the other carbons. In ν_{12} and ν_2, on the other hand, the motion is essentially that of the triangle $(C\text{-}H)_3$, the deuterium atoms and the other carbon atoms remaining practically at rest. The positions of ν_1 and ν_{12} — which appear anomalous from the point of view illustrated by Fig. 3 — are thus simply to be understood as the result of the special mechanical situation existing in sym-benzene-d_3. When a straightforward quantitative calculation of the frequencies is carried out, experiment and calculation agree.

Table XII.

	Amplitudes in 10^{-10} cm.				Transformation coefficients		Change of polarisability in 10^{-25} c. c.		Intensity	Depolarization
	C_H	C_D	H	D	ξ	η	A	γ	I	ϱ
ν_1	0.830	4.805	0.927	6.083	0.799	0.0407	4.97	1.53	1.00	0.10
ν_{12} . . .	5.015	−0.148	5.681	−0.193	0.683	0.0014	4.10	1.18	0.67	0.09
ν_2	0.939	−0.003	−9.869	0.002	0.001	0.7043	−2.97	−2.34	0.75	0.40
ν_{13} . . .	0.007	−1.612	0.018	7.573	−0.113	−0.6064	−3.24	−2.22	0.76	0.34

b. Approximate Calculation of Intensities in Sym-Benzene-d_3.

If one regards the A_1' vibrations as approximately those of two independent equilateral triangles, one can explain in a simple and pictorial fashion several features of the Raman spectra of benzene and its symmetrical tri derivatives. For example it is possible to estimate in the following way the intensity relationships of the A_1' frequencies from the intensities of the A_{1g} vibrations in benzene and benzene-d_6. It is known[1] that the polarizability changes, Δa and $\Delta a'$,

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[1] Lord and Teller, J. Chem. Soc., London, 1937, p. 1728.

for ν_1 in benzene and benzene-d_6 are nearly equal, the decreased amplitude of the carbon atoms in the latter being more or less counterbalanced by an increased amplitude of the deuterium atoms. Provided that this same sort of compensation holds for the vibrations of the triangles[1], the intensity of ν_1, the deuterium triangular vibration, should be about equal to that of ν_{12}, the hydrogen triangular vibration. The sum of the two should be rather close to that of ν_1 in A_{1g}, since the amplitudes in ν_1 and ν_{12} in A'_1 are respectively larger than those of ν_1 in benzene-d_6 and in benzene by about $\sqrt{2}$. This compensates for the fact that only one triangle contributes to the individual intensities in A'_1 rather than two superposed and cooperating triangles as in A_{1g}. Small deviations from the approximation of equality can be estimated by noting in Table XII, Column 2, that the "hydrogen triangle" does contribute a little to the polarizability change due to ν_1, and that the other triangle lowers the change in ν_{12} a trifle. The addition to $\varDelta a'$ in ν_1 is about 17 %, and the decrement in ν_{12} about 3 %. Hence the intensity ratio of ν_{12} to ν_1 in A'_1 should be

$$\frac{I_{12}}{I_1} = \left(\frac{\varDelta a\ (1-0.03)}{\varDelta a'\,(1+0.17)}\right)^2 = \frac{0.94}{1.37} = 0.69.$$

The intensity of the two lines together should be about equal to that of ν_1 in benzene or in benzene-d_6.

Since the anisotropy of ν_1 is about equal in benzene and benzene-d_6, we should expect ν_1 and ν_{12} in A'_1 to exhibit the same depolarization factor, namely $\varrho = 0.09$.

The above reasoning, combined with the observed

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[1] It should hold, because the amplitude ratios $C_H : H$ and $C_D : D$ both in ν_1 and in ν_{12} are very nearly equal to their respective values in ν_1 in benzene and benzene-d_6.

equality of intensity of ν_2 in benzene and in benzene-d_6, leads also to the conclusion that the intensities of ν_2 and ν_{13} in A_1' should be very nearly equal (no correction is necessary here) and should be approximately half of the intensity of ν_2 in benzene. ϱ for ν_2 in A_1' should be 0.4 and for ν_{13}, 0.35[1].

In addition it is possible on the basis of the "triangle picture" of the A_1' vibrations to understand the striking constancy of the 1000 cm.$^{-1}$ frequency found in symmetrical tri-derivatives of benzene[2]. If the mass of the deuterium atoms be greatly increased, it is found from Equations (1) that the amplitudes D and C_D in ν_{12} and ν_2 practically become zero, and that amplitudes H and C_H change very little from the tabulated values. Thus we can see that as long as the force system of the "hydrogen triangle" $(CH)_3$ is essentially unaltered, the totally symmetrical vibrations of the triangle, ν_{12} and ν_2, will be independent of the nature and mass of the symmetrically substituted groups. Not only will the frequency remain constant in these derivatives, but also the intensity and polarization of the Raman line. We can therefore explain the high intensity—it should be half as intense as the 992 cm.$^{-1}$ line in benzene—and strong polarization — $\varrho = 0.09$ in principle — of this line which led observers[3] to attribute it to the same mode of vibration as ν_1 in benzene, and to conclude therefrom that benzene had D_{3h} symmetry.

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[1] Cf. LORD and TELLER, loc. cit., p. 1736.

[2] KOHLRAUSCH, Physik. Zeitschr. **37**, 58 (1936).

[3] KOHLRAUSCH, Zeitschr. phys. Chem. B, **30**, 308 (1935) and references there cited. KOHLRAUSCH has recently shown (Naturwiss. **39**, 635 (1937)) on general dynamical grounds that ν_{12} in symmetrical tri-derivatives should lie in the approximate range 990—1010 cm.$^{-1}$. His method of proof gives no insight into the nature of the vibration, however, and cannot be directly applied to yield information concerning intensities and depolarization factors.

The same point of view leads to the prediction that all symmetrical tri derivatives of benzene-d_6 (except sym-$C_6H_3D_3$) should possess a strong line of very nearly half the intensity of ν_1 in benzene-d_6, and with a depolarization factor 0.09, quite close to 950 cm.$^{-1}$.

c. Precise Calculation of Intensities in Sym-benzene-d_3.

From the amplitudes of the A_1' frequencies in sym-benzene-d_3 as listed in Table XII it is possible to make a precise calculation of intensities and polarizations of the Raman lines of the A_1' class by the method of Lord and Teller[1]. By their method the first step is to relate the various amplitudes in the A_1' vibrations to the amplitudes in those vibrations whose intensities serve as a standard of comparison. In our instance the latter are the vibrations of classes A_{1g} and B_{1u} in benzene. The relations have the form:

$$\left.\begin{aligned}
\chi_{C_H} &= \xi\chi_{C_1} + \zeta\chi_{C_{12}} + \eta\chi_{C_2} + \vartheta\chi_{C_{13}} \\
\chi_{C_D} &= \xi\chi^*_{C_1} + \zeta\chi^*_{C_{12}} + \eta\chi^*_{C_2} + \vartheta\chi^*_{C_{13}} \\
\chi_{H} &= \xi\chi_{H_1} + \zeta\chi_{H_{12}} + \eta\chi_{H_2} + \vartheta\chi_{H_{13}} \\
\chi_{D} &= \xi\chi^*_{H_1} + \zeta\chi^*_{H_{12}} + \eta\chi^*_{H_2} + \vartheta\chi^*_{H_{13}}
\end{aligned}\right\} \quad (2)$$

In these equations the χ's are amplitudes, the nature of each being specified by its subscript. The four on the left are those listed for any one frequency of class A_1' in Table XII. The χ's on the right hand side of each equation represent amplitudes in benzene. χ_{C_1} means, for example, the amplitude of the carbon atoms in ν_1. The *'s denote the amplitudes of carbon and of hydrogen atoms 1, 3, and 5 (cyclic enumeration) as distinguished from carbon and

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[1] Lord and Teller, loc. cit.

hydrogen atoms in the 2nd, 4th and 6th positions. ξ, ζ, η and ϑ are purely numerical coefficients having one set of values for each of the four frequencies in class A_1'. The utility of the coefficients lies in the fact that by means of them the polarizability changes due to each of the four frequencies in A_1' may be reckoned from the polarizability changes in the four frequencies of symmetry A_{1g} and B_{1u} in benzene. For example, the relationships for ν_1 in A_1' are:

$$A_{1'} = \xi_1 A_1 + \zeta_1 A_{12} + \eta_1 A_2 + \vartheta_1 A_{13}$$

and

$$\gamma_{1'} = \xi_1 \gamma_1 + \zeta_1 \gamma_{12} + \eta_1 \gamma_2 + \vartheta_1 \gamma_{13}$$

in which $A_{1'}$ and $\gamma_{1'}$ are the respective symbols[1] for the isotropic and anisotropic parts of the polarizability change due to ν_1 in sym-benzene-d$_3$. The A's and γ's on the right are the corresponding quantities for the benzene frequencies whose numbers they carry as subscripts. Similar equations obtain for A and γ in the other three A_1' frequencies.

The well-known expression:

$$I_{\text{rel}} = \text{const.}\ (5A^2 + 13\gamma^2)$$

gives the relation between the quantities A and γ and the intensity, I_{rel}, of the Raman line, say ν_1 in A_1', referred to some standard intensity (e.g., that of ν_1 in benzene). The value of the proportionality constant depends of course on the standard chosen. The depolarization factor, ϱ, is:

$$\varrho = \frac{6\gamma^2}{5A^2 + 7\gamma^2}.$$

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[1] Note that $A_{1'}$ is a symbol for a physical quantity, and is not to be confused with A_1', which has an entirely different, purely descriptive significance as the symbol for a symmetry class.

To calculate I_{rel} and ϱ we take the values of A_1, A_2, γ_1 and γ_2 from the paper of LORD and TELLER. The fact that A_{12}, A_{13}, γ_{12} and γ_{13} are zero because of symmetry frees us from the necessity of determining the coefficients ζ and ϑ. The coefficients ξ and η for the four A_1' frequencies are found without the necessity of computing B_{1u} amplitudes by using the relationships $\chi_{C_{12}} = -\chi^*_{C_{12}}$; $\chi_{C_{13}} = -\chi^*_{C_{13}}$ and $\chi_{H_{12}} = -\chi^*_{H_{12}}$; $\chi_{H_{13}} = -\chi^*_{H_{13}}$ which are required by the B_{1u} symmetry.

The results of calculations made in this way are listed in the last four columns of Table XII. The intensities are referred to the intensity of ν_1 in A_1' as unity. If it is desired to convert them to the scale used by LORD and TELLER (ν_1 in benzene $= 10$) it is only necessary to multiply each by a factor of seven.

We should point out here that our calculation of intensities has been made from amplitudes corresponding to an assumed potential system. In their calculations LORD and TELLER had sufficient data to utilize a perfectly general potential system, and their amplitudes are exact within the limits of the assumption of a harmonic force field. The amplitudes given in Table XII are probable pretty close to the correct values, however, because we have found that the WILSON potential system gives almost exactly the values listed by LORD and TELLER for ν_1 and ν_2 in benzene and benzene-d_6, and because the equations (1) come very close to giving the observed A_1' frequency values.

d. Perturbation Calculation of $\frac{I_{12}}{I_1}$.

If we were able to carry out calculations similar to the preceding for the other "anomalous" separations and intensities of ν_1 and ν_{12}, the same sort of agreement with experiment would doubtless be found. It is simpler and more fruitful, however, to consider the frequency relationships of ν_1 and ν_{12} from a somewhat different standpoint. Let us suppose that instead of replacing the hydrogen atoms stepwise by deuterium in preparing the deuterated benzenes, we had simply increased the mass of all the H-atoms by one-sixth atomic unit at each step. We would then obtain five molecules, all of D_{6h} symmetry, intermediate between benzene and benzene-d_6. The values of ν_1 and ν_{12} for these five should certainly be given by the dotted lines in Fig. 3, since ν_1 and ν_{12} can never interact in molecules of D_{6h} symmetry. If we perturb slightly the vibrations ν_1 and ν_{12} in the D_{6h} molecules by a redistribution of the total hydrogen mass[1] we may investigate the resulting interaction of ν_1 and ν_{12}, if any, by applying perturbation theory in the manner of FERMI[2].

The energy of the D_{6h} vibrations ν_1 and ν_{12} in terms of their normal coordinates q_1 and q_{12} is:

$$2H = \dot{q}_1^2 + \dot{q}_{12}^2 + 4\pi^2\nu_1^2 q_1^2 + 4\pi^2\nu_{12}^2 q_{12}^2 .$$

By making the substitution $\nu_{12} + \nu_1 = S$, $\nu_{12} - \nu_1 = \Delta$ we rearrange to

$$2H = \dot{q}_1^2 + \dot{q}_{12}^2 + \pi^2 S^2 (q_1^2 + q_{12}^2) + 2\pi^2 \Delta S (q_{12}^2 - q_1^2) + \\ + \pi^2 \Delta^2 (q_1^2 + q_{12}^2) .$$

If the distribution of mass among the hydrogen atoms now be changed, the symmetry of the molecule will alter and changes must therefore be made in the energy expression.

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[1] E. g. by changing from the hypothetical molecule $C_6H_6^{1.5}$ to one of the isomers of $C_6H_3D_3$, or by going from $C_6H_6^{1.67}$ to a $C_6H_2D_4$ isomer.

[3] FERMI, Zeitschr. f. Phys., **71**, 250 (1931); cf. also PLACZEK, Handb. d. Radiolog. Bd. VI/2, p. 316 ff.

By far the most important of these changes should be the introduction of a quadratic term involving the crossproduct $q_1 q_{12}$. The coefficient, β, of the crossterm is zero in the D_{6h} molecules because of symmetry. Other changes include the addition of small corrective terms involving the $\dot{q}$'s, but these ought to be quite small because the total mass of the hydrogen atoms remains constant. The energy expression then takes the form:

$$\left.\begin{aligned} 2H = {} & \dot{q}_1^2 + \dot{q}_{12}^2 + \pi^2 S^2 (q_1^2 + q_{12}^2) && \text{(a)} \\ & + 2\pi^2 \Delta S (q_{12}^2 - q_1^2) + 2\beta q_1 q_{12} && \text{(b)} \\ & + \pi^2 \Delta^2 (q_1^2 + q_{12}^2) + f(\dot{q}_1, \dot{q}_{12}) && \text{(c)} \end{aligned}\right\} \quad (3)$$

Since in the D_{6h} molecules $\Delta \simeq 0.01\,S$, we shall feel justified in regarding the terms in (a) as our unperturbed energy expression, the terms in (b) as a small perturbation, and those in (c) as negligible.

The energy levels and wave functions corresponding to (a) are simply those of a doubly-degenerate harmonic oscillator. The levels are given by:

$$W_n^0 = (n+1)\frac{hS}{2}$$

in which n is the total vibrational quantum number. Associated with the n^{th} level are $n+1$ wave functions. Since the Raman frequencies ν_1 and ν_{12} are chiefly due to transitions from the level $n = 0$ to the level $n = 1$, we shall write down the form of the wave functions for the first two levels. For $n = 0$,

$$\psi_0^0 = N_0\, e^{-\frac{\pi^2 S}{h}(q_{12}^2 + q_1^2)}$$

in which N_0 is a numerical factor. For $n = 1$ there are two wave functions:

$$\psi^0_{1_{10}} = N_1 e^{-\frac{\pi^2 S}{h}(q_{12}^2 + q_1^2)} q_{12}$$

$$\psi^0_{1_{01}} = N_1 e^{-\frac{\pi^2 S}{h}(q_{12}^2 + q_1^2)} q_1$$

N_1 is a numerical factor. It will be noticed that the algebraic symmetry properties of $\psi^0_{1_{10}}$ are those of the normal coordinate q_{12}, and of $\psi^0_{1_{01}}$, those of q_1.

These energy levels and wave functions are to be corrected for the perturbation terms (b) by means of the perturbation theory of degenerate levels[1]. The correction to W^0_0 and to ψ^0_0 is zero. To W^0_1 we must add the corrective term W'_1 obtained by solving the secular determinant:

$$\begin{vmatrix} \frac{h\Delta}{2} - W'_1 & \frac{h\beta}{4\pi^2 S} \\ \frac{h\beta}{4\pi^2 S} & \frac{-h\Delta}{2} - W'_1 \end{vmatrix} = 0.$$

Thus we find:

$$\begin{aligned} W_1 &= W^0_1 + W'_1 \\ &= W^0_1 \pm \sqrt{\left(\frac{h\Delta}{2}\right)^2 + \left(\frac{h\beta}{4\pi^2 S}\right)^2}. \end{aligned} \qquad (4)$$

The double level W^0_1 therefore splits symmetrically into two under the action of the perturbation. The wave functions of the two split levels have the form:

$$\left.\begin{aligned} \psi_{1_{10}} &= A(B\psi^0_{1_{10}} - C\psi^0_{1_{01}}) \\ \psi_{1_{01}} &= A(C\psi^0_{1_{10}} - B\psi^0_{1_{01}}) \end{aligned}\right\} \quad (5)$$

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[1] See, for example, PAULING and WILSON, Quantum Mechanics, (McGraw-Hill, New York. 1935). Page 165.

where the coefficients of the ψ^0's are:

$$A = \left[\left(\frac{h\beta}{4\pi^2 S}\right)^2 + \left(\frac{h\Delta}{2} + \sqrt{\left(\frac{h\Delta}{2}\right)^2 + \left(\frac{h\beta}{4\pi^2 S}\right)^2}\right)^2\right]^{-\frac{1}{2}}$$

$$B = \left[\frac{h\Delta}{2} + \sqrt{\left(\frac{h\Delta}{2}\right)^2 + \left(\frac{h\beta}{4\pi^2 S}\right)^2}\right]$$

$$C = \frac{h\beta}{4\pi^2 S}.$$

The formulation of each ψ_1 by combination of the ψ_1^0's shows that the characteristics of the perturbed levels will be a mixture of the properties of the unperturbed ones. The numerical coefficients AB and AC are analogous to the ξ's and η's by which the amplitudes of the A_1' frequencies in sym-benzene-d_3 were expressed in terms of the A_{1g} and B_{1u} frequencies in benzene. AB and AC depend essentially on Δ and β alone. It is therefore helpful to consider the following limiting cases:

(1) If we allow $\beta \rightarrow 0$, Δ being kept constant and finite,

$$\psi_{1_{10}} \rightarrow \psi^0_{1_{10}}; \quad \psi_{1_{01}} \rightarrow \psi^0_{1_{01}};$$

and

$$W_1 \rightarrow W_1^0 \pm \frac{h\Delta}{2} \left(\text{i.e., } \frac{3}{2} h\nu_1 \text{ and } \frac{3}{2} h\nu_{12}\right).$$

That is, removal of the interaction between ν_1 and ν_{12} leads, as we should expect, to the original wave functions and energy levels of the D_{6h} molecule.

(2) If $\Delta \rightarrow 0$, β remaining constant and finite,

$$\psi_{1_{10}} \rightarrow \frac{1}{\sqrt{2}}(\psi^0_{1_{10}} - \psi^0_{1_{10}}); \text{ i. e., } \psi_{1_{10}} \rightarrow \text{const.} \cdot e^{-\frac{\pi^2 S}{h}(q_{12}^2 + q_1^2)} \cdot (q_{12} - q_1)$$

$$\psi_{1_{01}} \rightarrow \frac{1}{\sqrt{2}}(\psi^0_{1_{10}} + \psi^0_{1_{01}}); \text{ i. e., } \psi_{1_{01}} \rightarrow \text{const.} \cdot e^{-\frac{\pi^2 S}{h}(q_{12}^2 + q_1^2)} \cdot (q_{12} + q_1)$$

and $$W_1 \rightarrow W'_1 \pm \frac{h\beta}{4\pi^2 S}$$

The physical significance of the ψ's in limiting case (2) may be grasped by considering the factors $(q_{12} - q_1)$ and $(q_{12} + q_1)$. Here the normal coordinates q_1 and q_{12} differ only in that the amplitudes of atoms in the 2, 4 and 6-positions in the molecule have opposite signs in the two coordinates[1], i. e., have all positive signs in q_1 and all negative in q_{12}. Hence the amplitudes of all six atoms in the 2, 4 and 6-positions must be zero when ψ contains $(q_{12} + q_1)$ as a factor, and those of the 1, 3 and 5 atoms must vanish if ψ contains $(q_{12} - q_1)$. Symmetry requires the amplitudes of all carbon atoms as well as of all hydrogen atoms to be equal in q_1. Therefore if the accidental degeneracy of ν_1 and ν_{12} is exact, the two vibrations are independent "triangular" vibrations of the sort discussed on page 30. Thus in the limit (2) the result we have found to hold approximately for ν_1 and ν_{12} in the A'_1 vibrations of sym-benzene-d_3 holds precisely in any perturbed D_{6h} derivative.

To discover how closely ν_1 and ν_{12} in the various deuterated benzenes approach one or another of the above extremes, it is necessary to consider the relative magnitudes of Δ and β. We have seen that in all the hypothetical D_{6h} molecules between C_6H_6 and C_6D_6 Δ has a value of about 16 cm.$^{-1}$. This is small compared with S, but by no means zero. We should therefore expect to find the limit (2) approached only if β were to become quite large. We can state at once, however, that we know from considerations

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[1] This difference follows from the symmetry of the A_{1g} and B_{1u} vibrations, from the assumption (experimentally reasonable) that $\nu_2 = \nu_{13}$ both in benzene and in benzene-d_6 and from the assumption (which is not correct experimentally, but which limiting case (2) implies) that $\nu_1 = \nu_{12}$ both in benzene and in benzene-d_6.

of symmetry that β is identically zero for perturbations of C_{2v}^* and V_h symmetry, i. e. in the four ortho and para deuterium derivatives. Hence in these compounds limiting case (1) obtains, and we expect to find no perturbation interaction of ν_1 and ν_{12}. We have no independent way of finding the values of β in the other compounds, but we can estimate them in a relative way as follows: Let us adopt as a standard the value, β_1, of β in benzene-d_1. If the introduction of one deuterium atom into benzene gives rise to the term $\beta_1 q_1 q_{12}$ in the potential energy expression, the introduction of a second should be expected to give rise to a like term. When the second atom is introduced ortho or para to the first, however, the sign of the term is reversed and we find, as we have just stated, that the value of β for ortho and para derivatives is zero. On the other hand we should find in meta-benzene-d_2 that the terms are of like sign and therefore expect that β in this compound should have twice the value of β_1. The same reasoning leads to $3\beta_1$ for β in sym-benzene-d_3, and to β_1 for the other derivatives except those of symmetry C_{2v}^* and V_h. We can now evaluate β_1 empirically from the separation of ν_1 and ν_{12} in benzene-d_1 (for example), and determine the energy levels in the remaining compounds by Equation (4). The separations of the levels calculated in this way are listed in Table XIII. The whole number n listed in column 3 is the numerical factor by which β_1 must be multiplied to obtain the value of β for the compound under consideration. The actual frequencies of ν_1 and ν_{12} can be found by adding and by subtracting half the splitting to, and from, $\frac{S}{2}$. The calculated and observed splittings are in agreement except for the two meta- and the symmetrical tri compounds. The separations for these compounds have been overestimated, but at least we can explain in a semi-quantitative fashion the irregularities in the positions of ν_1 and ν_{12} in all the deuterated benzenes.

The wave functions (5) may be used in straightforward fashion (following Placzek, loc. cit. p. 321) to determine the intensity ratio of ν_{12} to ν_1. The derivation of the expression for this ratio is much simplified when we make use of the fact that the polarizability change due to ν_{12} in a D_{6h} molecule is zero by symmetry. We therefore obtain (cf. Placzek, Eq. (12) p. 321)

Table XIII.

Separation and Relative Intensities of ν_1 and ν_{12}.

Compound		S (calc.)	n	Splitting (calc.)	Splitting (obs.)	$\frac{I_{12}}{I_1}$ (calc.)	$\frac{I_{12}}{I_1}$ (obs.)
C_6H_6		2000	0	15.5	—	(0)	—
C_6H_5D		1994	1	(27.7)	27.7	0.28	0.37
$C_6H_4D_2$	o	1968	0	15.5	16.8	(0)	0.15
	m	1968	2	48.8	35.6	0.39	0.47
	p	1968	0	15.5	—	(0)	—
$C_6H_3D_3$	s	1953	3	71.6	47.3	0.51	0.63*
	v	1953	1	28.0	27.0	0.27	0,35
	u	1953	1	28.0	21.0	0.15	0.24
$C_6H_2D_4$	o	1937	0	15.5	13.6	(0)	0.18
	m	1937	2	49.6	32.6	0.36	0.35
	p	1937	0	15.5	—	(0)	—
C_6HD_5		1921	1	28.3	26.2	0.26	0.30
C_6D_6		1906	0	15.5	—	(0)	—

$$\frac{I_{12}}{I_1} = \frac{2W_1' - \varDelta}{2W_1' + \varDelta} \qquad (6)$$

where $2W_1'$ is the observed splitting of the levels, and $\varDelta$ is their unperturbed separation. The intensity ratios given

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* Cf. also the calculated values on p. 32 and in Table XII.

by this expression are shown in Column 6 of Table XIII. These may be compared with the micro-photometrically measured values in Column 7. The agreement is as satisfactory as can be expected. The finite intensity observed for ν_{12} in the two ortho compounds is not in real contradiction to the calculated value zero. Although no intensity should accrue to ν_{12} because of interaction with ν_1 in these compounds, the small intensity actually observed arises from an allowed but very weak interaction with frequencies other than ν_1 (cf. Fig. 2).

The perturbation procedure leads also to the conclusion that ν_1 and ν_{12} should have, except in the ortho derivatives, the same depolarization factor. We cannot say a priori what this factor will be in the several derivatives, but it may be inferred from the equality of ϱ for ν_1 in benzene and benzene-d_6 that ν_1 in the intermediate hypothetical D_{6h} compounds should exhibit this same value of ϱ. This fact, coupled with the procedure by which Equation (6) was derived, leads to the conclusion that ν_1 and ν_{12} should possess the same depolarization factor, 0.09, in all the deuterated benzenes except the ortho and para di and tetra derivatives. ϱ for ν_{12} in the ortho compounds should be $\frac{6}{7}$ by symmetry.

The pertubation procedure we have used in computing the various separations and intensities of ν_1 and ν_{12} perhaps appears crude, and the results obtained with it may seem disappointingly approximate in character. Certainly no one would resort to such approximation methods if it were possible to use more rigorous procedures. The example of our calculations for ν_1 and ν_{12} in sym-benzene-d_3 illustrates the point. Here one can make more precise calculations of frequencies and intensities[1]. A comparison of these cal-

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[1] On the basis of an assumed potential function, however.

culations with those made on the assumption of resonance interaction shows that at least the latter give a quite correct qualitative picture, and approach rather closely to a correct quantitative one.

The chief value of the perturbation calculations, however, is the corroboration which they lend to the D_{6h} structure. If a D_{6h} structure be assumed for benzene, the explanation we have given of the positions and relative intensities of ν_1 and its companion follows readily and quite completely. On the assumption of any other symmetry, and in particular of such symmetries as D_{3h} (KEKULÉ structure) and D_{3d} (bent structure), the irregularities of frequency and intensity may be explained only in complex and ad hoc fashion. The structures other than D_{6h} cannot be excluded by a strictly logical process, but when we may choose between a simple (D_{6h}) and a complicated structural basis for explaining observed spectra, our choice is clear. It is in this sense that the variations in ν_1 and ν_{12} in the deuterated benzenes may be said to offer "strong support" to the D_{6h} structure.

e. Fine Structure of ν_1.

The discussion just given of the interaction between ν_1 and ν_{12}, and of the intensity changes resulting therefrom, is of assistance in explaining the complicated structure of ν_1 in benzene. Under high dispersion this frequency appears not as a single line but as a strong central line with four weak satellites, a pair on each side. The fine structure has been studied by a number of investigators since its original discovery by HOWLETT[1]. The results of four of these investigations are summarized in Table XIV. While there are one

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[1] HOWLETT, Nature **128**, 796 (1931).

or two minor differences in the results, it will be seen that the four studies are essentially in very good agreement as to the relative spacings of the components. Other investigations[1] have generally been carried out with spectrographs of lower dispersion than those used in the four researches listed in the Table.

Table XIV.

Component	Frequency in cm.$^{-1}$ and Separation from Component III				
	a	b	c	d	Average
I	980.3 — 11.9	979.0 — 13.5	979.4 — 13.6	— —	979.6 — 13.0
II	983.9 — 8.3	984.0 — 8.5	983.3 — 8.9	984.5 — 8.2	983.9 — 8.5
III	992.2	992.5	992.2	992.7	992.4
IV	998.8 6.6	999.0 6.5	999.1 6.9	— —	999.0 6.7
V	1005.3 13.1	1005.0 12.5	1004.8 12.6	— —	1005.0 12.7

Reference a: Howlett, Can. Journ. Res. **5**, 572 (1931).
b: Grassmann and Weiler, Zeitschr. f. Phys. **86**, 321 (1933).
c: Epstein and Steiner, Zeitschr. phys. Chem. **B 26**, 131 (1934).
d: Cheng, Hsueh and Wu, Journ. Chem. Phys. **6**, 8 (1938).

An examination of the fine structure was made by one of us (A. L.) in 1931, although the results of the study had not been published previous to our earlier communication on this subject[2]. The frequencies and relative spacings obtained in 1931 agree well with the averages listed in Table XIV.

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[1] Cf. the summary of Angus, Ingold and Leckie, J. Chem. Soc. (London) **1936**, p. 928.

[2] Langseth and Lord, Journ. Chem. Phys. **6**, 203 (1938).

At the same time visual estimates of the relative intensities were made which agree roughly with estimates by other investigators (refs. a, b, d in Table XIV). All the visual estimates are in accord that satellite V is by far the weakest, that II and IV are of about equal intensity, and that I is approximately half as strong as II. Because visual estimates are of little more than qualitative significance, and because our interpretation of the fine structure enables a quantitative intensity calculation for the components, we have made a microphotometric determination of the intensities.

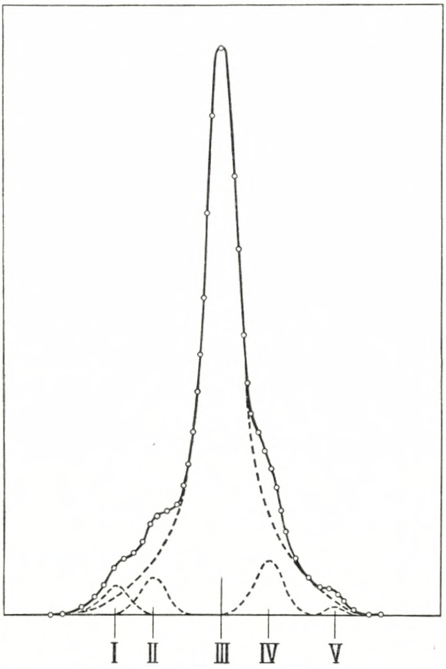

Fig. 4.

An intensity curve for the complex line is shown in Fig. 4. It was obtained from a microphotometer tracing with the help of the blackening-intensity calibration curve characteristic of the type of plate used in photographing the spectrum (Ilford Zenith). Experience has shown the blackening-intensity curve for this kind of plate varies little from one plate to another. Therefore it has been possible to translate blackening into intensity even though no graduated intensities had been recorded on the plate itself. No correction for the variation of plate sensitivity with wavelength has been necessary since the range of wavelength is very narrow.

The curve has been resolved into its components by assuming the shape shown in Fig. 4 for component III and then subtracting the intensity of that component from the total. The relative intensities have been determined by integration of the curves of each component. Since the assumption of the shape of III is to a certain extent arbitrary, the intensities of the satellites may be somewhat in error even if the outline intensity is accurately plotted. It is not likely that the positions of the maxima in cm.$^{-1}$ are much in error, however, because they are less sensitive than the areas to the choice of the shape of component III. For this reason we shall adopt the frequency values given by Figure 4 as the "best" values for the components rather than try to average our values with those of other observers. As one can see from Table XV, this decision is not an important one, since the values found from Fig. 4 agree well with the averages given in Table XIV. The various results yielded by Fig. 4 are listed in the rows marked "c" in Table XV.

Since the calculation of the ratio of intensities of components I and IV depends on the experimental intensity ratio of the components of the doublet at 1600 cm.$^{-1}$ in benzene, we have made a determination of the latter ratio. Fig. 5 gives the intensity curves for the doublet obtained in just the same way as the curves in Fig. 4. The integrated intensities of the doublet components have a ratio of 0.60 ± 0.05, the lower frequency being the more intense.

Table XV.

Component		I	II	III	IV	V
Frequency in cm.$^{-1}$	a	979.6	983.9	992.4	999.0	1005.0
	b	979.6	983.8	992.5	997.9	1005.5
	c	978.9	983.8	992.5	998.2	1006.4
	d	979.5	[986.3]	(992.5)	997.8	[ca. 1003]
Separation from Component III	a	−13.0	−8.5	—	6.7	12.7
	b	−12.9	−8.7	—	5.4	13.0
	c	−13.6	−8.7	—	5.7	13.9
	d	−13.0	−6.2	—	5.3	—
Intensity Relative to Component III	b	5	10	100	10	1
	c	3.5	4.2	100	5.3	0.6
	d	4.1	5.3	100	6.9	0.7
	e	4.5	(5.3)	(100)	6.8	0.8

a: Average values from Table XIV.
b: Visual measurements (1931).
c: Microphotometric measurements (1938).
d: Theoretical values.
e: Microphotometric intensities corrected.

Satellite II was first attributed to ν_1 in the molecule $C_5^{12}C^{13}H_6$ by Gerlach[1]. If one calculates the position of ν_1 in this molecule[2], one expects a decrease of 6.2 cm.$^{-1}$ from the position of ν_1 in benzene. The observed decrease, 8.7 cm.$^{-1}$, is 2.5 cm.$^{-1}$, or about 40 %, larger (Table XV). This anomalously large decrease is similar to that found

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[1] Gerlach, Sitz. Math.-Nat. Bayr. Akad. **1932**, 39.

[2] By computing ν_1 in the hypothetical molecule $C_6^{12.167}H_6$; cf. Teller, loc. cit. p. 142 ff.

for ν_1 in benzene-d_1, and may be attributed to the same cause, namely, interaction between ν_1 and ν_{12}. If interaction were not present ν_{12} should shift from 1010 cm.$^{-1}$ in benzene to about 1003 cm.$^{-1}$ in $C_5^{12}C^{13}H_6$. Interaction decreases the size of the actual shift, however, and also leads to a transfer of intensity to ν_{12} from ν_1 such as we have found in the deuterated benzenes. It is therefore quite in accordance

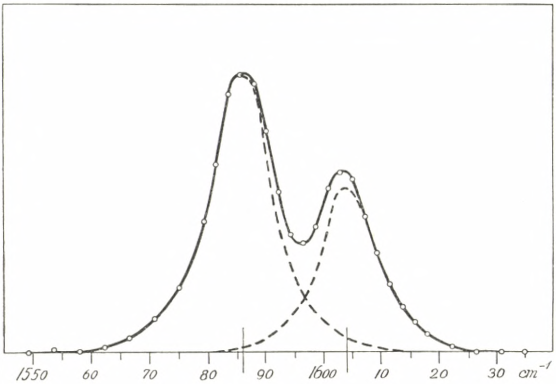

Fig. 5.

with our expectations that satellite II is accompanied by a weaker satellite (V) at 1005 cm.$^{-1}$. The intensity ratio of V to II may be computed by Equation (6), p. 43. For $2W_1'$ we may use the frequency difference between V and II, i. e. 22.6 cm.$^{-1}$ (see Table XV), and for $2W_1' - \varDelta$, twice the observed displacement of ν_1, 2×2.5 or 5.0 cm.$^{-1}$. We thus find $\varDelta = 17.6$ cm.$^{-1}$ (in fair agreement with the value used in Table XIII and in Fig. 3) and $2W_1' + \varDelta = 40.2$ cm^{-1}. The intensity ratio is thus 0.124; hence satellite II ought to be eight times as strong as V. This agrees very well with the value of seven which may be calculated from data in Table XV, row c.

The total intensity of ν_1 and ν_{12} in $C_5^{12}C^{13}H_6$ ought to be that of the unperturbed ν_1, and since this is approximately equal to the intensity of ν_1 in benzene, the total intensity of satellites II and V should be just that of III except for the rarity of $C_5^{12}C^{13}H_6$ molecules. If we assume the concentration of these to be six in one hundred molecules of benzene, we calculate that the individual intensities of II and V should be respectively 5.3 and 0.66, the intensity of the central line being set at 100. The calculated frequencies and intensities for II and V are shown in Table XV. The calculated frequencies are enclosed in square brackets to emphasize that these are not to be compared with experiment, since they are computed without taking account of resonance between ν_1 and ν_{12}.

The existence of satellites I and IV depends on the fact that the frequency of one of the non-totally symmetrical fundamentals in benzene, ν_8 at about 1600 cm.$^{-1}$, accidentally coincides with the sum of ν_1 and a lower frequency, ν_6 (vide infra, p. 56). This fortuitous resonance causes the same sort of splitting as that illustrated in Fig. 3, and results in a mixing of the wave functions of ν_8 and of $\nu_1 + \nu_6$ similar to that depicted by Equation (5). As a consequence of the mixing, a vibrational transition starting from the first exited level of ν_6 and ending on either of the first pair of resonance levels gives rise to Raman scattering very nearly equivalent, save for a numerical factor, to the scattering arising from a transition from the zero to the first excited level of ν_1. The frequencies of the two transitions starting from ν_6 are given simply by the difference between ν_6 (606.4 cm.$^{-1}$) and the frequencies of the doublet (1585.9 and 1604.2 cm.$^{-1}$; see Table X). These differences agree closely with the frequencies of satellites I and IV[1].

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[1] The same interpretation of satellite I is given without further com-

A precise calculation[1] of intensities for the two transitions shows that the sum of the two should be very close to the intensity of ν_1 ($0 \rightarrow 1$ transition). Therefore to find the total intensity of satellites I and IV we need only to multiply the standard intensity of III (100) by the factor which determines the relative number of molecules occupying the first excited level of ν_6, namely: $2 \times \exp\left(\frac{-hc\tilde{\nu}_6}{kT}\right)$. Furthermore with the help of the mixed wave functions one finds that the intensity ratio of I to IV is the same as the ratio of the intensity of the upper component of the resonance doublet to that of the lower, provided that one neglects polarizability changes due to second-order transitions (i. e., the transition from the first excited level of ν_6 to the unperturbed first excited level of ν_8). Experimentally this ratio is 0.60 (see Fig. 5 above), and therefore the intensities of I and IV should be 4.1 and 6.9 at room temperatures.

The calculated frequencies and intensities for the various components are given in the rows marked "d" in Table XV. Comparison of the calculated frequencies with the average of the observed values shows excellent agreement for satellites I and IV, and a discrepancy for II which is well understandable in light of the existence of V. The closeness of the agreement strengthens our confidence in the validity of the interpretation.

The agreement of experimental and calculated intensities (rows "c" and "d", foot of Table XV) is not quite so good.

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ment in Table 2 of the article of GRASSMANN and WEILER (ref. b, Table XIV). It is curious that they apparently overlooked the parallel interpretation of IV.

[1] The details of a similar calculation for the fine structure of the totally symmetrical frequency in carbon tetrachloride are given by HORIUTI, Zeitschr. f. Phys. **84**, 380 (1933).

The assumptions on which the calculations are based are doubtless more reliable than the intensity measurements, so that we may ascribe the discrepancies to experimental trouble. It is possible that the errors are the result of estimating incorrectly the shape of the lower part of component III in Fig. 4. More probably the error lies in the difficulty of measuring simultaneously and with accuracy the intensities of very strong and very weak lines. This difficulty is accentuated in the present instance because we have not determined directly the blackening curve for the spectrographic plate. To correct for this source of error we may multiply the intensities of all components except III by a factor 1.3, which is the factor required to raise the observed intensity of component II, 4.2, to the theoretical value 5.3. When this correction has been made, all the intensities agree very well with theory, as may be seen by comparing the last two rows of Table XV. We may say, therefore, that the observed intensities of components I, II, IV and V relative to one another are in good accord with theory, and that while their intensities with respect to III are uniformly too low by one-fourth, the discrepancy is not surprising in view of the difficulty of measuring accurately intensities differing by a factor of twenty.

The fine structure expected for ν_1 in benzene-d_6 is simpler than that in benzene. ν_8 appears in benzene-d_6 as a single line only, and therefore a satellite due to $\nu_8 - \nu_6$ should be lacking, since the product of the Boltzmann factor (0.1) and the intensity expected of second-order tones (<0.01) is overwhelmingly small. The component $(\nu_1 + \nu_6) - \nu_6$ should coincide with ν_1.

The calculated shift of ν_1 in $C_5^{12}C^{13}D_6$ is 5.0 cm.$^{-1}$, and the observed one 5.7 cm.$^{-1}$. Here the difference is more readily ascribable to experimental error than in benzene, but if we attribute all of it to interaction with ν_{12}, we may compute the intensity ratio of ν_{12} to ν_1 in $C_5^{12}C^{13}D_6$ as 0.03, i.e. ν_{12} should have only about $^1/_4$ the relative intensity of satellite V in benzene. ν_{12} should be higher than ν_1 by very nearly the same amount as in benzene, and therefore should lie in the neighborhood of 960 cm.$^{-1}$. Actually there is an extremely faint line at 962 cm.$^{-1}$, but its assignment is not entirely conclusive, because both ortho- and para-benzene-d_4 have their strongest lines at this point (at 960.0 ± 0.4 cm.$^{-1}$) and it is conceivable that the extended exposures which revealed the line may have been able to record the benzene-d_4 frequencies even though the total concentration of these lower deuterated benzenes was probably less than 0.02 $^0/_0$. That the line may actually be ν_{12} is given some support by the failure to observe the strongest frequency of meta-benzene-d_4 at 954 cm.$^{-1}$. This frequency should appear with not less than half the intensity of the 962 line if the latter is really due to the other benzene-d_4's.

Table XVI.
Fine Structure of ν_1 in Benzene-d_6.

No.	Frequency of Components in cm.$^{-1}$		Intensity of Components	
	Observed	Calculated	Observed	Calculated
I	939.5	940.2	10	5.8
II	945.2	(945.2)	(100)	(100)
III	962.1	960	0.1	0.2

The fine-structure data on benzene-d_6 are summarized in Table XVI. Not included in the Table are two very faint lines observed at 950.7 and 977.3 cm.$^{-1}$, which belong to benzene-d_5, and which are not to be expected in hydrogen-free benzene-d_6. The latter of these lines has also been reported by ANGUS, INGOLD and LECKIE[1]. The difference tone $\nu_8 - \nu_6$ should lie in this neighborhood (ca. 975 cm.$^{-1}$), but, for reasons just given, should not be expected to make its appearance.

It should be added that the arguments mentioned on page 44 may be used to show that the four companions of ν_1 in benzene and the two in benzene-d_6 should have the same depolarization factor as the parent line. This agrees qualitatively with the observations of GRASSMANN and WEILER[2] and of CHENG, HSUEH and WU[3], who report that component II is highly polarized in benzene. The latter authors set an upper limit of 0.4 to ϱ.

A carbon isotope effect in ν_1 indicates that the effect may be present in other frequencies. In order for the effect to be observed, however, special conditions must prevail. ν_1 is an intense and a highly polarized (ergo very sharp) line, so that the C^{13} displacement of 8 cm.$^{-1}$ may be resolved by a powerful spectrograph. The remaining lines due to carbon frequencies in benzene are fuzzy because they are depolarized; furthermore they are much weaker than ν_1. Therefore a correspondingly weaker C^{13}-satellite as close as 8 cm.$^{-1}$ may be expected to fuse undetectably into the parent line. For this reason we need not pay further heed to the influence of C^{13} on the Raman lines of benzene.

The effect of the C^{13} isotope in the deuterium derivatives is complicated by the fact that the isotope may occupy several essentially different places in the carbon ring. For example in sym-benzene-d_3, there are two non-equivalent

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[1] ANGUS, INGOLD and LECKIE, loc. cit. p. 930.

[2] Table XIV, ref. b.

[3] Table XIV, ref. d.

places for the isotope. As a result, the isotope in one place should produce a companion to ν_1 and in the other a companion to ν_{12} (cf. the discussion of the A_1' frequencies, page 30). Low frequency satellites have in fact been observed accompanying both ν_1 and ν_{12} in sym-benzene-d_3, with respective separations of 6.3 and 8.2 cm.$^{-1}$. In the other derivatives, the effect is more complicated in principle because the number of non-equivalent positions is larger (except in the para compounds). Practically, however, the effect is similar to that observed in sym-benzene-d_3. It is not of great interest and we will not consider it further.

2. The Remaining Planar Carbon Vibrations.

Except for ν_1, the degenerate vibrations ν_6 and ν_8 are the only Raman-active carbon frequencies in benzene. ν_6 is essentially a bending vibration which lies at 606 cm.$^{-1}$. There are no planar frequencies in its immediate neighborhood, and its undisturbed course through the various deuterium derivatives can easily be traced. The total decrease in ν_6 from benzene to benzene-d_6 is 27 cm.$^{-1}$, and the expected stepwise decrement of 4.5 cm.$^{-1}$ per deuterium atom is usually observed rather closely. The degeneracy of the frequency is released in all intermediate derivatives except sym-benzene-d_3 and therefore the line should appear double in their spectra. Actually the separation of the doublet is so small (ca. 5 cm.$^{-1}$) and the lines are so fuzzy that it has been possible to secure definite resolution of the components only in two instances.

