

Finally, we can observe a *spherolite* of the hexahydrate with a radial structure which now grows centrifugally to the large well-known semi-spheroidal spherolites of ferric chloride (fig. 3c).

§ 13. This experiment proves that the abrogation of the metastable condition, or at all events of a liquid condition which is possible under the influence of *phenomena* of retardation may happen owing to the formation of *spherolites which are preceded by the differentiation of the fusion into an aggregate of liquid globules*. True, the latter are here isotropous in contrast with the phytosterol esters just described, but the anisotropism of the latter liquids may be caused also by factors which are of secondary importance for the apparently existing connection between: metastability of liquid conditions, their abrogation by spherolite formation and the possible appearance of liquid globules as an intermediate phenomenon. I will just call attention to the fact that if we set aside a solution to crystallise with addition of a substance which retards the crystallisation, this will commence with the separation of originally isotropous liquid globules, so-called globulites, which BEHREND and VOGELSANG commenced to study long time ago.

All this leads to the presumption that the formation of the anisotropous liquid phases as aggregates of doubly-refracting liquid globules may have its origin in a kind of *phenomena* of retardation, the nature of which is still unknown to us at the present. Before long, I hope to revert again to this question.

Zaandam, 21 Nov. 1906.

**Physics.** — “Some additional remarks on the quantity  $H$  and MAXWELL’s distribution of velocities.” By Dr. O. POSTMA. (Communicated by Prof. H. A. LORENTZ).

§ 1. In these proceedings of Jan. 27<sup>th</sup> 1906 occur some remarks by me under the title of: “Some remarks on the quantity  $H$  in BOLTZMANN’s Vorlesungen über Gastheorie”.

My intention is now to add something to these remarks, more particularly in connection with GIBBS’ book on Statistical Mechanics <sup>1)</sup>, and a paper by Dr. C. H. WIND: “Zur Gastheorie” <sup>2)</sup>.

In my above-mentioned paper I specially criticised the proofs given

<sup>1)</sup> J. WILLARD GIBBS “Elementary Principles in Statistical Mechanics”, New-York, 1902.

<sup>2)</sup> Wien. Sitzungsber. Bd. 106, p. 21, Jan. 1897.

by BOLTZMANN and JEANS that MAXWELL'S distribution of velocities in a gas should give the most probable state, and demonstrated that they wrongly assume an equality of the probabilities a priori that the point of velocity of an arbitrary molecule would fall into an arbitrary element of the space.

The question, however, may be raised whether it would not be possible to interpret the analysis given by BOLTZMANN and JEANS in a somewhat different way, so that avoiding the incorrect fundamental assumption, the result could all the same be retained. And then this proves really to be the case. When the most probable distribution of velocities is sought from the ensemble of equally possible combinations of velocities with equal total energy, we make only use of the fact that the different combinations of velocities *are* equally possible, how they have *got* to be so is after all of no consequence. Or else, it had not been necessary to occupy ourselves with the separate velocities of the molecules and make an assumption as to them.

This way of looking upon the matter is of exactly the same nature as that constantly followed by GIBBS in his above-mentioned work. GIBBS treats in his book all the time instead of a definite system, an ensemble of systems of the same nature and determined mostly by the same number of general coordinates and momenta ( $p_1 \dots p_n, q_1 \dots q_n$ ), which he follows in their general course. Such an ensemble will best illustrate the behaviour of a system (e.g. a gas-mass), of which only a few data are known and of which the others can assume all kinds of values. He calls such an ensemble *micro-canonical* when all systems, belonging to it, have an energy lying between  $E$  and  $E + dE$  and for the rest the systems are uniformly distributed over all possibilities of phase or uniformly distributed over the whole *extension-in-phase* the energy of which lies between  $E$  and  $E + dE$ . When the energy of a gas-mass is given (naturally only up to a certain degree of accuracy) we should have reason according to GIBBS to study the microcanonical ensemble determined by this energy, and to consider the gas-mass as taken at random from such an ensemble. The extension-in-phase considered is thought to be determined by