The stretching frequency ν_8 lies at 1600 cm.$^{-1}$ in benzene and at 1553 cm.$^{-1}$ in benzene-d_6. It appears as a doublet in the former because ν_8 is fortuitously close to the sum

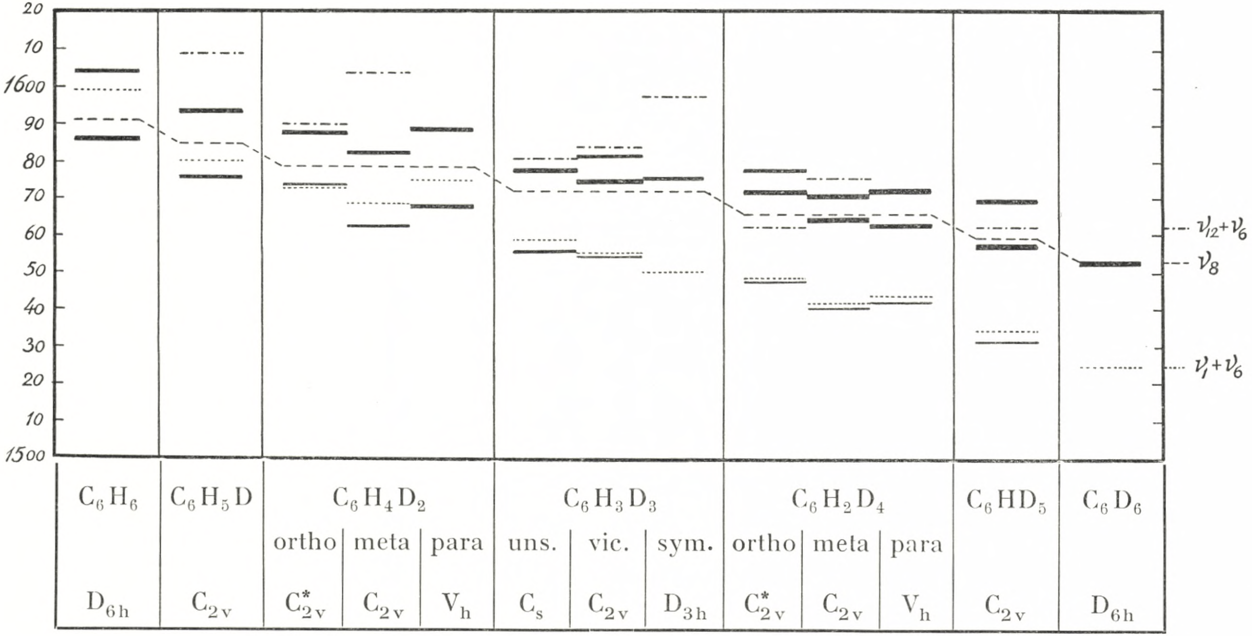

Fig. 6.

The solid lines indicate observed frequencies and the various broken lines the calculated values. In the text the overtone $\nu_1 + \nu_6$ is denoted I and $\nu_{12} + \nu_6$ II for the sake of brevity.

of ν_1 and ν_6, and the consequent interaction of the fundamental with the overtone leads to splitting. The accidental coincidence no longer obtains in benzene-d_6, and if there is interaction, it is imperceptible. The proximity of ν_8 to the overtone complicates the problem of interpreting ν_8 in the deuterated compounds. Further complication ensues because ν_{12} lies close to ν_1 and therefore the combination $\nu_6 + \nu_{12}$ can also interact with ν_8. This interaction is forbidden by symmetry in benzene, but in all the derivatives except para-benzene-d_2 and para-benzene-d_4, and of course benzene-d_6, some combination of ν_{12} and one of the components of ν_6 (i.e., ν_{6a} or ν_{6b}) is permitted to interact with one or the other of the components of ν_8. It is possible to compute rather closely the unperturbed positions of all these overtones and to obtain therefrom some idea of the structure to be expected of the line due to ν_8 in the various derivatives. Unfortunately it is an extremely difficult experimental problem to resolve this structure. ν_8 is doubly degenerate and therefore usually splits into two close components of which at least one is completely depolarized and is correspondingly difficult to separate from its companion (cf. the discussion of ν_6). In Fig. 6 the observed components of ν_8 are plotted together with the predicted stepwise shift in ν_8* and with the overtone $\nu_1 + \nu_6$ (I) and $\nu_{12} + \nu_6$ (II). No attempt has been made to estimate theoretically the splitting of ν_8 when the degeneracy is released. The overtones, which are in principle doublets, are also plotted as single lines since it seems unlikely, from experience with ν_6, that they will be resoluble.

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* Calculated as for ν_1 in Fig. 3. The unperturbed position of ν_8 in benzene is estimated to be just as far below the midpoint of the resonance doublet as the calculated position of $\nu_1 + \nu_6$ is above it.

The observed structure of the line generally agrees with that expected from the positions of the overtones. In benzene-d_1 and the benzene-d_2's ν_8 appears as a doublet of about the same separation as that in benzene, in accord with the fact that unperturbed ν_8 and overtone I lie close together. Overtone II appears as a weak line at the predicted point in benzene-d_1. In ortho-benzene-d_2 II lies so near one of the doublet lines that resolution is hardly to be expected, while in the para compound it is forbidden. It has not been found at the predicted place in meta-benzene-d_2. ν_8 lies halfway between I and II in sym-benzene-d_3, and since the separation of the overtones is almost 50 cm.$^{-1}$, it is not surprising that there seems to be no interaction. The line remains single and the overtones are not observed. The position of II is much closer to ν_8 in the other benzene-d_3's but its perturbing effect seems to be slight. It is possible to resolve ν_8 in the vicinal compound into two components of unequal intensity and about 7 cm.$^{-1}$ apart. This doublet is probably the result of the released degeneracy of ν_8, although it is of course conceivable that it arises from interaction of ν_8 with II. In unsym-benzene-d_3 ν_8 is a single line. Apparently neither release of degeneracy nor interaction with II is effective enough to make the components spectroscopically separable. The overtone I is found at the proper place in both compounds — just below its predicted position.

The structure of ν_8 in the remaining compounds (excluding benzene-d_6) is very similar to that in vic-benzene-d_3. The principal line is double and is accompanied by a weak satellite some 25 cm.$^{-1}$ below it. The doublet may be ascribed to the two components of ν_8, or, excepting the case of p-benzene-d_4, where interaction is forbidden by symmetry, to interaction with II. The satellite is due to overtone I — its observed position is always a wave number or two lower than predicted, which is to expected from interaction with ν_8.

The foregoing discussion shows that there is no feature of the complex group of lines due to ν_8 which cannot be understood on the basis of what we know about this frequency in benzene and benzene-d_6. The purpose of our rather detailed study was to make as certain as possible that the observed structure of ν_8 could be quite completely understood without the necessity of postulating the influence of a nearly fundamental. If a fundamental of the proper symmetry existed in the 1600 cm.$^{-1}$ region, it might exert on ν_8 a perturbing effect like that of ν_{12} on ν_1. There is reason to suspect the existence of such a fundamental. The frequency calculated by Wilson's equations for the trigonal stretching vibration ν_{14} would place it about 1800 cm.$^{-1}$, but it might well lie 200 cm.$^{-1}$ lower. There is no evidence from the structure of ν_8, however, which can be interpreted unequivocally as an indication of the presence of ν_{14} in the immediate neighborhood. Indeed we are inclined to say, on the basis of the evidence just considered, that ν_{14} lies outside the range 1560—1640 cm.$^{-1}$ in benzene and 1520—1600 cm.$^{-1}$ in benzene-d_6.

The region between 1600 and 2000 cm.$^{-1}$ in the Raman spectrum of benzene is entirely free from lines having an intensity greater than about 1 $^0/_0$ of that of ν_1. Indeed it is only by very prolonged exposures that any lines at all have been found here, and these may be explained satisfactorily as allowed overtones[1]. Somewhat surprisingly the same freedom from lines in this region prevails in all the deut-

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[1] Angus, Ingold and Leckie, loc. cit.

erated benzenes. We might have expected that ν_{14}, which from a formal standpoint is Raman-active in eight of the compounds, should appear somewhere within a 200 cm.$^{-1}$ range of its calculated position at 1800 cm.$^{-1}$. Its failure to appear in this region may of course mean only that the polarizability change due to ν_{14} is nearly equal to zero because amplitude changes produced by deuterium substitution are slight. An equally plausible interpretation, however, is that ν_{14} has been miscalculated, and actually lies below the 1560 cm.$^{-1}$ boundary set for benzene. There are numerous weak lines in the region 1200—1500 cm.$^{-1}$ in the spectra of the deuterated benzenes. While it may be that most of these are hydrogen deformation frequencies, it is quite possible that a line due to ν_{14} is lurking among them. Until they have been definitely classified as belonging to other forms of vibration, the possibility remains that ν_{14} has been observed but not identified.

The only planar carbon frequency which remains to be discussed is the infrared-active ν_{19}. The benzene—benzene-d_6 shift of this frequency, from 1480 to 1330 cm.$^{-1}$, is so large that it cannot be considered a purely carbon frequency. Therefore we may except it to vary somewhat irregularly in the deuterated benzenes, although it should never step outside the limits 1300 and 1500 cm.$^{-1}$. The expected irregularity in frequency and the fact that there are several weak lines in this region of the spectra of the derivatives necessitate an identification procedure which is somewhat different from that we have been using. We shall consider ν_{19} together with the planar hydrogen frequencies.

3. The Planar Hydrogen Vibrations.

Each derivative has a total of six hydrogen "stretching" frequencies, namely ν_2, ν_{13} and the two components of ν_7 and of ν_{20}. A part of the six (equal to the number of deuterium atoms in the molecule of the derivative) lie within 15 cm.$^{-1}$ of 2280 cm.$^{-1}$, and the remainder at 3055 ± 10 cm^{-1} There is no difficulty in identifying the spectroscopically active fundamentals in this region, although sometimes fewer strong lines are observed than are permitted. This means only that the lines are so close that it is not possible to resolve them. The neighborhood of each high frequency fundamental is rich in weak lines which may rather safely be attributed to combination tones. The latter have more intensity than usual, probably because of interaction between the overtones and the fundamentals.

We have now localized twelve of the twenty one planar frequencies. To find the remaining ones — Nos. 3, 14 and 15 (non-degenerate) and Nos. 9, 18 and 19 (double) — we consider first the spectrum of sym-benzene-d_3. The symmetry of this molecule forbids the presence of the three non-degenerate frequencies in the Raman effect. The double frequencies are allowed, but they must appear as single lines since the presence of the three-fold axis preserves their degeneracy. They have been found in benzene and benzene-d_6 to lie within the range 800—1500 cm.$^{-1}$, and therefore may reasonably be expected to occur within these extremes in sym-benzene-d_3. In addition to the two totally symmetrical lines, which have already been identified, there are two fairly strong and four weak lines in this region. Of the weak lines, the one at 1072 cm.$^{-1}$ may be eliminated from consideration because it cannot be included in any combination which satisfies the product rule for the E′ frequencies (Table VIII). Another of the faint lines, at 815 cm.$^{-1}$, is so near to the much stronger line at 834 cm.$^{-1}$, that it satisfies the product rule almost as well as the strong line, provided that the latter be omitted from consideration. Because of its intensity, the stronger line must be included, and on this ground the 815 cm.$^{-1}$ is ruled out as an E′ fundamental. The two remaining weak lines lie very close together at 1400 cm.$^{-1}$, and it is not possible (nor important) to decide between them by applying the product rule. The lower component, at 1396 cm.$^{-1}$, is somewhat the stronger, and therefore is assigned to a fundamental, viz. ν_{19}, which should lie between 1330 and 1440 cm.$^{-1}$. As we shall show later, the upper component may be satisfactorily interpreted as an overtone. The two strong lines, 834 and 1102 cm.$^{-1}$, are assigned to ν_{18} and ν_9 respectively.

The identification of frequencies 9, 18 and 19 in sym-benzene-d_3 serves as a basis for classifying observed frequencies in many of the other derivatives. When the degeneracy of the E′ frequencies is released by removal of the three-fold axis, components 9a, 18a and 19a[1] preserve a two-fold axis passing through two para carbon atoms (cf. page 9). In order for the axis to be preserved during these vibrations, the four atoms lying on it must not move off the axis. The only possible motion for the para hydrogen atoms therefore is one which stretches the C—H bond. Since vibrations 9a, 18a and 19a are hydrogen bending frequencies, it is probable that the para hydrogen atoms do not participate significantly in the motion, and therefore should not influence the values of these frequencies appreciably. The frequencies should accordingly have the

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[1] — Except in the two ortho derivatives (C_{2v}^{*}).

same values in all derivatives having the same distribution of deuterium atoms among the four non-para hydrogen atoms. The arrangement is the same for meta-benzene-d_2, vic- and sym-benzene-d_3, and meta-benzene-d_4. The frequencies which we have assigned to 9 a, 18 a and 19 a in these four compounds are listed for comparison in Table XVII.

Table XVII.

Frequency No.	Observed Frequency in $cm.^{-1}$ in			
	meta-d_2	vic-d_3	sym-d_3	meta-d_4
9 a	1108	1096	1102	1096
18 a	838	839	834	833
19 a	1397	1386	1396	1374 1409

The same reasoning leads us to expect these three frequencies to have nearly equal values in benzene, benzene-d_1 and para-benzene-d_2, and in para-benzene-d_4, benzene-d_5 and benzene-d_6. Insofar as selection rules permit, our expectations are fulfilled save that ν_{19a} is not observed in benzene-d_1. Vibrations 18 a and 19 a are not Raman-active in the para-derivatives, but ν_{9a} is found in both compounds close to its predicted place.

We have now considered all the planar frequencies except ν_3 and ν_{15}. The former is Raman-active in the para-derivatives, and since we have identified all the other active planar frequencies except 9 b in these compounds, it is not difficult to complete the identification. In para-benzene-d_2 there are five lines, all of moderate intensity or greater, in the range where ν_3 and ν_{9b} should appear, namely 860—1180 $cm.^{-1}$. Two of these have been assigned (ν_1 at 978.5 and ν_{9a} at 1176 $cm.^{-1}$). Of the three remaining, the one lying close to ν_1 at 966 cm.$^{-1}$ is eliminated because it is somewhat less intense than the other two, and because it fits another assignment to be discussed later. We therefore assign the lines at 911 and 1167 cm.$^{-1}$ to ν_{9b} and ν_3 respectively.

The same region in para-benzene-d$_4$ exhibits two faint lines in addition to the five of higher intensity. The assignment of the moderately strong lines at 950 and 1137 to ν_3 and ν_{9b} is supported by an application of the product rule for class B_{2g} of V_h (Table IX). The only other combination which leads to reasonably close agreement with the τ given by the product rule is 927 and 1137 cm.$^{-1}$. The value of τ calculated from these two frequencies is too large, whereas it should be too small by about 1 $^0/_0$ because of anharmonicity.

It will be noticed that in both the para compounds, one of the lines considered lies close to ν_1 on the low-frequency side, and therefore might be interpreted as due to the C^{13} isotope. The characteristics of the lines are in opposition to this view: in both cases it is too diffuse and too far removed from ν_1. In addition the intensities of both lines are too great to be attributed to the presence of C^{13}.

Identification of ν_3 in the para derivatives enables us to calculate its value in benzene and benzene-d$_6$ by applying the product rule (Table IX). We find from its location in para-benzene-d$_2$ that $\nu_3 = 1202$ cm.$^{-1}$ in benzene, and from para-benzene-d$_4$ that $\nu_3 = 924$ cm.$^{-1}$ in benzene-d$_6$. Because of anharmonicity, it is to be expected that the value for benzene has been calculated a little too high, and that for benzene-d$_6$ too low. The ratio of the two actual frequencies should be a trifle lower than that given by the product rule, viz. 1.29, whereas the ratio of the calculated frequencies is 1.30, or about 1 % too high. To correct the calculated values, we deduct 0.5 % from the benzene frequency and add 0.5 % to that of benzene-d_6. The corrected frequencies are 1195 and 930 $cm.^{-1}$.

The remaining planar frequency, ν_{15}, is a hydrogen bending vibration which is Raman-active only in the C_{2v}, C^*_{2v} and C_s derivatives. Even if one could identify it with certainty in the spectra of these compounds, it would not be possible to apply the product rule to a calculation of its value in benzene because the position of ν_{14} is unknown. ν_{15} may be estimated to lie in the neighbourhood of 1150 $cm.^{-1}$ in benzene and 850 $cm.^{-1}$ in benzene-d_6. In the intermediate derivatives there are six hydrogen in-plane bending frequencies (3, 9ab, 15 and 18ab), all of which will lie in the range 800—1180 $cm.^{-1}$. Since this region may also include out-of-plane hydrogen frequencies, it is necessary to consider the out-of-plane vibrations before attempting to assign observed frequencies in the derivatives of low symmetry.

4. The Non-Planar Vibrations.

There are six out-of-plane frequencies in benzene. Two are carbon vibrations involving considerable distortion of the carbon ring, two are hydrogen vibrations in which the carbon ring is distorted slightly, and two are hydrogen vibrations in which the ring is not distorted at all. One of each pair is doubly degenerate. Only the last pair is spectroscopically active, one frequency in the Raman effect (the doubly degenerate ν_{10}) and the other in infrared absorption (ν_{11}).

The positions of the two carbon frequencies depend on the resistance of the ring to distortion. Since there is no a priori way in which this resistance may be determined, the location of the frequencies has remained in doubt, and the possibility of observing them in the deuterated benzenes was one of the reasons for undertaking the present work. On the basis of evidence furnished by heat capacity measurements, it has been suggested[1] that one of the frequencies (16ab) lies at 400 cm.$^{-1}$ and the other (4) somewhat higher. This suggestion is supported by the temperature-dependence of the intensities of certain bands in the ultra-violet absorption spectrum of benzene, which has recently been the object of special study by Kistiakowsky and Solomon[2].

The most promising spectrum for finding ν_{16} should be that of sym-benzene-d$_3$, because it is the simplest in which ν_{16} is active (class E″ of D_{3h}). A line is indeed observed in this spectrum at 373 cm.$^{-1}$. While it is of low intensity, it is rather too strong for a combination tone. Its proximity to 400 cm.$^{-1}$ lends support to its interpretation as ν_{16}.

In all the other derivatives except para-benzene-d$_4$ there are definite indications of one, and sometimes two, frequencies in the region between 350 and 400 cm^{-1}*. The lines vary considerably in intensity, but their persistent occurrence in a narrow region around 373 cm.$^{-1}$ indicates that they arise from the same source as the line at that

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[1] Lord and Andrews, loc. cit.

[2] Kistiakowsky and Solomon, Journ. Chem. Phys. **5**, 609 (1937).

* The one found at 400 cm^{-1} in para-benzene-d$_2$, provided that it is actually due to ν_{16} in that molecule, appears in contravention of selection rules, and probably arises from the same source as the 400 cm^{-1} line in benzene, i. e., from $C_5^{12}C^{13}H_4D_2$ or from violation of selection rules because of liquid forces. The fact that no corresponding line has been found in para-d$_4$ may be due to the obscuring effect of a diffuse overtone at 2158 cm^{-1}, which, when excited by Hg-4047 Å, covers the region of the plate where lines of 390 cm^{-1} excited by Hg-4358 Å lie.

frequency in sym-benzene-d_3. They may therefore be assigned to ν_{16} (a or b).

Before considering the other carbon frequency, it is helpful to complete the assignment of observed fundamentals in sym-benzene-d_3. We have already accounted for nine of the twelve lines lying below 2000 cm.$^{-1}$. The other three are a strong line at 712 and two faint ones at 815 and 1072 cm.$^{-1}$. The intensity of the strong line indicates that it is to be ascribed to ν_{10}, a frequency which is Raman-active in benzene. This assignment is borne out by the fact that a strong line is observed at 711 ($\pm$ 1) cm.$^{-1}$ in the three compounds—meta-d_2, vic-d_3 and meta-d_4—in which ν_{10a} should have precisely the same frequency as ν_{10} in sym-benzene-d_3. We have seen above (page 64) that certain of the planar frequencies have approximately equal values in these four compounds. Similar considerations of symmetry require that each of the frequencies ν_{10a}, ν_{16a} and ν_{17a} have exactly the same value in all four derivatives. These frequencies preserve the two-fold axis present in derivatives, and since atoms participating in out-of-plane vibrations move only perpendicular to the plane, the atoms lying on the two-fold axis do not take part in the motion. Therefore the masses of the atoms on the axis are not a factor in the frequency values, and changing the masses has no effect on the frequencies. For the same reason we may expect the values of the same three frequencies to be identical in benzene, benzene-d_1 and para-benzene-d_2, and in para-d_4, benzene-d_5 and benzene-d_6. The assignment of frequencies is considerably facilitated by this circumstance.

It is not easy to decide which of the weak lines at 815 and 1072 cm.$^{-1}$ should be attributed to ν_{17}. Both are faint, although the latter is perhaps a little stronger. Both appear in the proper C_{2v} derivatives, but with varying intensity and wavelength which may be attributed to the difficulty of measuring weak and diffuse lines, particularly when they happen to lie, as both 815 and 1072 do, near stronger lines. The basis for our choice between the two is the rather negative one that it is easy to explain the line at 1072 as an overtone if the other is chosen as ν_{17}, while there is no satisfactory explanation for 815 cm.$^{-1}$ except as a fundamental.

If we assign 815 cm.$^{-1}$ to ν_{17}, 1072 cm.$^{-1}$ may be interpreted as a combination tone with the help of the infrared data of INGOLD et al.[1]. As we shall see presently, there is an infra-red active frequency of 691 cm.$^{-1}$ which may belong to a fundamental of class A_2''. The combination of this frequency with the E'' vibration at 375 cm.$^{-1}$ would give a frequency of symmetry E' at 1066 cm.$^{-1}$. It should be both Raman- and infrared-active, and there is indeed an infrared band observed at 1065 cm.$^{-1}$. The appearance of the combination tone in the Raman effect may be due in part to interaction with the nearby fundamental at 1102 cm.$^{-1}$. That such interaction is an important factor in the spectroscopic activity of combination tones is shown by their prevalence in the neighborhood of the strong lines around 2280 and 3060 cm.$^{-1}$, which we have previously noticed (p. 62). The same explanation holds for the doublet structure of the E' line at 1400 cm.$^{-1}$ (cf. p. 63), since the first overtone of the E'' fundamental at 711 cm,$^{-1}$ should lie quite near the fundamental.

The assignment of the 815 line to ν_{17} enables us to cal-

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[1] BAILEY, BEST, GORDON, HALE, INGOLD, LECKIE, WELDON and WILSON, Nature **139**, 880 (1937).

culate the product of ν_{16} and ν_{17} in benzene. We find from the product rule that $\nu_{16} \times \nu_{17}$ is 342,700 cm,$^{-2}$. The τ for the E_u^+ frequencies in D_{6h} is 1.414 (Table VII) and therefore $\nu_{16} \times \nu_{17}$ in benzene-d_6 is 242,200 cm.$^{-2}$. If the very weak line at 406 in the Raman spectrum of benzene be attributed to ν_{16}, the product rule then gives $\nu_{17} = 845$ cm.$^{-1}$. The evidence for ν_{16} in benzene-d_6 is not so definite. Angus, Ingold and Leckie[1] report an extremely faint line at 337 cm.$^{-1}$. We have found traces of this line, although at slightly higher frequencies than 337 cm.$^{-1}$. In any case the measured frequency is uncertain. If we somewhat arbitrarily set the value of the frequency at 350 cm.$^{-1}$, we may calculate that ν_{17} is about 690 cm.$^{-1}$ in benzene-d_6.

To identify ν_4 we consider first the uninterpreted lines of the spectra of the para derivatives, in which ν_4 is active. Omitting from consideration the extremely faint line at 400 cm.$^{-1}$, we have yet to assign vibrations to frequencies at 634, 738, 850, 966 and 1273 cm.$^{-1}$ in para-benzene-d_2. ν_4 should be the lowest of these, and we therefore assign it to 634 cm.$^{-1}$. This frequency is more than 200 cm.$^{-1}$ above ν_{16}, but calculation[2] indicates that ν_4 should be considerably the higher. ν_{10a} must lie at 850 cm.$^{-1}$, the position of ν_{10} in benzene, and since ν_{10b} should be somewhat lower, in the range 660—850 cm.$^{-1}$, we assign to it the line at 738 cm.$^{-1}$.

Thus there remains a choice between 966 and 1273 cm.$^{-1}$ for ν_5. Before attempting a decision, we must consider the spectrum of para-benzene-d_4. Here the unassigned lines are 662, 765, 927 and 1253 cm.$^{-1}$, which have moderate intensity or greater, and 605, 630, 842, 1051 and 1098 cm.$^{-1}$, which are faint. We can assign immediately the lines at

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[1] Angus, Ingold and Leckie, loc. cit.

[2] Cf. Lord and Andrews, loc. cit., p. 155.

662 and 765 cm.$^{-1}$ to 10a and 10b respectively. The faint line 605 is presumed to be ν_4 (it is somewhat more intense than the nearby line at 630 cm.$^{-1}$, which is extremely weak), and the other faint lines are deemed to belong to other sources than fundamental frequencies. The moderately strong lines at 927 and 1253 cm.$^{-1}$ are therefore eligible for assignment to ν_5.

The product rule for class B_{3g} of V_h (Table IX) gives a value of τ, 1.030, which is satisfied either by the combination

$$\frac{(634 \times 738 \times 966)}{(605 \times 765 \times 927)}$$

or by the alternative one in which 966 and 927 are replaced respectively by 1273 and 1253. The latter combination gives better agreement (1.027) with the theoretical τ, but the former (1.053) does not exceed the limits of error in applying the product rule, particularly in view of the difficulty of measuring both the 966 cm.$^{-1}$ frequency in para-benzene-d_2 and the faint line 605 in para-benzene-d_4. Hence the product rule does not permit here a clear cut decision between the two assignments.

The infrared absorption data for sym-benzene-d_3 may furnish evidence for the position of ν_5 in the para derivatives in the following way. By means of the product rule for class B_{3g} (Table IX) and the observed value of ν_{10} in benzene, the product of ν_4 and ν_5 in benzene may be calculated from the three B_{3g} frequencies in para-benzene-d_2. In turn the product of the three A_2'' frequencies of sym-benzene-d_3 may be computed with the help of the observed value of ν_{11} in benzene and the product rule. In the preliminary report of the infrared absorption spectrum of sym-benzene-d_3 given by INGOLD et al.[1], they report the numerical positions of the bands without intensity data. From the "parallel" structure of two bands at 533 and 914 cm.$^{-1}$, they assign the bands to A_2'' vibrations. If this indication of two of the A_2'' bands is correct, the third should lie either at 699 or at 921 cm.$^{-1}$, according to whether ν_5 in para-benzene-d_2 be assigned to the line at 966 or at 1273 cm.$^{-1}$. There is in fact a band observed at 691 cm.$^{-1}$, which would fit the former alternative. It is not reported as having parallel structure, but may be weaker than the two other parallel bands and correspondingly difficult to resolve. From the positions of ν_{11} in benzene and benzene-d_6, and of ν_4 in the para compounds, both these frequencies should be expected to appear in the neighbourhood of 600 cm.$^{-1}$ in sym-benzene-d_3. Therefore the assignment of ν_{11} to the 533 cm.$^{-1}$ band and ν_4 to 691 cm.$^{-1}$ is quite compatible with expectation. The A_2'' band at 914 cm.$^{-1}$ is on this interpretation assigned to ν_5.

On the other hand the alternative which would place the third A_2'' frequency at 921 cm.$^{-1}$ seems highly unlikely. There is no band reported within 80 cm.$^{-1}$ of the 914 band. In addition our prejudices with regard to the location of ν_4 and ν_{11} make it appear most improbable that either of these could have a frequency so high as 900 cm.$^{-1}$ in sym-benzene-d_3. If the assignment of the parallel bands is accepted, the allocation of ν_5 to the 966 frequency in para-d_2, to 914 in sym-d_3 and to 927 in para-d_4 is supported both in the Raman effect and in infrared absorption.

It is possible nevertheless to fit the Raman line at 1273 cm.$^{-1}$ in para-benzene-d_2 into an interpretative scheme as ν_5 if it be assumed that the bands at 533 and 691 cm.$^{-1}$ are A_2'' bands but that the 914 cm.$^{-1}$ band is not. In this

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[1] INGOLD et al., loc. cit.

case the product rule would place ν_5 at 1218 cm.$^{-1}$ in sym-benzene-d_3 and indeed there is a band observed at 1226 cm.$^{-1}$. The band is not reported as having parallel structure, but on the basis of such an interpretation ν_5 would have the thoroughly compatible values of 1273, 1226 and 1253 cm.$^{-1}$ in para-d_2, sym-d_3 and para-d_4 respectively. The 914 band might then be assigned to the overtone $\nu_{11} + \nu_{16}$, which has the symmetry E′ (both Raman and infrared-active) and a frequency of approximately 910 cm.$^{-1}$, but which should have a perpendicular rather than parallel structure in the infrared. This interpretation is therefore in direct contradiction to the parallel structure ascribed to the 914 cm.$^{-1}$ band.

We are faced with the necessity of deciding between the two interpretations. The first is quite satisfactory, but it leaves unexplained the two lines at 1253 and 1273 cm.$^{-1}$, of which the former has rather higher intensity than is ordinarily found in overtones. If they may be understood as overtones, there is no further objection. The second interpretation conflicts with the parallel structure observed for the 914 cm^{-1} infrared band in sym-d_3, and leaves lines at 966 and 927 cm.$^{-1}$ in para-d_2 and para-d_4 unexplained. The latter lines might also be ascribed to overtones. There is, however, no way of getting round the conflict with the observed parallel structure of the 914 band short of denying its existence. Therefore it seems to us that the first interpretation is the better. The question of overtones may best be evaded until a knowledge of the infrared absorption spectra of the para derivatives is available.

The product of ν_4 and ν_5 in benzene calculated from the product rule (Table IX) and the assignment of ν_5 to 966 cm.$^{-1}$ in para-benzene-d_2 is 704,000 cm.$^{-2}$. The same product in benzene-d_6, as calculated from para-benzene-d_4, is 486,200 cm.$^{-2}$. The ratio of these two numbers is 1.448, which is 2.4 $^0/_0$ above the product rule τ of 1.414 for B_{2g} frequencies (Table VII). If we attribute the discrepancy to anharmonicity we may correct the ratio by subtracting 1.2 $^0/_0$ from the product in benzene and adding 1.2 $^0/_0$ to that for benzene-d_6. The corrected products are 695,700 and 492,000 cm.$^{-2}$. Now let us assume that the shift in ν_4 in passing from benzene to para-benzene-d_2 is the same as that from para-d_2 to para-d_4, namely 30 cm.$^{-1}$. Therefore ν_4 in benzene is 664 cm.$^{-1}$, and from the product of ν_4 and ν_5, $\nu_5 = 1048$ cm.$^{-1}$. Similarly the values of ν_4 and ν_5 in benzene-d_6 are found to be 575 and 856 cm.$^{-1}$.

V. Summary of Frequency Assignments.

In the accompanying tables the assignments we have already made are summarized, and further assignments are made for the derivatives of low symmetry, whose observed frequencies have not been considered in detail. The frequencies are catalogued both as to number and symmetry class. It must be remembered, however, that the distribution of numbers among frequencies belonging to the same symmetry class is often arbitrary. It has little significance, for example, to differentiate by number between the various hydrogen planar bending frequencies in a compound of C_s symmetry. The assignment to classes, on the other hand, has been made on a more logical basis. In classifying the observed frequencies of compounds of low symmetry, the same auxilaries have been used as for the more symmetrical derivatives: product rule ratios, considerations of intensity, anticipated frequency shifts, etc. On the whole, the classification in Tables XX and XXI is reliable. When an assignment is considered doubtful, it is marked by an interrogation point.

Throughout the Tables, an observed frequency which is

Table XVIII.

Frequency Assignment for Compounds of D_{6h} and D_{3h} Symmetry.

Symmetry Class		Freq. No.	Frequency in $cm.^{-1}$		
D_{6h}	D_{3h}		Benzene	Sym-benzene-d_3	Benzene-d_6
A_{1g}	A_1'	1	992.5	956.6	945.2
		2	3061.5	3055.1	2293.2
B_{1u}		12	[1010]	1003.9	[962]
		13	[3060]	2283.8	[2290]
A_{2g}	A_2'	3	[1195]	—	[930]
B_{2u}		14	—	—	—
		15	—	—	—
E_g^+	E'	6	606.4	593.7	579.3
		7	3048.3	2272	2265.7
		8	1595	1575.9	1553.2
		9	1177.9	1101.7	869.1
E_u^-		18	1035*	834.3	813*
		19	1485*	1396.2	1333*
		20	3080*	(3055.1)	2294*
B_{2g}	A_2''	4	[664]	691*	[575]
		5	[1048]	914*	[856]
A_{2u}		11	671*	533*	503*
E_g^-	E''	10	849.7	711.7	663.5
E_u^+		16	406	373	350 ?
		17	[845]	815	[690]?

[ ] = calculated with help of the product rule.

( ) = one observed but unresolved frequency due to two or more vibrations.

* = observed in infrared only.

expected to be double and is found single is assigned to both of the expected vibrations. To denote the duplication, the second assignment is enclosed in parentheses. In Table XVIII certain frequencies which have not been observed have been calculated from the product rule. These are enclosed in square brackets. Frequencies observed in the infrared but not in the Raman spectrum are marked with an asterisk.

Table XIX.

Frequency Assignment for Derivatives of V_h Symmetry.

Symmetry Class	Freq. No.	Frequency in cm.$^{-1}$	
		para-benzene-d_2	para-benzene-d_4
A_{1g}	1	978.5	959.6
	2	3054.6	2283.0
	6 a	593.6	585.0
	7 a	2279.4	3042.9
	8 a	1589.2	1563.0
	9 a	1175.4	859.7
B_{2g}	3	1166.6	949.9
	6 b	598.8	(585.0)
	7 b	3042.3	2265.0
	8 b	1568.3	1571.7
	9 b	911.1	1137.4
B_{3g}	4	634	605
	5	966	927
	10 b	738	765.3
B_{1g}	10 a	850	662.3

( ) = one observed but unresolved frequency due to two or more vibrations.

It is also desirable to summarize in tabular form comparisons of the theoretical product rule ratios with τ's

Table XX.

Frequency Assignment for Derivatives of C_{2v} Symmetry.

Symmetry Class	Freq. No.	Observed Frequency in cm.$^{-1}$				
		benzene-d_1	meta-d_2	vic-d_3	meta-d_4	benzene-d_5
A_1	1	980.9	970.5	965.3	953.8	950.9
	2	3064.2	3058.8	3058.7	3051.4	3050.6
	6 a	598.5	598.4	592	589	584.8
	7 a	2269.8	2284.4	2288.1	2271.8	2268.3
	8 a	1593.8	1583.1	1575.3	1564.6	1557.9
	9 a	1176.5	1107.7	1095.5	1095.7	857.9
	12	1008.6	1006.1	992.3	986.4	977.1
	13	3055.5	3047	2280.8	2287.2	2288.8
	18 a	1032.4	838.1	838.7	832.5	836.4
	19 a	[1473]	1397.2	1385.6	1374	1323
	20 a	(3064.2)	(3058.8)	3050.6	(2287.2)	(2288.8)
B_1	3	1158.2	1168.4	1131.0	847.0	847.9
	6 b	602.0	(598.4)	(592)	(589)	(584.6)
	7 b	3040	2272.1	(2280.8)	(2271.8)	(2268.3)
	8 b	1575.7	1563.0	1582.2	1571.3	1570.4
	9 b	859.5	855	920?	(847)	(857.9)
	14	—	—	—	—	—
	15	(1176.5)	1177.2	1150.4	1175.9	1173.5
	18 b	(1032.4)	1030	863.4	(832.5)	812
	19 b	1418??	(1397.2)	1363.2?	—	1360
	20 b	(3064.2)	(3047)	(3050.6)	(3051.4)	(2268.3)
A_2	10 a	851.7	710.5	712.0	711.1	664.2
	16 a	403	374	374	375	(371)
	17 a	—	818	825	—	691.3
B_2	4	—	—	657?	632	614
	5	1077?	1051?	1031?	—	—
	10 b	780	818?	779.3	705	711.6
	11	—	—	—	—	—
	16 b	381	(374)	(374?)	(375)	371
	17 b	—	—	744	—	—

( ) = one observed but unresolved frequency due to two or more vibrations.

Table XXI.

Frequency Assignment for Derivatives of C^*_{2v} and C_s Symmetry.

Symmetry Class		Freq. No.	Observed Frequency in cm.$^{-1}$		
C^*_{2v}	C_s		ortho-d_2	unsym-d_3	ortho-d_4
A_1	A′	1	976.0	966.4	960.4
		2	3064	3055.7	3058.3
		6 a	598.3	593.5	589.3
		7 a	2280.8	2283.6	2289.9
		8 a	1573	1578	1578.1
		9 a	1177.5	1139.1	1170
		14	—	—	—
		15	1160	1128.3	932.3
		18 b	1055.4	1054.7	842.2
		19 b	1402.8	1390	1348.5
		20 b	3035.3	3045.1	2270.0
B_1		3	1130.7	841	(932.3)
		6 b	(598.3)	(593.5)	(589.3)
		7 b	2273.3	2270	(2270.0)
		8 b	1588	1556	1571.8
		9 b	(1177.5)	915	1136.5
		12	992.8	987.4	974.0
		13	3053	(3055.7)	3046.2
		18 a	856	(841)	813.1
		19 a	(1402.8)	(1390)	1372.3
		20 a	(3064)	(2270)	(2289.9)
A_2	A″	4	—	635	625.4
		5	—	927	—
		10 b	841.6	707	688.3
		16 a	384	395?	369
		17 a	—	822.7	778
B_2		10 a	782.1	772.2	738.7
		11	581.6	562	—
		16 b	(384)	(395?)	(369)
		17 b	825?	785	(778)

( ) = one observed but unresolved frequency due to two or more vibrations.

computed from the frequency assignments. In the course of our analysis such liberal use has been made of the product rule in computing unobserved frequencies that

Table XXII.

τ's in V_h Derivatives.

D_{6h}	$\underbrace{A_{1g}\ E_g^+}$	$\underbrace{E_g^-}$	$\underbrace{A_{2g}\ E_g^+}$	$\underbrace{B_{2g}\ E_g^-}$
V_h	A_{1g}	B_{1g}	B_{2g}	B_{3g}
C_6H_6: obs.	1.397	1.000	—	—
p-$C_6H_4D_2$ calc.	1.414	1.000	1.367	1.324
p-$C_6H_4D_2$: obs.	1.442	1.283	1.350	1.053
p-$C_6H_2D_4$ calc.	1.414	1.286	1.370	1.030

Table XXIII.

τ's in C_{2v} and C_{2v}^* Derivatives.

C_6H_6:	τ for Class A_1 in C_{2v}		τ for Class B_1 in C_{2v}^*	
	observed	calculated	observed	calculated
C_6H_5D	*	1.405	—	—
ortho- $C_6H_4D_2$	—	—	1.881	1.909
meta- $C_6H_4D_2$	1.972	1.975	—	—
vic-$C_6H_3D_3$	2.790	2.776	—	—
ortho- $C_6H_2D_4$	—	—	3.572	3.655
meta- $C_6H_2D_4$	3.901	3.901	—	—
C_6HD_5	5.291	5.484	—	—

* ν_{19a} not observed.

all but one of the classes in Table XVIII contain frequencies determined in this way. Clearly it serves no useful purpose to compare τ's for these classes with their theoretical values.

The one class in Table XVIII for which all frequencies have been actually observed is E′. The observed τ (C_6D_6:sym-$C_6H_3D_3$) is 1.97 whereas theory (Table VIII) is 1.959. The agreement is satisfactory.

Table XXIV.

Vibrations to which No Frequencies Have Been Assigned.

C_6H_6	C_6H_5D	$C_6H_4D_2$			$C_6H_3D_3$			$C_6H_2D_4$			C_6HD_5	C_6D_6
		ortho	meta	para	sym	vic	unsym	ortho	meta	para		
					3							
	4	4	4									
		5						5	5		5	
	11		11	11		11		11	11	11	11	
				12						12		
				13						13		
14	14	14	14	14	14	14	14	14	14	14	14	14
15				15	15					15		15
				16 a b						16 a b		
	17 a b	17 a	17 b	17 a b					17 a b	17 a b	17 b	
				18 a b						18 a b		
				19 a b					19 b	19 a b		
				20 a b						20 a b		

In Table XXII are listed the τ's calculated from observed frequencies and from theory for the Raman-active symmetry classes of V_h. Only the ratios benzene/para-benzene-d_2, and para-benzene-d_2/para-benzene-d_4 are given. The para-benzene-d_4/benzene-d_6 ratios must be correct if the others are, because the benzene/benzene-d_6 ratios are correct.

We have also calculated the theoretical τ-ratios for the totally symmetrical frequencies (A_1) of the C_{2v} derivatives and for the B_1 frequencies of C^*_{2v}. The observed and calculated τ's for six compounds are given in Table XXIII. For a seventh, benzene-d_1, only the theoretical value is given, because one of the totally symmetrical vibrations, ν_{19a}, has not been observed. It has been possible to calculate the value of the unobserved frequency from the product rule, since it is the only one missing. This value is listed in square brackets in Table XX.

The agreement between observed and theoretical τ's in Table XXIII is quite satisfactory in view of the fact that some eleven frequencies are involved in each product. The close agreement found for meta-benzene-d_2 and meta-benzene-d_4 is entirely fictitious, since the observed values should be circa 2 % too low because of anharmonicity. Hence these two observed τ's, together with that for vic-benzene-d_3, which is too high, are the least satisfactory in the Table.

To complete the tabulation we have assembled in Table XXIV a list of the vibrations in the various derivatives to which no frequencies have been assigned. The large number of unassigned V_h frequencies is of course due to the fact that the V_h molecules have a centre of symmetry and hence a large number of Raman-inactive frequencies. Their determination must be made with the help of a study of their infrared absorption spectra.

Table XXV summarizes all of the unassigned observed frequencies and suggests assignments for some of them. There are about a hundred frequencies, of which roughly half lie above 2000 cm.$^{-1}$. It seems quite clear that these latter are combination tones. The others may be combination tones or unassigned fundamentals. The selection principles for combination tones are considerably more lax in the deuterium derivatives than in benzene itself, and the num-

Table XXV. Unassigned Observed Fre

Benzene-d_1		Benzene-d_2						Benzene-			
		ortho		meta		para		sym.		vic.	
Freq. cm.$^{-1}$	A	Freq. cm.$^{-1}$	A	Freq. cm.$^{-1}$	A	Freq. cm.$^{-1}$	A	Freq. cm.$^{-1}$	A	Freq. cm.$^{-1}$	A
1610	$\nu_1 + \nu_{12}$	658	ν_4?	1082	$\nu_{10a} + \nu_{16}$	1273	$2\nu_4$?	1072	$\nu_4 + \nu_{16}$	1056	$2\nu_{11}$
2313	$2\nu_3$	692	—	1144	—	2223	$\nu_4 + \nu_{8a}$	1415	$2\nu_{10}$	1555	$\nu_1 + \nu$
3168	$2\nu_8$	774	$2\nu_{16}$	1419	$2\nu_{10a}$	2261	—	2241	$\nu_{18} + \nu_{19}$	2240	—
		1035	—	2249	$\nu_{10b} + \nu_{19}$	3155	$2\nu_{8b}$?	2975	$2\nu_{14}$?	2260	$2\nu_3$
		1077	—	2265	$\nu_{10a} + \nu_{8b}$	3175	$2\nu_{8a}$	3148	$2\nu_8$	2312	$2\nu_{15}$
		1248	—	2308	$\nu_{10a} + \nu_{8a}$					2982	$2\nu_{14}$
		1385	$\nu_6 + \nu_{10a}$	2337	$2\nu_3$						
		2258	$2\nu_3$	2992	$2\nu_{14}$?						
		2298	$\nu_3 + \nu_{9a}$	3153	$2\nu_{8ab}$						
		2314	$2\nu_{15}$								
		2993	$2\nu_{14}$?								
		3001	—								

ber of distinct active fundamental frequencies is considerably larger. It is therefore nearly always possible to find some combination of lower frequencies satisfying selection principles which will add up to a given frequency value within the limits of experimental error and of anharmonic departure from strict additivity. The validity of most of the assignments in Table XXV will remain in doubt until the infrared spectra of the derivatives are known. The assignuencies and Suggested Assignments.

		Benzene-d_4						Benzene-d_5	
unsym.		ortho		meta		para			
req. m.$^{-1}$	A	Freq. cm.$^{-1}$	A	Freq. cm.$^{-1}$	A	Freq. cm.$^{-1}$	A	Freq. cm.$^{-1}$	A
996	—	710	$2\nu_{16}$?	994	—	630	—	632	—
1070	—	1004	—	1057	—	1051	—	1034	—
1270	$2\nu_4$	1057	$\nu_{10\,b} + \nu_{16}$	1198	$\nu_{16} + \nu_{18\,a}$	1098	—	1099	—
1366	$\nu_6 + \nu_{10\,a}$	1069	—	1209	»	1253	$\nu_6 + \nu_{10\,a}$	1140	—
1461	$\nu_{14} + \nu_{17\,a}$	1099	$\nu_{10\,a} + \nu_{16}$	1409	$2\nu_{10}$	1542	$\nu_1 + \nu_6$	1225	$2\nu_4$
2270	$\nu_4 + \nu_{8\,a}$	1252	$2\nu_4$	1541	$\nu_1 + \nu_6$	2113	—	1412	$2\nu_{10\,b}$
2234	$\nu_3 + \nu_{19}$	1289	$\nu_3 + \nu_{16}$	2199	$\nu_4 + \nu_8$	2158	$\nu_6 + \nu_{8\,b}$	1532	$\nu_1 + \nu_6$
2297	—	1478	$2\nu_{10\,a}$	2223	$\nu_3 + \nu_{19}$	2219	—	2221	$\nu_{8\,a} + \nu_{10\,a}$
3023	$2\nu_{8\,b}$	1548	$\nu_1 + \nu_6$			2245	—	2246	$\nu_{8\,a} + \nu_{17\,a}$
3087	$2\nu_{8\,a}$	2160	$\nu_6 + \nu_{8\,b}$					2256	$\nu_{8\,b} + \nu_{17}$
		2187	$\nu_4 + \nu_{8\,b}$						
		2209	$\nu_4 + \nu_{8\,a}$						
		2251	$\nu_{8\,b} + \nu_{10\,b}$						
		2984	$2\nu_{14}$?						

ments which for one reason or another appear particularly doubtful are marked with interrogation points.

The authors wish to express their respective thanks to the Carlsberg Fond (A. L.) for generous financial support of this investigation, and to the U. S. National Research Council (R. C. L.) for the grant of a Fellowship.

VI. Summary.

The Raman spectra of the eleven deuterium derivatives intermediate between benzene and benzene-d_6 have been obtained, and with the help of the selection principles and Teller's product rule, have been analyzed. The results of the analysis are:

1. Convincing evidence in support of the D_{6h} structure for benzene has been obtained.

2. The locations of seven of the nine spectroscopically inactive frequencies in benzene have been determined from the positions of analogous active frequencies in the derivatives.

3. The frequencies of the two ring distortion vibrations have been established, and are found to agree satisfactorily with those previously suggested on the basis of thermal evidence.

4. The fine structure of the Raman line due to the totally symmetrical carbon frequency in benzene has been given a quantitative explanation. The frequency, intensity and state of polarization of the line's components have been calculated, and agree well with the experimental data.

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ON THE ORIGINAL ORBITS OF COMETS

1925 I, 1902 III AND 1897 I

BY

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1742

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This paper gives the results of calculations concerning the original orbits of comets 1925 I, 1902 III and 1897 I.

The first of these comets — comet 1925 I Orkisz — is one for which the basis of the calculation of the original orbit is excellent, the period of observation being more than one year, and the number of observations close to 600. The definitive orbit has been determined by Orkisz, who took account of the perturbations by Mercury, Venus, the Earth, Mars, Jupiter and Saturn. The agreement between observation and theory is exceptionally good, the mean errors of the resulting elements are consequently quite small. While the orbit determined by Orkisz is hyperbolic, the calculated original orbit is found to be elliptical.

For the second comet — comet 1902 III Perrine-Borrelly — the original orbit has already been investigated (cf. Publ. Copenhagen Observatory No. 19). The resulting original orbit was slightly hyperbolic, the mean error of $\frac{1}{a}$ being so large, however, compared with the numerical value of $\frac{1}{a}$, that the hyperbolicity was illusory. An investigation by Mr. Rasmusen showed that the comet a few years before the passage through perihelion had been rather close to the planet Neptune. It was quite possible, therefore, that a calculation of the original orbit, when account was taken of the perturbations by Neptune also, might to an appreciable extent modify the result of the previous investigation. The calculation was made, and led to the result that the original orbit was slightly elliptical.

The third of the comets mentioned, namely comet 1897 I Perrine, has also been investigated previously (Publ. Cop. Obs. No. 19). The calculation of the definitive orbit (loc. cit. p. 52) gave an hyperbolic value of $\frac{1}{a}$. The calculation, with the aid of Encke's method, of the original orbit gave for 1891 Feb. 20.0 Berlin M. T. an elliptical orbit $\left(\frac{1}{a} = +0.0000367\right)$. A continuation of the calculation still further back in time with the aid of equation (21) in Publ. 19 gave for the beginning of the year 1883 a quite insignificant change of this value $\left(\frac{1}{a} = +0.0000368\right)$, but the numbers given on p. 54 in Publ. 19 show that this value would have been changed a little — probably by 10 to 20 units of the 7th decimal — if the calculation had been continued some years further. In order to have, for one particular comet, a complete check on the method of Publ. 19 just referred to we have carried out a calculation of the original orbit according to the method of direct integration of rectangular co-ordinates, going backwards from 1891 Feb. 20.0 as far as 1880 March 9.0. For this epoch the resulting value of $\frac{1}{a}$ agreed within 28 units of the 7th decimal with the value found in Publ. 19.

The results obtained for the three comets are given in more detail on the following pages.

1. Comet 1925 I Orkisz.

Comet 1925 I Orkisz was observed during a period of 402 days, the number of observations amounted to 598. The following definitive elements were calculated by L. Orkisz[1]. Perturbations by Mercury, Venus, the Earth, Mars, Jupiter and Saturn were taken into account in the calculation. The perturbations by Uranus and Neptune were negligible.

Epoch of osculation 1925 Oct. 25.0 Greenwich M.T.

$$T = 1925 \text{ April } 1.5111585 \text{ G.M.T.}$$

$$\left.\begin{aligned} \omega &= 36^\circ\ 11'\ 40''.1 \\ \Omega &= 318 \quad 3 \quad 41\ .5 \\ i &= 100 \quad 0 \quad 57\ .0 \end{aligned}\right\} 1925.0$$

$$q = 1.1095947 \pm 0.0000118$$

$$e = 1.0006286 \pm 0.0000344$$

Elements and equatorial constants reduced to the standard equinox 1950.0 are:—

Epoch of osculation 1925 Oct. 25.0 G.M.T.

$$T = 1925 \text{ April } 1.5111585 \text{ G.M.T.}$$

$$\left.\begin{aligned} \omega &= 36^\circ\ 11'\ 33''.1 \\ \Omega &= 318\ 24\ \ 36\ .9 \\ i &= 100 \quad 1 \quad 6\ .5 \end{aligned}\right\} 1950.0$$

$$q = 1.1095947 \pm 0.0000118$$

$$e = 1.0006286 \pm 0.0000344$$

$$\frac{1}{a} = -0.0005665 \pm 0.0000310$$

$$\left.\begin{aligned} P_x &= +0.5354076 & Q_x &= -0.5348396 \\ P_y &= -0.7933299 & Q_y &= -0.0529366 \\ P_z &= +0.2897696 & Q_z &= +0.8432938 \end{aligned}\right\} 1950.0$$

From these the following equatorial co-ordinates and

---

[1] L. Orkisz, Die definitive Bahn des Kometen 1925 I (Orkisz), Warschau 1931.

velocity components for the epoch of osculation 1925 Oct. 25.0 are found:—

$$x = -2.0703958 \qquad 10\frac{dx}{dt} = -0.1033548$$

$$y = +0.5481689 \qquad 10\frac{dy}{dt} = +0.0833989$$

$$z = +2.2554015 \qquad 10\frac{dz}{dt} = +0.0375121$$

Basing on these co-ordinates and velocity components the motion of the comet has been followed backwards through a period of 20 years with the aid of the method of direct integration of rectangular co-ordinates. The attractions by the sun and the 8 major planets were taken into account. The following table gives the computed co-ordinates referred to the equinox 1950.0.

Equatorial Co-ordinates. Equinox 1950.0.

G. M. T.	x	y	z
1925 Nov. 6.0	—2.192989	+0.647853	+2.298875
Oct. 27.0	2.091026	0.564838	2.262860
— 17.0	1.987050	0.481280	2.224665
— 7.0	1.880942	0.397207	2.184080
Sept. 27.0	1.772574	0.312659	2.140870
— 17.0	1.661808	0.227690	2.094760
— 7.0	1.548498	0.142375	2.045440
Aug. 28.0	1.432485	+0.056816	1.992546
— 18.0	1.313606	—0.028853	1.935660
— 8.0	1.191692	0.114449	1.874295
July 29.0	1.066571	0.199730	1.807879
— 19.0	0.938087	0.284371	1.735747
— 9.0	0.806102	0.367937	1.657120
June 29.0	0.670529	0.449846	1.571092
— 19.0	0.531367	0.529317	1.476617
— 9.0	0.388764	0.605313	1.372514
May 30.0	—0.243099	—0.676461	+1.257493

G. M. T.	x	y	z
1925 May 20.0	— 0.095109	— 0.740983	+ 1.130235
— 10.0	+ 0.053957	0.796652	0.989563
April 30.0	0.202182	0.840835	0.834714
— 20.0	0.346906	0.870708	0.665745
— 10.0	0.484857	0.883698	0.483933
March 31.0	0.612586	0.878103	0.291979
— 21.0	0.727152	0.853631	+ 0.093741
— 11.0	0.826734	0.811533	— 0.106480
— 1.0	0.910877	0.754226	0.304786
Febr. 19.0	0.980280	0.684658	0.498235
— 9.0	1.036360	0.605736	0.684978
Jan. 30.0	1.080822	0.519982	0.864098
— 20.0	1.115368	0.429425	1.035335
— 10.0	1.141547	0.335620	1.198842
1924 Dec. 30.5	1.160700	0.239730	1.354995
— 20.5	1.173948	0.142604	1.504278
— 10.5	1.182225	— 0.044862	1.647205
Nov. 30.5	1.186295	+ 0.053048	1.784286
— 20.5	1.186791	0.150808	1.916001
— 10.5	1.184233	0.248185	2.042793
Oct. 31.5	1.179048	0.345017	2.165065
— 21.5	1.171598	0.441190	2.283180
— 11.5	1.162180	0.536626	2.397464
— 1.5	1.151045	0.631272	2.508213
Sept. 11.5	1.124444	0.818083	2.720121
Aug. 22.5	1.093146	1.001504	2.920710
— 2.5	1.058145	1.181560	3.111435
July 13.5	1.020189	1.358337	3.293495
June 23.5	0.979850	1.531956	3.467880
— 3.5	0.937572	1.702558	3.635414
May 14.5	0.893704	1.870285	3.796796
April 24.5	0.848526	2.035277	3.952616
— 4.5	0.802261	2.197673	4.103383
March 15.5	+ 0.755093	+ 2.357601	— 4.249534

G. M. T.	x	y	z
1924 Febr. 24.5	+ 0.707173	+ 2.515184	— 4.391450
— 4.5	0.658624	2.670537	4.529465
Jan. 15.5	0.609552	2.823768	4.663873
1923 Dec. 26.5	0.560043	2.974975	4.794933
— 6.5	0.510170	3.124253	4.922876
Nov. 16.5	0.459997	3.271687	5.047909
Oct. 27.5	0.409578	3.417359	5.170218
Sept. 17.5	0.308174	3.703714	5.407314
Aug. 8.5	0.206256	3.983863	5.635323
June 29.5	0.104045	4.258283	5.855207
May 20.5	+ 0.001710	4.527396	6.067770
April 10.5	— 0.100619	4.791571	6.273697
March 1.5	0.202843	5.051139	6.473576
Jan. 20.5	0.304884	5.306395	6.667911
1922 Dec. 11.5	0.406681	5.557601	6.857145
Nov. 1.5	0.508188	5.804996	7.041663
Sept. 22.5	0.609367	6.048795	7.221806
Aug. 13.5	0.710191	6.289192	7.397877
July 4.5	0.810638	6.526363	7.570145
May 25.5	0.910690	6.760472	7.738854
March 6.5	1.109565	7.220082	8.066436
1921 Dec. 16.5	1.306753	7.669074	8.382132
Sept. 27.5	1.502227	8.108340	8.687186
July 9.5	1.695985	8.538655	8.982644
April 20.5	1.888041	8.960687	9.269396
Jan. 30.5	2.078419	9.375022	9.548201
1920 Nov. 11.5	2.267151	9.782178	9.819717
Aug. 23.5	2.454275	10.182612	10.084516
June 4.5	2.639829	10.576731	10.343102
March 16.5	2.823855	10.964903	10.595920
1919 Dec. 27.5	3.006397	11.347456	10.843362
Oct. 8.5	3.187497	11.724689	11.085760
July 20.5	3.367199	12.096874	11.323495
May 1.5	— 3.545547	+12.464256	—11.556787

G. M. T.	x	y	z
1919 Febr. 10.5	− 3.722582	+ 12.827064	− 11.785914
1918 Nov. 22.5	3.898347	13.185505	12.011110
June 15.5	4.246233	13.890041	12.450540
Jan. 6.5	4.589528	14.579251	12.876570
1917 July 30.5	4.928539	15.254336	13.290454
Febr. 20.5	5.263553	15.916361	13.693255
1916 Sept. 13.5	5.594831	16.566276	14.085883
April 6.5	5.922609	17.204939	14.469118
1915 Oct. 29.5	6.247085	17.833128	14.843639
May 22.5	6.568432	18.451548	15.210037
1914 Dec. 13.5	6.886785	19.060838	15.568837
July 6.5	7.202252	19.661572	15.920506
Jan. 27.5	7.514918	20.254268	16.265462
1913 Aug. 20.5	7.824848	20.839385	16.604093
March 13.5	8.132096	21.417332	16.936747
1912 Oct. 4.5	8.436706	21.988472	17.263749
April 27.5	8.738719	22.553126	17.585400
1911 Nov. 19.5	9.038177	23.111580	17.901976
June 12.5	9.335120	23.664087	18.213742
Jan. 3.5	9.629592	24.210873	18.520937
1910 July 27.5	9.921638	24.752126	18.823772
Febr. 17.5	10.211321	25.288072	19.122514
1909 Sept. 10.5	10.498686	25.818833	19.417306
April 3.5	10.783802	26.344570	19.708356
1908 Oct. 25.5	11.066735	26.865421	19.995836
May 18.5	11.347564	27.381513	20.279911
1907 Dec. 10.5	11.626370	27.892965	20.560733
July 3.5	11.903245	28.399892	20.838445
Jan. 24.5	12.178288	28.902407	21.113176
1906 Aug. 17.5	12.451602	29.400627	21.385044
March 10.5	12.723297	29.894671	21.654158
1905 Oct. 1.5	12.993479	30.384669	21.920609
April 24.5	13.262255	30.870759	22.184480
1904 Nov. 15.5	− 13.529719	+ 31.353090	− 22.445840

For 1905 Oct. 1.5 G.M.T., when the comet was at a distance of 40 astronomical units from the sun, i. e. outside the orbit of Neptune, the following co-ordinates and velocity components $\left(x, y, z, \frac{dx}{dt}, \frac{dy}{dt}, \frac{dz}{dt}\right)$, and reductions to the center of gravity of the sun and the 8 major planets $\left(\xi, \eta, \zeta, \frac{d\xi}{dt}, \frac{d\eta}{dt}, \frac{d\zeta}{dt}\right)$, and the resulting reduced co-ordinates and velocity components $\left(\bar{x}, \bar{y}, \bar{z}, \frac{d\bar{x}}{dt}, \frac{d\bar{y}}{dt}, \frac{d\bar{z}}{dt}\right)$ were obtained:—

$$\begin{array}{lll}
x = -12.993479 & y = +30.384669 & z = -21.920609 \\
\xi = -4853 & \eta = -3166 & \zeta = -1179 \\
\hline
\bar{x} = -12.998332 & \bar{y} = +30.381503 & \bar{z} = -21.921788
\end{array}$$

$$\begin{array}{lll}
160\frac{dx}{dt} = +0.2694623 & 160\frac{dy}{dt} = -0.4880198 & 160\frac{dz}{dt} = +0.2651485 \\
160\frac{d\xi}{dt} = +8819 & 160\frac{d\eta}{dt} = -8235 & 160\frac{d\zeta}{dt} = -3702 \\
\hline
160\frac{d\bar{x}}{dt} = +0.2703442 & 160\frac{d\bar{y}}{dt} = -0.4888433 & 160\frac{d\bar{z}}{dt} = +0.2647783
\end{array}$$

From these we find:—

$$\bar{r} = \sqrt{\bar{x}^2 + \bar{y}^2 + \bar{z}^2} = 39.65548,$$

while the square of the velocity is:—

$$\bar{V}^2_{160} = \left(160\,\frac{d\bar{x}}{dt}\right)^2 + \left(160\,\frac{d\bar{y}}{dt}\right)^2 + \left(160\,\frac{d\bar{z}}{dt}\right)^2 = 0.3821613.$$

The equation of conservation of energy is:—

$$\bar{V}^2_{160} = w^2k^2(1+\Sigma m)\left(\frac{2}{\bar{r}} - \frac{1}{\bar{a}}\right)$$

or

$$\frac{1}{\bar{a}} = \frac{2}{\bar{r}} - \frac{\bar{V}^2}{w^2k^2(1+\Sigma m)}.$$

Inserting the values of $\bar{r}$ and $\overline{V}^2$ given above, $w^2 k^2 = 7.5753525$ and $1 + \Sigma m = 1.00134197$ the following value of $\frac{1}{a}$ for 1905 Oct. 1.5 G.M.T. is found:—

$$\frac{1}{a} = +0.0000540.$$

Thus the hyperbolic value of $\frac{1}{a}$ from the calculation of the definitive orbit has been changed into an elliptic value.

2. Comet 1902 III Perrine-Borrelly.

The calculation of the definitive elements was based on 1182 observations distributed over a period of 212 days (cf. Publ. Cop. Obs. No. 19, p. 57):—

Epoch of osculation $= T$.

$T = 1902$ Nov. 23.89393 M.T. Berlin

$$\left.\begin{aligned} \omega &= 152^\circ\ 57'\ 25''.3 \\ \Omega &= 49\ \ \ 19\ \ \ 10\ .3 \\ i &= 156\ \ \ 20\ \ \ 50\ .7 \end{aligned}\right\} 1900.0$$

$$\log q = 9.603225 \pm 0.000001$$

$$e = 0.9999675 \pm 0.0000074$$

$$\frac{1}{a} = +0.0000810 \pm 0.0000184$$

The calculation of original elements published in Publ. No. 19 was based on these elements. Perturbations from Jupiter and Saturn were taken into account. The elements referred to the center of gravity were derived for 1896 Oct. 31.0 M.T. Berlin, and $\frac{1}{a}$ was found to be -0.0000204. The original value of $\frac{1}{a}$ was found to be $\frac{1}{a} = -0.0000168$.

This is the only case of a cometary orbit which has changed in hyperbolic direction in going back to the original orbit.

A closer investigation showed that in 1890 the comet passed Neptune at a distance of 2 astronomical units, to the North. The perturbations by Neptune therefore must have been appreciable. In order to get a more accurate value of the original $\frac{1}{a}$ the perturbed co-ordinates of the comet were computed for the period 1896—1884, account being taken of the perturbations from Jupiter, Saturn, and Neptune. The result was that $\frac{1}{a}$ in 1884 had the value $+0.0000054$. The main steps of the calculation are given below.

With the aid of the data given in Publ. No. 19 the following ecliptical co-ordinates and velocity components for 1896 Oct. 31.0 M.T. Berlin were obtained (1900.0). The rectangular co-ordinates of Jupiter and Saturn were taken from Publ. Cop. Obs. No. 19 (cf. footnote 2 on page 15 in this paper), the co-ordinates of Neptune were calculated from the polar co-ordinates in Berliner Jahrbuch.

$$x = +9.534042 \qquad y = +15.572743 \qquad z = -1.277228$$

$$160\frac{dx}{dt} = -0.3627868 \quad 160\frac{dy}{dt} = -0.8281268 \quad 160\frac{dz}{dt} = +0.1161004$$

With these values perturbed ecliptical co-ordinates were computed with the aid of numerical integration back to 1884.

Ecliptical Co-ordinates. Equinox 1900.0.

M. T. Berlin	x	y	z
1897 April 9.0	+9.165243	+14.734619	−1.160325
1896 Oct. 31.0	+9.534042	+15.572743	−1.277228

M. T. Berlin	x	y	z
1896 May 24.0	+ 9.891244	+ 16.391468	— 1.392556
1895 Dec. 16.0	10.238010	17.192434	1.506394
July 9.0	10.575299	17.977041	1.618820
Jan. 30.0	10.903911	18.746513	1.729906
1894 Aug. 23.0	11.224512	19.501899	1.839715
March 16.0	11.537680	20.244163	1.948310
1893 Oct. 7.0	11.843901	20.974154	2.055745
April 30.0	12.143602	21.692660	2.162071
1892 Nov. 21.0	12.437163	22.400399	2.267334
June 14.0	12.724928	23.098039	2.371578
Jan. 6.0	13.007220	23.786203	2.474844
1891 July 30.0	13.284345	24.465460	2.577165
Febr. 20.0	13.556600	25.136340	2.678575
1890 Sept. 13.0	13.824268	25.799320	2.779096
April 6.0	14.087620	26.454824	2.878743
1889 Oct. 28.0	14.346920	27.103218	2.977526
May 21.0	14.602431	27.744814	3.075475
1888 Dec. 12.0	14.854401	28.379898	3.172635
July 5.0	15.103056	29.008735	3.269049
Jan. 27.0	15.348606	29.631564	3.364752
1887 Aug. 20.0	15.591232	30.248594	3.459774
March 13.0	15.831102	30.860018	3.554139
1886 Oct. 4.0	16.068360	31.465999	3.647869
April 27.0	16.303138	32.066689	3.740983
1885 Nov. 18.0	16.535547	32.662222	3.833501
June 11.0	16.765682	33.252722	3.925438
Jan. 2.0	16.993621	33.838302	4.016811
1884 July 26.0	17.219422	34.419070	4.107635
Febr. 17.0	+ 17.443128	+ 34.995127	— 4.197925

From this table we get for 1884 July 26.0 M.T. Berlin: —

$x = +17.219422 \qquad y = +34.419070 \qquad z = -4.107635$

$\xi = + \quad 1987 \qquad \eta = - \quad 7258 \qquad \zeta = + \quad 47$

$\bar{x} = +17.221409 \qquad \bar{y} = +34.411812 \qquad \bar{z} = -4.107588$

$$160\frac{dx}{dt} = -0.224748 \qquad 160\frac{dy}{dt} = -0.578396 \qquad 160\frac{dz}{dt} = +0.090554$$

$$160\frac{d\xi}{dt} = +1111 \qquad 160\frac{d\eta}{dt} = +679 \qquad 160\frac{d\zeta}{dt} = -31$$

$$160\frac{d\bar{x}}{dt} = -0.223637 \qquad 160\frac{d\bar{y}}{dt} = -0.577717 \qquad 160\frac{d\bar{z}}{dt} = +0.090523$$

$$\frac{1}{a} = 0.0516808 - \frac{0.391965}{7.575353 \times 1.0012923} = +0.0000054,$$

i. e. a slightly elliptic value.

3. Comet 1897 I Perrine.

The reasons for carrying out the investigations of this comet here presented were of a nature of principle. The method used in Publ. 19 in the calculation of original orbits of comets which, in the inner parts of the solar system, that is in the neighbourhood of perihelion, had proved to move in hyperbolic orbits, was largely based on the use of Encke's method of special perturbations, this method being used to follow the comet for a certain number of years back in time. The calculation of exact perturbations according to this method, however, involves a very great amount of labour. As a consequence, the calculations according to Encke's method were not carried as far back in time as would have been desirable from certain points of view. On the other hand equation (33) in Publ. No. 19 provided a means of determining an upper limit to that part of the perturbations which had not been allowed for in the calculations. This equation, however, gives a value which is far greater than the actual uncertainty of the results, because its derivation is based on the assumption of the most unfavourable conditions in every respect. Actually, therefore, there was no doubt that the accuracy of the calculation of the original $\frac{1}{a}$ was far greater than found according to equation (33) [cf. the remark on page 19].

Calculations of perturbations by Encke's method through a considerably longer period than that adopted in Publ. No. 19 would have involved a considerable increase in the amount of labour. It therefore meant a great help in this problem, when the method of direct integration of rectangular co-ordinates was gradually introduced. When this method is used in connection with the tables published by Comrie[1] and those published by the authors[2–4] the saving of labour is very considerable.

After this method had been adopted we have been able to increase considerably the period through which the comet was followed backward in time. It was also desirable to carry out comparison, in one or more special cases, between the results obtained earlier and results derived from a calculation by the method of direct integration of rectangular co-ordinates used over a considerably longer period. As an example we have chosen comet 1897 I.

The calculation of the definitive orbit for this comet had given the following result (Publ. No. 19, p. 52):—

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[1] L. J. Comrie, Planetary co-ordinates for the years 1800—1940, referred to the equinox of 1950.0, London 1933, Naut. Alm. Office.

[2] E. Strömgren, Koordinaten der Planeten Jupiter und Saturn nebst den diesen zwei Planeten entstammenden Störungskomponenten der Sonne von 1871 Febr. 5 bis 1904 Dez. 9, alles auf 1900.0 bezogen. Copenhagen 1914, Publ. Cop. Obs. No. 19 p. 28—35.

[3] H. Q. Rasmusen, Äquatoreale Jupiter- und Saturn-Koordinaten für den Zeitraum 1800—1900 bezogen auf das Äquinoctium 1950.0, Kiel 1936, A. N. 6172 and Publ. Cop. Obs. No. 107.

[4] H. Q. Rasmusen, Hilfstafeln für die numerische Integration der rechtvinkligen Koordinaten eines Himmelskörpers, Kiel 1936, A. N. 6235—36 and Publ. Cop. Obs. No. 109.

Epoch of osculation 1897 Jan. 29.0 M.T. Berlin.

$$
\begin{aligned}
T &= 1897 \text{ Feb. } 8.140779 \text{ M.T. Berlin} \\
\left.\begin{aligned}
\omega &= 172^\circ\ 19'\ \ 2''.02 \\
\Omega &= \ \ 86\ \ \ 31\ \ \ \ 3\ .51 \\
i &= 146\ \ \ \ 8\ \ 14\ .49
\end{aligned}\right\} & 1900.0 \\
\log q &= \ \ \ \ 0.0264443 \pm 0.0000034 \\
e &= \ \ \ \ 1.0009270 \pm 0.0000506 \\
\frac{1}{a} &= -0.0008722 \pm 0.0000476
\end{aligned}
$$

i. e. an hyperbolic orbit.

The calculation of the perturbations from Jupiter and Saturn with the aid of Encke's method gave the following perturbed co-ordinates and velocity components for 1891 Feb. 20.0 M.T. Berlin (Ecliptic 1900.0):—

$$x = +6.173828 \qquad y = +16.003986 \qquad z = +3.483160$$

$$160\,\frac{dx}{dt} = -0.1444654 \quad 160\,\frac{dy}{dt} = -\ 0.9166608 \quad 160\,\frac{dz}{dt} = -0.0601508$$

From these starting-values the co-ordinates of the comet were calculated by direct integration as far back as the beginning of 1880:—

Ecliptical Co-ordinates. Equinox 1900.0.

M. T. Berlin	x	y	z
1892 Jan. 6.0	+ 5.865270	+ 14.122429	+ 3.352011
1891 July 30.0	6.024685	15.075696	3.420431
Febr. 20.0	6.173828	16.003986	3.483160
1890 Sept. 13.0	6.314013	16.909769	3.540958
April 6.0	6.446330	17.795127	3.594436
1889 Oct. 28.0	6.571695	18.661826	3.644097
May 21.0	+ 6.690886	+ 19.511375	+ 3.690359

M. T. Berlin	x	y	z
1888 Dec. 12.0	+ 6.804570	+ 20.345079	+ 3.733574
July 5.0	6.913323	21.164063	3.774043
Jan. 27.0	7.017637	21.969312	3.812020
1887 Aug. 20.0	7.117943	22.761686	3.847727
March 13.0	7.214612	23.541945	3.881358
1886 Oct. 4.0	7.307966	24.310761	3.913080
April 27.0	7.398283	25.068733	3.943043
1885 Nov. 18.0	7.485803	25.816395	3.971382
June 11.0	7.570730	26.554232	3.998211
Jan. 2.0	7.653240	27.282677	4.023638
1884 July 26.0	7.733475	28.002128	4.047758
Febr. 17.0	7.811553	28.712950	4.070658
1883 Sept. 10.0	7.887569	29.415483	4.092415
April 3.0	7.961595	30.110047	4.113100
1882 Oct. 25.0	8.033683	30.796944	4.132779
May 18.0	8.103871	31.476476	4.151511
1881 Dec. 9.0	8.172188	32.148937	4.169352
July 2.0	8.238655	32.814619	4.186351
Jan. 23.0	8.303292	33.473814	4.202558
1880 Aug. 16.0	8.366113	34.126816	4.218021
March 9.0	8.427134	34.773920	4.232788
1879 Oct. 1.0	+ 8.486372	+ 35.415422	+ 4.246908

From these values the following co-ordinates and velocity components, and reductions to the center of gravity of the sun, Jupiter and Saturn, and the resulting reduced co-ordinates and velocity components were obtained:—

1880 March 9.0 M.T. Berlin.

$$\begin{array}{lll} x = +8.427134 & y = +34.773920 & z = +4.232788 \\ \xi = - \quad 7257 & \eta = - \quad 441 & \zeta = + \quad 221 \\ \hline \bar{x} = +8.419877 & \bar{y} = +34.773479 & \bar{z} = +4.233009 \end{array}$$

$$\begin{array}{lll}
160\,\dfrac{dx}{dt} = -0.060127 & 160\,\dfrac{dy}{dt} = -0.644253 & 160\,\dfrac{dz}{dt} = -0.014435 \\
160\,\dfrac{d\xi}{dt} = + \qquad\quad 12 & 160\,\dfrac{d\eta}{dt} = - \qquad 1446 & 160\,\dfrac{d\zeta}{dt} = + \qquad\qquad 7 \\
\hline
160\,\dfrac{d\bar{x}}{dt} = -0.060115 & 160\,\dfrac{d\bar{y}}{dt} = -0.645699 & 160\,\dfrac{d\bar{z}}{dt} = -0.014428
\end{array}$$

and from these values we find for the original $\frac{1}{a}$:—

$$\frac{1}{\bar{a}} = +0.0000396$$

i. e. a value, which agrees within 28 units in the 7th decimal with that given in Publ. No. 19 $\left(\frac{1}{\bar{a}} = +0.0000368\right)$.

The numerical calculations the results of which are published in this communication have been made by Mr. Hans Q. Rasmusen. Mag. scient. B. Svanhof has checked certain steps of the calculations. Economic support from the Carlsbergfond is gratefully acknowledged.

Observatory, Copenhagen. Elis Strömgren.

Postscript: Recently from other sides two investigations made after the principles used in the Copenhagen papers have been published on the original orbits for two comets which in the neighbourhood of perihelion moved in hyperbolic orbits. One of these, concerning comet 1932 VI Geddes, has been carried out by G. van Biesbroeck (Publ. Yerkes Observatory VIII, 3). The other, concerning comet 1922 II Baade, has been made by A. Gennaro (Publ. Padua Observatory No. 54). In both cases an hyperbolic orbit was changed into a slightly elliptic orbit.

Dr. GENNARO in his paper makes an investigation for the comet 1922 II following the method outlined on p. 25 of Publ. Cop. Obs. No. 19: — «Es ist zu der Anwendung der Formel (33) zu bemerken, dass wir für $\left|\triangle\left(\frac{1}{a}\right)\right|$, d. h. für die Maximalgrenze der unberücksichtigten Störung in $\frac{1}{a}$, immer in jedem konkreten Fall einen bedeutend niedrigeren Wert feststellen können, ohne dass wir genötigt wären, die Störungsrechnung weiter rückwärts zu führen. Bei der Ableitung der Formel (33) haben wir für b und für $P_n^3(\cos\Phi)$ ihre theoretischen Maximalwerte benutzt. Es ist aber leicht, in jedem konkreten Fall, d. h. für jede Kometenbahn, je nach den Werten der Bahnelemente, spezielle Maximalwerte zu berechnen, die einen niedrigeren Betrag aufweisen».

As was to be expected, the value for the upper limit of the neglected perturbation in $\frac{1}{a}$ thus obtained by Dr. GENNARO for the comet investigated by him was considerably smaller than the value following from the general equation (33) in Publ. 19.

E. S.

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Mathematisk-fysiske Meddelelser. **XVI,** 8.

THE β-RAY SPECTRUM OF RADIO-HELIUM

BY

T. BJERGE AND K. J. BROSTRØM

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When beryllium is bombarded with fast neutrons (of energies greater than about 2 million electron volts), a radioactive isotope of helium, ${}^{6}_{2}\mathrm{He}$, is formed by the process[1,2]:

$$ {}^{9}_{4}\mathrm{Be} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{6}_{2}\mathrm{He} + {}^{4}_{2}\mathrm{He}. \tag{1} $$

The ${}^{6}_{2}\mathrm{He}$ disintegrates in the following way:

$$ {}^{6}_{2}\mathrm{He} \rightarrow {}^{6}_{3}\mathrm{Li} + e^{-} \tag{2} $$

the half-value period being 0.8 ± 0.1 sec.[3] As already pointed out in a preliminary note[4] the results of an investigation of the energy distribution of the β-particles from the radiohelium support the interpretation of the processes of its formation and disintegration indicated by the above formulae. This is discussed more completely at the end of the present paper which also gives a full description of the experiments, in which a special technique had to be used owing to the short half-value period of the radio-helium.

Experimental arrangement.

We used a Wilson expansion chamber constructed by Dr. J. C. Jacobsen; the arrangement is shown in fig. 1. The

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[1] T. Bjerge, Nature **138**, 400 (1936).

[2] T. Bjerge, Studier over kunstig Radioaktivitet med kort Halveringstid, Dissertation, Copenhagen (1938).

[3] T. Bjerge, loc. cit., see also Nahmias and Walen, J. de Phys. et le Rad., **8**, 153 (1937).

[4] T. Bjerge and K. J. Brostrøm, Nature **138**, 400 (1936).

top glass plate, which has a diameter of 15 cm., rests on a glass ring of 5 cm. height, and the movable bottom is a rubber plate *R*. The volume beneath *R*, which contains air or another gas at an adjustable pressure, can be connected suddenly to the evacuated vessel *A* through a ground cone valve; this makes *R* fall down upon the brass plate *B* under the expansion of the gas in the chamber above *R*. The top plate, the ring and the rubber plate are held firmly against the brass plate *B*, and the system is made gas-tight by means of rubber washers. The rubber plate *R* is stiffened by an aluminium (or ebonite) plate, which covers the central part of *R* so that only a narrow region along the circumference remains soft; this is done by making *R* of two sheets fused together with the stiff plate between them. Thus the bottom of the expansion chamber is always approximately plane.

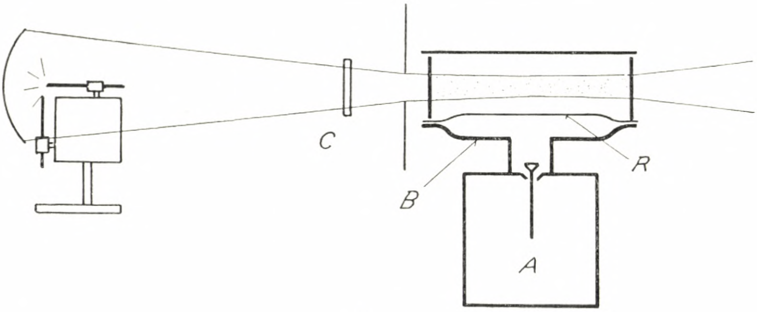

Fig. 1.

The expansion ratio, i. e. the ratio of the volume of the expansion chamber after and before an expansion, can be adjusted by adjusting the pressure in the gas beneath *R* before the expansion. Air saturated with ether and alcohol vapour was used as gas in the chamber, the bottom of *R* being covered with a layer of collodium.

The source of light was the positive electrode of a carbon arc with copper-plated "effect" carbons (Siemens Koh-I-Noor, 8 mm.). The beam was concentrated by a spherical mirror as shown in fig. 1. *C* is a cylindrical lens spreading the light beam in the horizontal plane. The chamber was illuminated for 0.2 sec. just after expansion by opening a shutter and at the same time short-circuiting the series-resistance of the arc (burning on 220 volts D. C.), thus allowing a current of 100 to 200 amperes to pass.

The tracks were photographed by two cameras with double anastigmatic objectives 1 : 4.5, and 12.5 cm. focal length. They were placed 80 cm. above the expansion chamber with a mutual lateral distance of 7.5 cm. Under these circumstances the reproduction will be sufficiently sharp for tracks of any altitude within the illuminated part of the chamber, which has a height of 2 cm. The film material used was mostly Agfa Isochrom or Isopan.

Fig. 2 shows the arrangement for activating the beryllium and bringing it quickly into the expansion chamber. The beryllium layer *S* was stuck to the outside of a small light brass cylinder by means of shellac. This cylinder was attached to an arm *A* movable around an axis *B* and held by a small electromagnet m_1 in such a position that *S* surrounded the neutron source *N* (2—300 millicuries of radon mixed vith beryllium powder). When the current in m_1 was broken a spiral spring working on the shaft *B* would make the arm move so as to bring the beryllium-cylinder into the thin-walled (0.05 mm.) brass tube *C* inserted in the top plate of the chamber (*C* had 1.5 cm. diameter and 5 cm. depth); in this position it was held by the electromagnet m_2. The movement was also used to release a falling weight which in due course short-circuited the series-resistance of the carbon-arc, opened and closed the shutter, and caused the expansion of the chamber.

The β-rays emitted from the beryllium layer were bent into circular paths by a magnetic field produced by two coils *M* arranged symmetrically above and below the illuminated part of the chamber in approximately the "Helmholtz positions". Each coil had 1200 turns of 1.4 mm. enamelled copper wire wound on a holder of 2 mm. copper plate; the lower coil was supported by a wooden stand, the upper coil was spaced from the lower one by wooden blocks. The magnetic field produced by a 10 amp. current through the coils was measured with a test coil and ballistic galvanometer, the Wilson chamber being removed; it was practically circular symmetric. In Fig. 3 the field is plotted against the distance from the center for a current of 20 amperes.

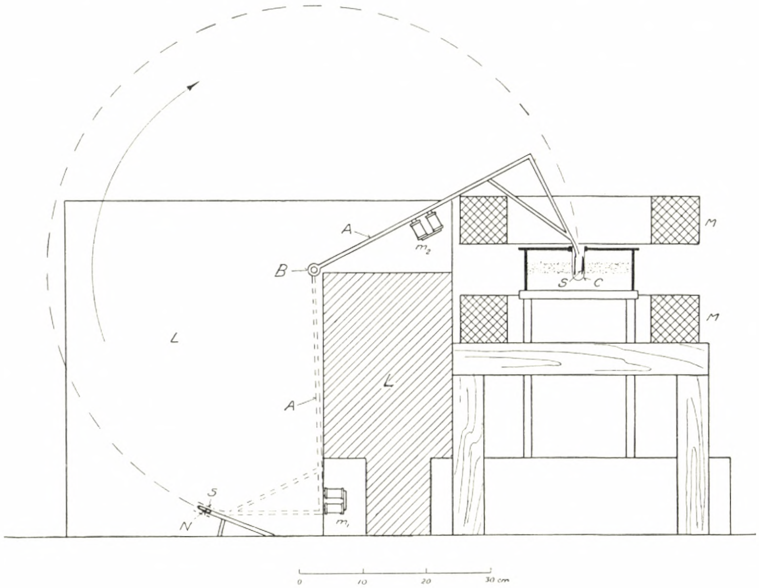

Fig. 2.

As a magnetic field of 1500 Ørsteds is suitable for the determination of β-particle energies of a few million e-volts, it was necessary to pass a current of 20 amperes through the coils. Each coil had a resistance of 10 Ohms, so that the total effect developed was about 8 kilowatts; thus it was only possible to feed the coils for a very short time at every expansion, because the heating would otherwise very soon disturb the functioning of the Wilson chamber. The switch for the current in the coils was therefore mechanically coupled to the switch starting the movement of the arm, which brought the beryllium sample from the neutron source into the chamber in 0.4 sec. In the course of this time the magnetic field would reach its maximum value within 0.5 per cent, as can be calculated from the self-inductance (1.5 henries) and resistance. After expansion the current was broken by the last switch released by the falling weight mentioned above, and in order to minimize the spark the coils (which were in series) were constantly

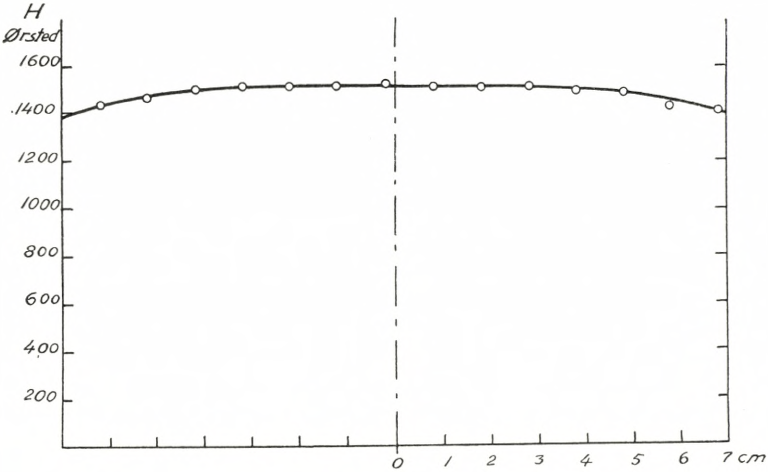

Fig. 3.

shunted with 40 Ohms. In this way the current only flowed for 0.7 sec. at each expansion; further the lower part of the chamber was cooled by surrounding it with a copper-plate cylinder to which was soldered a copper tube cooled by a stream of water, and the top part of the chamber could be air-cooled by a fan. When photographs were taken only at one-minute intervals the chamber would work satisfactorily.

At each expansion the current in the coils was determined; the ammeter used did not come to rest within 0.7 sec., but was adjusted as a kind of "ballistic" instrument.

In order to shield the chamber from the γ-rays from the neutron source the latter was surrounded with blocks of lead (L in fig. 2) except for a slit to allow the passage of the moving arm.

The evaluation of the photographs.

A part of the photographs were, of course, spoiled for various reasons such as fog in the chamber, insufficient illumination, etc. On the more successful 1 or 2 tracks, on an average, are seen starting from the cylinder in the middle of the chamber, as shown by the examples in fig. 4 and 5. The track in fig. 4 was produced by a negative elektron; this is also the case for the track A of fig. 5, but for the track B, which is a closed circle, it is not possible to decide the sign of the electron. The total number of tracks found on the photographs was 120; most of these could unambiguously be ascribed to negative electrons, no one could unambiguously be ascribed to a positive electron, and the number of those which from their appearance could be either positive or negative was not greater than could be expected if all the particles emitted were negative electrons.

Thus the radioactive substance created by bombardment of beryllium with neutrons (the helium isotope of mass 6) emits negative electrons and there is no sign that it should also emit positive electrons.

The radius of curvature of the tracks was measured by direct comparison of the photograph with a set of concentric circles photographed by the same camera at the same distance. This actually gives the projection of the path on a horizontal plane, but the error introduced by neglecting the vertical component of the velocity will in general not amount to more than one or two per cent of the energy and as the uncertainty in the determination of the energy in our experiments was greater than this, the error was not important. Although in this way the more troublesome method of reprojecting the stereoscopic pictures was not used, the two different aspects of the tracks very often facilitated the evaluation.

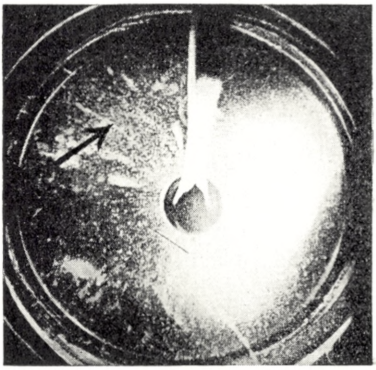

Fig. 4.

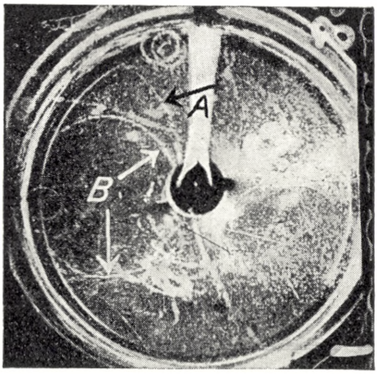

Fig. 5.

The radius of curvature ϱ was multiplied with the corresponding value for the magnetic field H (taken from the curve of fig. 3 using the proper value of the current), and $H\varrho$ was corrected as described below. From $H\varrho$ the energy was deduced, and the 120 particles were divided into energy groups with intervals of 0.5 million e-volts (m. e. v.). In fig. 6 the number of particles in each group is plotted against the energy in m. e. v.

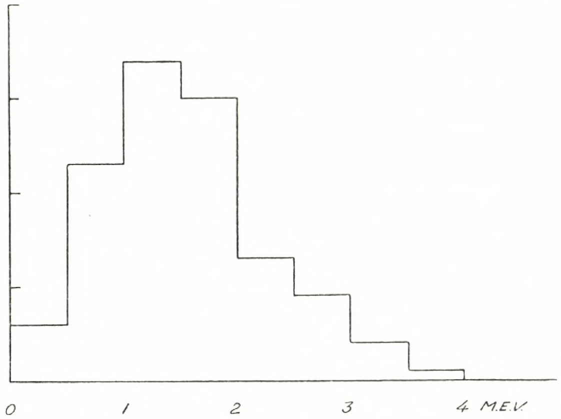

Fig. 6.