$\int dp_1 \dots dq_n$ , but in the case of a gas-mass with simple equal molecules this is proportional to

$$\int dx_1 dy_1 dz_1 \dots dx_n dy_n dz_n, d\dot{x}_1 d\dot{y}_1 d\dot{z}_1 \dots d\dot{x}_n d\dot{y}_n d\dot{z}_n,$$

so that we may say that every combination of velocities and configuration is of equally frequent occurrence in the ensemble.

It is now easy to see that when the energy is purely kinetic the

same cases occur in such an ensemble, *with regard to the distribution of velocities*, as are considered as equally possible cases by BOLTZMANN and JEANS. The difference in the way of treatment of GIBBS on one side, and that of BOLTZMANN and JEANS on the other consists besides in the fact that the one occupies himself with separate velocities and the other not, in this that GIBBS treats the configuration and the distribution of velocities at the same time (both belong to the idea phase), whereas JEANS treats the latter separately, and BOLTZMANN does not occupy himself with the configuration in this connection.

Every phase of BOLTZMANN (combination of velocities) corresponds with as many phases of GIBBS (combination of velocities and configuration) as the molecules can be placed in different ways with that special combination of velocities. This number being the same for every combination of velocities according to the independence of the distribution of velocities and configuration following from the fundamental assumption, it will be of no consequence, comparing the different combinations of velocities inter se, whether we also take the configuration of the molecules into account or not. So when seeking the most probable distribution of velocities (that, with which the most combinations of velocities coincide), we must arrive at the same result whether we follow GIBBS or BOLTZMANN.

It is obvious that the phases of the microcanonical ensemble meant here are what GIBBS calls the specific phases. GIBBS distinguishes namely between specific and generic phases: in the former we consider as different cases those where we find at the same place and with the same velocity, other, even though quite equal molecules, in the latter we do not. In other words: in the former we consider also the individual molecules, in the second only the number of the molecules. So we may now say that in such a microcanonical ensemble the most probable distribution of velocities and that which will also occur in the great majority of cases (compare JEANS' analysis discussed in the first paper) will be that of MAXWELL. When therefore an arbitrary mass of gas in stationary state may be considered as taken at random out of such a microcanonic ensemble, MAXWELL's distribution of velocities or one closely resembling it will most probably occur in it. In this way a derivation of the law has been obtained to which the original objection no longer applies, though, of course, the assumption of the microcanonical ensemble remains somewhat arbitrary <sup>1)</sup>.

<sup>1)</sup> With the more general assumption of a *canonical* ensemble MAXWELL's law is derived by LORENTZ: "Abhandlungen über Theoretische Physik", Lpzg. 1906 I, p. 295.

Finally the question might be raised, when we want to consider the separate velocities, whether it is possible to arrive at the equally possible combinations under discussion on another supposition a priori about the chances of every value for the velocity than the one indicated by BOLTZMANN and JEANS. The supposition must of course be such, that the chance is independent of the direction of the velocity, so that the chance of a velocity  $c$ , at which the point of velocity falls into a certain element of volume  $d\zeta d_\eta d_\xi$ , may be represented by  $f(c)d\zeta d_\eta d_\xi$ . When we moreover assume that the probabilities for the different molecules are independent of each other, the probability of a certain combination of velocities is proportional to  $f(c_1)f(c_2)\dots f(c_n)$ , and this must remain the same when the kinetic energy  $L$ , or because the molecules are assumed to be equal,  $\sum c^2$  remains the same. For every change of  $c_k$  and  $c_l$  into  $c'_k$  and  $c'_l$ , so that  $c_k^2 + c_l^2 = c'^2_k + c'^2_l$ , must  $f(c_k) \cdot f(c_l) = f(c'_k) \cdot f(c'_l)$ . This is an equation which frequently occurs in the theory of gases, from which follows  $f(c) = a e^{bc^2}$ . As a special case follows from this:  $f(c) = a$ , i. e. the assumption of BOLTZMANN and JEANS, that the probability a priori would be equal for every value of the velocity.

§ 2. In the second place I wish to make some remarks in connection with the proof that BOLTZMANN gives in his "Gastheory", that for an "ungeordnetes" gas with simple suppositions on the nature of the molecules in the stationary state MAXWELL'S distribution of velocities is found. Dr. C. H. WIND shows in his above-mentioned paper that in this BOLTZMANN makes a mistake in the calculation of the number of collisions of opposite kind. BOLTZMANN, namely, assumes, that when molecules whose points of velocity lie in an element of volume  $d\omega$ , collide with others whose points of velocity lie in  $d\omega_1$ , so that after the collision the former points lie in  $d\omega'$  and the latter in  $d\omega'_1$ , now the elements of volume  $d\omega$  and  $d\omega'$ ,  $d\omega_1$  and  $d\omega'_1$  would be equal, so that now  $d\omega' d\omega'_1 = d\omega d\omega_1$ . He further assumes that when molecules collide whose points of velocity lie in  $d\omega'$  and  $d\omega'_1$ , they will be found in  $d\omega$  and  $d\omega_1$  after the collision. These last collisions he calls collisions of opposite kind. WIND now shows that this assumption is untrue;  $d\omega$  is not  $= d\omega'$ ,  $d\omega_1$  not  $= d\omega'_1$ , nor even  $d\omega d\omega_1 = d\omega' d\omega'_1$ , except when the masses of the two colliding molecules are equal<sup>1)</sup>.

Further the points of velocity of colliding molecules which lay in  $d\omega'$  and  $d\omega'_1$ , do not always get to  $d\omega$  and  $d\omega_1$  after collision,

<sup>1)</sup> I point out here that even then it is not universally true, but only when the elements of volume  $d\omega$  and  $d\omega_1$  have the shape of rectangular prisms or cylinders whose side or axis has the direction of the normal of collision.

so that another definition is necessary for collisions of opposite kind, viz. such for which the points of velocity get in  $d\omega$  and  $d\omega_1$  after the collision. WIND proves further that the number of collisions of opposite kind is all the same represented by the expression which BOLTZMANN had found for it.

It is then easy to change (what WIND does not do) the proof given by BOLTZMANN in § 5 of his "Gastheory", that Maxwell's distribution of velocities is the only one possible, in such a way that it is perfectly correct. But the error in question makes itself felt all through BOLTZMANN's book. Already with the proof of the  $H$ -theorem given in more analytical form in a footnote to § 5 we have some difficulty in getting rid of this error.

We meet the same thing when the molecules are treated as centres of force, and when they are treated as compound molecules. At the appearance of the second volume of his work, BOLTZMANN had taken notice of WIND's views, but the inaccurate definition for collisions of opposite kind has been retained<sup>1)</sup>.

In connection with this error, made by BOLTZMANN in a geometrical treatment of the phenomena of collision, is another error of more analytical nature, so that also JEANS, who treats the matter more analytically, gives a derivation which in my opinion is not altogether correct. Though preferring the geometrical method, BOLTZMANN repeatedly refers to the other<sup>2)</sup>. The method would then consist in this, that the components of the velocities after the collision  $\xi'\eta'\zeta'\xi'_1\eta'_1\zeta'_1$  are expressed by  $f(\xi\eta\zeta\xi_1\eta_1\zeta_1)$  and then by means of JACOBI's functional determinant  $d\xi'd\eta'd\zeta'd\xi'_1d\eta'_1d\zeta'_1$  is expressed in  $d\xi d\eta d\zeta d\xi_1 d\eta_1 d\zeta_1$ . We find then that here this determinant is = 1 and so

$$d\xi'd\eta'd\zeta'd\xi'_1d\eta'_1d\zeta'_1 = d\xi d\eta d\zeta d\xi_1 d\eta_1 d\zeta_1 \text{ or } d\omega'd\omega'_1 = d\omega d\omega_1.$$