The upper limit of the energies is presumably situated between 3.5 and 4.0 m. e. v. The most energetic particle found had 3.6 m. e. v.; on account of the scarcity of particles with energies near the upper limit it is reasonable to assume that the latter is lying somewhat above the maximum energy found for any particle. On the other hand the uncertainty in the determination of the energies of the individual particles, which is shown below to be about 10 per cent, will make the energy spectrum blurred, thus tending to give an increase in the apparent upper energy. Taking these facts into account and judging from the general appearance of fig. 6, we consider the most probable value of the upper energy limit for the β-particles in question to be 3.7 ± 0.5 m. e. v.

Corrections and Uncertainty.

Before reaching the expansion chamber the β-particles have to pass the thin-walled brass cylinder and part of the beryllium layer, and this gives rise to a loss of velocity. The diminution of the quantity $H\varrho$ can be calculated from the formula

$$\frac{\delta(H\varrho)}{\sigma}\cdot\beta^3 = 5.10\cdot\frac{Z}{A}\left(96.1-\log_e\frac{A}{Z}+\log_e\sigma-\log_e\frac{1-\beta^2}{\beta^2}-\beta^2-2C\right)^1$$

where σ is the thickness of the layer expressed in cg./cm.^{2}, Z the atomic number, A the atomic weight, β the velocity expressed as a fraction of the velocity of light, and C is a quantity depending on the atomic structure. Putting $C = 41$ this formula seems to be in fairly good agreement with experimental results. For the brass cylinder $\sigma = 5$ cg./cm.^{2}, which gives $\delta_1(H\varrho) = 250$ or 300 Ørsteds·cm. for the β-particle velocities in question. For the beryllium layer $\sigma = 12$ cg./cm.^{2}; on an average the electrons will pass through half of this layer, i. e. 6 cg./cm.^{2}, which gives $\delta_2(H\varrho) = 300 \pm 300$ Ørsteds·cm. The total correction, taking into account that the particles have in general an oblique path through the layers, amounts to about

$$\delta(H\varrho) = 800 \pm 400 \text{ Ørsteds·cm.}$$

The uncertainty 400 Ørsteds·cm. in $H\varrho$ corresponds to an uncertainty in the energy $\Delta_1 E = 0.12$ m. e. v. for particles of energy greater than 1 m. e. v. For slower β-particles $\Delta_1 E$ is smaller.

For a helical path the tangent of which makes an angle α with the horizontal plane, the value found for $H\varrho$ in

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[1] Rutherford, Chadwick and Ellis, Radiations from radioactive substances, Cambridge (1930), p. 439.

the way described above gives the horizontal component of the momentum, and the total momentum could be obtained by division with $\cos\alpha$. Energy and momentum being approximately proportional for $E > 1$ m. e. v., the energies found ought to be divided by $\cos\alpha$. With the given dimensions of the illuminated part of the chamber this correction will, however, only in exceptional cases amount to more than a few per cent; considering the fairly large uncertainty in the determination of $H\varrho$, we have, therefore, not carried out the troublesome stereoscopic determination of the paths but left out the correction for their obliquity as unimportant.

Another correction which we have neglected is the correction for the decrease of the magnetic field near the edge of the chamber (see fig. 3). For a path passing this zone the mean radius of curvature (this is what can be measured) will be slightly increased, but the deviation rarely exceeds a few per cent, and the error introduced by neglecting this will counteract the error from neglecting the obliquity. The total effect of leaving out these two corrections will be an uncertainty $\Delta_2 E$ in the energy determination amounting to 2 or 3 per cent.

Besides $\Delta_1 E$ and $\Delta_2 E$ there are the following two sources of uncertainty in the energy determination:

1. The scattering of the β-particles. With air in the chamber the corresponding uncertainty in the mean radius of curvature will, according to genenal experience, amount to 5 or 10 per cent. This gives $\Delta_3 E = 5$ or 10 per cent (for energies > 1 m. e. v.). This is the principal source of uncertainty; it can be considerably reduced by using hydrogen in the chamber instead of air, but the illumination we could obtain was only just sufficient with air

in the chamber and would have been insufficient with hydrogen.

2. The personal factor in evaluating the radius of curvature. Both of us measured all the tracks independently and the results were the same within an uncertainty $\Delta_4 E$ of a few per cent.

Thus the total uncertainty $\Delta_1 E + \ldots \Delta_4 E$ in the energy determination will be about 10 per cent, for the slowest particles perhaps somewhat more.

Discussion.

The maximum energy 3.5 ± 0.5 m. e. v. of the β-particles emitted in process (2) permits calculation of the mass of the $^{6}_{2}\mathrm{He}$ atom. Using the atomic masses from table LXXIII in "Nuclear Physics C" by LIVINGSTON and BETHE[1] one has $^{6}_{3}\mathrm{Li} = 6.0169 \pm 0.0002$, and hence by reaction (2):

$$^{6}_{2}\mathrm{He} = 6.0169 + 0.0039 = 6.0208 \pm 0.0005.$$

This gives for the energy release in reaction (1):

$$9.0150 + 1.0090 - (6.0208 + 4.0039) = -0.0007 \quad \text{mass units}$$

or

$$-0.65 \pm 0.5 \text{ m. e. v.}$$

This result is in agreement with the following two facts:

1° — Process (1) is insensitive to surrounding the beryllium sample and neutron source with paraffin, ɔ: slow neutrons are not active in the process.

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[1] M. STANLEY LIVINGSTON and H. A. BETHE, Rev. Mod. Phys., **9**, 245 (1937).

2° — Oliphant has found that neutrons of energy down to c. 2 m. e. v. are able to produce the radioactivity in question[1]. Such neutrons are emitted in the process

$$ {}^{2}_{1}\mathrm{H} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{3}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n} $$

in the backward direction from the bombarding beam of deuterons, when the energy of the latter is 0.4 m. e. v. If the incident neutron in (1) has a kinetic energy of c. 2 m. e. v. there will only be 1.2 ± 0.5 m. e. v. as kinetic energy to share between the resulting particles ${}^{4}_{2}\mathrm{He}$ and ${}^{6}_{2}\mathrm{He}$; this however, corresponds to a sufficient mutual repulsion for the particles to penetrate their mutual potential barrier practically instantanously even if the lower value is chosen[2].

This numerical agreement thus supports the interpretation contained in (1) and (2) of the processes of formation and disintegration of a radioactive body when beryllium is bombarded with neutrons. Taking into account the fact that the active body is a gas there are only two other possibilities of an interpretation, viz.:

$$ {}^{9}_{4}\mathrm{Be} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{6}_{3}\mathrm{Li} + {}^{4}_{1}\mathrm{H} \qquad (3) $$

with a radioactive hydrogen isotope disintegrating as follows:

$$ {}^{4}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + e^{-}, \qquad (4) $$

and

$$ {}^{9}_{4}\mathrm{Be} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{5}_{2}\mathrm{He} + {}^{5}_{2}\mathrm{He} \qquad (5) $$

followed by the radioactive disintegration

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[1] M. L. E. Oliphant, Copenhagen Conference, June 1936 (unpublished).

[2] Compare the remarks on penetrability of potential barriers for α-particles contained in the paper by T. Bjerge, Proc. Roy. Soc., **164**, 243 (1938).

$$^{5}_{2}\mathrm{He} \rightarrow {}^{5}_{3}\mathrm{Li} + \mathrm{e}^{-} \qquad (6)$$

The first of these possibilities can be excluded because the radioactive gas can be conducted through hot copper oxide and afterwards through an air-trap cooled with solid carbon dioxide and alcohol without losing its activity[1]. The second possibility, expressed by (5) and (6), would involve that the energy difference between the $^{5}_{2}$He and the $^{5}_{2}$Li in question should be 3.7 ± 0.5 m. e. v. Now $^{5}_{2}$He might be formed from $^{4}_{2}$He by addition of a neutron, $^{5}_{3}$Li by addition of a proton, and the binding forces are probably small and not very different, so that the energy difference could hardly be much more than the 0.8 m. e. v. due to the mass difference between a neutron and a hydrogen atom. Thus the present experiments should exclude the processes (5) and (6) as an explanation of the radioactivity in question, and only the explanation given by (1) and (2) remains.

This argument we consider to be fairly safe, but as recent experiments have thrown new light upon the existence of a helium isotope of mass 5, a brief discussion of these experiments and their bearing on the present problem may have some interest.

Williams, Shepherd and Haxby[2] have given evidence for the process

$$^{7}_{3}\mathrm{Li} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{5}_{2}\mathrm{He} + {}^{4}_{2}\mathrm{He} \qquad (7)$$

The mass of the $^{5}_{2}$He determined by means of the range of the homogeneous group of α-particles is found to be 5.0137; this is more than the mass of $^{4}_{2}$He plus a neutron,

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[1] T. Bjerge, Studier over kunstig Radioaktivitet med kort Halveringstid, Dissertation, Copenhagen (1938).

[2] J. H. Williams, W. G. Shepherd and R. O. Haxby, Phys. Rev. **52** 390 (1937).

and accordingly the ${}^{5}_{2}\mathrm{He}$ splits up into these particles after a mean life of about $5 \cdot 10^{-20}$ seconds (as found from the uncertainty in the energy of the ${}^{4}_{2}\mathrm{He}$-group), i. e. long before it can reach a detecting apparatus.

Joliot, and Zlotowski[1], on the other hand, find that on bombardment of deuterium with polonium α-particles protons are released which they explain by the reaction

$$ {}^{4}_{2}\mathrm{He} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{5}_{2}\mathrm{He} + {}^{1}_{1}\mathrm{H} \qquad (8) $$

From the proton tracks in a Wilson-chamber the mass of ${}^{5}_{2}\mathrm{He}$ is found to be 5.0106 which is less than that of ${}^{4}_{2}\mathrm{He}$ plus a neutron, thus indicating a stable ${}^{5}_{2}\mathrm{He}$. One might perhaps assume that in process (7) the ${}^{5}_{2}\mathrm{He}$ is left in an excited state of about 3 m. e. v. and thus reconcile the results of Williams, Shepherd and Haxby with those of Joliot anb Zlotowski.

Neither of these two ${}^{5}_{2}\mathrm{He}$ nuclei could, however, be identical with the β-radioactive helium isotope produced by bombarding beryllium with neutrons. The ${}^{5}_{2}\mathrm{He}$ of Williams, Shepherd and Haxby only exists for about 10^{-20} seconds and is thus excluded. The ${}^{5}_{2}\mathrm{He}$ of Joliot and Zlotowski has the mass 5.0106 ± 0.0005; if we suppose this ${}^{5}_{2}\mathrm{He}$ to split up in a process like (6) with the maximum β-ray energy of 3.7 ± 0.5 m. e. v. the resulting ${}^{5}_{3}\mathrm{Li}$ atom would have the mass 5.0067 ± 0.0007. This would mean, however, that ${}^{6}_{3}\mathrm{Li}$, which has the mass 6.0169, would have more mass than ${}^{5}_{3}\mathrm{Li}$ plus a neutron and would thus be unstable. As a matter of fact, ${}^{6}_{3}\mathrm{Li}$ is quite stable, and a stable ${}^{5}_{3}\mathrm{Li}$ has not been found.

Also in the light of the new evidence of the existence

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[1] F. Joliot and J. Zlotowski, Comptes rendus **206**, 1256 (1938).

of ${}^{5}_{2}$He we may, therefore, conclude that the only possibility of explaining that a radioactive helium isotope is produced by bombarding beryllium with fast neutrons is the one expressed by reactions (1) and (2).

The present work was carried out at the Institute of theoretical Physics of the University of Copenhagen. We wish to express our thanks to Professor N. Bohr for his kind interest in the work and to Dr. J. C. Jacobsen for the loan of the Wilson chamber. Our thanks are also due to the Radium Institute of Copenhagen for the gift of the emanation.

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Færdig fra Trykkeriet den 28. November 1938.

Det Kgl. Danske Videnskabernes Selskab.
Mathematisk-fysiske Meddelelser. **XVI,** 9.

ÜBER DIE ABHÄNGIGKEIT DES TEMPERATURSPRUNGES VON DEM AKKOMMODATIONSKOEFFICIENTEN NEBST EINIGEN VERWANDTEN WÄRMELEITUNGSPROBLEMEN IN GASEN

VON

SOPHUS WEBER

KØBENHAVN
EJNAR MUNKSGAARD
1939

Printed in Denmark.
Bianco Lunos Bogtrykkeri A/S, København.

§ 1. Seitdem Kundt und Warburg[1] die Aufmerksamkeit darauf lenkten, dass nach der kinetischen Gastheorie ein Temperatursprung an der Grenzfläche zwischen Gase und fester Wand, wenn ein Temperaturgradient in der Richtung der Nomale im Gase herrscht, bestehen muss, sind mehrere experimentellen Untersuchungen hierüber ausgeführt.

M. von Smoluckowski[2], der im Anschluss an die Arbeiten von Maxwell[3] und von Kundt & Warburg, sich mit dem Wärmeaustausch zwischen einem Gase und einer festen Wand eingehend beschäftigte, hat nicht nur experimentelle Untersuchungen über den Temperatursprung ausgeführt, sondern auch diese Erscheinung, ausgehend von den Maxwell'schen Voraussetzungen in Bezug auf die Zurückwerfung der Gasmoleküle von einer festen Wand, theoretisch untersucht.

Kundt und Warburg definierten den Temperatursprung, $\Delta \Theta$, durch:

$$\Delta \Theta = -\gamma \cdot \frac{d\Theta}{dn},$$

wo Θ die Temperatur und n die Richtung der Normale angibt.

Smoluckowski fand experimentell, dass der Temperatursprungskoefficient, γ, innerhalb einem sehr grossen Druck-

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[1] A. Kundt und E. Warburg: Pogg. Ann. 156 (1875) p. 177.

[2] M. v. Smoluckowski: Wied. Ann. 64 (1898) p. 101.

[3] J. C. Maxwell: Scient. Pap. 11, p. 681.

bereich mit der mittleren freien Weglänge, λ, im Gase proportional ist, welches auch aus den gleichzeitigen Observationen von BRUSH[1] hervorgeht.

Später hat GEHRCKE[2] mit einem sehr verbesserten Apparat die Messungen von SMOLUCKOWSKI wiederholt und das Resultat von SMOLUCKOWSKI bestätigt und ausserdem gefunden, dass der Wert von $\frac{\gamma}{\lambda}$ bei den allerniedrigsten Drücken abnimmt.

Während SMOLUCKOWSKI und GEHRCKE für die Bestimmung von dem Temperatursprung die totale Wärmeleitung zwischen zwei Oberflächen untersuchten, hat LAZAREFF[3] den Temperaturverlauf zwischen den Platten direkt gemessen und hieraus den Wert für $\frac{\gamma}{\lambda}$ bestimmt.

SMOLUCKOWSKI hat mit Hilfe der kinetischen Gastheorie den Wert für γ theoretisch berechnet; erst laut der einfachen kinetischen Theorie von CLAUSIUS und später, ausgehend von der eksakten kinetischen Theorie von Maxwell, für Moleküle, welche sich wie nach der umgekehrten 5ten Potenz von der Entfernung abstossende Kraftcentra verhalten.

Später hat MARTIN KNUDSEN[4] im Zusammenhang mit seinen bekannten Untersuchungen über die molekulare Wärmeleitung der Gase sich mit dem Temperatursprung beschäftigt und den Zusammenhang zwischen dem Temperatursprung und dem Akkommodationskoefficienten, a, auseinandergesetzt.

SMOLUCKOWSKI[5] fand theoretisch nach der kinetischen Gastheorie für einatomige Gase:

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[1] C. F. BRUSH: Phil. Mag. 45 (1898) p. 31.

[2] E. GEHRCKE: Ann. d. Ph. 2 (1900). p. 102.

[3] P. LAZAREFF: Ann. d. Ph. 37 (1912) p. 233.

[4] MARTIN KNUDSEN: Ann. d. Ph. 34 (1911) p. 651.

[5] M. VON SMOLUCKOWSKI: Wiener Ber. 108 (1899) p. 5; Wied. Ann. 64 (1898) p. 101.

$$\gamma = \frac{15}{16} \sqrt{2\pi}\, \frac{2-a}{a} \cdot \frac{\eta}{\sqrt{p\varrho}}, \tag{1}$$

wo η, ϱ und p der innere Reibungskoefficient, bezw. die Dichte und der Druck des Gases sind.

Führen wir in diesem Ausdruck die mittlere freie Weglänge, λ, nach S. Chapman[1] ein, dann finden wir, weil:

$$p\lambda = \frac{1}{0{,}499} \sqrt{\frac{\pi}{8}} \cdot \frac{\eta_0}{\sqrt{{}_1\varrho_0}} \left(\frac{T}{T_0}\right)^{1+n} = \sqrt{\frac{\pi}{2}} \cdot \frac{\eta_0}{\sqrt{{}_1\varrho_0}} \left(\frac{T}{T_0}\right)^{1+n} = {}_1\lambda_0 \left(\frac{T}{T_0}\right)^{1+n},$$

dass der Temperatursprungskoefficient für einatomige Gase wird:

$$\gamma = \frac{15}{4} \cdot \frac{2-a}{2a} \cdot \lambda$$

§ 2. Wie bereits erwähnt, können die vorliegenden experimentellen Untersuchungen in zwei Klassen geteilt werden, nämlich die Bestimmungen von γ aus der totalen Wärmeleitung zwischen zwei Oberflächen und die Bestimmungen von γ durch direkte Messung von dem Temperaturverlauf zwischen den Oberflächen mit verschiedener Temperatur. Nach der ersten Methode untersuchten v. Smoluckowski und Gehrcke atmosphärische Luft und Wasserstoff, während Lazareff nach der zweiten Methode untersuchte atm. Luft, Wasserstoff und Kohlensäure; die verwendeten Oberflächen, wozwischen die Wärmeleitung von statten ging, waren entweder reine Glasoberflächen oder blanke, glatte Metalloberflächen.

Die Resultate von diesen Messungen sind in der Tabelle I zusammengestellt, wo sowohl die Werte von $\frac{\gamma}{\lambda_M}$ (λ_M = die O. E. Meyer'sche freie Weglänge), wie auch die Werte von

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[1] S. Chapman: Vgl. J. H. Jeans: The Dyn. Theory of Gases, 1925, p. 276.

$\frac{\gamma}{\lambda}$ (λ = die Chapman'sche freie Weglänge) aufgenommen sind; wie man sieht, ist die Übereinstimmung zwischen den Resultaten von den zwei Messmethoden befriedigend, wenn in Betracht gezogen wird, dass die verwendeten Oberflächen verschieden sind.

Tabelle I.

	Smoluckowski	Gehrcke	Lazareff
	$\frac{\gamma}{\lambda_M}$	$\frac{\gamma}{\lambda_M}$	$\frac{\gamma}{\lambda_M}$
H_2	6.95	5.70	7.68
Atm. Luft	1.70	1.83	1.67
CO_2	—	—	1.69
	$\frac{\gamma}{\lambda}$	$\frac{\gamma}{\lambda}$	$\frac{\gamma}{\lambda}$
H_2	11.22	9.20	12.40
Atm. Luft	2.75	2.96	2.70
CO_2	—	—	2.73

Die experimentelle Untersuchung von Lazareff ist sehr schön durchgeführt, und sein Apparat ist so konstruiert, dass es nicht zu erwarten ist, dass die Temperaturverteilung zwischen den Platten durch entstehende thermische Gleitströme, bezw. Konvektionsströme, beeinflusst worden ist. —

Später haben W. Mandell und West[1] diese Untersuchungen nach der Methode von Lazareff wiederholt und sehr abweichende Resultate gefunden, u. A. Temperaturunterschiede zwischen den Platten und dem Gase, die nur durch Konvektionsströmungen erklärt werden können; wenn man aber die Konstruktion des von M. und W. verwendeten Messapparates kritisch untersucht, sieht man sofort, dass die zwei

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[1] W. Mandell and J. West: Proc. Phys. Soc. London 37 (1925) p. 20.

Oberflächen, wozwischen der Temperaturverlauf gemessen wird, direkt durch einen Kupfercylinder verbunden sind; durch den Temperaturgradienten in dieser Cylinderfläche entstehen thermische Gleitströmungen der Cylinderfläche entlang, und diese Strömungen, die wahrscheinlich in dem Apparat von M. und W. sehr regelmässig gewesen sind, bleiben bis zu den niedrigsten Drücken bestehen und beeinflüssen den Temperaturverlauf zwischen den Platten; auch in dem von Lazareff verwendeten Apparat werden diese Gleitströmungen entstehen können, aber werden durch die besondere Konstruktion des Apparates *nicht* zwischen den Messflächen durchdringen.

Aus den Untersuchungen von Mandell und West, die der weniger glücklichen Konstruktion des Messapparates wegen bei den höheren Drücken ganz falsche Resultate von der Grösse des Temperatursprunges geben, geht aber hervor, dass bei den allerniedrigsten Drücken der Temperaturverlauf zwischen den Platten in Luft und Wasserstoff sich nicht mehr ändert, sondern konstant wird, und dass die Temperatur des Gases in diesem Falle gegeben ist durch:

$$T = \frac{1}{2}\,(T_1 + T_2),$$

so wie man auch nach den Untersuchungen von Martin Knudsen über die molekulare Wärmeleitfähigkeit erwarten müsste, jedenfalls wenn die Akkommodationskoefficienten von den zwei Platten dieselben sind.

In diesem Falle, also $\bar{p} \rightarrow 0$ oder $\frac{d}{\lambda} \overset{\rightarrow}{=} 0$, wird der Temperatursprung bei den Platten:

$$\varDelta T = T_1 - \frac{1}{2}\,(T_1 - T_2) = \frac{1}{2}\,(T_1 - T_2)$$

§ 3. In einer Reihe von Experimentaluntersuchungen habe ich[1] früher Präcisionsbestimmungen von der Wärmeleitfähigkeit der Gase ausgeführt; diese Bestimmungen wurden nach einer verbesserten Schleiermacher'schen Methode gemacht, und teilweise wurden sie auch kontrolliert durch Messungen mit verschiedenen Doppelapparaten nach Goldschmidt; die verwendeten Apparate waren alle so konstruiert, dass die Bestimmungen von der Wärmeleitfähigkeit nicht durch Konvektion oder bekannte Fehlerquellen beeinflüsst waren; gleichzeitig mit der Bestimmung von der Wärmeleitfähigkeit des Gases wurde für die untersuchten Gase der Temperatursprung gegenüber glatten, blanken Platinoberflächen bestimmt.

Bei den Messungen von dem Temperatursprung wurde mit 4 verschiedenen Apparaten gearbeitet; App. I und II waren verbesserte Schleiermacher'sche Apparate mit dickem Draht, während die Apparate 4 und 6 nach der Methode von Goldschmidt gebaut waren; in der Tabelle II sind die Konstanten für diese Apparate angegeben; $2r_0$ ist der Diameter des verwendeten Platindrahtes, und $2R_0$ ist der innere Diameter des umgebenden Glasrohres; die nähere Umschreibung und Konstruktion sind in den citierten Abhandlungen zu finden.

Tabelle II.

App. I (Schl.)	$2r_0 = 0.040784$ cm	$2R_0 = 2.3441$ cm
„ II (Schl.)	„ $= 0.040746$ cm	„ $= 2.5424$ cm
„ 4 (Golds.)	„ $= 0.005246$ cm	„ $= 1.526$ cm
„ 6 (Golds.)	„ $= 0.005246$ cm	„ $= 1.449$ cm

Aus der observierten Wärmeabgabe des geheissten Platindrahtes Q_∞ für $p \rightarrow \infty$ und Q_p bei dem Druck p wurde

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[1] Sophus Weber: Ann. d. Ph. Bd. 54 (1917) p. 326 und p. 437; Comm. Kamerlingh Onnes Lab. Leiden. Suppl. No. 42 b, 1918; Ann. d. Ph. Bd. 82 (1927) p. 479.

γ_1 bei dem Druck p für die geheisste Platinoberfläche bestimmt durch die bekannte Formel:

$$\gamma_1 = \frac{ln \frac{R_0}{r_0}}{\frac{1}{r_0} + \frac{1}{R_0} \cdot \frac{\gamma_2}{\gamma_1}} \left\{ \frac{Q_\infty}{Q_p} - 1 \right\} \tag{2}$$

γ_2 ist der Wert des Temperatursprungskoefficienten an der Glasoberfläche, $2 \pi R_0$, und bei der Berechnung wurde in Übereinstimmung mit den Messungen von Martin Knudsen angenommen, dass γ denselben Wert für Glas und blankes, glattes Platin hat; wo es sich ausserdem in diesen Messungen, weil $\frac{r_0}{R_0}$ sehr klein ist, nur um eine kleine Korrektion für γ_1 handelt, ist ein kleiner Unterschied zwischen γ_1 und γ_2 ohne grössere Bedeutung für die Bestimmung von γ_1.

Aus den Messungen geht hervor, dass $\gamma \cdot p$, bezw. $\frac{\gamma}{\lambda}$, in einem grossen Bereich konstant ist; das Endresultat von den Messungen, nachdem diese neuberechnet sind, ist in Tabelle III, Kolonne 7, angegeben; insbesondere sind die Bestimmungen mit dem App. 6 gut, aber die gegenseitige Übereinstimmung der Versuchsreihen ist durchaus befriedigend; der Wert für CO_2 ist in guter Übereinstimmung mit dem Wert von Lazareff; hierauf werde ich in dem Folgenden zurückkommen.

Aus dieser Tabelle III geht hervor, dass die von mir bestimmten Werte gut mit einander und auch mit den früheren observierten Werten übereinstimmen; dieses gilt sowohl für zweiatomige Gase, als auch für mehratomige, wie z. B. CO_2; wenn wir die beobachteten Werte in Kolonne 7 vergleichen mit den Werten in Kolonne 11, die nach der Formel von Smoluckovski für einatomige Gase und mit den

Tabelle III.

		$\left(\frac{\gamma}{\lambda}\right)_{T_0 = 273 \cdot 1}$ (λ nach S. Chapman)				Warscheinlichster Wert für $\left(\frac{\gamma}{\lambda}\right)_{T_0}$	$(p\lambda)_{T_0}$	Akkommodationskoefficienten, a_{T_0}		$\left(\frac{\gamma}{\lambda}\right)_{T_0}$ ber. aus $3{,}75 \cdot \frac{2-a}{2a}$	Akkommodationskoeff. a_{T_0} berechnet aus $\frac{\gamma}{\lambda}$
		App. I	App. II	App. 4	App. 6			nach Knudsen[1]	nach Schmidt[2]		
1)	Ar.	. .	2.54	. .	. .	2.54	6.29	0.852	—	2.52	—
2)	He	8.48	8.54	. .	. .	8.50	17.72	0.338	0.336	9.25	. .
3)	Ne	3.58	3.64	3.93	. .	3.90	12.56	0.653	0.670	3.88	. .
4)	H_2	11.70	11.72	. .	. .	11.70	11.31	0.278	0.283	11.63	. .
5)	O_2	. .	2.74	. .	. .	2.74	6.45	0.80	. .	2.81	. .
6)	N_2	. .	2.44	. .	. .	2.44	5.98	—	0.855	2.50	. .
7)	Atm. Luft	. .	2.95	. .	2.77	2.85	6.04	0.80	. .	2.81	. .
8)	CO	. .	. .	. .	. .	. .	5.94	. .	. .	. .	. .
9)	CO_2	. .	2.80	. .	2.74	2.74	3.91	0.81	. .	2.78	. .
10)	N_2O	. .	3.23	. .	. .	3.23	4.85	—	—	—	0.74
11)	CH_4	. .	2.64	. .	. .	2.64	3.89	. .	. .	. .	0.83

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[1] Martin Knudsen: Ann. d. Phys., 46 (1915) p. 641.

[2] G. Schmidt: Comm. Kamerlingh Onnes Lab., Leiden, 242^c.

bekannten Werten für die Akkommodationskoefficienten berechnet sind, dann sehen wir, dass die Übereinstimmung sehr befriedigend ist, obwohl die Übereinstimmung für Helium etwas nachlässt; der Faktor $k_1 = \frac{15}{4} = 3{,}75$ in der Formel von Smoluckowski gilt also nicht nur für einatomige Gase, sondern ist auch für mehratomige Gase gültig; diese experimentelle Tatsache ist sehr interessant und von grosser Bedeutung, weil es hierdurch möglich wird den Akkommodationskoefficienten, a, aus einer Messung von dem Temperatursprung zu bestimmen; dieses ist in der Tabelle für N_2O und CH_4 zum Ausdruck gebracht.

§ 4. In der Ableitung von der Formel (1) für den Temperatursprung hat Smoluckowski[1] die mathematisch eksakte Maxwell'sche Berechnungsmethode verwendet und also angenommen, dass die Moleküle als Kraftcentra, die sich gegenseitig mit einer Kraft, umgekehrt proportional mit der 5ten Potenz der Entfernung, abstossen, aufgefasst werden können; diese Berechnung, die im Allgemeinen der Grösseordnung nach richtige Resultate gibt, wie auch die späteren theoretischen Untersuchungen von S. Chapman[2] und D. Enskog[3] gezeigt haben, ist in der kinetischen Gastheorie sehr zu empfehlen, obwohl die Methode wenig anschaulich und übersichtlich ist.

In dem Folgenden werden wir aber den Temperatursprung näher betrachten, indem wir ausgehen von der mehr anschaulichen Methode, welche Martin Knudsen[4] bei seinen Betrachtungen über den Zusammenhang zwischen der molekularen Wärmeleitung und der Maxwell'schen Wärme-

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[1] M. von Smoluckowski: loc. cit.

[2] S. Chapman: Phil. Trans. 216 (A) (1915) p. 279.

[3] D. Enskog: Inaug. Diss., Upsala, 1917.

[4] Martin Knudsen: loc. cit.

leitung verwendet hat; ich werde nachweisen, dass diese Methode auch für die kinetische Theorie numerisch richtige Resultate gibt[1]; dieses findet m. E. seine Erklärung darin, dass die individuellen Eigenschaften der Moleküle, herrührend von den molekularen Kraftfeldern, in der Temperaturabhängigkeit der mittleren freien Weglänge zum Ausdruck kommen.

Wie aus dem Folgenden hervorgeht, gibt die Knudsen'sche Methode eine übersichtliche Ableitung von den Unterschieden in den Formeln für ein- und mehratomige Gase.

Zu diesem Zweck betrachten wir ein Gas in dem Maxwell'schen Zustand, d. h. den Zustand, in welchem die mittlere freie Weglänge, λ, sehr klein gegenüber den massgebenden Abmessungen des Apparates ist; für den Maxwell'schen Zustand gilt also $\frac{\lambda}{d} \overset{\rightarrow}{=} 0$; wird aber $\frac{d}{\lambda} \overset{\rightarrow}{=} 0$ gültig, haben wir den Knudsen'schen Zustand des Gases; in dem Maxwell'schen Zustand sind die Wärmeleitfähigkeit, K, und innere Reibung, η, unabhängig von der Dichte.

Wenn in dem Gase ein Temperaturgradient herrscht, betrachten wir, Fig. 1, am einfachsten zwei parallele Metallplatten, A und B, mit dem Abstand, d, und mit den Temperaturen T_1 und T_2; wir setzen nun voraus: $\frac{\lambda}{d} \rightarrow 0$. Zwischen den Platten und parallel mit diesen denken wir uns zwei Flächen, V_1 und V_2, deren Abstand, b, klein gegenüber λ ist; die Wärmemenge, Q, die in dem stationären Zustand per Sek. und per cm^2 zwischen diesen beiden

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[1] Wenn man den Einfluss von magnetischen oder elektrischen Feldern auf der Wärmeleitung oder der inneren Reibung der Gase theoretisch untersuchen will um den observierten Effekt zu erklären, ist es wahrscheinlich empfehlungswert erst den Einfluss der Felder in dem Knudsen-Zustand der Gase zu untersuchen (vgl. Hermann Senftleben und O. Riechenmeyer: Ann. der Ph. 6, 105, 1930; Hermann Senftleben: Phys. Z. S., 31, 961, 1930 und Z. f. Phys. 74, 757, 1932.)

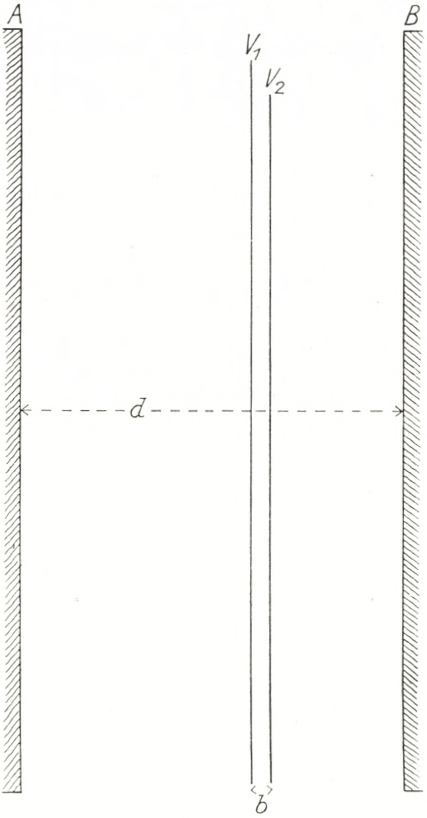

Fig. 1.

Flächen, V_1 und V_2, transportiert wird, lässt sich, wenn ε die molekulare Wärmeleitung bezeichnet, schreiben:

$$Q = \varepsilon \cdot p \cdot \Delta t$$

p ist der Druck des Gases und Δt die Temperaturdifferenz der durch die Flächen in entgegengesetzter Richtung sich bewegenden Moleküle.

Dieser Ausdruck muss nach Knudsen so aufgefasst werden, dass man, falls die Geschwindigkeiten der von rechts kommenden Moleküle sich steigerten, so dass sie gleiche

Geschwindigkeiten wie die von links kommenden Moleküle bekämen, an dieser Stelle der Gasmasse ein homogenes Gas mit der Temperatur, t_1, haben würde; die Temperatur, t_2, der von rechts kommenden Moleküle wird in ähnlicher Weise aufgefasst; man hat dann:

$$\Delta t = t_1 - t_2.$$

Indem wir Δt als verschwindend klein gegenüber der absoluten Temperatur des Gases ansehen dürfen, wird die Temperatur von dem Gase zwischen den Flächen, V_1 und V_2, gleich an $t = \frac{1}{2}(t_1 + t_2)$ sein, und von dieser Stelle aus wird die Temperatur sich nach beiden Seiten linear ändern, so dass:

$$t + x_1 \cdot \frac{dt}{dx} = t_1 \quad \text{und} \quad t - x_1 \cdot \frac{dt}{dx} = t_2$$

oder:

$$t_1 - t_2 = \Delta t = 2\,x_1 \cdot \frac{dt}{dx}.$$

Die Moleküle, die durch die Flächen, V_1 und V_2, fliegen, werden dann im Mittel solche Geschwindigkeiten oder Eigenschaften, z. B. Bewegungsmenge, translatorische und innere Energie, haben, als wären sie alle aus den Entfernungen, x_1, von den Flächen V_1 und V_2 gekommen; eine einfache Überlegung zeigt, dass x_1 proportional mit der mittleren freien Weglänge, λ, sein muss; wir setzen also:

$$2\,x_1 = k_1 \cdot \lambda, \quad \text{woraus} \quad x_1 = \frac{1}{2} \cdot k_1 \cdot \lambda.$$

Nach der einfachen kinetischen Gastheorie würde man erwarten, dass $x_1 = \lambda$ wäre, und also $k_1 = 2$. Es ist aber einleuchtend, dass der Wert von x_1, bezw. k_1, nicht derselbe sein wird für den Transport von Bewegungsmenge (innere Reibung der Gase) und kinetischer Energie (Wärmeleitung der Gase), weil in dem letzten Falle die Transportgeschwindigkeit und die transportierte Menge nicht von einander unabhängig sind[1]; dasselbe gilt auch für den Transport von der translatorischen Energie und der inneren Energie der Moleküle, wenn wir nach der Hypothese von Martin Knudsen annehmen werden, dass die innere Energie ganz unabhängig von der translatorischen Energie über die Moleküle verteilt ist, aber doch so, dass der mitt-

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[1] Es ist vielleicht nicht ohne Interesse den Energietransport in einem Gase näher zu betrachten. Für ein Gas mit der Temperatur T und N Molekülen per cm^3 ist der Energieinhalt per cm^3 an translatorische Energie, $N \cdot \frac{1}{2} m \overline{\Omega^2} = N \cdot \frac{3}{2} kT$ und an innere Energie, $f \cdot N \cdot \frac{3}{2} kT$; hierin ist $f = \frac{2}{3} \frac{1}{\varkappa - 1} - 1$, wo $\varkappa = \frac{c_p}{c_v}$.

Besteht im Gase ein Temperaturgradient, erhalten wir, dass der Energietransport für die translatorische Energie in der molekularen Wärmeleitung $\frac{4}{3} \cdot \frac{1}{2} m \overline{\Omega^2} = 2\,kT$ per Moleküle ist; dasselbe gilt auch für den Energietransport in der Molekularströmung; die Erklärung hierfür ist, wie bekannt, zu finden in der Abhängigkeit zwischen der Energie pro Moleküle $\frac{1}{2}$ m$\overline{\Omega^2}$ und der molekularen Transportgeschwindigkeit $\overline{\Omega}$ in Verband mit dem Maxwell'schen Verteilungsgesetz; für die innere Energie besteht nach der Hypothese von Martin Knudsen dieser Verband nicht, und in diesem Falle wird der Energietransport für die innere Energie per Moleküle $f \cdot \frac{3}{2} kT$; der ganze Energietransport per Moleküle wird also in der molekularen Wärmeleitung:

$$E = 2\,kT + f \cdot \frac{3}{2} kT = 2\,kT \left[1 + \frac{3}{4} \cdot f\right],$$

oder der Wert, den Knudsen angegeben hat.

Etwas besonderes ist es aber, dass die transportierte Energie per Moleküle für ein strömendes Gas in dem Maxwell'schen Zustand, z. B. in der Poiseulleströmung, nicht $\frac{3}{2} kT$ ist, sondern $\frac{5}{2} kT = \frac{3}{2} kT + kT$; die Erklärung hierfür ist, dass in dieser Strömung auch eine Arbeit $p \cdot v = kT$ durch das Querschnitt geht (vgl. Sophus Weber: Z. f. Ph. Bd. 24, 1924, p. 267).

lere Wert der einen dem mittleren Wert der andern proportional ist; ausserdem gilt für beide das Maxwell'sche Verteilungsgesetz.

Wenn wir vorläufig nur die translatorische Energie, bezw. einatomige Moleküle, betrachten, haben wir:

$$\Delta t = k_T \cdot \lambda \frac{dt}{dx}, \quad \text{woraus} \quad Q = k_T \cdot \varepsilon_T \cdot p \lambda \frac{dt}{dx}.$$

Die Wärmemenge, Q, ist aber in dem Maxwell'schen Zustand des Gases gleich an $K \frac{dt}{dx}$, wo K die bekannte Wärmeleitfähigkeit des Gases ist; diese ist, wie bekannt, unabhängig von dem Druck, wenn $\frac{\lambda}{d} \to 0$.

Wir erhalten also in dem stationären Zustand:

$$K = k_T \cdot \varepsilon_T \cdot p \lambda,$$

und in diesem Ausdruck sind alle Grössen bekannt mit Ausnahme von k_T.

Um den Wert von k_T zu bestimmen, ist es am einfachsten den gefundenen Wert für K mit dem Resultat von Chapman und Enskog für einatomige Gase in dem Maxwell'schen Zustande zu vergleichen. —

Wir nennen die spezifische Wärme bei konstantem Volumen für einatomige Gase, C_v, und für mehratomige Gase, c_v.

Aus der kinetischen Gastheorie folgt die bekannte Relation:

$$K = P \cdot c_v \cdot \eta,$$

die für einatomige Gase nach den Berechnungen von Chapman und Enskog wird:

$$K = \frac{5}{2} \cdot C_v \cdot \eta.$$

Wenn wir nun diese zwei Werte für K — z. B. bei 0° C — vergleichen, dann erhalten wir den Wert für k_T. —

Nach CHAPMAN haben wir:

$$\eta = 0.499 \frac{m\,\bar{\Omega}_0}{\sqrt{2}\cdot\pi\,\sigma^2} = \frac{1}{2}\,Nm\,\bar{\Omega}_0 \frac{1}{\sqrt{2}\cdot\pi\,\sigma^2\cdot N},$$

woraus:

$$\eta_0 = \frac{1}{2}\,Nm\,\bar{\Omega}_0\lambda_0 \text{ und } (p\,\lambda)_0 = \sqrt{\frac{\pi}{2}}\,\frac{\eta_0}{\sqrt{{}_1\varrho_0}},$$

weil:

$$Nm = {}_1\varrho_0\cdot p;\ \bar{\Omega}_0 = \sqrt{\frac{8}{\pi}}\,\frac{1}{\sqrt{{}_1\varrho_0}} \text{ und } \lambda = \frac{1}{\sqrt{2}\cdot\pi\,\sigma^2\cdot N}.$$

Für einatomige Gase, die nur translatorische Energie besitzen, haben wir nach KNUDSEN:

$$\varepsilon_T = \sqrt{\frac{2}{\pi}}\cdot\frac{1}{\sqrt{{}_1\varrho_0}}\cdot\frac{1}{T_0},$$

sodass wir bekommen:

$$K = k_T\cdot\varepsilon_T\cdot p\,\lambda = k_T\cdot\frac{\eta_0}{{}_1\varrho_0}\cdot\frac{1}{T_0}.$$

Aus der CHAPMAN-ENSKOG'schen Formel für einatomige Gase wird erhalten:

$$K = \frac{5}{2}\cdot\frac{3}{2}\cdot\frac{1}{T_0}\cdot\frac{1}{{}_1\varrho_0}\cdot\eta_0, \text{ weil } C_{v,\,0} = \frac{3}{2}\cdot\frac{1}{T_0}\cdot\frac{1}{{}_1\varrho_0}.$$

Hieraus folgt:

$$k_T = \frac{15}{4}.$$

§ 5. Bevor wir nun zu der Wärmeleitung für mehratomige Gase übergehen, werden wir erst den analogen Fall für den Transport von Bewegungsmenge (innere Reibung) betrachten; in diesem Falle würde man $k_1 = 2$ erwarten, weil die transportierte Menge und die Transportgeschwindigkeit von einander unabhängig sind.

In einer früheren Abhandlung über Wärmeleitfähigkeit von Gasgemischen[1] habe ich in Analogie mit der molekularen Wärmeleitung die molekulare Reibung, μ, in der folgenden Weise eingeführt:

Wir betrachten wieder zwei parallele Platten, V_1 und V_2, in einem Gase, wobei der Abstand der Platten sehr viel kleiner als die mittlere freie Weglänge, λ, sei; bewegt sich die Platte V_2 in ihrer eigenen Ebene mit der Geschwindigkeit, v, so wird per cm² und per Sek. an die Platte V_1 die Bewegungsmenge, M, übergeführt, wo:

$$M = \frac{1}{4} N m \overline{\Omega} v = \frac{1}{\sqrt{2\pi}} \cdot \sqrt{\frac{273 \cdot 1}{T}} \cdot \sqrt{{}_1\varrho_0} \cdot p \cdot v = \mu \cdot p \cdot v,$$

$$\text{wo } \mu = \frac{1}{\sqrt{2\pi}} \cdot \sqrt{\frac{273 \cdot 1}{T}} \cdot \sqrt{{}_1\varrho_0}$$

die molekulare Reibung ist.

Durch eine analoge Betrachtung, wie oben für die Wärmeleitung durchgeführt, in welcher nur $\frac{dt}{dx}$ durch $\frac{dv}{dx}$ ersetzt wird, erhalten wir:

$$\eta = k_\eta \cdot \mu \cdot p\lambda.$$

Vergleichen wir diesen Ausdruck mit dem obenerwähnten Ausdruck für η von CHAPMAN:

$$\eta_0 = \frac{1}{2} \cdot \frac{m\overline{\Omega}}{\sqrt{2} \cdot \pi\sigma^2} = \frac{1}{2} N m \overline{\Omega} \lambda = \frac{1}{2} \sqrt{\frac{8}{\pi}} \cdot \sqrt{{}_1\varrho_0} \cdot p\lambda,$$

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[1] SOPHUS WEBER: Ann. d. Ph., Bd. 54, (1917) p. 482.

dann erhalten wir:

$$k_\eta \cdot \mu_0 \cdot p\lambda = \sqrt{\frac{2}{\pi}}\sqrt{{}_1\varrho_0} \cdot p\lambda,$$

oder:

$$k_\eta = 2, \text{ weil } \mu_0 = \frac{1}{\sqrt{2\pi}}\sqrt{{}_1\varrho_0}.$$

In diesem Falle wird also $k_\eta = 2$, wie auch zu erwarten wäre.