The number of collisions of opposite kind =  $f'F'_1d\omega'd\omega'_1\sigma^2g \cos \vartheta d\lambda dt$  according to BOLTZMANN, and so also =  $f'F'_1d\omega d\omega_1\sigma^2g \cos \vartheta d\lambda dt$ . In this the mistake is made, however, that  $d\xi'd\eta'd\zeta'd\xi'_1d\eta'_1d\zeta'_1$  the volume in the space of 6 dimensions that would correspond with the volume  $d\xi d\eta d\zeta d\xi_1 d\eta_1 d\zeta_1$  before the collision, is thought as bounded by planes such as  $\xi' = c$ , which is not the case. JEANS too equates the products of the differentials, in which according to him,  $d\xi' \dots d\xi'_1$  being arbitrary, the  $d\xi \dots d\xi_1$  must be chosen in such a way, that the values of  $\xi' \dots \xi'_1$  calculated by the aid of the functions  $\xi' = f(\xi \dots \xi_1)$  etc. fall within the limits fixed by  $d\xi'$  etc<sup>3)</sup>. This, however, is impossible.

<sup>1)</sup> Cf. § 78, 2nd paragraph.

<sup>2)</sup> Cf. among others volume I, p. 25 and 27.

<sup>3)</sup> Cf. "The dynamical Theory of Gases" p. 18.

In my opinion the correct principle that the calculation of the extension occupied by the combinations of the points of velocity after the collision when that before the collision is known and vice versa, would come to the same thing as a transition to other variables in an integration, has not been applied in exactly the correct way. The property in question says that in an integral with transition from the variables  $\xi'_1 \eta'_1 \zeta'_1 \xi'_1 \eta'_1 \zeta'_1$  to  $\xi_1 \eta_1 \zeta_1 \xi_1 \eta_1 \zeta_1$  the product of the differentials  $d\xi'_1 d\eta'_1 d\zeta'_1 d\xi'_1 d\eta'_1 d\zeta'_1$  may be replaced by  $\frac{d(\xi'_1 \eta'_1 \zeta'_1 \xi'_1 \eta'_1 \zeta'_1)}{d(\xi_1 \eta_1 \zeta_1 \xi_1 \eta_1 \zeta_1)}$   $d\xi_1 d\eta_1 d\zeta_1 d\xi_1 d\eta_1 d\zeta_1$ , if we integrate every time with respect to the corresponding regions, *but these expressions are not equal for all that*. The first expression may be said to represent the elementary volume in the space of 6 dimensions, bounded with regard to  $\xi'_1 \dots \zeta'_1$ , the second the elementary volume bounded with regard to  $\xi_1 \dots \zeta_1$ <sup>1)</sup>.

We have a simple example when in the space of three dimensions we replace  $\int p dx dy dz$ , which e.g. represents the weight of a body, by  $\int p r^2 \sin \vartheta dr d\vartheta d\varphi$ , which represents the same thing, without  $dx dy dz$  having to be equal to  $r^2 \sin \vartheta dr d\vartheta d\varphi$ .