Während wir für den Maxwell'schen Zustand der einatomigen Gase nach Chapman haben:

$$f'' = \frac{K}{C_v \cdot \eta} = \frac{k_T}{k_\eta} \cdot \frac{\varepsilon_T p\lambda}{\mu \cdot p\lambda} \cdot \frac{1}{C_v} = \frac{15}{8} \cdot \frac{\varepsilon_T}{\mu} \cdot \frac{1}{C_v} = \frac{5}{2},$$

erhalten wir für das Verhältnis f'' für einatomige Gase in dem Knudsen-Zustand der Gase[1]:

$$f'' = \frac{\varepsilon_T}{\mu \cdot C_v} = \frac{4}{3},$$

woraus hervorgeht, dass für $\frac{d}{\lambda} \geqq \infty$, $f'' = \frac{5}{2}$, während $f'' = \frac{4}{3}$ für $\frac{d}{\lambda} \geqq 0$.

§ 6. Wir werden nun zu den mehratomigen Gasen übergehen und gehen aus von der Hypothese von Knudsen. Nennen wir den mittleren Wert von der translatorischen Energie der Moleküle, e_1, und von der Atomenergie, e_2, dann haben wir:

$$\frac{e_1 + e_2}{e_1} = k_{1,2} = \frac{2}{3} \cdot \frac{1}{\frac{c_p}{c_v} - 1} = \frac{2}{3} \cdot \frac{1}{\varkappa - 1}.$$

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[1] Sophus Weber: Doktordisputats, København, 1916, p. 110.

Tabelle IV

	$K_0 \cdot 10^5$	$\eta_0 \cdot 10^5$	$(p\,\lambda)_{T_0}$	$\left(\frac{c_p}{c_v}\right)_{\text{theor.}}$	$\left(\frac{c_p}{c_v}\right)_{\text{beob.}}$	$\frac{K_0}{\varepsilon_0 \cdot p\,\lambda}$	$k'' = \frac{9\varkappa - 5}{\varkappa + 1}$	
He	34.3	18.76	17.72	$1 + \frac{2}{3}$	—	3.68	$\frac{15}{4} = 3.75$	mit $\varkappa = \frac{5}{3}$
Ne	11.12	29.11	12.56	„	—	3.76	„	
Ar	3.82	21.02	6.29	„	—	3.72	„	
H_2	41.3	8.50	11.31	$1 + \frac{2}{5}$	. .	3.34	$\frac{19}{6} = 3.17$	mit $\varkappa = \frac{7}{5}$
O_2	5.83	19.31	6.45	„	. .	3.22	„	
N_2	5.66	16.74	5.98	„	. .	3.17	„	
Luft	5.74	17.22	6.04	„	. .	—	„	
CO	5.37	16.65	5.94	„	. .	3.06	„	
CO_2	3.43	13.74	3.91	—	1.299^5	2.88	2.91	mit $\varkappa = 1{,}30$
N_2O	3.61	13.66	3.89	—	1.302	3.08	„	
CH_4	7.20	10.29	4.86	—	1.304	2.97	„	mit $\varkappa = 1{,}30$

Durch eine kritische Untersuchung von den Werten von K_0, η_0 und $\frac{c_p}{c_v}$ wäre es möglich, dass die Übereinstimmung noch etwas besser wird.

Betrachten wir nun wieder den Wärmetransport zwischen den zwei Flächen, V_1 und V_2, dürfen wir in diesem Falle, wie bereits oben erwähnt, nicht annehmen, dass der Abstand x_1 für die translatorische und die innere Energie derselbe ist; wir müssen also schreiben:

Für die translatorische Energie:

$$t_1 - t_2 = \Delta t = 2\, x_1 \cdot \frac{dt}{dx} = k_T \cdot \lambda \cdot \frac{dT}{dx},$$

und für die innere Energie:

$$t_1' - t_2' = \Delta t' = 2\, x_1' \cdot \frac{dt}{dx} = k_A \cdot \lambda \cdot \frac{dT}{dx},$$

woraus:

$$t_1' - t_2' = \frac{k_A}{k_T} (t_1 - t_2),$$

und für den totalen Energietransport im Gase:

$$Q = \varepsilon_T \cdot p\,(t_1 - t_2) + \varepsilon_A \cdot p\,(t_1' - t_2')$$

$$= (k_T \cdot \varepsilon_T + k_A \cdot \varepsilon_A) \cdot p\, \lambda \frac{dT}{dx} = K \cdot \frac{dT}{dx}.$$

Nach dem Vorhergehenden ist $k_T = \frac{15}{4}$; für die innere Energie müssen wir aber, wenn wir von der Hypothese von Knudsen ausgehen, in Analogie mit dem Transport von Bewegungsmenge (innere Reibung), $k_A = 2$ setzen, weil auch die innere Energie in diesem Falle unabhängig von der molekularen Transportgeschwindigkeit ist; wir erhalten hieraus:

$$Q = \left(\frac{15}{4} \varepsilon_T + 2\, \varepsilon_A\right) p\, \lambda \frac{dT}{dx} = K \frac{dT}{dx} = k'' \varepsilon\, p\, \lambda \frac{dT}{dx},$$

$$\text{wo } \varepsilon = \varepsilon_T + \varepsilon_A.$$

Nun ist aber: $\varepsilon_A = \frac{3}{4}\cdot f\cdot\varepsilon_T$, wo $f = \frac{2}{3}\cdot\frac{1}{\varkappa - 1} - 1$, und man bekommt also hieraus für mehratomige Gase:

$$K = k''\cdot\varepsilon\cdot p\lambda = \frac{9\varkappa - 5}{\varkappa + 1}\cdot\varepsilon\cdot p\lambda,$$

$$\text{oder } k''_{\text{teor.}} = \frac{9\varkappa - 5}{\varkappa + 1}.$$

Wir können nun diesen theoretischen Wert, $k''_{\text{teor.}} = \frac{9\varkappa - 5}{\varkappa + 1}$, vergleichen mit dem experimentellen Wert, $k''_{\text{obs.}} = \frac{K}{\varepsilon p\lambda}$; das Resultat wird in der Tabelle IV gesehen.

Aus der Tabelle IV sehen wir, dass die Übereinstimmung zwischen dem experimentellen Wert: $k''_{\text{obs.}} = \frac{K}{\varepsilon p\lambda}$ und dem theoretischen Wert: $k''_{\text{teor.}} = \frac{9\varkappa - 5}{\varkappa + 1}$ sehr befriedigend ist, sowohl für einatomige, als für mehratomige Gase, und wir dürfen also hieraus schliessen, dass der verwendete Wert, $k_A = 2$, auch für diesen Fall richtig ist.

§ 7. Wir können nun auch für mehratomige Gase den Faktor P in der Formel:

$$K = P\cdot c_v\cdot\eta \tag{3}$$

bestimmen.

Setzen wir in dieser Formel die gefundenen Werte für K und η ein, dann bekommen wir:

$$\frac{9\varkappa - 5}{\varkappa + 1}\cdot\frac{1}{4}\sqrt{\frac{2}{\pi}}\cdot\frac{\varkappa + 1}{\varkappa - 1}\cdot\frac{1}{\sqrt{{}_1\varrho_0}}\cdot\frac{1}{T_0}\cdot p\lambda = P\cdot c_v\cdot\sqrt{\frac{2}{\pi}}\sqrt{{}_1\varrho_0}\cdot p\lambda,$$

weil nach Knudsen:

$$\varepsilon = \varepsilon_T + \varepsilon_A = \varepsilon_T\left(1 + \frac{3}{4}f\right) = \frac{1}{4}\sqrt{\frac{2}{\pi}} \cdot \frac{\varkappa + 1}{\varkappa - 1} \cdot \frac{1}{\sqrt{{}_1\varrho_0}} \cdot \frac{1}{T_0}.$$

Wo aber:

$$c_v = C_v \cdot \frac{\frac{2}{3}}{\varkappa - 1} = \frac{3}{2} \cdot \frac{1}{{}_1\varrho_0} \cdot \frac{1}{T_0} \, \frac{\frac{2}{3}}{\varkappa - 1},$$

erhalten wir:

$$P = \frac{1}{4}(9\varkappa - 5). \tag{4}$$

Dieser Ausdruck von P ist bereits von A. Eucken[1] angegeben; ausgehend von der Knudsen'schen Hypothese, dass die innere Energie unabhängig von der translatorischen Energie über die Moleküle verteilt ist, nimmt Eucken an, dass die Wärmeleitung für mehratomige Gase geschrieben werden kann:

$$K = \frac{5}{2} \cdot c_t \cdot \eta + c_r \cdot \eta;$$

c_t und c_r bezeichnen den der Translationsenergie bezw. Rotationsenergie entsprechenden Anteil der spezifischen Wärme bei konstantem Volumen, woraus allgemein:

$$c_t + c_r = c_v.$$

Man hat aber:

$$c_t = C_v \text{ und } c_r = C_v \cdot \frac{\frac{5}{3} - \varkappa}{\varkappa - 1}, \text{ woraus:}$$

$$K = \frac{1}{4}(9\varkappa - 5)\, c_v \cdot \eta. \tag{5}$$

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[1] A. Eucken: Phys. Z. XIV, 1913 p. 324.

Die Übereinstimmung zwischen dem theoretischen Wert für $P = \frac{1}{4}(9\varkappa - 5)$ und dem observierten Wert $\frac{K}{c_v \cdot \eta}$ ist, wie bekannt, besonders schön (Vgl. JEANS: Theory of Gases, 1925, Tabelle auf Seite 301).

Hieraus geht also auch hervor, dass der Wert von $k_A = 2$ richtig ist.

Es ist vielleicht in diesem Verband nicht ohne Interesse zu erwähnen, dass man für mehratomige Gase in dem Knudsen-Zustand erhält:

$$P_{\to 0} = \frac{\varepsilon_T + \varepsilon_A}{\mu \cdot c_v} = \frac{1}{2}(\varkappa + 1).$$

§ 8. Wir werden nun, nachdem k_T und k_A in dieser Weise bestimmt sind, den theoretischen Wert für den Temperatursprung betrachten, indem wir untersuchen werden, wie der Wärmeaustausch bei der Platte A, Fig. 1, vonstatten geht; erst untersuchen wir diesen Fall für ein einatomiges Gas.

Bei der Platte, A, hat man eine Gruppe von einströmenden und eine Gruppe von zurückgeworfenen Molekülen; wir nennen für die erste Gruppe die mittlere Geschwindigkeit der Moleküle Ω'_1 und die entsprechende Temperatur t_1; für die zweite Gruppe sind die entsprechenden Grössen Ω'_2 und t_2; ist die Temperatur der Platte, T_1 hat man nach der Definition des Akkommodationskoefficienten, a:

$$\overline{\Omega}'^2_2 = \overline{\Omega}'^2_1 + a\,(\overline{\Omega}^2_1 - \overline{\Omega}'^2_1)$$

$$\text{oder } 'E_2 = 'E_1 + a\,(E_1 - 'E_1)$$

$$\text{oder } \quad t_2 = t_1 + a\,(T_1 - t_1),$$

$$\text{weil } \frac{1}{2} m\,\overline{\Omega}^2 = E = \frac{3}{2} kT.$$

Die Temperatur der an der Platte A grenzenden Gasschicht wird dann $t = \frac{1}{2}(t_1 + t_2)$, und der Temperatursprung:

$$\Delta T = T_1 - t = T_1 - \frac{1}{2}(t_1 + t_2),$$

oder:

$$\Delta T = \frac{2 - a}{2\,a}(t_1 - t_2).$$

Die von der Platte A, pro Sek. und cm², weggeführte Wärmemenge, wird:

$$Q = \varepsilon_T \cdot p\,(t_1 - t_2) = K\,\frac{dT}{dx} = k_T \cdot \varepsilon_T \cdot p\,\lambda\,\frac{dT}{dx},$$

woraus:

$$t_1 - t_2 = k_T \cdot \lambda \cdot \frac{dT}{dx}, \quad \text{mit} \quad k_T = \frac{15}{4}.$$

Hieraus erhalten wir:

$$\Delta T = \frac{2 - a}{2\,a}\,k_T \cdot \lambda\,\frac{dT}{dx} = \frac{15}{4} \cdot \frac{2 - a}{2\,a} \cdot \lambda\,\frac{dT}{dx} \tag{6}$$

oder genau die Formel von SMOLUCKOWSKI für einatomige Gase.

Wir gehen nun zu den mehratomigen Molekülen über und betrachten wieder den Wärmeaustausch bei der festen Wand A; für die Moleküle der einströmenden Gruppe dürfen wir, wenn der Wärmezustand stationär ist, annehmen, dass die translatorische und innere Energie in Temperaturgleichgewicht (Äquipartition) sind, weil die Moleküle kommen aus einer Gasmasse in dem Maxwell'schen Zustand; in diesem Falle entspricht sowohl die translatorische als die innere Energie der Temperatur t_1. Wenn diese Moleküle gegen die feste Wand A stossen, sind zwei Möglichkeiten vorhanden, d. h. entweder ist der Akkommodationskoefficient für die zwei Sorten Energie derselbe, oder man muss mit verschiedenen Akkommodationskoefficienten für die zwei Sorten Energie rechnen. Der erste Fall ist nach den Untersuchungen von Martin Knudsen[1] der wahrscheinlichste, weil er durch seine Arbeit über Radiometerkraft und Wärmeleitung in Helium und Wasserstoff für blanke und »schwarze« Oberflächen nachgewiesen hat, dass der Akkommodationskoefficient für die translatorische und die innere Energie der Wasserstoffmoleküle derselbe ist; in diesem Falle ist es deutlich, dass der Gleichgewichtszustand zwischen der translatorischen und inneren Energie in der einströmenden Molekülgruppe nach der Zurückwerfung nicht gestört sein wird; für die Moleküle in der ausgehenden Gruppe wird also auch Temperaturgleichgewicht zwischen den zwei Sorten Energie herrschen, und beide werden der Temperatur, t_2, entsprechen.

Bei der Berechnung des Temperatursprunges kann man in diesem Falle entweder den Energieaustausch für die gesammte Energie oder für eine der zwei Sorten, z. B. die translatorische Energie, untersuchen.

Wenn wir erst den Energieaustausch für die translatorische Energie untersuchen, dann erhalten wir genau dieselbe Berechnung wie für einatomige Gase und finden also wieder die Formel von Smoluckowski; wir können dieses am einfachsten zeigen, wenn wir von der obengenannten Hypothese von Eucken ausgehen. Der Teil der Wärmeleitung, der nur von der translatorischen Energie herrührt, ist nach Eucken:

$$K_t = K - c_r \cdot \eta, \text{ weil } K = \frac{5}{2} c_t \cdot \eta + c_r \cdot \eta .$$

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[1] Martin Knudsen: Kgl. D. Vid. Selsk., Mat. fys. Medd. XI. I. 1930.

Nun ist nach dem Vorhergehenden:

$$c_t + c_r = c_v = C_v \frac{\frac{2}{3}}{\varkappa - 1} = C_v k_{1,2},$$

wo aber:

$$c_t = \frac{c_v}{k_{1,2}}, \text{ wird } c_t = C_v,$$

woraus:

$$K_t = \frac{5}{2} \cdot C_v \cdot \eta.$$

Laut der Transportgleichung haben wir:

$$Q_T = \varepsilon_T \cdot p\,(t_1 - t_2) = \frac{5}{2} \cdot C_v \cdot \eta \cdot \frac{dT}{dx},$$

woraus:

$$t_1 - t_2 = \frac{\frac{5}{2} \cdot \eta \cdot C_v}{\varepsilon_T \cdot p} \cdot \frac{dT}{dx} = \frac{15}{4} \lambda \frac{dT}{dx}.$$

Wo der Temperatursprung gegeben ist durch:

$$\varDelta T = \frac{2 - a}{2\,a} (t_1 - t_2),$$

erhalten wir auch in diesem Falle:

$$\varDelta T = \frac{15}{4} \cdot \frac{2 - a}{2\,a} \cdot \lambda \frac{dT}{dx}.$$

Betrachten wir noch eben in diesem Falle den Austausch der totalen Energie; wir können wieder für den Energieaustausch bei der festen Wand schreiben:

$$'E_2 = {}'E_1 + a\,[E_1 - {}'E_1],$$

wobei vorausgesetzt ist, dass der Akkommodationskoefficient, a, derselbe ist für die zwei Sorten Energie; werden die entsprechenden Temperaturen, bezw. t_1 und t_2, der Molekülgruppen eingeführt, erhält man wieder:

$$t_2 = t_1 + a(T_1 - t_1),$$

und für den Temperatursprung:

$$\Delta T = \frac{2-a}{2a}(t_1 - t_2).$$

Die Gleichung für den Energieaustausch bei der festen Wand wird in diesem Falle:

$$Q = \varepsilon_T \cdot p(t_1 - t_2) + \varepsilon_A \cdot p(t'_1 - t'_2);$$

wo nach dem Vorhergehenden:

$$t_1 - t_2 = k_T \cdot \lambda \frac{dT}{dx} \text{ und } t'_1 - t'_2 = k_A \cdot \lambda \frac{dT}{dx}.$$

Hieraus folgt:

$$Q = \varepsilon_T \cdot p(t_1 - t_2) + \varepsilon_A \cdot \frac{k_A}{k_T}(t_1 - t_2) = K \frac{dT}{dx}.$$

Nun ist aber:

$$K \frac{dT}{dx} = (k_T \varepsilon_T + k_A \varepsilon_A)\, p \lambda \frac{dT}{dx},$$

woraus:

$$t_1 - t_2 = \frac{k_T \varepsilon_T + k_A \cdot \varepsilon_A}{\varepsilon_T + \frac{k_A}{k_T} \cdot \varepsilon_A} \cdot \lambda \frac{dT}{dx} = k_T \cdot \lambda \frac{dT}{dx}$$

und also auch für mehratomige Gase:

$$\Delta T = k_T \cdot \frac{2-a}{2a} \lambda \frac{dT}{dx} = \frac{15}{4} \cdot \frac{2-a}{2a} \cdot \lambda \frac{dT}{dx}.$$

Wir sehen hieraus, dass diese theoretischen Betrachtungen zeigen, dass der Faktor, k_T, in der Formel für den Temperatursprung derselbe ist für ein- und mehratomige Gase, wenn der Akkommodationskoefficient für die translatorische und die innere Energie derselbe ist; umgekehrt dürfen wir annehmen, dass, wenn wir für ein Gas mit bekanntem Akkommodationskoefficienten, a, den Faktor $k_T = \frac{15}{4}$ experimentell finden, der Akkommodationskoefficient für die translatorische und die innere Energie nicht wesentlich verschieden ist.

Nach Tabelle III ist dies also der Fall für die bis nun untersuchten Gase.

Hätte man in den obenstehenden Berechnungen nicht den Unterschied zwischen k_T und k_A berücksichtigt, sondern $k_T = k_A$ gesetzt, dann hätte man erhalten:

$$K\frac{dT}{dx} = (\varepsilon_T + \varepsilon_A)\cdot p\,(t_1 - t_2) = Q\,,$$

woraus:

$$k''\,(\varepsilon_T + \varepsilon_A)\,p\,\lambda\,\frac{dT}{dx} = (\varepsilon_T + \varepsilon_A)\,p\,(t_1 - t_2),$$

und also:

$$t_1 - t_2 = k''\cdot\lambda\,\frac{dT}{dx},$$

wo:

$$k'' = \frac{9\varkappa - 5}{\varkappa + 1}.$$

In diesem Falle würde also der Faktor, k_n, in der Formel für den Temperatursprung:

$$\varDelta T = k_n\,\frac{2-a}{2a}\,\lambda\,\frac{dT}{dx},$$

sich ändern mit dem Wert von $\varkappa$; die obenstehende Formel mit $k_n = k'' = \frac{9\varkappa - 5}{\varkappa + 1}$ ist von H. S. Gregory[1] abgeleitet. —

Diese Ableitung ist also nach dem Obenstehenden nicht einwandfrei und auch nicht in Übereinstimmung mit den experimentellen Ergebnissen (vgl. Tabelle III). —

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[1] H. Spencer Gregory: Phil. Mag. (7) 22, 257, 1936.

Offen bleibt noch die Frage, wie die Formel für den Temperatursprung sich ändern würde, wenn die Akkommodationskoefficienten für die translatorische und die innere Energie der Moleküle verschieden wären; in diesem Falle ist die mittlere, translatorische und innere Energie in der Gruppe von den zurückgeworfenen Molekülen nicht in Temperaturgleichgewicht, und es wird dann die Frage sein, welche mittlere Temperatur dieser Molekülgruppe zugemessen werden muss; nach der obenerwähnten Untersuchung von Martin Knudsen und dem Resultat in der Tabelle III, ist dieser Fall wohl wenig wahrscheinlich, und es hat darum vorläufig keinen Zweck hierüber theoretische Betrachtungen anzustellen.

§ 9. Aus den experimentellen Untersuchungen von Gehrcke und Lazareff ist hervorgegangen, dass der Ausdruck $\frac{\gamma}{\lambda}$ nur konstant ist, wenn das Gas in dem Maxwell'schen Zustand ist, also wenn $\frac{d}{\lambda} \rightarrow \infty$; laut dem Experiment stellt es sich heraus, dass $\frac{\gamma}{\lambda}$ abnimmt, wenn $\frac{d}{\lambda}$ kleiner wird.

Weil Gehrcke, wie auch Lazareff mit zwei parallelen Platten gearbeitet haben, wird es zweckmässig sein erst den Verlauf von dem Temperatursprung, bezw. Wärmeleitung und Temperaturverteilung zwischen zwei planparallelen Platten näher zu betrachten.

Betrachten wir, wie in Fig. 1, zwei planparallele Platten A und B mit den Temperaturen T_1 und T_2 und den Akkommodationskoefficienten a_1 und a_2, dann erhalten wir, wenn wir den Abstand zwischen den Platten, d, nennen, und wenn $\frac{d}{\lambda} \rightarrow \infty$, für den Temperatursprung:

$$\text{bei der Platte } A\colon\ \varDelta T_1 = T_1 - T_1' = k_T \frac{2 - a_1}{2\,a_1} \cdot \lambda \cdot \frac{dT}{dx},$$

und bei der Platte B: $\Delta T_2 = T_2' - T_2 = k_T \frac{2 - a_2}{2\,a_2} \cdot \lambda \cdot \frac{dT}{dx}$,

$$\text{wo } k_T = \frac{15}{4}.$$

$\frac{dT}{dx}$ ist der Temperaturgradient im Gase dort, wo der gewöhnliche Maxwell'sche Zustand gilt; wir können also in der Mitte zwischen den Platten setzen:

$$\left(\frac{dT}{dx}\right)_{x=\frac{d}{2}} = \frac{T_1' - T_2'}{d} = \frac{1}{1 + \frac{1}{2} k_T \left[\frac{2 - a_1}{2\,a_1} + \frac{2 - a_2}{2\,a_2}\right] \cdot \frac{\lambda}{d}} \cdot \frac{T_1 - T_2}{d}. \tag{7}$$

Wir sehen hieraus, dass wir eine Abnahme von $\frac{\Delta T}{\lambda}$ bezw. $\frac{\gamma}{\lambda}$ erwarten müssen, wenn die Grösse:

$$\frac{1}{2} k_T \left[\frac{2 - a_1}{2\,a_1} + \frac{2 - a_2}{2\,a_2}\right] \cdot \frac{\lambda}{d}$$

nicht mehr gegenüber 1 verschwindend klein ist, sowie dieses auch von Gehrcke experimentell nachgewiesen ist.

Betrachten wir die Wärmeleitung zwischen den Platten, erhalten wir:

$$Q = K \cdot \frac{dT}{dx} = K \frac{1}{1 + \frac{1}{2} k_T \left[\frac{2 - a_1}{2\,a_1} + \frac{2 - a_2}{2\,a_2}\right] \cdot \frac{\lambda}{d}} \cdot \frac{T_1 - T_2}{d}, \tag{8}$$

welche Formel für $a_1 = a_2$ bereits von Martin Knudsen[1] angegeben ist.

Aus der Formel (7) können wir sehen, wie $\frac{dT}{dx}$ zwischen den Platten sich mit $\frac{\lambda}{d}$ ändert, und diese Formel können

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[1] Martin Knudsen: loc. cit. pag. 656.

wir durch die Messungen von Lazareff über den Temperaturverlauf zwischen den Platten nachprüfen.

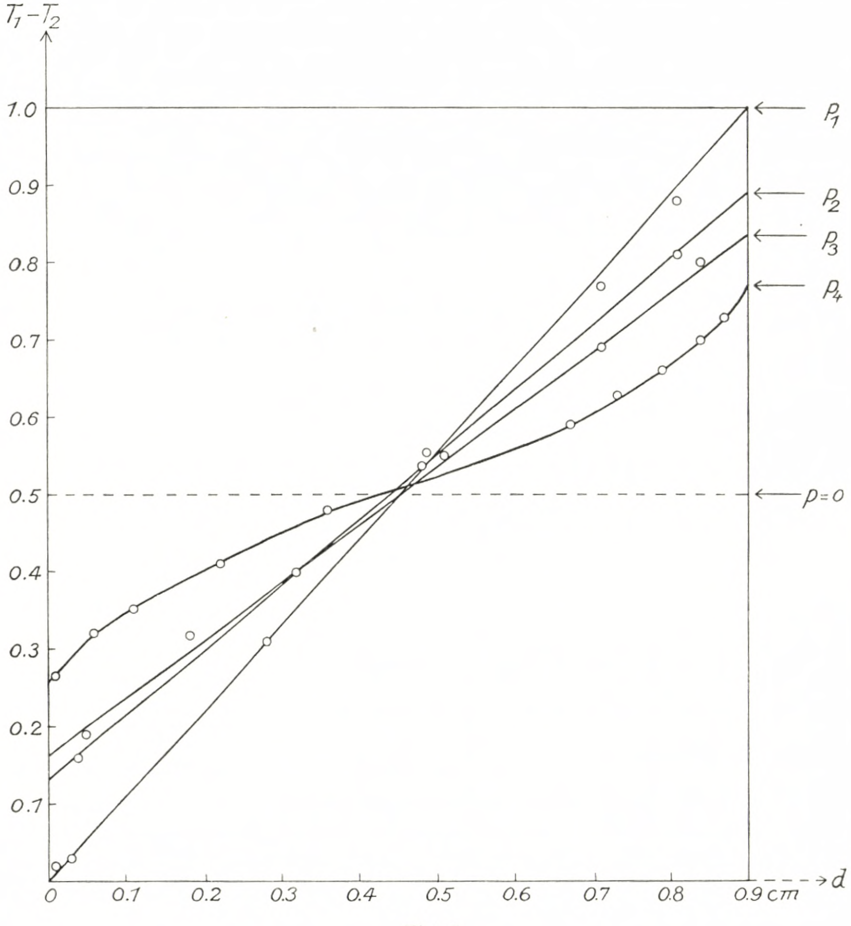

Fig. 2.

Lazareff[1] untersuchte mittels direkten Temperaturmessungen zwischen zwei Platten mit dem Abstand $d = 0.90$ cm den Temperaturverlauf zwischen den Platten; er verwendete atmosphärische Luft und bestimmte u. A. den Temperaturverlauf bei den Drücken:

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[1] P. Lazareff: loc. cit.

$$
\begin{aligned}
p_1 &= 760{,}0 \text{ mm Hg}\\
p_2 &= 0{,}087 \text{ mm Hg}\\
p_3 &= 0{,}065 \text{ mm Hg}\\
p_4 &= 0{,}019 \text{ mm Hg}
\end{aligned}
$$

Die Platten hatten denselben Akkommodationskoefficient, und bei hohem Druck fand Lazareff für atm. Luft $\frac{\gamma}{\lambda} = 2{,}70$, woraus:

$$\frac{15}{4} \cdot \frac{2-a}{2a} = 2{,}70 \text{ oder } a = 0{,}82,$$

wie auch zu erwarten wäre für atm. Luft und glatte Oberflächen.

Die Resultate der Temperaturmessungen sind in Fig. 2 graphisch wiedergegeben, nachdem diese auf einem Temperaturunterschied, $T_1 - T_2 = 1^\circ$ C, umgerechnet sind.

Aus diesen Kurven ist es einfach $\frac{dT}{dx}$ in dem Gebiet, wo das Gas in dem Maxwell'schen Zustand ist, zu bestimmen; diese Werte sind in der Tabelle V in der Kolonne $\left(\frac{dT}{dx}\right)_{\text{obs.}}$ wiedergegeben. Aus Formel (7) lässt sich nun für jeden Druck den Wert von $\frac{dT}{dx}$ berechnen; die auf diese Weise berechneten Werte für die Drücke p_1, p_2, p_3, und p_4 sind in der Tabelle unter $\left(\frac{dT}{dx}\right)_{\text{ber.}}$ angegeben.

Tabelle V

Atm. Luft, p in mm Hg		$\left(\frac{dT}{dx}\right)_{\text{obs.}}$ nach Lazareff	$\left(\frac{dT}{dx}\right)_{\text{ber.}}$ nach Form. 7.
$p_1 =$	760,0 mm	1,111	1,111
$p_2 =$	0,087 „	0,850	0,830
$p_3 =$	0,065 „	0,775	0,760
$p_4 =$	0,019 „	0,425	0,430
$p =$	0	—	0

Wir sehen hieraus, dass die Übereinstimmung zwischen $\left(\frac{dT}{dx}\right)_{\text{obs.}}$ und $\left(\frac{dT}{dx}\right)_{\text{ber.}}$ sehr befriedigend ist.

Aus der theoretischen Formel (7) geht hervor, dass für $p \rightarrow 0$, $\frac{dT}{dx} = 0$ wird; d. h. dass die Temperatur des Gases zwischen den Platten in diesem Falle konstant wird. Nennen wir die Temperatur x, dann finden wir für diesen Fall:

$$\frac{T_1 - x}{x - T_1} = \frac{2 - a_1}{2 - a_2} \cdot \frac{a_2}{a_1} \quad \text{oder}$$

$$T_1' = T_2' = x = \frac{1}{2} \cdot \frac{a_1 (2 - a_2) T_1 + a_2 (2 - a_1) T_2}{a_1 + a_2 - a_1 a_2}.$$

Ist $a_1 = a_2$ wird $x = \frac{1}{2}(T_1 + T_2)$; dieses wird auch bestätigt durch die Messungen von Mandell und West[1] bei den allerniedrigsten Drücken; die gefundenen kleinen Abweichungen können vollständig durch den Einfluss der Strahlung erklärt werden.

Die hier abgeleitete Formel für den Verlauf des Temperatursprunges findet sofort ihre Verwendung in der theoretischen Behandlung von dem absoluten Manometer von Martin Knudsen und von den experimentellen Untersuchungen von Martin Knudsen[2] und R. H. E. Rasmussen[3] über das Radiometereffekt von einem geheissten Band, wovon die zwei Seiten verschiedene Akkommodationskoefficienten haben. —

Obwohl m.W. keine vollständigen Messungsreihen für den Verlauf von dem totalen Wärmetransport zwischen zwei parallelen Platten in dem ganzen Gebiet $0 \leqq \frac{d}{\lambda} \leqq \infty$ vorliegen, werde ich in einer späteren Abhandlung auf dem Zusam-

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[1] Mandell und West: loc. cit.

[2] Martin Knudsen: Kgl. Danske Vid. Selsk. XI, 1, 1930.

[3] R. H. E. Rasmussen: Kgl. Danske Vid. Selsk. XI, 9, 1932 und XIII, 9, 1935.

menhang zwischen der totalen Wärmeleitung und dem Temperatursprung zwischen parallelen Platten und coaxialen Cylindern zurückkommen; für coaxiale Cylinder, bezw. ein dünnes Platinband, ausgespannt in der Achse eines umgebenden Glascylinders, liegt ein besseres und ziemlich vollständiges Versuchsmaterial vor. —

Zusammenfassung.

Ausgehend von der von Martin Knudsen angegebenen Relation zwischen der Maxwell'schen Wärmeleitfähigkeit, K, und der molekularen Wärmeleitfähigkeit, ε:

$$K = k \cdot \varepsilon \cdot p \cdot \lambda,$$

worin p der Druck und λ die mittlere freie Weglänge des Gases nach Chapman sind, wird erst für den Transport der translatorischen Energie die Konstante k in dieser Formel bestimmt durch Vergleichung mit der bekannten Chapman-Enskog'schen Formel für einatomige Gase:

$$K = \frac{5}{2} \cdot C_v \cdot \eta .$$

Für die translatorische Energie wird $k = k_T = \frac{15}{4}$ und für die innere Energie $k = k_A = 2$.

In Anschluss hieran wird der Temperatursprung, ΔT, bei einer Oberfläche mit dem Akkommodationskoefficienten, a, sowohl für einatomige, als für mehratomige Gase abgeleitet; geltend für alle Gase wird gefunden:

$$\Delta T = \frac{15}{4} \cdot \frac{2 - a}{2\,a} \cdot \lambda \cdot \frac{dT}{dx}.$$

In dieser Formel ist $\frac{dT}{dx}$ der Temperaturgradient in der Richtung der Normale an der Oberfläche, während λ durch die innere Reibung der Gase, η, bestimmt ist nach der CHAPMAN'schen Formel:

$$\eta = 0{,}499\, N \cdot m \cdot \overline{\Omega} \lambda = \frac{1}{2}\, N m \overline{\Omega} \lambda$$

Die Formel für $\varDelta T$ wird mit dem früheren und mit dem Beobachtungsmaterial des Verfassers, unter Benutzung von den bekannten Werten des Akkommodationskoefficienten, verglichen; die Übereinstimmung ist sowohl für einatomige, wie auch für mehratomige Gase, sehr befriedigend, sodass es hierdurch möglich wird den Akkommodationskoefficienten, a, aus einer Messung des Temperatursprunges zu bestimmen, während es aus dem Wert des Temperatursprunges bei bekanntem Wert von a möglich ist zu sehen, inwieweit die Akkommodationskoefficienten für die translatorische Energie und die innere Energie des Gases wesentlich von einander abweichen.

In Analogie mit dem molekularen Wärmeleitvermögen, ε, wird die molekulare Reibung, μ, definiert; die Ableitung gibt:

$$\mu = \frac{1}{\sqrt{2\pi}} \sqrt{\frac{273 \cdot 1}{T}}\, \sqrt{{}_1\varrho_0} \quad \text{und} \quad \eta = k_\eta \cdot \mu \cdot p \lambda,$$

Mit $k_\eta = 2$ erhält man $\eta = \frac{1}{2} N m \overline{\Omega} \lambda$ in Übereinstimmung mit CHAPMAN.

Aus der molekularen Wärmeleitfähigkeit, ε, und aus dem Ausdruck für die molekulare Reibung, μ, wird für mehratomige Gase den Wert von der Konstante, P, in der bekannten Formel:

$$K = P \cdot c_v \cdot \eta,$$

theoretisch abgeleitet.

Wird $\frac{c_p}{c_v} = \varkappa$ gesetzt, erhält man:

$$P = \frac{1}{4}(9\varkappa - 5),$$

in Übereinstimmung mit der Hypothese von A. Eucken und den Zahlenwerten.

Ausserdem wird, gültig für alle Gase, die Relation:

$$\frac{K}{\varepsilon \cdot p\lambda} = \frac{9\varkappa - 5}{\varkappa + 1},$$

abgeleitet und durch die bekannten Zahlenwerte nachgeprüft; die Übereinstimmung ist sehr befriedigend.

Zum Schluss wird der Temperaturverlauf zwischen zwei parallellen Platten mit Abstand, d, und Temperaturdifferenz $T_1 - T_2$, unter Verwendung der Formel für den Temperatursprung, abgeleitet; ist der Akkommodationskoefficient, a, für beide Oberflächen derselbe, erhält man in der Mitte zwischen den Platten:

$$\frac{dT}{dx} = \frac{T_1 - T_2}{d} \cdot \frac{1}{1 + \frac{15}{4} \cdot \frac{2-a}{2a} \cdot \frac{\lambda}{d}},$$

welcher Ausdruck durch die Lazareff'schen Messungen bestätigt wird. —

Auch bei dieser Gelegenheit möchte ich der Direktion des Dänischen Carlsbergfonds meinen Dank für gewährte Stütze aussprechen.

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DE THERMODYNAMISKE HOVEDSÆTNINGERS GRUNDLAG OG FORMULERING

AF

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1. Indledning.

I et foregaaende Arbejde[1] er der gjort et Forsøg paa en almindelig Karakteristik af de energetiske Fænomener, saaledes som de erfaringsmæssigt fremstiller sig for Iagttageren. Det var Grundtanken i dette Forsøg, at en i Naturen indtrædende Forandring af et stofligt System, der befinder sig i Hvile, altid er betinget af, og for de reversible Grænsetilfældes Vedkommende alene bestaar i, en Transport af energetiske Kvantiteter mellem Tilstande, der er kendetegnede ved deres energetiske Potentialer. En saadan Kvantitetstransport betegnedes derfor som en energetisk Grundproces. Det kunde godtgøres, at Studiet af de energetiske Fænomener ud fra dette Synspunkt frembød væsentlige Fordele, specielt kunde det vises paa Grundlag heraf, at der fandtes en simplere og mere harmonisk Relation mellem Varme og Arbejde end den hidtil i Thermodynamiken antagne.

Hvad der i særlig Grad kendetegner den nævnte Behandling af de energetiske Problemer, er den Symmetri, hvormed de forskelligartede Elementer indtræder i Beskrivelsen af Fænomenerne, og den formelle Almindelighed, der derved kommer til at beherske de tilhørende mathematiske Relationer. Erkendelsen af denne Symmetri fører

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[1] J. N. Brønsted: Om Relationen mellem Varme og Arbejde. D. kgl. danske Vidensk. Selsk. Math.-fys. Meddelelser, XV, 4 (1937).

til en simpel Skematisering indenfor Energetiken og bidrager til paa frugtbar Maade at overføre Synspunkter og Erfaringer fra et energetisk Omraade til et andet.

Det er nærværende Afhandlings Formaal udfra det beskrevne Betragtningsgrundlag at naa til en præcis og harmonisk Formulering af de energetiske Hovedsætninger, idet der herved betegnes de Principer af alment og omfattende Indhold, hvorved de i Naturen foregaaende makroskopiske Forandringer beskrives. At der ved Opstillingen af dette energetiske System i visse Henseender vil vise sig Afvigelser fra den traditionelle Thermodynamik, kan ventes allerede udfra den bestaaende Forskel i Opfattelsen af Varme-Arbejds-Relationen, som der ovenfor er hentydet til. Denne Forskel vil ogsaa i nærværende Afhandling blive gjort til Genstand for udførlig Betragtning, idet det ifølge Sagens Natur er vigtigt, at saadanne Afvigelser fra tidligere Synspunkter fremtræder med størst mulig Klarhed.

Til Gennemførelsen af dette Forsøg kræves i forskellige Retninger en videre Udbygning af Systemet i Detaljer og nøjere Definitioner af indgaaende Begreber. Navnlig gælder dette de thermiske Begreber, saavel Varme som Entropi og Temperatur. En væsentlig Del af Afhandlingen beskæftiger sig med Spørgsmaal af denne Art.

Det skal bemærkes, at der efter Thermodynamikens Grundlæggelse ved Mayer, Joule, Clausius og William Thomson og efter Fæstnelsen og Anerkendelsen af dette klassiske thermodynamiske System fra visse Sider har været forsøgt at indføre nye Synspunkter til Opnaaelse af formelle Simplifikationer i de thermodynamiske Problemers almindelige Behandling. Hidtil har disse Forsøg dog været uden større Held. Særlig maa den »Energetik«, som er opbygget af Wilhelm Ostwald, siges at have lidt

Skibbrud overfor Klassicismens energisk haandhævede Standpunkt. Der skal dog ikke lægges Skjul paa, at dette Resultat for en væsentlig Del skyldes Svagheden i den detaljerede Gennemførelse af Systemet, snarere end i dets grundlæggende Ide. Det kan derfor ikke paa Forhaand betragtes som udelukket, at fortsatte Bestræbelser for Simplifikation af Thermodynamikens Methode kan føre til brugbare Resultater.

Specielt maa den for det OSTWALD'ske System karakteristiske Spaltning af Energien i to Faktorer af væsensforskellige Egenskaber, som vistnok kan siges i særlig Grad at være kommen i Miskredit, allerede her betegnes som en Betragtning, der er af væsentlig Betydning for den thermodynamiske Methodik. Den er i nøje Overensstemmelse med Grundtanken ogsaa i nærværende Afhandlings Forsøg paa en simplificeret og rationaliseret Fremstilling af de energetiske Grundfænomener.

2. Det almindelige Arbejdsbegreb. Arbejdsprincipet.

Det almindelige Arbejdsbegreb er opstillet paa Grundlag af det mekaniske Arbejdsbegreb udfra Analogibetragtninger. Efter Mekanikens Terminologi er der til Transporten af en Massepartikel mellem to faste Punkter i et Kraftfelt knyttet et »Arbejde«, som under konstante Betingelser, d. v. s. naar Partiklen er tilstrækkelig lille til ikke kendeligt at paavirke Kraftfeltet, og idet den Vej, ad hvilken Partiklen transporteres fra Begyndelsespunktet 1 til Slutningspunktet 2, holdes uforandret, er proportional med den transporterede Masse. Under disse simple Betingelser vil altsaa følgende Ligning være gyldig:

$$\delta A = (\varphi_1 - \varphi_2)\, \delta m, \tag{1}$$

hvor δA er Arbejdet, nærmere bestemt Arbejdstabet, ved den betragtede Transport, δm den transporterede Masse og $\varphi_1 - \varphi_2$ en Størrelse, der er bestemt ved Beliggenheden af de faste Punkter, mellem hvilke Partiklen bevæger sig gennem Feltet. Dette er en Arbejdsdefinition for de specielt betragtede Processer, i hvilke alene Massen er variabel. Er Kraftens Retning fra 1 til 2, siges Differensen $\varphi_1 - \varphi_2$ at være positiv, Arbejdstabet δA i Ligning (1) vil i saa Fald ogsaa være positivt. Selve Transporten vil vi betegne som den mekaniske Grundproces.

Ligning (1) tillader Sammenligning af Arbejder, der er knyttet til Transporten af forskellige Masser ad samme Bane. Til Opstilling af det almindelige mekaniske Arbejdsbegreb som et Paradigma for det almindelige energetiske Arbejdsbegreb vil det være tilstrækkeligt at betragte Tilfælde, hvori Transporten af Masse foregaar saa langsomt, at Bevægelsesenergi kan udelukkes. I saa Fald vil efter Mekanikens Terminologi den totale til en sammenkoblet Transport af to eller flere Massepartikler knyttede Arbejdssum, d. v. s. den algebraiske Sum af alle Arbejdstab ved Processen, være Nul. Denne Sætning kan anses for at fremstille den almindelige mekaniske Arbejdsdefinition, idet det paa Grundlag heraf er muligt at bestemme Arbejdet ved en vilkaarlig mekanisk Proces i Forhold til Arbejdet i et valgt System, hvori kun Massen er variabel.

Vi har altsaa for to sammenkoblede mekaniske Grundprocesser: $\delta A' + \delta A'' = 0$, eller almindeligt: $\Sigma \delta A = 0$, idet det herved vel maa erindres, at δA har den ved (1) givne begrænsede Betydning. For to sammenkoblede Grundprocesser følger, at:

$$(\varphi_1' - \varphi_2')\,\delta m' = (\varphi_1'' - \varphi_2'')\,\delta m'', \tag{2}$$

saaledes, at Værdien for $\varphi_1'' - \varphi_2''$ kan bestemmes, naar Værdien for $\varphi_1' - \varphi_2'$ er konventionelt fastsat. Denne Fremgangsmaade kan ikke føre til Modsigelse.

Et mekanisk System, hvori alene den her beskrevne Grundproces har Lejlighed til at forløbe — bestaaende f. Ex. af et Lod, der har Adgang til at bevæge sig parallelt med Jordens Gravitationskraft — vil vi betegne som et mekanisk Arbejdsreservoir. Ved Sammenkobling af Arbejdsreservoiret med et vilkaarligt andet mekanisk System vil efter den ovenfor indførte Definition Arbejdstabet i dette kunne bestemmes som identisk med Arbejdsgevinsten i Reservoiret. Mekanisk Arbejde er saaledes direkte konstaterbart i de for Arbejdsreservoiret konventionelt fastsatte Enheder.

Efter Mekanikens Grundprinciper er imidlertid en Ligning af den ved (1) givne Form af langt mere almen Betydning, idet det Arbejde, der er knyttet til Transport af Masse mellem to givne Punkter, er uafhængigt af den Vej, ad hvilken Transporten ledes. Dette betyder, at de indgaaende Størrelser φ_1 og φ_2 kan erstattes af Funktioner Φ_1 og Φ_2, hvis Værdi ogsaa ved vilkaarlig Transportvej alene afhænger af de paagældende Punkters Beliggenhed i Kraftfeltet. Vi skriver i Overensstemmelse hermed:

$$\delta A = (\Phi_1 - \Phi_2)\,\delta m \tag{3}$$

og betegner de i Parenthesen indgaaende Funktioner som Potentialer. Samtidig vil Udtrykket:

$$\Sigma \delta A = 0, \tag{4}$$

der ovenfor var opstillet som en Definition af Arbejdsbegrebet under de indskrænkende Forudsætninger, at Transportvejen var fastlagt, forfremmes til Udtrykket for et Grundprincip for de mekaniske Processer. Vi vil betegne dette som det mekaniske Arbejdsprincip.

Vor Opgave er nu at overføre det mekaniske Arbejdsbegreb og det mekaniske Arbejdsprincip til Omraader af ikke-mekanisk Art. I Forsøget herpaa vil vi som første væsentlige Forudsætning for Behandlingen fastslaa den allerede i den foregaaende Afhandling gennemførte Grundforestilling, at alle i Naturen foregaaende Forandringer omfatter og for ideale Grænsetilfældes Vedkommende alene bestaar af Transport af energetiske Kvantiteter imellem forskellige Tilstande. Udover en saadan Transport af Kvantitet vil der rent logisk set kunne tænkes en Dannelse eller en Tilintetgørelse af Kvantitet, men saadanne Fænomener er efter vor Grundforestilling udelukket fra de nævnte ideale Grænsetilfælde. Den energetiske Grundproces, hvormed en saadan Kvantitetstransport vil blive betegnet, er derfor ganske analog med den som den mekaniske Grundproces betegnede Transport af Masse i et Kraftfelt.

De energetiske Kvantiteter er med Hensyn til deres energetiske Karakter at sidestille med Masse. De er i visse Tilfælde Størrelser, der er direkte givne ved simple fysiske Maalemethoder, f. Ex. gælder dette om Rumfang, Stof- og Elektricitetsmængde. I saa Tilfælde kan den indtrædende Forandring siges at være en umiddelbart iagttagelig Grundproces, karakteriseret paa aabenbar Maade af Kvantitetens Konstans. En analog Beskrivelse vil dog være af almindelig Gyldighed, f. Ex. omfatte ogsaa den thermiske Grundproces, som senere vil blive særlig behandlet, og hvori Entropien optræder som den energetiske Kvantitet.

I Overensstemmelse med Behandlingen af de rent mekaniske Processer vil vi til enhver energetisk Grundproces, der er karakteriseret ved Arten af den transporterede Kvantitet, og som er givet ved sit fuldstændige Forløb, koordinere en Arbejdsværdi, der i Analogi med Ligning (1) udtrykkes ved:

$$\delta A = (\varphi_1 - \varphi_2)\, \delta K. \qquad (5)$$

Kvantiteten δK er infinitesimal, hvorved sikres, at Transporten ikke forandrer Størrelserne φ_1 og φ_2, der i energetisk Henseende kendetegner henholdsvis Begyndelses- og Slutningstilstanden for Kvantiteten. Ifølge denne Definitionsligning er Arbejdet proportionalt med den overførte Kvantitetsmængde, idet kun denne er variabel. δA betegnes som Arbejdstabet. Ved Ændring af Processens Retning vil Arbejdstabet være udtrykt ved (5) efter Fortegnsforandring.

Til yderligere Udvikling af det almindelige Arbejdsbegreb vil vi indføre den erfaringsmæssigt begrundede Forudsætning, at den fuldstændige Reversibilitet, der er karakteristisk for de rent mekaniske Processer, ogsaa behersker Grundprocesser af anden, vilkaarlig Art. Betegnelsen »Reversibilitet« benyttes her som Udtryk for, at de paagældende Grundprocesser, hvis sammenknyttede Forløb er sikret ved en »Arbejdskobling«, forløber gennem en Ligevægtstilstand i den Forstand, at infinitesimale Ændringer i Størrelsen φ i Ligning (5), d. v. s. i de deltagende Systemers Tilstande, er tilstrækkelige til at fremkalde Ændring af Retningen i de sammenkoblede Grundprocesser. Realisationsbetingelsen herfor er paa iøjnefaldende Maade afhængig af Processens Art. I visse Tilfælde vil Reversibiliteten kunne sikres ved en direkte Kobling til mekaniske Arbejdsreservoirer, idet de paagældende Processer er rent mekanisk afbalancerede. I andre Tilfælde — f. Ex. gælder dette den thermiske Proces — maa Processen, hvis Reversibiliteten skal overholdes, gennemføres ad Omveje, f. Ex. under Anvendelse af en infinitesimal Kredsproces som den Carnot'ske, eller en Række af saadanne Kredsprocesser. Denne Forskel er i experimentel Henseende særdeles væsentlig, men principielt maa det siges at være uden Betydning, om Reversibiliteten er direkte eller indirekte realiserbar. Grundlaget for vor Betragtning er dens principielle Gennemførlighed i alle Tilfælde.

Udfra denne Forudsætning er det almindelige Arbejdsbegreb fixeret ved Ligningen $\Sigma\delta A = 0$, der udsiger, at det totale til reversible Grundprocesser knyttede Arbejdstab er Nul. For et vilkaarligt System, sammenkoblet med et Arbejdsreservoir ved direkte eller indirekte Kobling, saa at Systemet som Helhed fungerer reversibelt, følger heraf, at Arbejdstabet i det reagerende System er lig Arbejdsgevinsten i Arbejdsreservoiret. Til Arbejdstabet er der ved reversible Processer knyttet en ækvivalent Arbejdsgevinst, hvis Størrelse direkte kan konstateres i de for Arbejdsreservoiret konventionelt fastsatte Enheder.

De her fremførte Sætninger er Arbejdsdefinitioner. Vi vil i Analogi med Behandlingen af de mekaniske Processer udvide Betydningen af Ligning (5), idet vi postulerer, at Arbejdet δA er uafhængigt af Vejen. Dette betyder, at (5) kan omskrives til:

$$\delta A = (P_1 - P_2)\,\delta K, \tag{6}$$

hvori P_1 og P_2 er Potentialer, d. v. s. Funktioner, der alene afhænger af Tilstanden af de to Systemer, mellem hvilke Kvantitetstransporten finder Sted, og hvis Differens derfor kan bestemmes ved et enkelt Arbejdsforsøg. Samtidig med denne Transformation vil Ligningen

$$\Sigma \delta \mathrm{A} = 0\,, \tag{7}$$

der ovenfor var opstillet som en Definition af Arbejdsbegrebet under de indskrænkende Forudsætninger, at Transportvejen var fastlagt, forfremmes til et almindeligt Grundprincip. Vi vil betegne dette som Arbejdsprincipet.

En Grundproces, hvorved Kvantiteten transporteres fra et højere til et lavere Potential, har vi betegnet som positiv, medens en modsatrettet Grundproces er betegnet som negativ. Fortegnet for det ved (6) udtrykte Arbejdstab, der er det samme som Fortegnet for Grundprocessen, kan imidlertid ikke bestemmes ved Betragtninger af den anførte Art og lader sig i Virkeligheden kun fastsætte konventionelt. Man kan f. Ex. vedtage, at Gravitationspotentialet i Nærheden af Jordoverfladen tiltager med Højden over denne. Mest rationelt sker Fortegnsbestemmelsen ved Inddragning af irreversible Forandringer under Betragtningerne, idet man ved den hertil knyttede Grundproces fastsætter Kvantitetstransporten som positiv.

At Arbejdet ved en Grundproces er uafhængigt af Vejen, saaledes som Arbejdsprincipet postulerer, betyder, at en Proces, der forløber i et kvantitetsafsluttet, arbejdskoblet System, og som alene for Kvantiteten δK's Vedkommende har medført en endelig Potentialændring, idet denne Kvantitet i Begyndelsestilstanden I og Slutningstilstanden II befinder sig henholdsvis ved Potentialet P_1 og P_2, er karakteriseret af et bestemt Arbejdstab, hvis Størrelse er $(P_1 - P_2)\,\delta K$. Dette Arbejdstab i Systemet vil vise sig som Arbejdsgevinst i Reservoiret. Den samtidig indtrædende, infinitesimale Ændring af alle Potentialer i Systemet, der muligvis kunde opfattes som arbejdsforaarsagende, derved at endelige Kvantitetsmængder transporteredes gennem infinitesimale Potentialdifferenser, skal saaledes efter Grundlaget for vor Betragtning ikke medtages ved Arbejdsberegningen. Dette vigtige Forhold, der er i Sammenhæng med den Gibbs'ske for kemiske Systemer gyldige Fundamentalligning: $\Sigma \mathrm{KdP} = 0$, i hvilken Summationen skal udstrækkes over de indgaaende Potentialer, Temperatur, Tryk og kemisk Potential, vil blive belyst i anden Forbindelse i det følgende.

Er Tilstand I og II identiske, hvilket er ensbetydende med, at Systemet har gennemløbet en Kredsproces, er Arbejdstabet $= 0$, og der vil intet Arbejde kunne registreres i det tilkoblede Arbejdsreservoir. Da Processer af den her beskrevne Art ogsaa kan betegnes som Processer i Systemer af invariable Kvantitetsmængder, ses det, at der kan tillægges saadanne Systemer en alene af Tilstanden afhængende potentiel Energi, hvis Differens $\Pi_{\mathrm{I}} - \Pi_{\mathrm{II}}$ er identisk med Arbejdstabet. Er Systemet arbejdsafsluttet fra Omgivelserne, f. Ex. derigennem at det benyttede Arbejdsreservoir medregnes til Systemet, vil den potentielle Energi forblive konstant.

Den potentielle Energi er altsaa et Begreb, der indtræder som Arbejdsfunktion for Systemer, der er fuldstændig kvantitetsafsluttede fra Omgivelserne. Er der Adgang for Kvantiteter udefra, vil selve Arbejdsbegrebet vel være anvendeligt uden Indskrænkning, idet Kvantitetsflytningen indenfor Systemet kan foregaa uanfægtet, men Ændringen i potentiel Energi vil nu i Almindelighed være ubestemt. Hvis den i en vis Del af Processen tilførte Kvantitet fjernes i en anden Del af Processen, saaledes at Processen, bestemt ved Begyndelses- og Slutningstilstanden, kan siges at være kvantitetsafsluttet, vil Begrebet potentiel Energi naturligvis igen være anvendeligt, idet Kvantitetskommunikation af denne Art er identisk med Arbejdskommunikation. Tilføres Kvantiteten δK ved Potentialet P_2 og fjernes den ved Potentialet P_1, vil Arbejdstabet i Systemet være $(P_1 - P_2)\,\delta K$, men medens denne Forandring i det helt kvantitetsafsluttede System vilde være Resultatet af en Grundproces, hvis Ækvivalens maatte optræde i det paa Forhaand afgrænsede System, vil man i det her betragtede Tilfælde, hvor Processen er medført af Kvantitetskommunikationen, være henvist til at søge Arbejdsækvivalensen udenfor Systemet.

Det er endvidere vigtigt at lægge Mærke til, at Arbejdsprincipet, i Kraft af sin Stilling som det almengyldige Udtryk for Tilstedeværelse af Reversibilitet ved de energetiske Processer, maa danne Grundlaget for alle de almindelige og specielle Ligevægtsudtryk, der optræder i Thermodynamiken. Det vil ved Udledningen af disse, saaledes som vist i et enkelt Exempel i den tidligere Afhandling, ikke være nødvendigt at opsøge en praktisk gennemførlig eller anskuelig Reaktionsmekanisme, idet vi alment postulerer den principielle Gennemførlighed af en hvilkensomhelst energetisk Grundproces paa reversibel Maade. F. Ex. udledes den CLAPEYRON'ske Damptryksformel ved Anvendelse af Arbejdsprincipet paa den reversible Omdannelse:

$$\text{Vædske } (1) + \text{Damp } (2) \rightarrow \text{Vædske } (2) + \text{Damp } (1),$$

hvor (1) og (2) svarer til hver sin af hinanden uendelig nærliggende Faseligevægte. Formlen faas da umiddelbart ved i Udtrykket for Arbejdsprincipet at indsætte de sammenkoblede spatiske og thermiske Arbejder: $(v'' - v')\,dp$ og

$(S' - S'')\, dT$, som den til Realisation af den nævnte Proces nødvendige Transport af de angivne Kvantiteter gennem de infinitesimale Potentialdifferenser repræsenterer. Omvendt vil naturligvis en hvilkensomhelst af disse Ligninger, hvis den anses for bevist paa anden Maade, f. Ex. gennem den i den klassiske Thermodynamik anvendte Bevisførelse, kunne tjene som Grundlag for Opstillingen af Arbejdsprincipet i dets almindelige Form.

Det her fremførte Arbejdsbegreb er, som ovenfor betonet, baseret paa det energetiske Kvantitetsbegreb, der betragtedes som defineret udfra kendte fysiske Maalemethoder. Den thermiske Kvantitet, som vi anvendte i ovenstaaende Exempel, danner principielt ingen Undtagelse herfra. I visse Henseender vil man dog formentlig tillægge Entropien en særlig Stilling, dels paa Grund af Begrebets historiske Udvikling og den særlige Behandlingsmaade, det underkastes i den traditionelle Thermodynamik, dels paa Grund af dets tilsyneladende mindre haandgribelige Kvantitetskarakter. Det vil være vor Opgave i det følgende Afsnit at fuldstændiggøre vort Arbejdsbegreb ved Paavisning af, hvorledes Entropien paa simpel Maade kan indføres i Thermodynamiken som den thermiske Kvantitet.

3. Entropi-, Varme- og Temperaturdefinition.

Det er, som fremhævet i den foregaaende Afhandling, et Hovedsynspunkt for vor Behandling af energetiske Fænomener, at de reversible thermiske Processer ikke adskiller sig i væsentlige Henseender fra andre reversible energetiske Processer, og at derfor Begrebet den thermiske Grundproces, defineret som en Transport af den thermiske Kvantitet fra et thermisk Potential til et andet, optræder sideordnet med Grundprocesser af anden Art. For den thermiske Kvantitet indførtes herved Betegnelsen Entropi, idet det under Anvendelse af den sædvanlige thermodynamiske Temperaturskala kunde vises, at det saaledes indførte Begreb var identisk med Entropien i den traditionelle Betydning.

I Postulatet om de reversible Processers Formulering som Grundprocesser, d. v. s. som Processer, der er karakteriseret alene som Transport af Kvantitet, vil der i og for sig være indeholdt tilstrækkeligt Grundlag for Entropidefinition. Af Hensyn til den vigtige Sammenhæng, som kan opstilles mellem Entropi, Varme og Temperatur, og til vort Formaal, at undgaa som Basis for Fremstillingen at benytte thermiske Begreber, der alene hviler paa traditionelle thermodynamiske Forestillinger, vil det dog være nødvendigt nærmere at præcisere den antydede Definition af Kvantiteten og at udvikle Sammenhængen mellem denne og de øvrige thermiske Begreber paa uafhængigt Grundlag. Vi vil herved gaa ud fra, at Fysikens Methode til Paavisning af Temperaturulighed og til Sammenligning af smaa Temperaturdifferenser umiddelbart kan akcepteres.

Den thermiske Grundproces vil forløbe mellem to Systemer af forskellig Temperatur, naar disse bringes i reversibel, thermisk Kommunikation. Herved vil de to Systemer, som vi vil tænke os i Form af »Kalorimetre«, d. v. s. stoflige Systemer, der kun kommunicerer thermisk med Omgivelserne, begge undergaa visse Forandringer, som i Overensstemmelse med vor Opfattelse skyldes Optagelse og Afgivelse af den thermiske Kvantitet. Vor første Opgave vil være at definere Kvantiteten i Relation til den indtraadte Forandring. Denne vil bl. a. bestaa i »Temperaturændringer«, og man vil til Bestemmelse heraf kunne benytte Udslaget paa et »empirisk« Thermometer eller en Række af empiriske Thermometre, d. v. s. Systemer, der ved Temperaturændringer forandrer sig paa maalelig Maade. For smaa Temperaturændringer vil, som Erfaringen viser, de forskellige Thermometerudslag, naar bortses fra ganske specielle Muligheder, der er uden Betydning for vor Opgave, være indbyrdes proportionale. Et enkelt af dem vil altsaa kunne benyttes som Maal for Temperaturændringen.

Den Entropimængde, der optages i et Kalorimeter under givne Betingelser, vil vi paa Basis af disse Betragtninger definere som proportional med Temperaturændringen i Kalorimetret, maalt som ovenfor angivet. Den optagne Entropimængde vil blive regnet positiv, hvis den medførte Temperaturændring efter sædvanlig Konvention for Temperaturmaaling er positiv. Idet ogsaa den nævnte Proportionalitetsfaktors numeriske Værdi fastsættes konventionelt, er den under de givne Betingelser, d. v. s. i det givne Kalorimeter, optagne Entropimængde saaledes fuldstændig bestemt. Vi har faaet en speciel, under givne Betingelser brugbar Entropidefinition. Men det er naturligvis paa Basis heraf ikke muligt at sammenligne Entropimængder, optagne under ulige Betingelser, f. Ex. i Kalorimetre af forskelligt Kalorimetermateriale, eller ved forskellig Temperatur. Ja, Spørgsmaalet om et Størrelsesforhold for Entropimængder under ulige Betingelser er i Virkeligheden paa dette Stadium af vor Betragtning, hvor den almindelige Entropidefinition endnu ikke er fuldstændig fastslaaet, uden egentlig Mening.

I Overensstemmelse med den i den tidligere Afhandling antydede Fremgangsmaade vil vi definere Entropien almindeligt som en Størrelse, der tilfredsstiller den specielle Definition og tillige er reversibelt transportabel. Dette betyder, at vi, naar to Kalorimetre under vilkaarlige Betingelser er i reversibel thermisk Kommunikation, definitionsmæssigt vil fastsætte, at den af det ene Kalorimeter optagne Entropimængde er = den af det andet Kalorimeter afgivne. Denne Definition, der er i Overensstemmelse med Analogipostulatets Karakterisation af den thermiske Grundproces som en Kvantitetsflytning, fører, som man let ser, til en entydig Fastsættelse af Entropimængdens Størrelse. Er nemlig de konventionelle Temperaturændringer i Kalorimetrene I og II ved den betragtede Proces henholdsvis dt_1 og dt_2 og de tilsvarende optagne Entropimængder C_1dt_1 og C_2dt_2, hvor C_1 og C_2 er Konstanter (der kunde betegnes som Kalorimetrenes konventionelle Entropikapaciteter), og er i et analogt Forsøg, hvori den reversible Kommunikation imellem de to Kalorimetre foregaar ad en anden Vej, Temperaturændringerne henholdsvis dt_1 og dt'_2, de tilførte Entropimængder altsaa henholdsvis C_1dt_1 og $C_2dt'_2$, saa vil for den totale Proces, der faas ved Kombination af de nævnte to Processer, forløbende i modsatte Retninger, Entropitilvæksten være $C_2(dt_2 - dt'_2)$. Denne maa imidlertid ifølge Arbejdsprincipet for den reversible Proces være $= 0$, hvoraf $C_2dt_2 = C_2dt'_2$. Naar Kalorimeter I ved reversibel Kommunikation afgiver en vis Entropimængde, vil den i II optagne være uafhængig af Processens Mekanisme. Definitionen af Entropi som en reversibelt transportabel Størrelse vil altsaa ikke kunne føre til Modsigelse.

Det vil bemærkes, at der ikke er Tale om et Bevis for Ligestorhed af optagne og afgivne Entropimængder, men kun om en Paavisning af Tilladeligheden af den definitionsmæssige Fastsættelse af Identitet. Denne Forskel er sikkert særlig iøjnefaldende for Entropikvantiteten. Men det maa erkendes, at en Sammenligning af Kvantiteter under forskelligartede Betingelser ganske alment er principielt uigennemførlig, saa at man ikke uden specielle Definitioner er i Stand til at tillægge Paastanden om Kvantitetens Konstans en Mening, selv om vi har at gøre med Kvantiteter, hvis fysiske Bestemmelse forekommer umiddelbart let gennemførlig. I Virkeligheden maa Kvantitetsdefinitionen for at være energetisk tilfredsstillende ganske alment gøres afhængig af en Methode, der svarer til den for Entropien anvendte. Det vil dog formentlig være unødvendigt her at betragte dette mere erkendelsestheoretiske Spørgsmaal for de Kvantiteters Vedkommende, der ikke er af thermisk Art.

Den givne Definition af en Entropimængde som den reversibelt transportable thermiske Kvantitet har først og fremmest Betydning for Systemer af forskellig Temperatur. Ved Temperaturhomogenitet vil Entropitransport altid være reversibel, vi har da at gøre med den »neutrale« Grundproces. Ved Temperaturforskellighed derimod er Grundprocessen »aktiv«, d. v. s. den vil være knyttet til en Frembringelse enten af Varme eller af Arbejde. Det er med Lovene herfor, den thermiske Energetik i Hovedsagen beskæftiger sig.

Om Varmebegrebet, det 2det grundlæggende thermiske Begreb, hvormed Energetiken opererer, gælder, som allerede tidligere gjort opmærksom paa, at det, saalænge de betragtede Fænomener er reversible, ikke vil frembyde særlige Ejendommeligheder fremfor de analoge Begreber, der i den tidligere Afhandling blev betegnede som ækvipotentielle Energiarter. Det exceptionelle, der betegner Varmens Særstilling i Energetiken, fremkommer først ved Inddragning ogsaa af de irreversible Fænomener under vore Betragtninger. Varme er derfor trods den tilsyneladende

Simpelhed, hvormed den optræder i den sædvanlige Thermodynamik, i Forhold til Entropien et mere sammensat Begreb, hvis egentlige Karakter først fremgaar af en mere udførlig Analyse.

I den tidligere Afhandling er Sammenhængen mellem Entropi og Varme fremstillet paa Grundlag af det foreliggende traditionelle Temperaturbegreb. Det er imidlertid, som allerede nævnt, Formaalet her at udvikle de thermiske Begreber paa uafhængig Basis under Anvendelse af entydige Definitioner. Vi vil derfor nu søge en Fastsættelse af Varmebegrebet og af dettes Forhold til Entropien uden Anvendelse af de i den traditionelle Thermodynamik optrædende Relationer.

Denne Opgave vil ligesom den tilsvarende Opgave for Entropibegrebets Vedkommende falde i to Afsnit, af hvilke det første angaar Varmedefinitionen under tilnærmelsesvis konstante Betingelser, d. v. s. naar Varmen optages i et Kalorimeter, der herved forbliver tilnærmelsesvis uforandret. Vi vil i dette Tilfælde definere Varmeoptagelsen som proportional med Temperaturændringen i Kalorimetret, maalt paa et vilkaarligt »empirisk« Termometer. Denne Definition er aabenbart identisk med Entropidefinitionen. Idet vi iøvrigt indfører de samme Konventioner som ved Entropidefinitionen, er det saaledes klart, at der ved konstante Betingelser, d. v. s. ved Anvendelse af samme Kalorimeter, overhovedet ikke kan skelnes mellem tilført Entropi og tilført Varme, da Forholdet imellem dem er bestemt alene ved en konventionelt fixerbar Proportionalitetsfaktor.

Til almindelig Fixering af Varmebegrebet under vilkaarlige Betingelser vil vi definere Varmen som en Størrelse, der foruden at tilfredsstille den specielle Definition er irreversibelt transportabel. Dette betyder, at vi, naar to Kalorimetre under vilkaarlige Betingelser er i irreversibel thermisk Kommunikation, definitionsmæssigt vil fastsætte, at den af det ene Kalorimeter optagne Varmemængde er = den af det andet Kalorimeter afgivne. At denne Definition fører til et entydigt Varmebegreb, er et alment Erfaringsresultat, idet Forholdet imellem de indgaaende Varmemængder, hver for sig bestemt ved den for konstante Betingelser givne Methode, erfaringsmæssigt er uafhængigt af den irreversible Ledningsproces's særlige Mekanisme. Det vil ogsaa følge af Varmeprincipet paa Grundlag af Relationen mellem Varme og Entropi, som er opstillet i det følgende.

Det er aabenbart, at Entropi- og Varmemængde efter de givne Definitioner ikke kan skelnes fra hinanden ved Udførelsen af et enkelt Kalorimeterforsøg under givne Betingelser, ja overhovedet ikke ved Processer, der foregaar ved konstant Temperatur. Det er ved deres forskellige Transportabilitetsforhold ved varierende Temperatur at disse to Begreber udviser deres specielle Ejendommeligheder. Det er utvivlsomt, at det er de simple experimentelle Realisationsbetingelser for den irreversible Varmetransport, der har været bestemmende for den Stilling, som Varmen indtager i den traditionelle Thermodynamik som det oprindelige og grundlæggende thermiske Begreb, medens den i Praxis mere vanskeligt gennemførlige reversible Grundproces har anvist Entropien dens Plads som det afledede thermiske Begreb. Principielt set er Forholdet imidlertid netop det omvendte, idet Entropitransportens Karakter af en Grundproces, der er ganske analog med andre, f. Ex. mekaniske, kemiske og elektriske Grundprocesser, medfører den største Simpelhed med Hensyn til den thermodynamiske Opfattelse af selve Entropibegrebet. Med Varmetransporten og saaledes ogsaa med det almene Varmebegreb forholder det sig ganske anderledes. Den irreversible Varmeoverføring er en ensidig Proces, Varmen altsaa ikke alment transportabel, som Tilfældet er med en Kvantitet. Varmetransporten kan ikke betegnes som en Grundproces, og dens enestaaende Karakter bliver først forstaaelig i Forbindelse med Studiet af Lovene for de irreversible Processer i Almindelighed. Dette Spørgsmaal er allerede ret udførligt behandlet i den foregaaende Afhandling, men vi skal senere tilføje en supplerende Betragtning i Tilslutning til en Temperaturdefinition, der hviler paa de her givne Definitioner af Varme og Entropi.

Ud fra disse Definitioner af Varme og Entropi er nemlig det tredie thermiske Begreb, Temperaturen, simpelt tilgængelig. Ifølge det fremførte er Entropi- og Varmemængde proportionale ved enhver vilkaarlig valgt konstant Temperatur med en af Temperaturen paa entydig Maade afhængende Proportionalitetsfaktor. Man kan altsaa skrive:

$$\delta Q = T \delta S, \tag{8}$$

hvor δQ og δS er de optagne Mængder af henholdsvis Varme og Entropi, og T er en Proportionalitetsfaktor, der alene og entydigt afhænger af Temperaturen. Vi vil da uden Modsigelse kunne benytte selve denne Faktor som et Maal for Temperaturen, saaledes at Ligning (8) kan betragtes som en Temperaturdefinition. Anvendt paa en thermisk Overføring mellem to Temperaturer kan (8) skrives:

$$\frac{T_1}{T_2} = \left(\frac{\delta Q_1}{\delta Q_2}\right)_{\text{rev.}} = \left(\frac{\delta S_2}{\delta S_1}\right)_{\text{irrev.}}, \tag{9}$$

saaledes at Temperaturforholdet ses at være = Forholdet mellem de tilsvarende Varmemængder ved reversibel og = det omvendte Forhold mellem de tilsvarende Entropimængder ved irreversibel Kommunikation. Vi vil betegne den saaledes fastsatte Skala som den thermiske Temperaturskala.

Det skal her bemærkes, at det tilsyneladende vilde være en naturligere og med nærværende Fremstilling overensstemmende Methode at søge Temperaturen defineret paa Grundlag af Arbejdsprincipet, der for Forløbet af en enkelt Grundproces i Forbindelse med et Arbejdsreservoir kan udtrykkes ved:

$$\delta A = (P_1 - P_2)\, \delta K.$$

Hvis nemlig Kvantiteten allerede er defineret, kan denne Ligning, saaledes som paapeget i det foregaaende Afsnit, i al Almindelighed tjene til Fastsættelse af Potentialforskellen $P_1 - P_2$. Da vi nu i dette Afsnit har opstillet den almene Definition af en transportabel Entropimængde δS, vil den thermiske Arbejdsformel:

$$\delta A = (T_1 - T_2)\, \delta S \qquad (10)$$

jo netop fremstille en saadan Temperaturdefinition.

Der kan da heller ikke være Tvivl om, at vi ved denne Ligning har faaet fixeret et konsekvent og rationelt Temperaturbegreb. Vi vil betegne den herved givne Skala som den energetiske Temperaturskala. Men det maa bemærkes, at medens Definitionen af den thermiske Skala fixerer Temperaturens absolute Værdi eller, om man vil, Nulpunktet for Skalaen, kan man af (10) kun aflede en Temperaturdifferens, hvilket betyder, at vi ikke har Midler til at bestemme Nulpunktet paa den energetiske Skala. Ganske i Almindelighed har vi i Arbejdsprincipet et Middel til Fastsættelse af en Potentialskala, uden at det derved er muligt at fixere Potentialets Nulpunkt. Dette hænger sammen med den Tilknytning til Grundprocessen, som enhver Arbejdsformel er baseret paa, idet der jo herved altid kun er Tale om Flytning af Kvantitet mellem forskellige Potentialer. Absolutværdien for Potentialet vil kun indgaa i Relationer, der angaar Dannelse eller Tilintetgørelse af Kvantitet, og er derfor i Almindelighed uden Betydning i Energetiken. Kun for det thermiske Potential er Sagen anderledes. Muligheden for at fastsætte Temperaturen absolut i den thermiske Skala paa Basis af Kendskab til Varmemængden er nøje knyttet til det Faktum, at vi netop for den thermiske Kvantitets Vedkommende, og alene for denne, har at gøre med en Ændring af dens absolute Mængde, saaledes som vi iagttager ved Forløbet af den irreversible Proces.

Vi vil til Sammenligning af de to her fremstillede Skalaer betragte en thermisk Grundproces, bestaaende i reversibel Transport af Entropimængden δS fra Reservoir I, hvis Temperatur i den thermiske og energetiske Skala er henholdsvis Θ_1 og T_1, til Reservoir II, hvis tilsvarende Temperatur er Θ_2 og T_2. For denne i Systemet I—II forløbende Grundproces gælder Arbejdsudtrykket (10), d. v. s. der vil indenfor Systemet foregaa et Arbejdstab, givet ved:

$$\delta A = (T_1 - T_2)\,\delta S,$$

og samtidig blive opsamlet en Arbejdsgevinst af samme Størrelse i et tilkoblet Arbejdsreservoir. Saafremt de i Systemet frembragte Forandringer kompenseres ved Overføring af Entropimængden δS fra et ydre Reservoir R_I, hvis thermiske Temperatur er Θ_1, til Reservoiret I og Overføring af samme Entropimængde fra II til et ydre Reservoir R_{II}, hvis thermiske Temperatur er Θ_2, vil I—II-Systemet slet ikke være blevet forandret, og det ydre Arbejde kan siges at være dannet paa Bekostning af det thermiske Arbejdstab i R-Reservoirerne. Disse har, idet deres Funktion kun har bestaaet i neutral Varmeoverføring, ifølge Ligning (8) henholdsvis mistet Varmemængden $\Theta_1 \delta S$ og modtaget Varmemængden $\Theta_2 dS$, ialt altsaa mistet Varmemængden:

$$\delta Q = (\Theta_1 - \Theta_2)\,\delta S.$$

Da I—II-Systemet ikke har forandret sig, vil ifølge Varme-Arbejds-Ækvivalensprincipet, som vil blive opstillet i det følgende, Summen af Varme- og Arbejdstab i Omgivelserne være Nul. Vi faar altsaa:

$$(T_1 - T_2)\,\delta S = (\Theta_1 - \Theta_2)\,\delta S,$$

hvoraf man direkte kan fastslaa den thermiske og energetiske Skala som identiske. Men det maa udtrykkelig bemærkes, at denne Identitet af de to Skalaer ikke er forudsætningsløs, men, som fremhævet, er betinget af Ækvivalensprincipets Gyldighed.

Vi har ved disse Undersøgelser over Optagelse og Afgivelse af Entropi- og Varmemængder anvendt »Kalorimetre«, idet denne Betegnelse er benyttet i Overensstemmelse med ovenstaaende Definition og med almindelig fysisk Terminologi. Det indses imidlertid umiddelbart, at optagne eller afgivne Entropi- og Varmemængder ogsaa i Tilfælde af et System af ganske vilkaarlig Natur er underkastet de for disse thermiske Størrelser opstillede Transportabilitetsbetingelser. Det er derfor ikke forbundet med nogen Vanskelighed at bestemme de til et vilkaarligt System overførte Entropi- og Varmemængder, selv om de dertil svarende konventionelle Temperaturændringer som Følge af Systemets Komplicerthed ikke kan konstateres.

Naar vi ifølge det ovenfor fremsatte kan fastslaa, at der ved reversible Processer for Entropiens Vedkommende, ligesom for andre Kvantiteter, kun foregaar en Flytning fra en Tilstand til en anden, saa følger heraf, at Entropiforøgelsen i et System ved dets reversible og vilkaarligt kvantitetsvariable Overgang fra en given Tilstand I til en anden given Tilstand II er lige saa stor som Entropiformindskelsen i det Entropireservoir, hvorfra Entropien overføres. Hvis System + Reservoir gennemløber en reversibel Kredsproces, kan man derfor slutte, at Entropimængden i Systemet herved ikke forandres, idet den analoge Sætning nødvendigvis maa være gyldig for Reservoiret, der kun har været entropikommunicerende. I Systemer, der undergaar reversible Forandringer, er Entropien altsaa givet med Systemets Tilstand.

4. Energetisk Varmeudvikling.

Ved Siden af en Transport af Kvantitet, der er blevet fremstillet som karakteristisk for den reversible Proces, kan man som nævnt rent formelt tænke sig Processer, ved hvilke Kvantitet forsvandt eller opstod. Erfaringen lærer, at kun en enkelt af disse Processer i Virkeligheden er mulig, nemlig Dannelsen af Entropi, der er knyttet til den irreversibelt forløbende Grundproces. Denne Entropidannelse er ensbetydende med en Varmeudvikling, idet efter vor Opfattelse Ligning (8) i det foregaaende Afsnit er almengyldig. Da de i denne Ligning indgaaende Entropi- og Varmemængder kun er definerede som Størrelser, der tilføres et System udefra, bliver det Opgaven her at undersøge, hvorledes Mængderne af Entropi og Varme, der opstaar i et System ved irreversible Processer, principielt kan bestemmes, og hvorledes Almengyldigheden af den omtalte Ligning (8) kan bevises. Tillige vil der naturligvis samtidig opstaa Spørgsmaalet om Relationen mellem de frembragte thermiske Størrelser og det tilsvarende Arbejdstab.

For rent mekanisk irreversible Processer og visse andre Processer af lignende Simpelhed foreligger der med Hensyn til Bestemmelsen af udviklet Varme og Entropi i og for sig intet særligt Problem, idet de Systemer, der her er Tale om, har Karakter af »Kalorimetre«, i hvilke »udviklede« thermiske Størrelser direkte kan identificeres med tilførte. Hvis f. Ex. to Metalstykker ved Gnidning mod hinanden under Overholdelse af Temperaturhomogenitet udviser en vis Temperaturstigning, vil man heraf beregne en Udvikling af Varme, som er lige saa stor som den Mængde af tilført Varme, der foraarsager samme Temperaturstigning. Analogt gælder, hvis Temperaturstigningen fremkaldes i en Leder ved Passage af en elektrisk Strøm. I andre Tilfælde, f. Ex. hvis der foregaar kemiske eller spatiske Grundprocesser, er en saadan Simpelhed ikke til Stede.

Vi vil med det Formaal at søge en almindelig Fixering af Varmeudviklingsbegrebet først betragte en vilkaarlig differential Grundproces, bestaaende i Transport af en Kvantitet δK fra en given Tilstand med det højere Potential P_1 til en anden given Tilstand med det lavere Potential P_2. Efter vore tidligere meddelte Forudsætninger vil herved foregaa et Arbejdstab af Størrelsen:

$$\delta A = (P_1 - P_2)\, \delta K .$$

Hvis den differentiale Grundproces foretages paa reversibel Maade, vil et Arbejde af samme Størrelse som Arbejdstabet blive opsamlet i et tilkoblet Arbejdsreservoir.

Foregaar Processen derimod irreversibelt, vil intet ydre Arbejde blive registreret, og Systemets Slutningstilstand vil som Følge af det irreversible Fænomen, vi betegner som en Varmeudvikling, udvise en Temperatur, der er infinitesimalt højere end Slutningstilstanden ved den reversible Proces. Skal de to Processer udvise samme Slutningstemperatur, maa der i det reversible Tilfælde tilføres eller i det irreversible Tilfælde bortføres en positiv Varmemængde δQ. Da denne Varmemængde saaledes ved iøvrigt ganske identiske Tilstandsforandringer udøver samme thermiske Effekt som det Fænomen, vi har betegnet som Varmeudvikling, er det nærliggende at fastsætte, at Varmeudviklingen — hvis Betydning og Værdi det er vor Opgave at fixere — definitionsmæssigt er identisk med Varmemængden δQ, der er direkte tilgængelig for Maaling.

Varmeudviklingen ved en differential irreversibel Proces er saaledes defineret som den Varmemængde, der udefra maa tilføres ved den reversible Proces for at Reaktionsforløbet i de to Tilfælde skal blive det samme.

Er Processen af endelig Udstrækning, vil der ved dens irreversible Forløb naturligvis kunne ske endelige Ændringer i alle Potentialer. Idet vi atter identificerer Varmeudviklingen med den Varmemængde, der maa tilføres, naar samme Proces forløber reversibelt, er det aabenbart, at den totale Varmeudvikling maa være Summen af de i hvert Reaktionselement optrædende differentiale Varmeudviklinger. Det er derfor nødvendigt til Bestemmelse af den søgte Varmemængde under det reversible Forløb at tilføre Varmen paa en saadan Maade, at Forandringen i Systemet Element for Element er identisk med Forandringen ved den irreversible Proces. Man kan sige, at det drejer sig om en reversibel kinematografisk Reproduktion af det irreversible Reaktionsforløb. Den herved tilførte Varmemængde er da i Overensstemmelse med det for differentiale Processer anførte identisk med den irreversible Varmeudvikling. Definitionen gælder ikke alene for afsluttede Systemer, men ogsaa for det Tilfælde, at Kvantiteter i vilkaarlig Mængde tilføres udefra. Det er denne Varme, der i den tidligere Afhandling er indført under Betegnelsen energetisk Varmeudvikling. Denne er altsaa for en given irreversibel Proces defineret som den Varmemængde, der maa tilføres udefra, for at den givne irreversible Proces kan kinematografisk reproduceres paa reversibel Maade. Vi skal nedenfor vise, hvorledes Betingelserne i denne Definition kan fixeres skarpere paa Grundlag af Ækvivalensprincipet, samt betragte dens Forhold til Begrebet »Varmeudvikling« i den traditionelle Betydning.

Den ved den irreversible Grundproces frembragte Entropimængde faas paa Grundlag af en ganske analog Betragtning som den Entropi, der til reversibel kinematografisk Reproduktion af vedkommende Proces kræves tilført Systemet. Da tilført Varme og Entropi er sammenknyttet ved Ligning (8), vil den ovenfor beskrevne Tilførsel af Varmemængden δQ til det differentialt reagerende System være ensbetydende med Tilførsel af Entropimængden δS, bestemt ved denne Ligning. Følgelig vil ved den irreversible Proces samme Entropimængde være opstaaet i Systemet. Den i Begyndelsen af dette Afsnit fremsatte Anskuelse, at et Udtryk:

$$\delta Q = T \delta S, \tag{11}$$

konformt med (8), er af almen Betydning, gyldig saavel for tilførte som for irreversibelt frembragte Varme- og Entropimængder, ses saaledes at være verificeret. Paa samme Maade vil for den integrale Proces Udtrykket:

$$Q = \int_1^2 T \delta S \tag{12}$$

ses at være almengyldigt, uafhængigt af, om de indgaaende thermiske Størrelser er tilførte eller udviklede i Systemet.

Det blev i Slutningen af det foregaaende Afsnit paavist, at Entropimængden i et System, der gennemløber en kvantitetsvariabel Kredsproces paa reversibel Maade, ikke forandres. Er den paagældende Kredsproces delvis irreversibel, saaledes at Entropi opstaar under en Del af Forløbet, vil efter det ovenanførte denne Kredsproces kunne kinematografisk reproduceres paa reversibel Maade under Tilførsel af en Entropimængde, der er lig den irreversibelt frembragte. Systemets Entropiændring er altsaa den samme ved Kredsprocessens reversible og irreversible Forløb, saaledes at den for den reversible Kredsproces opstillede Entropisætning ogsaa maa være gyldig for den irreversible. Dette betyder, at Entropien i et System, der undergaar vilkaarlige Forandringer, er bestemt alene ved Systemets Tilstand, eller at den, i Overensstemmelse med sin Kvantitetskarakter, er en Tilstandsfunktion.

5. Ækvivalensprincipet.

Efter den i det foregaaende fremsatte Opfattelse af de reversible Processer som Processer, hvori energetiske Kvantiteter indgaar alene som transporterede, ikke som Størrelser, der frembringes eller tilintetgøres, vil det kunne hævdes, at ogsaa Varmeudvikling og Varmeforbrug efter den i det foregaaende Afsnit givne »energetiske« Definition er udelukket fra Optræden i Processer af den nævnte Art. Dette ses ogsaa umiddelbart ved Anvendelse af vort almindelige Postulat om Uigennemførligheden af Varme-Arbejds-Transformationen paa reversible Processer. Det følger heraf, at energetisk Varmeabsorption overhovedet er en Umulighed, og at energetisk Varmeudvikling med dertil knyttet positivt Arbejdstab er forbeholdt de irreversible Processer.

Som Indledning til den Undersøgelse over den kvantitative Sammenhæng imellem Arbejdstab og Varmeudvikling ved de irreversible Processer, som skal foretages i dette Afsnit, vil det være hensigtsmæssigt at betragte det traditionelle Princip om Ækvivalensen mellem Varme og Arbejde. Det er utvivlsomt at denne, ogsaa som Mayer-Joule-Princippet betegnede, Sætning ikke omhandler Arbejde i den almindelige Betydning, hvori Begrebet optræder i den nærværende Afhandling, men alene mekanisk Arbejde eller visse andre Arbejdsformer af lignende Simpelhed. Ogsaa Varmeudviklingsbegrebet, der indgaar i Ækvivalensprincipet, er det simplere Begreb, hvis Størrelse er tilgængelig ved den sædvanlige Kalorimeteranordning. Det er Identiteten af disse Størrelser:

$$\delta A = \delta Q,$$

som det klassiske Ækvivalensprincip postulerer.

Om denne Ligning er først at bemærke, at den simple Sammenhæng, der udtrykkes heri mellem Varme og Arbejde, er betinget af, at en Varmemængde bestemmes paa den i Afsnit 3 angivne Maade som en Størrelse, der er irreversibelt transportabel. Hvis man i Forsøg med to Kalorimetre under ulige Betingelser omdanner samme Arbejdsmængde til Varme, vil Ækvivalensprincipet m. a. O.

forlange, at de thermiske Effekter, der frembringes i de to Kalorimetre, staar i numerisk samme Forhold til hinanden som de tilsvarende thermiske Effekter ved direkte thermisk Kontakt mellem Kalorimetrene. Man finder imidlertid i den traditionelle Thermodynamik Ækvivalensprincipet ofte begrundet med Henvisning til den experimentelle Paavisning af, at der altid kræves samme Mængde Arbejde til Frembringelse af en bestemt Temperaturstigning i et givet Kalorimeter[1]. Dette er naturligvis en ganske utilstrækkelig Fixering af Begrebet. I visse Tilfælde, f. Ex. i den CLAUSIUS'ske Behandling af Varmekraftmaskinen, anses Varmen for reversibelt transportabel. Endvidere finder man undertiden Varmen defineret ved Hjælp af Ækvivalensprincipet[2], uden at der dertil er knyttet en Paavisning af dens karakteristiske Transportabilitetsbetingelser. Dette kan naturligvis ikke føre til nogen Ækvivalenslov. Til Trods for den Usikkerhed, der saaledes præger Varmebegrebet definitionsmæssigt, kan det dog siges, at det almindeligvis med Hensyn til sin Anvendelse indføres i Overensstemmelse med den i Afsnit 3 givne Definition, og vi vil derfor antage, at denne Definition kan opstilles ogsaa som den klassiske Thermodynamiks. Naturligvis er det kun Varme som tilført eller bortført, der herved defineres.

Men dernæst maa der med Hensyn til den experimentelle Begrundelse af Ækvivalensprincipet henledes Opmærksomheden paa følgende almindelige Forhold. Foreligger der som Opgave at sammenligne eller paavise Ligestorheden af to energetiske Størrelser, vil dette kunne foretages, saafremt de umiddelbart maales og udtrykkes i identiske En-

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[1] Jfr. f. Ex. EUCKEN: Energie und Wärmeinhalt, p. 2, 1929.

[2] M. BORN: Phys. Zeitschr. **22**, 222 (1921).

heder. Man kan saaledes sammenligne og finde Udtryk for Forholdet imellem to Mængder af samme energetiske Kvantitet. Denne Metode kan ikke finde Anvendelse i det foreliggende Tilfælde, da det thermiske Arbejde og Varmen ganske vist begge udtrykkes som Produkt af Entropi og Temperatur, men den absolute Temperaturværdi, som ifølge Paavisningen i Afsnit 3 er nødvendig til Beregning af Varmemængden, først er tilgængelig netop paa Grundlag af det Ækvivalensprincip, hvis Gyldighed skal prøves. Men dernæst er en tilsvarende Mulighed for Sammenligning til Stede, saafremt to Størrelser af forskellig Art viser en fuldstændig gensidig Transformabilitet. Dette finder Udtryk ved Anvendelsen af Arbejdsprincipet, tiltrods for at de indgaaende Objekter, hvis indbyrdes Forhold man søger, maales i forskellige Enheder. Man taler i saa Tilfælde vel snarere om Ækvivalens end om Identitet. At 1 Volt-Coulomb er ækvivalent med 10^7 erg, betyder ikke alene, at det elektriske Arbejde 1 Volt-Coulomb kan omdannes til det mekaniske Arbejde 10^7 Erg, men ogsaa at den modsatte Omdannelse af 10^7 Erg til 1 Volt-Coulomb er mulig. Den fuldstændige Reciprocitet i Omdannelsen er Betingelsen for, at Ækvivalensen kan fastslaas.

Men denne Betingelse er jo i Forholdet mellem Varme og Arbejde ikke til Stede. Som udførligt paavist i den tidligere Afhandling, er Relationen ensidig, idet Arbejde vel kan omdannes til Varme, men den modsatte Proces under alle Omstændigheder er uigennemførlig. Hvad Erfaringen lærer os, er derfor ene og alene, at Arbejde ved Omdannelse til Varme præsterer en Varmemængde, der er proportional med Arbejdstabet. Den tillader meget vel den Mulighed, at Tilstedeværelsen af et ikke-energetisk Middel til Maaling af de paagældende Størrelser i samme Enhed vilde afsløre en svigtende Ækvivalens ved Arbejdets Varmetransformation.

Naar Resultatet af de talrige Undersøgelsesmethoder, der har ført til Bestemmelse af det mekaniske Varmeækvivalent, synes at hvile paa Maalinger, der ikke alene angaar den irreversible Omdannelse af Arbejde til Varme, men ogsaa en reversibel Omdannelse af Arbejde til Varme eller af Varme til Arbejde, og naar denne genetiske Ækvivalens saa stærkt understreges i den traditionelle Behandling af Thermodynamiken, saa maa herom siges paa Basis af ovenstaaende almindelige Synspunkt, at saadanne Resultater altid vil være tilgængelige for, og efter nærværende Afhandlings Forudsætninger altid maa være underkastet, en Fortolkning, der principielt afviger fra den af den klassiske Thermodynamik givne. Man vil let se, at alle Methoder i Virkeligheden beror paa en Sammenligning af Arbejde, ydet i en reversibel Proces, med Varme, udviklet i den tilsvarende irreversible, idet det, der varierer fra Tilfælde til Tilfælde, alene er den Varme, der i samme Mængde tilføres udefra under det reversible og det irreversible Forløb.

Udfra Umuligheden af paa thermodynamisk Grundlag at bevise Existensen af den Ækvivalens af Varme og Arbejde, som Thermodynamiken hidtil har regnet med som en af dens Hovedsætninger, kunde det synes nærliggende at søge Ækvivalensprincipet erstattet med et ensidigt »Proportionalitetsprincip«, der holder sig til det rent erfaringsmæssige. Det er dog klart, at netop Umuligheden af Varmens Omdannelse til Arbejde forhindrer Ækvivalensprincipet i at kunne føre til nogen som helst thermodynamisk Modsigelse. Heller ikke Værdien af »Varmeækvivalentet«, d. v. s. det Antal mekaniske Arbejdsenheder, der medgaar til Frembringelse af en Varmeenhed, berøres af Valget imellem de to Alternativer. Naar det endvidere betænkes, at Ækvivalensprincipet har en sikker ikke-thermodynamisk Basis, vil der, selv om vi erkender og fastholder dets i thermodynamisk Henseende svigtende Grundlag, ikke være Grund til at indføre noget Forbehold i Anvendelse af dette Princip paa de Omraader, indenfor hvilke det hidtil har været anvendt.

Det er tværtimod Formaalet i nærværende Afsnit at udvide Ækvivalensprincipets Domæne til Omfattelse af alle Arbejdsomraader. De nye Fænomener, der viser sig, naar vi gaar over til at betragte Varmefrembringelsen ved ikke-mekaniske Processer, og som utvivlsomt har været den væsentlige Aarsag til den Begrænsning i Principet, som karakteriserer den klassiske Thermodynamik, bestaar i de samtidig med det irreversible Reaktionsforløb indtrædende Forandringer, som viser sig i det reagerende Systems »indre« energetiske Egenskaber, og som er ejendommelige for Grundprocessen, og derfor bestaar, selv om den irreversibelt dannede Varme udvikles udenfor Systemet. Saadanne Forandringer er vel principielt ogsaa til Stede, f. Ex. naar en Stofmængde flyttes fra et Gravitationspotential til et andet, men de er her af saa ringe Dimensioner, at de er uden Betydning for Problemet. Ved de kemiske, thermiske og spatiske Processer vil der derimod foraarsages Ændringer i alle de indgaaende »indre« Potentialer, d. v. s. Tryk, Temperatur og kemisk Potential, og de mekaniske Processers Simpelhed vil ikke længere være til Stede.

Vi har imidlertid i det foregaaende opstillet de almindelige Principer, hvorefter saavel Arbejdstab som Varmeudvikling ved den irreversible Proces kan bestemmes uafhængigt af deres Art. For Arbejdstabet gælder definitionsmæssigt Ligning (3), hvilket saavel for differentiale som for integrale Processer betyder, at Arbejdstabet er lige saa stort som Arbejdstabet i Systemet, naar den betragtede irreversible Proces reproduceres kinematografisk paa reversibel Maade. Og for Varmeudviklingen gælder definitionsmæssigt, at den er lig den Varmemængde, som maa tilføres ved denne reversible Reproduktion af Processen.

Idet vi i Overensstemmelse med Hovedtanken i nærværende Fremstilling generaliserer de for mekaniske Processer anerkendt gyldige Love til almen Anvendelighed, vil vi for irreversible Processer af vilkaarlig Art, og idet ovennævnte Definitioner for Arbejdstab og Varmeudvikling indføres, postulere, at det til de irreversible Processer knyttede Totalarbejdstab og den samtidig ved Processen udviklede Varmemængde er numerisk ækvivalente. Det kvantitative Indhold af dette Postulat, der kan formuleres ved Hjælp af Udtrykket:

$$\Sigma \delta A = \delta Q, \qquad (13)$$

vil vi betegne som det almindelige Ækvivalensprincip. Men det bør dog ikke overses, at Iagttagelsesgrundlaget ogsaa angaar Fortegnet for de i (13) indgaaende Størrelser.

Vi opstiller dette Princip som gyldigt for de irreversible Processer, der her særlig har været taget i Betragtning, nemlig de kvantitetsafsluttede Processer. Men da selve Arbejdsbegrebet, som tidligere bemærket, bestaar uantastet, naar der foruden Kvantitetstransporten foregaar en Tilførsel af Kvantitet, og da ogsaa Varmeudviklingsbegrebet er lige vel defineret i afsluttede og ikke afsluttede Systemer, vil vi betragte Ækvivalensprincipet som alment.

Med Hensyn til den experimentelle Verifikation af Principet gælder, at det herfor nødvendige Materiale til en vis Grad kan betragtes som identisk med det, den klassiske Thermodynamik har indsamlet som Bevis for »Energisætningen«. Det vil i alle Tilfælde principielt dreje sig om Betragtning af Processer, der kan forløbe i fuldstændig Afslutning fra Omgivelserne, idet Tilstanden I irreversibelt omdannes til Tilstanden II. Om en saadan Proces vil den klassiske Thermodynamik summarisk postulere, at den forløber uden Energiændring, selvom Tilstand I omdannes til Tilstand II i Kommunikation med Omgivelserne. Nærværende Fremstilling vil derimod, hvis der under den samme Tilstandsforandring optages Varmemængden Q fra Omgivelserne og udrettes Arbejdet A til Omgivelserne, definitionsmæssigt identificere disse Størrelser med henholdsvis Varmeudvikling og Arbejdstab ved den irreversible Proces. Ligestorheden af A og Q følger derefter paa Grundlag af Ækvivalensprincipet.

Problemer af denne Art vil iøvrigt blive nærmere behandlet i Afsnit 7, der omhandler Energibegrebet i Almindelighed. Paa dette Sted vil vi kun undersøge Ækvivalensprincipets Anvendelse paa de irreversible, rent thermiske Processer, der, som allerede berørt i den tidligere Afhandling, i visse Henseender frembyder særlig Simpelhed.

Den irreversible Proces, der forløber, naar to Varmereservoirer eller Kalorimetre bringes i thermisk Kontakt, er i det foregaaende anvendt som Grundlag for selve Varmebegrebet, idet det definitionsmæssigt fastsættes, at den af det ene Kalorimeter afgivne Varme er lige saa stor som den af det andet Kalorimeter modtagne. Denne Varmetransport er imidlertid et Naturfænomen, der i sin ydre Form er uden Sidestykke. Uden en Analyse, der kan bringe den ind under almindeligere Synspunkter, maa Varmen fortolkes substantielt som en Kvantitet, hvilket fører til thermodynamisk Konflikt, eller Tydningen maa baseres alene paa den molekularkinetiske Opfattelse. I det tidligere Arbejde er Varmebegrebet fortolket ved Paapegelsen af, at Varmeledningsprocessen er en Entropitransport, der som Følge af irreversibelt Forløb er ledsaget af en Varmeudvikling. Den fremstiller m. a. O. Virkeliggørelsen af den irreversible thermiske Grundproces, og dens enestaaende Art beror paa, at det alene er ved denne, at transporteret og frembragt Kvantitet er af identisk Art. At denne Opfattelse fører til en kvantitativ Overensstemmelse med Erfaringen, kunde vises paa Grundlag af Ækvivalenssætningen, og idet der benyttedes samme Temperaturskala ved Anvendelsen af det thermiske Arbejdsudtryk $\delta A = (T_1 - T_2)\, \delta S$ og ved Udtrykket $\delta Q = T \delta S$, der sammenknytter Varme og Entropi. Korrektheden af denne Behandling følger af den i Afsnit 3 af nærværende Afhandling givne Paavisning af, at de to nævnte Temperaturskalaer netop under den indførte Betingelse, at Ækvivalensprincipet er gyldigt, vil være identiske.

Derimod kan der overfor denne Fortolkning af Varmeledningsfænomenet gøres gældende, at den ikke helt har frigjort sig for et Element af ufortolket Varmetransport, idet nemlig den Varme, som opstaar ved Irreversibiliteten, og som dannes i den mellem de to Kalorimetre etablerede Leder, hvis Temperatur varierer fra T_1 til T_2, ifølge Ræsonnementet ledes videre til Omraader af lavere Temperatur ved en Proces, der er identisk med den, hvis Fortolkning søges.

Det er imidlertid ikke forbundet med Vanskelighed at opstille en fuldstændig energetisk Theori for Varmeledningsfænomenet paa det allerede benyttede Grundlag, idet enhver Varmetransport opfattes som en under Varme- eller Entropidannelse foregaaende Entropistrømning. Vi vil til dette Øjemed tænke os en stationær thermisk Strøm gennem en Leder, der forbinder to Varmereservoirer, hvis Temperatur er T_1 og T_2, maalt paa den thermiske Skala. Den stationære Tilstand er bestemt derved, at der overalt i Lederen gennem hvert Tværsnit passerer samme Mængde Varme Q pr. Tidsenhed. Den samtidig passerende Entropimængde S er i hvert Tværsnit givet ved:

$$Q = TS, \tag{14}$$

hvor T er Tværsnittets Temperatur. Entropistrømmen er saaledes ikke konstant, men vokser i Styrke med Afstanden fra den højere Temperatur T_1.

Ved Passage af Entropimængden S gennem Temperaturintervallet dT vil det thermiske Arbejdstab være:

$$\delta A = -SdT, \tag{15}$$

hvor T maales efter den energetiske Skala. Som vi har set, kan denne erstattes af den thermiske Skala, under Forudsætning af Ækvivalensprincipets Gyldighed. Under samme Forudsætning vil der ved den irreversible Passage i Stedet for Arbejdet δA opstaa en lige saa stor Varmemængde:

$$\delta q = -SdT = -Q d\ln T \tag{16}$$

og følgelig Entropien:

$$\delta s = -Sd\ln T = -Q\frac{dT}{T^2}. \tag{17}$$

Da denne deltager i Entropistrømningen, vil Mængden af strømmende Entropi gennem de forskellige Tværsnit af Lederen ændres efter Ligningen:

$$dS = -S d \ln T, \tag{18}$$

hvoraf ved Integration fra T_1 til T_2:

$$\ln \frac{S_1}{S_2} = -\ln \frac{T_1}{T_2}, \tag{19}$$

idet S_1 er den Entropimængde, der forlader T_1, og S_2 den, der ankommer til T_2. Da (19) ogsaa kan skrives:

$$T_1 S_1 = T_2 S_2,$$

eller ifølge (14):

$$Q_1 = Q_2, \tag{20}$$

ses det, at den givne Fortolkning af Ledningsprocessen som en i Overensstemmelse med Ækvivalensprincipet forløbende Entropistrømning umiddelbart fører til den i det foregaaende givne Beskrivelse af Varmen som irreversibelt transportabel. Klarlæggelse af Ledningsprocessens energetiske Mekanisme giver saaledes samtidig den energetiske Forstaaelse af selve Varmebegrebet.

Ovenstaaende Analyse giver tillige et klart Indtryk af Betydningen af den Temperatur, ved hvilken den irreversible Varmedannelse foregaar, for Størrelsen af den frembragte Varme i en Proces, der er givet ved sin Begyndelses- og Slutningstilstand. Hvis f. Ex. det mekaniske Arbejde A omdannes til Varme i et Kalorimeter af Temperaturen T under Overholdelse af Temperaturhomogenitet under hele Forsøget, vil efter Ækvivalensprincipet den udviklede Varmemængde Q være uafhængig af T. I en Række af forskellige Forsøg af denne Art, afvigende fra hinanden alene ved Kalorimetrenes Temperatur, er Q altsaa uforandret. Foretages derimod Varmetilførslen til et Kalorimeter paa »indirekte« Maade, saaledes at Varmen først udvikles ved Temperaturen T_1 og derfra ledes ned til den lavere Temperatur T_2, hvorved Begyndelsestilstanden og Slutningstilstanden bliver identiske med Begyndelses- og Slutningstilstanden i det tilsvarende »direkte« Forsøg ved T_2, saa vil Varmeudviklingen være forskellig i de to Tilfælde, idet der i det »indirekte« Forsøg til Varmemængden Q vil adderes den ved den irreversible Ledningsproces fra T_1 til T_2 udviklede Varme, hvis Værdi efter Formel (16) er:

$$Q'' = Q \ln \frac{T_1}{T_2}. \tag{21}$$

Lignende Forhold vil naturligvis gøre sig gældende ganske almindeligt ved de irreversible mekaniske eller lignende Processer, hvis den frembragte Entropi deltager i paafølgende irreversible Processer, saaledes f. Ex. hvis der ved Gnidning opstaar Temperaturforskelle, der derefter udjævnes ved thermisk Ledning. Forudsætningen for at den energetiske Varmeudvikling ved en mekanisk Proces kan bestemmes ved et simpelt Kalorimeterforsøg, d. v. s. Forudsætningen for, at den er identisk med den thermometriske, er altsaa, at der ikke under Forsøget opstaar Temperaturer, der i væsentlig Grad afviger fra Kalorimeterets Middeltemperatur i det paagældende Øjeblik.

Der skal sluttelig gøres opmærksom paa, at Gyldigheden af det almindelige Ækvivalensprincip tillader en skarpere Definition af de Betingelser, hvorunder den i det foregaaende Afsnit fastsatte Methode til Bestemmelse af Arbejdstabet og den energetiske Varmeudvikling kan gennemføres. Hvis det nemlig er givet, at den reversible Reproduktion af en irreversibel Proces kræver tilført udefra en Varmemængde, der er lige saa stor som det samtidig i et Arbejdsreservoir opsamlede Arbejde, saa vil denne Varmemængde for hvert enkelt Reaktionselements Vedkommende, og saaledes ogsaa for Totalprocessen, kunne tilvejebringes ved irreversibel Transformation af det tilsvarende Arbejdselement, efter at dette er opsamlet i Arbejdsreservoiret og dets Størrelse er konstateret. Der kræves i saa Fald ikke tilknyttet ydre Varmekilder af ubestemt Karakter, men den reversible Proces vil foregaa i et System, der i samme Grad som den irreversible, den reproducerer, er afsluttet fra Omgivelserne.

6. Det traditionelle Varmetoningsbegreb og Varme-Arbejds-Relationen.

Medens der efter Hovedsynspunkterne i nærværende Fremstilling ved de reversible Processer foregaar en Omsætning mellem forskellige Arbejdsarter i Overensstemmelse med Arbejdsprincipet, uden at Varme herved forbruges eller opstaar, vil der efter de traditionelle Forestillinger ved disse Processer kunne optræde saavel »Udvikling« som »Absorption« af Varme. Et saadant kalorisk Fænomen betegnes med et fra Thermokemien hentet Udtryk som Varmetoning. Vi skal nu underkaste denne Paastand en nærmere Prøvelse.

Der skal først erindres om, at den paa Arbejdsprincipet hvilende Beskrivelse af de reversible Processer udmærker sig ved den fuldstændige Symmetri, hvormed alle energetiske Kvantiteter og Potentialer indgaar saavel i de almindelige som i de specielle Formler. Paa Grundlag heraf maa, som ogsaa tidligere bemærket, enhver Usymmetri, der indføres i de reversible Processers Behandling, paa Forhaand henføres til en Skævhed allerede i Problemstillingen. Naar den traditionelle Opfattelse mener ved Siden af det thermiske Arbejde, der indtræder i de reversible Processer paa Linie med andre Arbejdsformer, at maatte indføre en anden, speciel thermisk Energiform, maa det derfor meget nøje undersøges, hvormed en saa paafaldende Antagelse er begrundet.

Denne Undersøgelse vanskeliggøres noget derved, at Theorien for det reversible Varmefænomen paa intet Sted i den traditionelle Thermodynamik er fremstillet blot nogenlunde i Sammenhæng. Der findes ingen Angivelse af de almindelige Principer, hvorefter man kan paavise en optrædende reversibel Varmetoning eller maale dens Størrelse. Et Studium af de Tilfælde, hvori det omhandlede Varmefænomen betragtes som en særlig fastslaaet Realitet, giver dog det Indtryk, at det er Temperaturændringen i Systemet, der efter de traditionelle Synspunkter tjener som Kriterium for en optrædende Varmetoning, og at dennes Fortegn er bestemt ved Temperaturændringens Fortegn. Hvad angaar Størrelsen af den frembragte eller forbrugte Varmemængde, synes den at blive beregnet i Overensstemmelse hermed som den Varmemængde, der skal fjernes fra det reagerende System eller tilføres dette, for at den paagældende Proces skal foregaa isothermt. Det er i Henhold til denne Opfattelse, at den traditionelle Fremstillings Varmetoning i det tidligere Arbejde er blevet betegnet som den thermometriske Varmetoning, idet dog denne Betegnelse vil blive anvendt paa det nævnte thermometriske Fænomen saavel for reversible som for irreversible Processer.

Idet vi i Mangel af en klar Definition indenfor selve det Videnskabsomraade, der hævder Realiteten af den reversible Varmetoning, antager, at Begrebet lader sig fastsætte i Overensstemmelse med ovenstaaende Antagelse, viser der sig overfor dette Begreb straks den ovenfor omtalte principielle Betænkelighed, beroende paa den herved i Behandlingen indførte Usymmetri. Det maa nemlig hævdes, at en Temperaturændring ved den reversible Proces i ingen Henseende kan gøre Krav paa en principielt væsentligere Betydning end en Ændring i andre energetiske Potentialer, f. Ex. Tryk og kemisk Potential, som samtidig optræder i Systemet. Det er derfor vilkaarligt og irrationelt at antage Dannelsen af en ny Energiart paa Basis af en Temperaturstigning uden at gøre nogen tilsvarende Antagelse paa Basis af en Ændring i Tryk og kemisk Potential.

Denne Betragtning er af saa afgørende Betydning, at der allerede heri synes at være tilstrækkeligt Grundlag for Afvisning af den traditionelle Paastand om det reversible Varmetoningsfænomen. Men end mere slaaende viser sig Nødvendigheden heraf, naar man betænker Arbejdsprincipets Fordring, at det totale Arbejdstab i et reversibelt lukket System er Nul. Hvis Varme opstod eller forsvandt i et lukket System ved reversible Processer, vilde en saadan Proces kollidere med Ækvivalens- og Energiprincipet, idet der intet Ækvivalent vilde kunne paapeges for den opstaaede eller forbrugte Varme.

Ogsaa uden Antagelse af Arbejdsprincipet i dets fulde Almindelighed vil denne Konklusion kunne drages ved Betragtning af simple Tilfælde, i hvilke Arbejdsomsætningen fra alle Synspunkter er utvivlsom. Er det paagældende System f. Ex. en Luftart, der ændrer sit Rumfang reversibelt i Kommunikation med et Arbejdsreservoir, vil Arbejdstabet $p\delta v$ i Luftarten være knyttet til Arbejdsgevinsten δA i Reservoiret. Da disse to Arbejdsmængder ved Maaling i samme mekaniske Enheder viser sig fuldstændig identiske, vil det efter Ækvivalensprincipet være udelukket, at der herved kan ske Dannelse eller Forbrug af Varme, der jo dog ogsaa efter de klassiske Anskuelser er en Form for Energi, hvis Opstaaen kræver sit Ækvivalent.

Den her nævnte Proces har for ideale Luftarters Vedkommende spillet en vigtig Rolle i Theorien for de reversible Varmefænomener og for Varme-Arbejds-Transformationen i det hele, idet den har været anset for paa en særlig anskuelig Maade at illustrere den formentlige Overgang fra Varme til Arbejde og omvendt. Komprimeres en ideal Luftart i thermisk Kommunikation med et stort Varmereservoir, vil nemlig den i Reservoiret optagne Varmemængde være lige saa stor som det tilførte Arbejde, og den komprimerede Luftart kan nu expandere irreversibelt uden at ændre sin Temperatur, hvorved Systemets oprindelige Tilstand genoprettes. Samtidig kan som det faktiske Nettoresultat noteres et kalorisk Fænomen, bestaaende i, at det tilførte Arbejde er omdannet til en ækvivalent Varmemængde. Efter den klassiske Thermodynamik[1] er det den reversible Kompression, der foraarsager det ydre Arbejdstab og Dannelse af den ækvivalente Varmemængde, der overføres til Reservoiret, medens den efterfølgende irreversible Expansion er et uvirksomt Tillægsfænomen, der foregaar uden »Energiomsætning«. Efter nærværende Fremstilling derimod sker Arbejdstab og Varmedannelse naturligvis ved den irreversible Del af Processen, medens den reversible, hvis Totalarbejdstab er Nul, kun er ansvarlig for den Temperaturstigning, der optræder sammen med Ændring af de andre energetiske Potentialer, og som tillader den neutrale Overføring af en endelig Varmemængde til Reservoiret at finde Sted.

De særlig simple Forhold, der i fysisk Henseende udmærker de ideale Luftarter, gør disse til en vis Grad til far-

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[1] Jfr. f. Ex. Müller Pouillet: Lehrbuch d. Physik III, 654 (1907).

lige Objekter for de energetiske Undersøgelser, der har principielle og almene Lovmæssigheder som Maal. Betragtning af det specielle er ofte en uheldig Vej til Forstaaelse af det almindelige. Ovenstaaende traditionelle Fortolkning af Expansionsprocessen og Resultater af lignende Art, der er omtalt i den tidligere Afhandlings Afsnit 6, er bemærkelsesværdige Exempler i denne Henseende. Til den herskende Uklarhed har utvivlsomt ogsaa bidraget Indførelsen af molekulartheoretiske Argumenter i den energetiske Betragtning, idet man identificerer den kinetiske Molekylenergi med »Varme«, opfattet mere som en abstrakt Artsbetegnelse end som en Størrelse eller Mængde, der er skarpt energetisk defineret[1].

Saavel af Symmetrigrunde som af Hensyn til Opretholdelse af Varme-Arbejds-Ækvivalensprincipet er det saaledes nødvendigt at afvise Antagelsen af en Dannelse eller et Forbrug af Varme ved den reversible Proces. Spørgsmaalet kan imidlertid ikke anses for paa udtømmende Maade diskuteret, uden at det særlige Forhold, som den klassiske Thermodynamik har opstillet i Forbindelse med Varme-Arbejds-Transformationen, er taget i Betragtning. Det er velbekendt, at en saadan Transformation ikke anses for mulig som isoleret Proces, men menes kun at foregaa i Forbindelse med visse ledsagende Processer, der betegnes som Kompensationer. Det er paa ingen Maade ualmindeligt, at dette Krav paa mere eller mindre aabenlys Maade tilsidesættes ved de til dette Emne knyttede Betragtninger, men i Realiteten er Fordringen derom utvivlsomt til Stede, og selve 2den Hovedsætning i Thermodynamiken er i den W. THOMSON'ske Formulering et Udtryk

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[1] Jfr. f. Ex. R. CLAUSIUS: Die kinetische Theorie der Gase, p. 16 (1889—91).

for Nødvendigheden heraf. Til Afgørelse af, hvilken Rolle man kan tillægge disse Kompensationsprocesser, vil det nu være formaalstjenligt først at opstille en almindelig, rent skematisk Inddeling af Reaktionsformernes logiske Muligheder. Vi vil hertil benytte den klassiske Karakteristik, der er baseret paa Processens Entropiændring, og som ogsaa nærværende Fremstilling, i Overensstemmelse med Betragtningen i Afsnit 9, kan slutte sig til.

Vi finder, idet vi betragter kvantitetsafsluttede Systemer, følgende Muligheder:

1. Processer, ved hvilke Entropien forøges. Isolerede Processer af denne Art er irreversible.

2. Processer, ved hvilke Entropien ikke forandres. Disse Processer er reversible.

3. Processer, ved hvilke Entropien formindskes. Disse Processer, tagne for sig, er efter alle Synspunkter uigennemførlige.

Som allerede tidligere bemærket, vil en i Naturen virkeligt forløbende Proces altid kunne opfattes som sammensat af Delprocesser, der i Tilfælde af reversible Totalprocesser alene vil være Grundprocesser, tilhørende den ovenstaaende Kategori 2. Ved denne Sammensætning af den reversible Totalproces vil Arbejdsprincipet overholdes og Entropikonstansen fremkomme som en naturlig Konsekvens af Reversibiliteten. Rent skematisk vil imidlertid den reversible Totalproces ogsaa kunne sammensættes af Processer, hørende under Kategorierne 1 og 3, idet Entropigevinsten i den ene tænkes at kompensere Entropitabet i den anden. M. a. O. den reversible Totalproces kan rent skematisk sammensættes af eller spaltes i to Delprocesser, af hvilke den ene er irreversibel og den anden umulig.

En nærmere Undersøgelse af dette Spørgsmaals Behandling vil vise, at den ovenfor skildrede Methode i den traditionelle Thermodynamik ikke alene betragtes som en skematisk Sammensætning af den reversible Totalproces, men ogsaa som dens genetiske Fortolkning i en Række vigtige Tilfælde. Tankegangen er den, at den umulige Proces bliver muliggjort ved Tilknytning af den irreversible som »Kompensation«. For visse Enkeltprocesser, særlig Varmekraftmaskinens Funktion, er denne Fortolkning behandlet i den tidligere Afhandling, og der skal herom eller om den thermiske Grundproces i Almindelighed her kun gøres opmærksom paa, at det ikke er muligt ved dens skematiske Sammensætning efter klassisk Methode at præcisere Processen i en saadan Grad, at Temperaturen af den Varmemængde, der er Genstand for den formentlige Arbejdstransformation, lader sig bestemme. I hvilket Omfang, den nævnte Fortolkning tænkes gennemført almindeligt i den traditionelle Behandling, kan vanskeligt afgøres, da Problemet slet ikke synes at have paakaldt Opmærksomheden, men da der ikke er fastslaaet noget Princip, der tillader at adskille de for de forskelligartede Fortolkningsmethoder tilgængelige Tilfælde fra hinanden, og det heller ikke ses, paa hvilken Basis et saadant Princip skulde kunne opstilles, maa man principielt anse denne Methode for alment karakteriserende for den traditionelle Behandling af de reversible Processer.

Der kan dog ikke være Tvivl om, at den fuldkomne Vilkaarlighed, hvormed den omtalte Spaltning af den reversible Proces lader sig realisere, i sig selv berøver Methoden og de paa dens Anvendelse beroende Konklusioner enhver theoretisk Betydning. Er Totalprocessen:

$$X \rightarrow Y \qquad \text{(I)}$$

og Delprocesserne:

$$X_1 \rightarrow Y_1 \qquad \text{(II)}$$

og:

$$X_2 \rightarrow Y_2, \qquad \text{(III)}$$

vil man nemlig som Partialproces (II) kunne indsætte en hvilkensomhelst imaginær Proces, idet Kompensationsprocessen (III) derefter altid vil kunne indrettes paa en saadan Maade, at:

$$X_1 + X_2 = X,$$

$$Y_1 + Y_2 = Y,$$

d. v. s. saaledes at Totalprocessen (I) fremkommer. F. Ex. skulde den reversible Udladning af et Akkumulatorbatteri kunne opfattes som en Omdannelse af Varme til elektrisk Arbejde og paafølgende irreversibelt, kompenserende Forløb af den kemiske Udladningsproces, medens omvendt Opladningen skulde opfattes som en spontan, mod Affiniteten foregaaende kemisk Ladningsproces, kompenseret af det tilførte elektriske Arbejdes Omdannelse til Varme. En saadan Opfattelse vilde være analog med Clausius's Fortolkning af Varmekraftmaskinen. De ovenstaaende Betragtninger udelukker dog saadanne i sig selv ganske unaturlige Fortolkninger fra nogen Realitetsbetydning, og den derpaa hvilende Argumentation for Muligheden af en Varme-Arbejds-Transformation maa erkendes ikke at føre til det tilsigtede Maal.

Det er et afgørende Punkt i de ovenstaaende Betragtninger, at en Temperaturændring ikke i al Almindelighed kan tages som Tegn paa en i Systemet foregaaende kalorisk Proces, naar der herved forstaas Dannelse eller

Forbrug af en Varmemængde, hvortil der svarer et Arbejdsækvivalent. At der optræder en »thermometrisk Varmetoning« er utvivlsomt, thi denne er, efter det ovenstaaende, defineret ved Temperaturændringen, men dette er et rent Terminologispørgsmaal, og at tillægge den Karakter af Varme i energetisk Forstand vilde føre til Konflikt med Energiprincipet. Kun hvis Systemet har »Kalorimeterkarakter«, er der — saaledes som benyttet i selve Varmedefinitionen — en simpel Sammenhæng mellem Temperaturændring og Varmemængde. Det følger heraf, at heller ikke til Bestemmelse af den til irreversible Processer knyttede og med Arbejdstabet ækvivalente Varmeudvikling vil et Temperaturudslag kunne tjene, idet et saadant kun for en Del er betinget af Irreversibiliteten. Bestemmelse af denne Varmemængde maa, som beskrevet i forrige Afsnit, ske paa en anden Maade.

Til den Varmemængde, der beregnes paa Basis af et Temperaturudslag i et reagerende System, og som vi har betegnet som den thermometriske Varmetoning, knytter der sig dog i visse Tilfælde først og fremmest for isotherme, irreversible Processer betydelig Interesse. Erindres det, at den ifølge den ovenfor vedtagne Definition, for en given Proces er identisk i Størrelse med den Varmemængde, som maa fjernes fra det reagerende System eller tilføres dette, for at den paagældende Proces kan forløbe isothermt, saa ses det, at denne Definition umiddelbart kun kan anvendes paa differentiale Processer. Ved Processer af endelig Udstrækning faas Varmetoningen ved Integration af de differentiale Varmetoningselementer fra Begyndelses- til Slutningstilstanden gennem et endeligt Temperaturinterval.

7. Energi.

Det egentlige Grundlag for Thermodynamikens Energibegreb er Sætningen om Varmens og Arbejdets Ækvivalens. Saalænge vore Betragtninger er indskrænkede til de reversible Processer, der paa udtømmende Maade er beskrevne ved Gyldighed af Arbejdsprincipet $\Sigma \delta A = 0$, vil Betegnelsen af Arbejdet som »Energi« og af Arbejdstabet som et Energitab ikke medføre nogen ny Begrebsdannelse eller i det hele taget have nogen Realitetsbetydning. Lige saa lidt vil Betegnelsen af Varmen som »Energi« paa nogen Maade være et nyt Karakteristikum for Varme ved saadanne Processer, hvori der kun foregaar en Varmetransport paa reversibel Maade, d. v. s. ved konstant Temperatur. Hvis vi derimod under vore Betragtninger inddrager ogsaa de irreversible Processer, ved hvilke Arbejde efter vore Forudsætninger alment omdannes til Varme, vil den numeriske Ækvivalens, som herved viser sig at være til Stede, tilkendegive Existensen af et Fællesbegreb, der omfatter begge disse Størrelser, og for hvilket det vil være naturligt og nyttigt at indføre en særlig Betegnelse. Det er paa denne Basis, Energibegrebet i Thermodynamiken er frembragt. Hvis vi definerer den Energimængde, der opstaar i et i alle Henseender afsluttet System som Følge af deri foregaaende Processer, ved Ligningen:

$$\delta E'' = \delta Q'' - \delta A'', \tag{22}$$

der udtrykker, at denne Energimængde er den udviklede Varme minus Arbejdstabet, og hvis vi i denne Ligning indfører Ækvivalensprincipet: $\delta Q'' = \delta A''$, saa følger heraf:

$$\delta E'' = 0, \tag{23}$$

en Sætning, der betegnes som Energiprincipet. Der udsiges herved, at der ikke kan ske Energiændringer i et System, der er fuldstændig afsluttet fra Omgivelserne, idet Tilvækst og Tab indenfor Systemet vil ophæve hinanden. Sætningen kaldes ogsaa Thermodynamikens 1ste Hovedsætning eller Loven om Energiens Konstans. Da (22) er en Energidefinition, ses det dog let, at denne under forskellige Betegnelser optrædende Grundsætning ikke gaar ud over det, der allerede i Ækvivalensprincipet er postuleret som et direkte Udtryk for energetiske Erfaringer.

Der kendes i Thermodynamiken ingen Processer, der er sideordnede med Arbejds-Varmetransformationen. Energiprincipet er derfor en Lov af særlig Karakter, principielt ganske forskellig fra Loven om »Materiens Konstans«, med hvilken den ofte parallelliseres. En Relation imellem Stof og Energi, som Relativitetstheorien forlanger, ligger udenfor Thermodynamiken.

Energibegrebet er dog ikke udtømmende beskrevet ved Relationen (22), der alene redegør for Processer i afsluttede Systemer. Vi vil definitionsmæssigt fastsætte, at en Ligning af Formen (22) fremstiller Energitilvæksten i et System ogsaa for de Tilfælde, hvor Arbejdet og Varmen tilføres udefra til Systemet. Den almindelige Energidefinition gaar imidlertid videre, idet den ogsaa tager saadanne Forandringer af et System i Betragtning, som hidrører fra Tilførsel udefra af Kvantiteter af vilkaarlig Art. Vi vil med W. Gibbs[1] og i Overensstemmelse med de i den foregaaende Afhandling fremsatte Betragtninger definere Energien alment ved Udtrykket:

$$dE = \Sigma P dK, \qquad (24)$$

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[1] W. Gibbs: Collected Works I, Thermodynamics, p. 63 (1928).

idet dE betegner den Energimængde, som tilføres til det betragtede System, naar dette ved det deri herskende Potential P faar Kvantitetstilvæksten dK. For Energi, der efter (24) hidrører fra Kvantiteter, der kan betegnes som faktisk tilførte, er denne Ligning af ganske formel Karakter. At den kan anvendes som et almindeligt Energiudtryk, der ogsaa omfatter de ved (22) fremstillede Energiarter, følger deraf, at ogsaa disse sidste kan skrives paa den ved (24) givne Form. Vi har jo nemlig for Arbejdstabet og Varmeudviklingen de i det foregaaende opstillede og begrundede Formler:

$$\Sigma \delta A = \Sigma (P_1 - P_2)\, \delta K \qquad (25)$$

og:

$$\delta Q = \Sigma T \delta S, \qquad (26)$$

der begge er konforme med (24). Vi vil understrege denne Forskel ved at spalte den totale Energitilvækst i to Led:

$$\delta E = \delta E' + \delta E'', \qquad (27)$$

af hvilke:

$$\delta E' = \Sigma' P \delta K \qquad (28)$$

og:

$$\delta E'' = \Sigma'' P \delta K \qquad (29)$$

fremstiller de Energioptagelser, der hidrører henholdsvis fra tilførte og indenfor Systemet transporterede eller opstaaede Kvantiteter, idet vi herved lader »Systemet« omfatte ogsaa de Afsnit af »Omgivelserne«, hvormed det kun er arbejdskommunicerende.

Ved Indførelse af (23) i (27) faas:

$$\delta E = \delta E' = \Sigma' P \delta K, \qquad (30)$$

der direkte udtrykker, at Energitilvæksten i et System er = den udefra optagne Energi, og at derfor, i Overensstemmelse med Ækvivalensprincipets Fordringer, Energien i et afsluttet System er konstant.

Det er af Betydning at bemærke den Væsensforskel, der karakteriserer de to Energibestanddele $\delta E'$ og $\delta E''$, hvori den totale Energitilvækst kan spaltes. Leddet $\delta E''$ er, som udtrykt ved Ligning (22), sammensat af Energimængder, der er genetisk og kvantitativt sammenknyttede ved de existerende Varme-Arbejds-Relationer. Energien $\delta E'$ derimod, der hidrører fra Kvantitetstilførsel udefra, repræsenteres ikke i noget Ækvivalensprincip og lader sig ikke almindeligt beregne paa Grundlag af dens faktorielle Sammensætning. En Omdannelse til andre Energiformer vilde nemlig kræve, at Kvantiteten δK enten blev frembragt eller tilintetgjort. Og en Beregning af Energimængden vilde fordre, at Potentialets absolute Værdi var energetisk tilgængelig. F. Ex. maatte man for Rumfangsenergiens Vedkommende kræve, at i Udtrykket $dE = -pdv$ Rumfanget dv kunde tilintetgøres, og Trykket p bestemmes absolut. Ingen af disse Muligheder er til Stede. Kun hvis Entropi er den tilførte Kvantitet, er Forholdet anderledes, idet saavel Entropien kan opstaa, og Varme derfor dannes af Arbejde, som ogsaa det tilhørende Potential, Temperaturen, som vist i Afsnit 3, er tilgængelig for absolut energetisk Bestemmelse, netop paa Grundlag af Entropimængdens Inkonstans. Det er herigennem, at Varmen eller Produktet $T\delta S$ opnaar en Tilknytning til Arbejdet, som andre analoge Energier af Formen $P\delta K$ ikke er i Besiddelse af.

Den almindelige Ligning (24) har saaledes udelukkende formel Betydning. En Energitilvækst, som et System undergaar ved Tilførsel af et herhenhørende δK kan kun kompenseres ved Fjernelse af denne Kvantitet under Betingelser i Systemet, der er identiske med Betingelserne under dens Tilførsel.

Ved Siden af den ved (23) udtrykte Sætning, der omfatter afsluttede Systemer, er der i den traditionelle Thermodynamik opstillet et Energiprincip, der omfatter Systemer, der er aabne for Kvantitetstilførsel. Dette Princip postulerer, at Energien er en Tilstandsfunktion, eller at Energiændringen ved Overgang af et System fra en Tilstand I til en Tilstand II vil være uafhængig af den Vej, ad hvilken Overgangen sker. Vi vil til Undersøgelse af denne Sætnings Forhold til Arbejds- og Ækvivalensprincipet og til Energidefinitionen (24) lade det betragtede System gennemløbe en reversibel Kredsproces i Kommunikation med et Arbejdsreservoir og et Antal Kvantitetsreservoirer. Er Potentialerne i Systemet P og i Reservoirerne P°, vil den i Systemet og i Reservoirerne optagne Energi være henholdsvis:

$$\Delta E = \oint P_1 dK_1 \tag{31}$$

og:

$$\Delta E^\circ = \oint P_1^\circ dK_1^\circ . \tag{32}$$

Er Arbejdstabet i Arbejdsreservoiret ΔA, gælder endvidere for Totalsystemet:

$$\Delta E + \Delta E^\circ = \Delta A . \tag{33}$$

Da Systemet, som Følge af Kvantitetetens Karakter af Tilstandsfunktion, under en Del af Processen vil have afgivet til et Reservoir den samme Mængde af den paagældende Kvantitet, som det har modtaget fra samme Reservoir i en anden Del af Processen, og da Potentialet i Reservoiret, der kun kommunicerer med Hensyn til en enkelt Kvantitet, alene afhænger af den heraf i ethvert Stadium af Processen afgivne Mængde, maa den Energimængde, som ialt er optaget i Reservoirerne, ved Kredsprocessens Afslutning være Nul:

$$\Delta E^{\circ} = 0. \qquad (34)$$

Det samme maa da gælde for det reagerende System + Arbejdsreservoiret, da disse i Forening med Kvantitetsreservoirerne udgør det afsluttede Totalsystem. Da det reagerende System er vendt tilbage til sin oprindelige Tilstand, og et Arbejdsudslag i Arbejdsreservoiret derfor vilde være opstaaet uden et dertil svarende Ækvivalent i andre Dele af Totalsystemet, maa man ifølge Arbejdsprincipet sætte $\Delta A = 0$. Men heraf følger:

$$\Delta E = 0, \qquad (35)$$

hvilket betyder, at Reaktionssystemets Energi efter Kredsprocessen er uforandret.

Er den betragtede Kredsproces irreversibel, udkræves yderligere til Beviset et Entropireservoir, til hvilket den i Systemet irreversibelt dannede Entropi overføres. I saa Fald vil, som det let ses, Indførelse af Ækvivalensprincipet i Stedet for Arbejdsprincipet føre til samme Resultat som ovenfor.

Vi finder altsaa, at det er muligt paa Basis af disse to Principer og Energidefinitionen (24) at aflede et Energiprincip, der udtrykkes ved Paastanden om, at Energien af et System ikke ændrer sig, naar Systemet i vilkaarlig Kommunikation med Omgivelserne gennemløber en Kredsproces. Denne Sætning er ensbetydende med, at Energien er en Tilstandsfunktion, og med andre tidligere nævnte

Former, hvorunder Energiprincipet for aabne Systemer optræder i den traditionelle Fremstilling.

Det samme ses udfra vor almindelige Energidefinition (24) ved den Gibbs'ske Integrationsmethode. Tænkes et givet System opbygget af dets infinitesimale Kvantitetselementer, omfattende Stof, Rumfang og Entropi, paa en saadan Maade, at disse tilføres fra givne Reservoirer i det Forhold, hvori de er til Stede i Systemet, vil alle kemiske Potentialer, saavel som Tryk og Temperatur, forblive konstante under Opbygningen. Ved Integration af Ligning (24), der under de fastsatte Betingelser er let gennemførlig, faas som almindeligt Udtryk for et Systems Energi:

$$\mathrm{E} = \Sigma \mathrm{P}_1 \mathrm{K}_1. \tag{36}$$

Denne Ligning viser, at E er en Tilstandsfunktion, da alle de sammensættende Faktorer P og K er Tilstandsfunktioner.

Efter Ligning (36) kan Energien af et System opfattes som sammensat af forskellige Energiformer, der hver for sig er Tilstandsfunktioner, og hvis Sum er Totalenergien:

$$\mathrm{E} = \mathrm{E}_1 + \mathrm{E}_2 + \ldots\ldots\ldots, \tag{37}$$

hvor:

$$\mathrm{E}_1 = \mathrm{P}_1 \mathrm{K}_1,$$
$$\mathrm{E}_2 = \mathrm{P}_2 \mathrm{K}_2,$$

o. s. v. Tænkes Systemet opbygget alene af Entropi, Rumfang og Stof, bliver Energiudtrykket:

$$\mathrm{E} = \mathrm{TS} - \mathrm{pv} + \mu_1 \mathrm{n}_1 + \mu_2 \mathrm{n}_2 + \ldots\ldots\ldots, \tag{38}$$

hvor man kan sætte:

$E_S = TS \quad = $ Thermisk Energi.

$E_v = -pv = $ Rumfangs- eller spatisk Energi.

$E_{n_1} = \mu_1 n_1 = $ Kemisk Energi (1).

$E_{n_2} = \mu_2 n_2 = $ Kemisk Energi (2)

o. s. v.

Ved almindelig Differentiation af (36) vil Energiændringen for hver Energiarts Vedkommende dele sig i to Led:

$$dE_1 = P_1 dK_1 + K_1 dP_1, \tag{39}$$

af hvilke det første repræsenterer den Tilvækst i den paagældende Energiart, som skyldes Tilførsel, Transport eller Produktion af den tilhørende Kvantitet, medens det andet hidrører fra en Potentialtilvækst, som er en Følge af Systemets vilkaarlige Ændring. Summen af de førstnævnte Energiændringer giver efter (24) den totale Energiændring, medens den sidstnævnte, som man let ser, i Følge den Gibbs'ske Fundamentalligning:

$$\Sigma K_1 dP_1 = 0 \tag{40}$$

har Summen Nul.

Ligning (40) kan betragtes som Udtrykket for et specielt »Energiprincip«, der indenfor de ved dets Form bestemte Rammer er af universel Gyldighed, i Modsætning til det analoge Udtryk (35), der kun gælder for afsluttede Systemer. Det er altsaa meget vel muligt for hver enkelt Energiart at operere med et Differential, der bestemmes af Potentialændringen ved konstant eller variabel Kvantitet, men ved Beregningen af den totale Energiændring vil disse Differentialer automatisk forsvinde.

Det er paa Grundlag af denne Betragtning aabenbart, at ingen Energimængde af Formen KdP kan indgaa i energetiske Processer som Ækvivalent for Arbejde eller Energiændringer af Formen PdK, der ifølge (24) giver et fuldstændigt Udtryk for de Ændringer, som et Systems Energi undergaar i eller uden Kommunikation med Omgivelserne. Det vilde derfor være fuldstændig misvisende f. Ex. at opfatte den thermiske Energi TS som Varme efter den Definition, der i det foregaaende er givet af Begrebet en Varmemængde. Dette Synspunkt er af Interesse i det navnlig i Afsnit 6 behandlede Spørgsmaal om den reversible Varme-Arbejds-Transformation og bidrager til at belyse Arten af de Argumenter, hvorved den traditionelle Thermodynamik har søgt at løse dette Problem.

Den ovenstaaende Fremstilling benytter, som det ses, den i og for sig nærliggende Fremgangsmaade at definere Energien af et System og postulere de for Energien gældende Love paa Grundlag af de Forandringer, der foregaar med selve Systemet. Den klassiske Methode er forskellig herfra, idet det efter W. Thomson og Planck er almindeligt at definere Energiændringen af et System ved dets Overgang fra Tilstand I til Tilstand II som det mekaniske Ækvivalent af alle »ydre Virkninger«, der ledsager denne Overgang, og at opstille dette Ækvivalents Uafhængighed af den særlige Mekanisme, hvorefter denne Overgang fra I til II finder Sted, som det egentlige Energiprincip[1]. Hvis vi betegner »Systemet« med A og Omgivelserne med B, saaledes at A + B er et fuldstændig afsluttet Totalsystem, er det altsaa den klassiske Methode til Bestemmelse af Energiændringen i A at undersøge Forandringerne i B. Da A og B imidlertid maa betragtes som principielt ganske sideordnede Enheder, maa denne

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[1] William Thomson: Trans. Roy. Soc. Edinburgh **20**, 475 (1853). M. Planck: »Das Prinzip der Erhaltung der Energie«, p. 104 (1913), og Thermodynamik, 9te Aufl., p. 40 (1930).

Methode umiddelbart synes formaalsløs. Den kan naturligvis være fordelagtig, i det Tilfælde at A er et indviklet System og B et simpelt, f. Ex. et Arbejdsreservoir. Men da dette ikke kan alment forudsættes, og f. Ex. ogsaa den Mulighed er til Stede, at A er simpelt og B indviklet, saa ses det ikke, at der i den anviste Methode skulde være givet et Energidefinitionsprincip, der paa nogen Maade har almindelig eller principiel Betydning.

Det maa endvidere bemærkes, at det »mekaniske Ækvivalent« af ydre Virkninger kun er principielt tilgængeligt, naar disse »Virkninger« er repræsenterede af de forskellige Arbejdsarter og Varme. Hvis der til Systemet eller dets Omgivelser føres Kvantitet, f. Ex. en kemisk Komponent, kan det mekaniske Ækvivalent heraf ikke umiddelbart angives. Selv uden en Definition af dette Ækvivalent kan Energiprincipet for aabne Systemer — saaledes som ovenfor vist ved Anvendelse af Ligning (24) — dog afledes og udtrykkes ved Paastanden om Energiens Tilstandsfunktionskarakter. Bestaar Problemet derimod i Angivelse af Størrelsen af den Energiændring, som et System undergaar ved en vilkaarlig Tilstandsforandring, saa kræves der, som i det hele taget ved Anvendelse af de thermodynamiske Funktioner, en Standardisering af de forskellige Kvantiteters Potentialer i valgte Normaltilstande. Dette er naturligvis Forudsætningen for Beregning af Energiændringen efter (24) og alle andre Ligninger, der udtrykker Energiændringen som Funktion af et Potential, der er forskelligt fra Temperaturen. Men det maa ogsaa være Forudsætningen for den klassiske Energidefinition, saafremt den skal udstrækkes til Gyldighed for Systemer, der paa vilkaarlig Maade er udsat for Indgreb fra Omgivelsernes Side.

8. Arbejdet og den integrale Proces.

Arbejdsbegrebet er i 1ste Afsnit blevet udviklet paa Basis af Betragtninger over den differentiale Proces, d. v. s. en Proces, i hvilken infinitesimale Kvantiteter transporteres gennem endelige Potentialdifferenser. At Arbejdet ved Processer af endelige Dimensioner kan faas ved Integration af det differentiale Arbejdsudtryk, naar Integrationsvejen er fastlagt, har ogsaa været benyttet som en selvfølgelig Slutning ved forskellige Problemers Behandling i det foregaaende. I dette Afsnit skal Spørgsmaalet om det integrale Arbejde betragtes med særligt Henblik paa de Synspunkter, der er herskende ved den traditionelle Behandling af dette Emne.

I Undersøgelsen af det Arbejde, der er knyttet til en integral Proces, vil det System, som omfattes af Processen, kunne være defineret som et fuldstændig afsluttet System, eller det kan være koblet til et ydre Arbejdsreservoir, eller der kan være Adgang for Tilførsel til det af vilkaarlige Kvantiteter. Afhængende af de fastsatte Betingelser, vil Arbejdssætningen fremtræde i forskellig Form.

Vi vil opstille Opgaven i Overensstemmelse med den traditionelle Behandling, idet der spørges: Hvilket Arbejde kan vindes, d. v. s. registreres i et tilkoblet Arbejdsreservoir, ved reversibel Overgang af et givet System til et andet?

Saafremt de to Systemer er givne med samme Indhold af hver af de indgaaende Kvantiteter, vil den reversible Omdannelse: System I → System II kunne foregaa kvantitetsafsluttet fra Omgivelserne. I dette Tilfælde vil alene Anvendelsen af Arbejdsprincipet vise, at Arbejdet, som registreres i Arbejdsreservoiret, er uafhængigt af den Vej, ad hvilken Processen forløber. I Overensstemmelse hermed kan der, som berørt i Afsnit 1, tillægges saadanne Systemer en potentiel Energi, der kun afhænger af Tilstanden, og hvis Differens i to givne Tilstande angiver det paagældende Arbejde.

Saafremt derimod Indholdet af Kvantitet i de to givne Systemer ikke er det samme, idet Kvantitetsmængden i System I er:

$$\mathrm{K}_1^{\mathrm{I}},\ \mathrm{K}_2^{\mathrm{I}},\ \mathrm{K}_3^{\mathrm{I}},\ldots\ldots$$

og i Systemet II:

$$\mathrm{K}_1^{\mathrm{II}},\ \mathrm{K}_2^{\mathrm{II}},\ \mathrm{K}_3^{\mathrm{II}},\ldots\ldots,$$

saaledes at der til Omdannelse af det givne Begyndelsessystem I til det givne Slutningssystem II kræves tilført Kvantiteterne:

$$\mathrm{K}_1^{\mathrm{II}}-\mathrm{K}_1^{\mathrm{I}},\ \mathrm{K}_2^{\mathrm{II}}-\mathrm{K}_2^{\mathrm{II}},\ldots\ldots,$$

saa er aabenbart Spørgsmaalet om, hvilket Arbejde der kan vindes ved denne Proces, fuldkommen ubestemt og uden Mening, idet der ved Spørgsmaalets Formulering intet er givet om, hvorfra de paagældende Kvantiteter skal hentes, om Arbejdet, der vindes ved Overføring af disse til Systemet, skal medregnes til det søgte Arbejde, eller i Tilfælde heraf, om Overføringen skal foretages paa reversibel eller irreversibel Maade.

Vi skal ved Undersøgelsen af den almindelige Behandling af dette Problem først betragte visse Specialtilfælde. Lad den paagældende Proces være en adiabatisk Gasexpansion. Dette betyder, at Begyndelsessystemet er en Luftart af et Rumfang v^{I} og Slutningssystemet samme Luftart af Rumfanget v^{II}, og at Rumfanget er den eneste Kvantitet, med Hensyn til hvilken de to Systemer differerer.

Det Arbejde, der kan vindes ved denne Proces, er efter den traditionelle Opfattelse:

$$A = \int_{I}^{II} pdv, \tag{41}$$

en Størrelse, der aabenbart har en bestemt, ved Tilstandene I og II given Værdi, da ved den adiabatiske Tilstandsforandring Integrationsvejen for Differentialet er fastlagt.

Forudsætningen for dette Udtryks Rigtighed er, som man let ser, dels at Rumfanget $v^{II} - v^{I}$, hvormed Systemet er blevet forøget, er hentet fra et Vakuum, dels at Overføringen fra Vakuum til Systemet er foregaaet reversibelt, og endelig, at Overføringsarbejdet er medregnet i det søgte Arbejde.

Som næste Specialtilfælde vil vi betragte samme Begyndelsessystem med Entropien S^{I}, medens Slutningssystemet har Entropien S^{II}, og iøvrigt alle andre Kvantiteter er identiske. Arbejdet A ved Omdannelsen af System I til System II er efter den traditionelle Opfattelse Nul. Forudsætningen for Rigtigheden heraf er aabenbart, at det Arbejde, som vindes ved den reversible Overføring af Entropien $S^{II} - S^{I}$ fra det Entropireservoir, hvorfra det hentes, til Systemet, enten ikke er medregnet, eller paa Grund af specielt Valg af Reservoiret har Værdien Nul, eller, som tredje Mulighed, at Overføringen er foregaaet paa irreversibel Maade.

Som tredje Specialtilfælde vil vi betragte samme Begyndelsessystem, men antage, at Slutningssystemet afviger fra Begyndelsessystemet baade med Hensyn til Rumfang og Entropi. Efter den traditionelle Opfattelse er i saa Tilfælde:

$$A = \int_{I}^{II} pdv, \tag{42}$$

en Størrelse, der ikke har nogen bestemt Værdi, da Integrationsvejen her vil afhænge af den Rækkefølge, i hvilken Elementer af den samlede Rumfangsændring $v^{II}-v^{I}$ og den samlede Entropiændring $S^{II}-S^{I}$ tilføres fra de respektive Reservoirer. Det er ofte det her nævnte Tilfælde, der i den traditionelle Thermodynamik henvises til som et simpelt Exempel paa Arbejdets Udefinerthed ved den integrale Proces. Forudsætningen for Rigtigheden af Udtryk (42) er aabenbart, at den Forskel i Beregningsmaaden for tilført Rumfang og tilført Entropi, der er vist at være til Stede i de to foregaaende Exempler, er bibeholdt i det nærværende. Med andre Ord at Rumfangstransporten antages reversibel og medregnes ved Beregning af A, medens der ikke regnes med en reversibel Entropitransport.

Foruden ved Rumfang og Entropiindhold vil de to Systemer, der sammenlignes, kunne afvige fra hinanden ved forskelligt Indhold af Stof, en Mulighed, hvormed den traditionelle Behandling dog ikke beskæftiger sig. Derimod regnes naturligvis med Stoftransport i Systemet, ligesom i det hele taget enhver Grundproces indenfor dette anses for mulig.

Den ganske forskelligartede Behandlingsmaade, som den traditionelle Thermodynamik anvender overfor Rumfang og Entropi, har utvivlsomt sin Oprindelse i den rent praktiske Forskel, der for disse to Kvantiteters Vedkommende er forbundet med den reversible Transport, idet denne jo er let gennemførlig for Rumfangets, men i Almindelighed vanskeligere gennemførlig for Entropiens Vedkommende. En principiel Forskel bestaar dog ikke i denne Henseende, og den traditionelle Behandlingsmaade maa derfor fra et principielt Synspunkt siges at være urationel.

Der maa knytte sig mere theoretisk Interesse til en Besvarelse af det opstillede Spørgsmaal, naar der gives de forskellige indgaaende Kvantiteter en ensartet og symmetrisk Behandling, idet det vil være let derefter at udsondre og beskrive de Tilfælde, som har særlig praktisk Betydning.

Vi vil først fastsætte, at Rumfang og Entropi ved Omdannelse af System I til System II i alle Tilfælde tages reversibelt fra givne Reservoirer, henholdsvis af Trykket p_0 og Temperaturen T_0, og iøvrigt tillade vilkaarlige Grundprocesser at foregaa reversibelt indenfor Systemet under dets Ændring fra Tilstand I til Tilstand II.

Det totale Arbejde, der herved opsamles i tilkoblede Arbejdsreservoirer, kan da udtrykkes ved:

$$A = A_i + A_v + A_s, \tag{43}$$

hvor A_i er Arbejdstabet, hidrørende fra Grundprocesser i Systemet, medens A_v og A_s er Arbejdstabet, hidrørende fra henholdsvis Rumfangs- og Entropitransporten. For Totalarbejdet gælder, idet man anvender Energiprincipet paa det samlede System, og E_i, E_v, E_s betegner Energien henholdsvis i Systemet, Rumfangs- og Entropireservoiret:

$$A = -\varDelta E = -\varDelta E_i - \varDelta E_v - \varDelta E_S. \tag{44}$$

Dette Arbejde er uafhængigt af Processens Mekanisme. Hvis man derfor i Spørgsmaalet om Arbejdet ved den betragtede Ændring af Systemet fra Tilstand I til Tilstand II medregner A_v og A_s, vil dette Arbejde være en Funktion alene af de to Tilstande.

Hvis de nævnte Transportarbejder ikke medregnes, er Arbejdet alene A_i. Vi har nu almindeligt, idet dK er Kvantitetstilvæksten i Systemet:

$$A_v + A_S = -\int_I^{II} (p_0 - p)\, dv + \int_I^{II} (T_0 - T)\, dS, \tag{45}$$

eller ved Indførelse af (43):

$$A_i = A + \int_I^{II} (p_0 - p)\, dv - \int_I^{II} (T_0 - T)\, dS. \tag{46}$$

Kombineres denne Ligning med (44), idet samtidig indføres det almindelige Energiudtryk (24):

$$dE = \Sigma P dK, \tag{47}$$

faas:

$$A_i = -\Delta E_i - \int_I^{II} p dv + \int_I^{II} T dS. \tag{48}$$

Da Værdien af de to Integraler under de gældende Forudsætninger er ubestemt, maa A_i, d. v. s. det Arbejde, der kan vindes ved den betragtede Ændring af Systemet fra Tilstand I til Tilstand II, naar Overføringsarbejderne for de tilførte Kvantiteter ikke medregnes, være afhængigt af den Vej, ad hvilken Processen ledes. I de særlige Tilfælde, hvor p og T er konstante under Processen, vil dog Arbejdet være fixeret ved Grænsetilstandene.

Hvis endelig det Tilfælde betragtes, at Arbejdet, saaledes som det er almindeligt i den traditionelle Behandling, kun for Rumfangsoverføringens, men ikke for Entropioverføringens Vedkommende, medregnes i den omspurgte Arbejdsværdi, vil denne blive bestemt ved $A_i + A_v$, og man finder da paa samme Maade som ovenfor:

$$A_i + A_v = -\Delta E_i - \Delta E_v + \int_I^{II} T dS \tag{49}$$

eller:

$$A_v = -\Delta E_v + \int_I^{II} p dv. \tag{50}$$

Arbejdet vil saaledes i Almindelighed være afhængigt af Vejen. Kun hvis T er konstant under Processen, bliver Arbejdsværdien aabenbart given alene ved Slutnings- og Begyndelsestilstanden.

Denne Paastand om Arbejdets Tilstandsbestemthed ved isotherme Processer er netop den klassiske Thermodynamiks og er, som vi ser, baseret paa den vilkaarligt valgte Beregningsmaade for Arbejdet. Det fra et alment Standpunkt irrationelle Forhold, at der for et enkelt af de energetiske Potentialer kræves en Særstilling ved Beskrivelsen af Begreber og Fænomener af ganske almen Art, finder altsaa sin Forklaring i det Moment af Vilkaarlighed, der fra et principielt Synspunkt findes allerede i Definitionen af det klassiske Arbejdsbegreb.

Betragtes Spørgsmaalet helt almindeligt, idet vi betragter et reversibelt reagerende System, aabent for en Række forskellige Kvantiteter, nemlig:

$$K_1,\ K_2,\ K_3 \ldots\ldots\ldots,$$
$$K'_1,\ K'_2,\ K'_3 \ldots\ldots\ldots,$$

for hvilke Overføringsarbejderne medregnes for den første Rækkes Vedkommende og ikke medregnes for den andens, vil det Arbejde, der vindes, være givet ved:

$$A_i + \Sigma A_{K_1} = -\Delta E_i - \Sigma \Delta E_{K_1} + \Sigma \int_I^{II} P'_1 dK'_1, \qquad (51)$$

hvor $\Sigma \Delta E_{K_1}$ er Summen af Energitilvæksterne i Rækken af K_1-, K_2- .... Reservoirer, og P'_1, P'_2 .... de i Systemet optrædende Potentialer, der hører til de paa tilsvarende Maade markerede Kvantiteter.

Hvis alle Arbejderne ved Overføring fra Reservoirer medregnes, reduceres (51) til:

$$A_i + \Sigma A_{K_1} = -\Delta E_i - \Sigma \Delta E_{K_1}. \qquad (52)$$

Hvis derimod ingen af disse Overføringsarbejder medregnes, reduceres (51) til:

$$A_i = -\Delta E_i + \Sigma \int_{I}^{II} P'_1 \, dK'_1. \qquad (53)$$

I første, men ikke i andet Tilfælde, er Arbejdet under vilkaarlige Betingelsesvariationer bestemt som en Tilstandsfunktion.

Endelig kan Formel (51) ogsaa bringes til Anvendelse paa en reversibel Kredsproces. Denne Betegnelse anvendes almindeligvis i Thermodynamiken om en Proces, ved hvilken »Systemets« to Grænsetilstande I og II er identiske, medens der er foregaaet en Ændring af Tilstanden i medvirkende Reservoirer, simplest bestaaende i to Grundprocesser, der er koblede gennem Systemet.

For saadanne Processer er for det første:

$$\Delta E_i = 0, \qquad (54)$$

saaledes at det almindelige Arbejdsudtryk for Kredsprocessen bliver:

$$A_i + \Sigma A_{K_1} = -\Sigma \Delta E_{K_1} + \Sigma \oint P'_1 \, dK'_1. \qquad (55)$$

Hvis der for hver af K_1-Kvantiteternes Vedkommende kun anvendes et enkelt Reservoir, er endvidere:

$$\Delta E_{K_1} = \Delta E_{K_2} = \ldots\ldots \Sigma \Delta E_{K_1} = 0, \qquad (56)$$

saaledes at man for Kredsprocessens Arbejde faar:

$$A_i + \Sigma A_{K_1} = \Sigma \oint P'_1 \, dK'_1. \qquad (57)$$

Anvendes dette Udtryk paa den simple Carnot'ske Kredsproces, for hvilken:

$$A_i = 0\,,$$

og, efter det klassiske Beregningsprincip:

$$\Sigma \oint P'_1\, dK' = \oint TdS\,,$$

faas, idet tillige (50) indføres, følgende Udtryk for det vundne Arbejde:

$$A_v = \oint TdS = \oint pdv\,. \tag{58}$$

Den almindelige Form (55) kan betragtes som Arbejdsudtrykket for den generaliserede Carnot'ske Kredsproces, i hvilken de fire Variable p, v, T og S, der indgaar i den simple Proces, er erstattede af vilkaarlige Par af korresponderende Potentialer og Kvantiteter, og hvor Processens Funktioner i tilsvarende Grad varieres.

Som det vil fremgaa af ovenstaaende, er den i den traditionelle Behandling tilstedeværende Usymmetri i Anvendelsen af Arbejdsbegrebet, der gør sig gældende f. Ex. i dens Indførelse af Differentialet pdv, men ikke TdS som et Arbejdselement, begrundet i en utilstrækkelig Erkendelse af den uløselige Forbindelse, hvormed Arbejdsbegrebet er knyttet til Grundprocessen, d. v. s. til en Kvantitetstransport, i hvilken Modtager- og Afsenderpotentialet nødvendigvis optræder jævnsides.

Dette Forhold gør sig gældende paa typisk Maade i den thermodynamiske Funktionstheori, hvor saadanne Funktioner som fri Energi og thermodynamisk Potential optræder som forskelligt benævnte »Arbejdsfunktioner«. Som det kan ventes, er denne Betragtning begrundet i en lignende usymmetrisk Opfattelse af de forskellige i Thermodynamiken optrædende Kvantitets-Potential-Produkter som den, der ovenfor er paapeget.

9. De thermodynamiske Hovedsætninger.

Ved Opstilling af de almindelige energetiske Grundprinciper paa Grundlag af det foreliggende Erfaringsmateriale, saaledes som det er nærværende Afhandlings Opgave, vil det ikke paa Forhaand være afgjort, hvorledes dette Materiale skal afgrænses, eller hvor elementære Iagttagelser der skal inddrages under Formuleringen. At Universet indeholder energetiske Kvantiteter, er f. Ex. en Erfaringssag, som maaske kunde kaldes et Grundprincip. Det vil dog være naturligt at unddrage Spørgsmaal, der nærmest kunde betegnes som erkendelsestheoretiske, fra Betragtning paa dette Sted og at formulere Principerne i Overensstemmelse med de Retningslinier, som har været ledende ved Opstillingen af de klassiske thermodynamiske Hovedsætninger.

Man vil da af de i de foregaaende Afsnit udviklede Betragtninger kunne uddrage som almindeligt Resultat og opstille som almindelig Grundsætning, at alle naturligt forløbende Processer er ledsaget af et positivt Arbejdstab og en positiv Varmeudvikling, som for det reversible Grænsetilfælde antager Værdien Nul, og som for alle Arter af Forandringer er numerisk ækvivalente. Dette Resultat kan mathematisk fremstilles ved Udtrykket:

$$\Sigma A = Q \geqq 0, \qquad (59)$$

hvor Lighedstegnet gælder for reversible og Ulighedstegnet for irreversible Processer.

I dette Udtryk er samlet de forskellige Principer, der er opstillet i det foregaaende. Formuleringen af disse Principer vil være til en vis Grad afhængig af den Orden, hvori de fremsættes. Det vil i formel Henseende være simplest at begynde med det almengyldige Udtryk:

$$\Sigma A = Q, \tag{60}$$

der er opstillet som Ækvivalensprincipet, idet herefter paa den ene Side Ulighederne:

$$\Sigma A > 0 \tag{61}$$

og:

$$Q > 0 \tag{62}$$

bliver alternative og ækvivalente Udtryk for det, der specielt karakteriserer de irreversible Processer, medens paa den anden Side Ligningerne:

$$\Sigma A = 0 \tag{63}$$

og:

$$Q = 0 \tag{64}$$

bliver alternative og ækvivalente Udtryk for det, der specielt karakteriserer de reversible Processer. Det ved (63) og (64) udtrykte er i det foregaaende blevet betegnet som Arbejdsprincipet. Det ved (61) og (62) udtrykte vil vi betegne som Varmeprincipet.

Det maa bemærkes, at denne i formel Henseende simpleste Fremgangsmaade ved Principernes Opstilling ikke giver Udtryk for den naturlige Rækkefølge af indhøstede energetiske Erfaringer, thi Iagttagelse af Retningen af en Proces maa i Almindelighed gaa forud for dens nøjere Undersøgelse i kvantitativ Henseende. Ved Joule's Forsøg over Varmeudviklingen ved den mekanisk irreversible Proces er utvivlsomt Iagttagelsen af Arbejdstabet og en Varmemængdes Udvikling en mere umiddelbar Erfaring end Fastsættelsen af den existerende numeriske Ækvivalens. For den konventionelle Thermodynamiks Vedkommende betyder denne Betragtning, saaledes som det vil fremgaa af det efterfølgende, at 2den Hovedsætning kan siges at være et Udtryk for mere elementær Iagttagelse end 1ste. Dette er ikke i Uoverensstemmelse med den historiske Rækkefølge, i hvilken Grundideen i disse Sætninger fremtræder i Thermodynamiken.

Vor Opgave er nu at undersøge de opstillede Principers Forhold til disse klassiske Hovedsætninger. For Ækvivalensprincipets Vedkommende er dette i det væsentlige sket allerede i de to foregaaende Afsnit. Vi har set, at 1ste Hovedsætning eller Sætningen om Energiens Bestaaen indeholder Ækvivalensprincipet som eneste Erfaringsprincip og kun antager en herfra forskellig Formulering ved Indførelse af Energidefinitionen, der omfatter utransformeret Energi. Men det maa erindres, at den som Ækvivalensprincipet ovenfor opstillede Sætning paa den ene Side implicite forudsætter den genetiske Relation (61)—(62), der ikke optræder som et Forbehold i det klassiske Energiprincip, paa den anden Side indholdsmæssigt gaar ud over dette, derved at det postulerer Ækvivalensen af Varme og Arbejde ogsaa i de Tilfælde, hvor Energiprincipet undlader at skelne disse Begreber fra hinanden som selvstændige Energiarter.

1ste Hovedsætning fremstilles iøvrigt i mange forskelligartede Former af ingenlunde identisk Indhold. En ofte benyttet Formulering for den er Perpetuum mobile Principet. Man kan sige, at dette Princip postulerer, at der til Opnaaelse af en positiv Arbejdsgevinst kræves et vist

Ækvivalent. Da Arten af dette Ækvivalent lades ganske ubestemt, er denne Formulering meget omfattende, men i tilsvarende Grad af mindre Indholdsværdi. Hvis Ækvivalentet identificeres med et Arbejdstab, gaar Perpetuum mobile Principet over til Arbejdsprincipet.

2den Hovedsætning optræder ligesom 1ste i talrige Formuleringer. Den findes f. Ex. udtrykt ved Postulatet om, at Entropien er en Tilstandsfunktion, en Paastand, hvori efter Born[1] Thermodynamiken naar til sit Højdepunkt. Den findes ogsaa formuleret ved Opstilling af Sætningen om Umuligheden af et Perpetuum mobile af 2den Art, hvortil der allerede er taget Stilling ved Paastanden om den ubetingede Uigennemførlighed af Varme-Arbejdstransformationen. Endvidere er den udtrykt ved Opstilling af det bekendte klassiske Udtryk for det thermiske Arbejde. Man kan dog antagelig gaa ud fra, at 2den Hovedsætnings væsentlige Indhold efter de herskende Anskuelser, hvortil den molekular-statistiske Behandling af Emnet ved Boltzmann og Planck har bidraget i væsentlig Grad, ikke kan udtrykkes ved en Ligning, men maa gives Form af en Ulighed og derfor er beslægtet med den Sætning, der ovenfor er udtrykt ved Varmeprincipet.

Den Ulighed, hvorved 2den Hovedsætning karakteriseres i den klassiske Thermodynamik, er som bekendt:

$$dS > 0\,, \tag{65}$$

der udtrykker, at alle irreversible Processer, der forløber uden Tilførsel af Varme, er ledsaget af Entropiforøgelse. Denne Sætning følger umiddelbart af Varmeprincipet og fører ogsaa umiddelbart til dette, da Entropi og Varme er alment sammenknyttede ved Ligningen

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[1] M. Born: Physik. Zeitschr. **22**, 219 (1921).

$$\delta Q = T \delta S .$$

At Entropiforøgelsen er uafhængig af Reaktionsmekanismen og alene bestemt ved Totalprocessens Grænsetilstande, følger naturligvis ogsaa direkte, da Entropien, som tidligere vist, er en Tilstandsfunktion. Som almindelig Karakteristik af det irreversible, naturlige Reaktionsforløb maa Udtrykkene (61), (62) og (65) derfor siges at være ækvivalente.

Det er næppe nødvendigt at erindre om, at δQ her er den energetiske Varmeudvikling, der for en kinematografisk fastlagt Proces, og saaledes for enhver Proces, der faktisk er foregaaet i Naturen, har en exakt defineret Betydning i Modsætning til det traditionelle Varmeudviklingsbegreb, der ved alle ikke-isotherme Processer er ubestemt. Samtidig bør det bemærkes, at den Tankegang, der i sin Tid har ført til den thermokemiske Theori om de frivillige kemiske Processers positive Varmetoning[1] ved konsekvent Gennemførelse utvivlsomt vilde have ført til Overensstemmelse med det her opstillede energetiske Varmeprincip.

I den traditionelle Thermodynamik er Udtrykkene (62) og (65) naturligvis ikke taget som ækvivalente Fremstillinger af 2den Hovedsætning, bl. a. fordi den slet ikke opererer med Begrebet energetisk Varmeudvikling. Afvisningen af (62) som et brugbart Udtryk har dog ogsaa en anden Begrundelse. Efter Planck[2] er det 2den Hovedsætnings Opgave ved en ved sine Grænsetilstande I og II given Proces, der forløber uden at medføre Forandringer i Omgivelserne, at afgive et alene paa disse Grænse-

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[1] Julius Thomsen: Bidrag til et thermo-kemisk System. K. Danske Vid. Selsk. Skrifter [5] **3**, p. 115 (1853).

[2] M. Planck: Thermodynamik, 9te Aufl., pp. 85—89 (1930).

tilstande baseret Kriterium for, om Processens Retning er I → II eller omvendt. Det er m. a. O. Opgaven at opstille en Tilstandsfunktion af saadanne Egenskaber, at den er bestemmende for den relative Stabilitet af to Systemer, der staar i det nævnte indbyrdes Forhold. Til Løsning af denne Opgave er naturligvis kun Entropien, d. v. s. Uligheden (65) brugbar, da kun Entropiændringen, ikke Varmeudviklingen er bestemt ved Processens Grænsetilstande. Men dette Resultat er jo en Følge af den valgte Problemstilling, og det ses ikke, at den deri indeholdte Begrænsning af Opgaven er forenelig med den Almindelighed, som maa være de thermodynamiske Hovedsætningers Formaal.

Iøvrigt maa det bemærkes, at de Forsøg, hvorved Entropitilvæksten ved den irreversible Proces konstateres og maales, er ganske identiske med dem, der tjener til Konstatering og Maaling af den energetiske Varmeudvikling. Fordringen, at Omgivelserne ikke maa forandres under Omdannelse af I til II eller omvendt, betyder, at Energi, Rumfang og Mængden af de indgaaende kemiske Stofkomponenter har samme Værdi i de to Grænsetilstande. En reversibel Overgang fra I → II eller omvendt, som Maalingen kræver gennemført, sker altsaa i Kommunikation med Arbejds- og Varmereservoirer paa en saadan Maade, at den samlede til Systemet afgivne Energimængde er Nul, d. v. s., at den ydre Arbejdsgevinst og den af Systemet optagne Varmemængde er lige store. Hvis Processen ledes i Overensstemmelse hermed, er ifølge Afsnit 4 den optagne Varmemængde definitionsmæssigt = den energetiske Varmeudvikling og den optagne Entropi definitionsmæssigt = Entropitilvæksten ved den irreversible Proces. Som vist af Relationen $\delta Q = T\delta S$, er den ene givet ved den anden, naar Systemets Temperatur er bekendt. Der kan derfor heller ikke paavises experimentelle Betingelser, der gør Entropitilvæksten mere egnet som almindeligt Udtryk for 2den Hovedsætning end den energetiske Varmeudvikling.

Formulering af 2den Hovedsætning som et Varmeprincip kan derimod siges at frembyde det Fortrin, at Varme og Arbejde i saa Fald bliver de eneste Begreber, der indgaar i de thermodynamiske Grundprinciper, og at disse herved kommer til at fremtræde som et System af Love af en særlig formel Simpelhed.

Sluttelig maa undersøges den Stilling, som Arbejdsprincipet indtager i Forhold til de traditionelle Hovedsætninger. Arbejdsprincipet, der ovenfor er udtrykt ved Ligning (63) og ved Hjælp af Ækvivalensprincipet kunde bringes paa den alternative Form (64), er opstillet i 1ste Afsnit som Grundformlen for alle reversible Processer og er som nævnt tillige Grundlaget for alle de specielle Formler, der udtrykker den thermodynamiske Ligevægtsbetingelse paa de særlige fysisk-kemiske Omraader. Da det er almindeligt at betragte 2den Hovedsætning som Grundlag for disse Ligninger, kunde det ligge nær at antage, at Arbejdsprincipet udgør et af 2den Hovedsætning betinget Specialprincip. Ved Prøvelse af denne Antagelse vil det bemærkes, at Arbejdsprincipet kan udledes af Ækvivalens- og Varmeprincipet under Indførelse af visse Forudsætninger. Hvis vi postulerer almindeligt, at Ulighedstegn, der optræder i Udtryk for de irreversible Processer, ved Overgang til reversible Processer degenererer til Lighedstegn, vil (63) fremkomme, dels som en direkte Konsekvens af (61), dels ved Kombination af (60) og (62). Paa dette Grundlag følger Arbejdsprincipet altsaa direkte af en af

Varmeprincipets alternative Former, eller ved Kombination af Varmeprincipets 2den alternative Form med Ækvivalensprincipet. Endvidere vil Arbejdsprincipet aabenbart fremkomme som en Konsekvens af Ækvivalensprincipet (60), hvis vi for de reversible Processer postulerer, at $Q = 0$. Endelig følger det, som ovenfor nævnt, af Perpetuum mobile Principet, naar det Ækvivalent, som er krævet heri, postuleres at være Arbejde.

I alle Tilfælde vil Arbejdsprincipet, som det saaledes ses, først vise sig at være en Følge af de to andre, i det væsentlige med de traditionelle Hovedsætninger sammenfaldende Principer, naar yderligere Postulater vedrørende Forholdet mellem de reversible og irreversible Processer indføres. Dette maa betyde, at Arbejdsprincipet ikke kan identificeres med Varme- eller Ækvivalensprincipet eller indføres i Thermodynamiken som en direkte Konsekvens af nogen af de traditionelle Hovedsætninger. Særlig maa dette understreges for 2den Hovedsætnings Vedkommende. Hvis de paa Arbejdsprincipet hvilende, for alle Grupper af Ligevægte gyldige Specialformler skulde kunne begrundes ved 2den Hovedsætning, maatte det være udelukket, at dennes karakteristiske Indhold kunde fremstilles ved en Ulighed som den i den klassiske Theori ved (65) og i nærværende Fremstilling ved (62) udtrykte.

Der er endnu et Synspunkt, under hvilket Arbejdsprincipet vil kunne betragtes, og hvorudfra Grundideen i nærværende Fremstilling maaske vil fremtræde med særlig Klarhed. Vi har som skematisk Basis for alle thermodynamiske Fænomener den numeriske Relation, der fremstilles af Ækvivalensprincipet:

$$A = Q \text{ (vilkaarlige Processer).}$$

Genetisk falder disse Fænomener, som allerede nævnt i det foregaaende udfra en Entropibetragtning, i tre Grupper. Den første af disse omfatter de irreversible Processer, ved hvilke der sker en Overgang af Arbejde til Varme. Efter vore Grundforestillinger er Overgang af Varme til Arbejde under alle Betingelser uigennemførlig, vi kan derfor som Parallel til de irreversible opstille de umulige eller imaginære Processer, ved hvilke der sker en Overgang af Varme til Arbejde. Disse Processer er altsaa definerede ikke ved deres skematiske, men ved deres genetiske Uigennemførlighed. Som tredje Gruppe kan opstilles de reversible Processer, der ikke kan indordnes under de to foregaaende, men som fremstiller de imellem disse liggende Grænsetilfælde. Karakteren af disse Grænsetilfælde fremtræder nu ud fra denne Betragtning ganske automatisk, idet Berøring imellem de to Grupper, for hvilke henholdsvis:

$$A \rightarrow Q \text{ (irreversible Processer)}$$

og:

$$A \leftarrow Q \text{ (imaginære Processer),}$$

kun er mulig for $Q = 0$. Under denne Betingelse bortfalder Retningsbestemtheden af de to Reaktionsgrupper, og de repræsentative Udtryk degenererer hver for sig til:

$$A = 0 \text{ (reversible Processer),}$$

d. v. s. til Arbejdsprincipet.

Det ses af ovenstaaende, at Skemaet for den irreversible Proces gaar over til Skemaet for den imaginære Proces ved Retningsforandring. Man kan ogsaa sige, at de to skematiske Reaktionsforløb er bestemt af Tidsfølgen og omdannes indbyrdes ved Ændring af denne. Hvis vi til

Fuldstændiggørelse af vor Karakteristik af de energetiske Naturfænomener indrullerer ogsaa den skematisk tilladelige, imaginære Proces i vort sammenfattende Udtryk (59), faas som den mest omfattende Formulering af de energetiske Principer Udtrykket:

$$\Sigma A = Q \begin{matrix} > \\ = \\ < \end{matrix} 0 \quad \begin{matrix} 1.\ \text{irrev.} \\ 3.\ \text{rev.} \\ 2.\ \text{imag.,} \end{matrix} \tag{66}$$

hvori, som anført, det øverste Ulighedstegn specielt gælder for de irreversible, naturligt eller frivilligt forløbende, det nederste Ulighedstegn for de imaginære, uigennemførlige Processer, og endelig det sidste af de to Lighedstegn for de reversible Grænsetilfælde.

Dette Udtryk indeslutter i sig alle andre tilladelige energetiske Postulater og de generelle Lovmæssigheder, der behersker saavel Reaktionsforløb som Ligevægt. Specielt indeholdes deri ogsaa det Postulat om Varme-Arbejds-Transformationens ubetingede Uigennemførlighed, som blev opstillet i den tidligere Afhandling, og som har været den vejledende Grundtanke ogsaa i nærværende Fremstilling af de energetiske Grundprinciper.

10. Oversigt.

Nedenfor er sammenstillet de vigtigste af de i denne Afhandling og i den tidligere om Varme-Arbejds-Relationen opnaaede Resultater. Oversigten er af beskrivende Art og de opstillede Sætninger ikke nødvendigvis indbyrdes uafhængige.

1. Der kan opbygges et almindeligt energetisk Princip-system paa Grundlag af Begreberne Kvantitet og Potential. Grundprocessen i Energetiken bestaar i en Transport af Kvantiteter. Alle reversible Fænomener i Naturen er sammensat alene af saadanne Grundprocesser.

2. Til enhver Grundproces er koordineret et Arbejdstab, der i Arbejdsformlen skrives som et Produkt af den transporterede Kvantitet og Forskellen i Potential mellem de to Tilstande, mellem hvilke Transporten foregaar: $\delta A = (P_1 - P_2)\,\delta K$. For reversible Processer er Summen af alle Arbejdstab lig Nul: $\Sigma\delta A = 0$. Denne Sætning betegnes som Arbejdsprincipet.

3. Den thermiske Grundproces er en Transport af Entropi mellem forskellige Temperaturer. Entropien er den thermiske Kvantitet og defineres alment paa Grundlag af sin reversible Transportabilitet.

4. Ved Tilførsel af Entropi til et System tilføres definitionsmæssigt tillige en dermed proportional Varmemængde. Varmen defineres alment paa Grundlag af sin irreversible Transportabilitet. Tilført Varme og Entropi er sammenknyttet ved Relationen: $\delta Q = T\delta S$, der definerer Temperaturen efter den »thermiske« Skala. Denne er under Forudsætning af Varme-Arbejds-Ækvivalens identisk med den »energetiske« Temperaturskala, der er defineret ved: $\delta A = (T_1 - T_2)\,\delta S$. Den er ogsaa identisk med KELVINskalaen.

5. Den irreversible Proces forløber under Arbejdstab og Varmeudvikling: $\Sigma\delta A > 0$, $\delta Q > 0$. Denne Sætning kaldes Varmeprincipet. Samtidig dannes Entropi, der ligesom tilført Entropi er sammenknyttet med Varmen ved Relationen: $\delta Q = T\delta S$.

6. Arbejdstabet ved den irreversible Proces er givet ved Arbejdsformlen. Det kan bestemmes som det ydre Arbejde, der vindes ved Processen, naar denne reproduceres paa reversibel Maade. Det Overskud af Varme, som maa tilføres udefra ved den reversible Reproduktion, er den energetiske Varmeudvikling.

7. Arbejdstabet ved den irreversible Proces er proportionalt med den energetiske Varmeudvikling. Paa Grundlag af denne Erfaring opstilles Ækvivalensprincipet: $\Sigma \delta A = \delta Q$.

8. Den særlige Stilling, som Varmen indtager i Energetiken, er forstaaelig udfra en energetisk Fortolkning af Varmeledningsprocessen. Hvis denne opfattes som en irreversibel Grundproces, ledsaget af en Entropi- og Varmedannelse, paa hvilken Ækvivalensprincipet kan bringes i Anvendelse, faas paa dette Grundlag Overensstemmelse med Erfaringen.

9. Det er ikke muligt paa energetisk Basis i al Almindelighed at bestemme eller definere Absolutværdien af de energetiske Potentialer. Kun for det thermiske Potential, Temperaturen er dette muligt ved Anvendelse af Ækvivalensprincipet paa den irreversible Proces, idet herved en Varmemængde af Formen $T\delta S$ opstaar.

10. Det kaloriske Fænomen er begrænset til irreversible Processer. Den traditionelle Thermodynamiks Paastand om reversibel Varmeudvikling og Varmeabsorption, for hvis Optræden en Temperaturændring tages som Udtryk, beror paa utilstrækkelig Analyse af de paagældende Fænomener. Varmetoninger af den nævnte Art kan ikke forenes med Gyldigheden af Ækvivalens- og Arbejdsprincipet.

11. Omdannelse af Varme til Arbejde er en ubetinget uigennemførlig Proces. Den traditionelle Thermodynamiks Fremstilling af den reversible Gasexpansion som Exempel paa en saadan Omdannelse undlader at tage i Betragtning det Arbejdstab, som Rumfangsændringen repræsenterer. Naar dette Arbejde medregnes, vil Antagelsen af et Varmeforbrug vise sig i Strid med Ækvivalens- og Arbejdsprincipet.

12. Varmekraftmaskinens Funktion kan beskrives som en thermisk Grundproces, i hvilken Entropien flyttes fra en højere til en lavere Temperatur i mekanisk Kobling. Arbejdsudtrykket for saadanne Processer: $\delta A = (T_1 - T_2)\,\delta S$ er i kvantitativ Overensstemmelse med det Clausius'ske Udtryk, der er erfaringsmæssigt verificeret.

13. Den traditionelle Clausius'ske Fortolkning af Varmekraftmaskinens Funktion som en, af en kompenserende Varmetransport ledsaget, Varme-Arbejds-Transformation er genetisk uantagelig, da Varmetransporten, der er irreversibel, ikke kan indgaa som en Bestanddel af en reversibel Proces. Indførelse af energetiske »Kompensationer« i Overensstemmelse med den klassiske Ide maa, paa Grund af den Vilkaarlighed, der udmærker Methoden, og dens Udnyttelse af imaginære Processer, overhovedet afvises som naturvidenskabeligt Fortolkningsprincip.

14. Den traditionelle Thermodynamiks Varmetoningsbegreb for saavel reversible som irreversible Processer er baseret paa Temperaturændringer i Systemet og er derfor i nærværende Fremstilling betegnet som thermometrisk Varmetoning. Den kan defineres som en Varmemængde, men for Udviklingen eller Absorptionen af en saadan Varmemængde foreligger der intet Arbejdsækvivalent, saaledes som Ækvivalens- og Energiprincipet forlanger.

15. Energibegrebet i Thermodynamiken hviler paa Varme-Arbejds-Ækvivalensen. Energiprincipets Realitetsindhold er udtrykt i Ækvivalensprincipet. Den almindelige Energidefinition: $dE = \Sigma P dK$ og andre, videregaaende Formuleringer af Energiprincipet er kun af formel Betydning.

16. Det Gibbs'ske Energiudtryk: $E = TS - pv + \Sigma \mu_1 n_1$ kan opfattes som omfattende de specielle Energiformer

thermisk, spatisk og kemisk Energi, repræsenterede ved deres tilsvarende PK-Produkter. Disse Energiformer er naturligvis hver for sig Tilstandsfunktioner. Den Gibbs'ske Fundamentalligning: $SdT - vdp + \Sigma n_1 d\mu_1 = 0$, kan betragtes som et universelt Energiprincip, medens den analoge Ligning: $TdS - pdv + \Sigma \mu_1 dn_1 = 0$, kun gælder for konstant Totalenergi.

17. Fastsættelse af det Arbejde, der kan vindes ved en integral Proces, der forløber i Kommunikation med Omgivelserne, kræver en skarpere Afgrænsning af Arbejdsbegrebet end den almindeligvis givne. Indførelse af en saadan Afgrænsning vil i visse Henseender modificere de traditionelle Arbejdslove. Den Carnot'ske Kredsproces, hvis Arbejde er spatisk, kan generaliseres ved i Stedet for de deri indgaaende Kvantiteter, Rumfang og Entropi, at indføre vilkaarlige Kvantitetsarter.

18. De energetiske Grundprinciper, omfattende Arbejds-, Varme- og Ækvivalensprincipet, kan sammenfattes i Udtrykket: $\Sigma \delta A = \delta Q \geqq 0$. Realitetsindholdet af Thermodynamikens 1ste Hovedsætning dækkes af Ækvivalensprincipet. Hvis 2den Hovedsætning fremstilles ved Uligheden $\delta S > 0$, vil den indholdsmæssigt være ækvivalent med Varmeprincipet. Arbejdsprincipet, der gælder for de reversible Processer, og som er Grundlaget for alle energetisk-thermodynamiske Ligevægtsformler, er ikke en direkte Konsekvens af de to Hovedsætninger i deres her antagne Formulering, men faas deraf ved Indførelse af visse Postulater. Det faas ogsaa som en Konsekvens af de reversible Processers Stilling som Grænsetilfælde mellem de irreversible og de skematisk tilladelige, men genetisk uigennemførlige Processer, vi har betegnet som imaginære.

INDHOLD

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