So we have here:

$$\int d\xi'_1 d\eta'_1 d\zeta'_1 d\xi'_1 d\eta'_1 d\zeta'_1 = \int \left| \frac{d(\xi' - \xi_1)}{d(\xi - \xi_1)} \right| d\xi_1 d\eta_1 d\zeta_1 d\xi_1 d\eta_1 d\zeta_1,$$

which two expressions represent the "extension" in the space of 6 dimensions after the collision. That before the collision is  $\int d\xi_1 d\eta_1 d\zeta_1 d\xi_1 d\eta_1 d\zeta_1$ , so that, when the determinant = 1, the extension remains unchanged by the collision. This proves really to be the case, as JEANS shows. We may, however also consider this property as a special case of the theorem of LIOUVILLE, and derive it from this<sup>2)</sup>. This theorem says, that with an ensemble of identical, mutually independent, mechanic systems, to which HAMILTON's equations of motion apply,  $\int dp_1 \dots dq_n = \int dP_1 \dots dQ_n$ , when  $p_1 \dots q_n$  represent the coordinates and momenta of the systems at an arbitrary point of time,  $P_1 \dots Q_n$  those at the beginning. GIBBS calls this law: the principle of conservation of extension-in-phase, which extension we must now think extended over a space of  $2n$  dimensions. When now the two colliding molecules are considered as a system which does not experience any influence of other systems, and it is assumed that during the

1) Cf. LORENTZ, l. c. Abhandlung VII.

2) As BOLTZMANN cursorily remarks: volume II p. 225.

collisions forces act which only depend on the place of the particles and not on the velocities, we may apply the formula  $\int dp'_1 \dots dq'_n = \int dp_1 \dots dq_n$  to an ensemble of such pairs of molecules, the former representing the extension-in-phase after, the latter that before the collision. In the case discussed by BOLTZMANN the masses of these molecules are  $m$  and  $m_1$  so that we get:

$$\begin{aligned} & \int dx' dy' dz' m^3 d\xi' d\eta' d\zeta' dx'_1 dy'_1 dz'_1 m_1^3 d\xi'_1 d\eta'_1 d\zeta'_1 = \\ & = \int dx dy dz m^3 d\xi d\eta d\zeta dx' dy' dz' m^3 d\xi' d\eta' d\zeta'. \end{aligned}$$

As we may consider the coordinates during the collision as invariable, it follows from this that:

$$\int d\xi' d\eta' d\zeta' d\xi'_1 d\eta'_1 d\zeta'_1 = \int d\xi d\eta d\zeta d\xi_1 d\eta_1 d\zeta_1.$$

§ 3. However as has been referred to above, we may, without assuming anything about the mechanism of the collision, prove the property by means of the formulae for the final velocities with elastic collision, making use of the functional determinant. Another method is followed by WIND in his above-mentioned paper (the second proof) and by BOLTZMANN (vol. II p. 225 and 226); this method differs in so far from the preceding one, that the changing of the variables takes place by parts (by means of the components of velocity of the centre of gravity), which simplifies the calculation<sup>1)</sup>. A third more geometrical method is given by WIND in his first proof. This last method seems best adapted to me to convey an idea of the significance of the principle of conservation of extension-in-phase in this special case. I shall, however, make free to apply a modification which seems an abridgment to me, by also making use of the functional determinant. So it might now also be called a somewhat modified first method.

In the first place I will call attention to the fact that with these phenomena of collision it is necessary to compare infinitely small volumes; if we, therefore, want to use the formula:

$$\int d\xi' d\eta' d\zeta' d\xi'_1 d\eta'_1 d\zeta'_1 = \int \left| \frac{d(\xi' \dots \xi'_1)}{d(\xi \dots \xi_1)} \right| d\xi d\eta d\zeta d\xi_1 d\eta_1 d\zeta_1$$

<sup>1)</sup> It seems to me that in this proof BOLTZMANN does not abide by what he himself has observed before (§ 27 and § 28, vol. II), viz. that the equality of the differential products means that they may be substituted for each other in integrals. The beginning of § 77 and the assumption of  $du dx dw$ , and  $dU dV dW$ , as reciprocal elements of volume, is, in my opinion, inconsistent with this

we must take infinitesimals of the 2<sup>n</sup><sup>l</sup> order. We can, however, also proceed in a somewhat different way. For how is the above formula derived? By making use of the fact, that with a volume  $d\tilde{\xi} d\eta d\tilde{\zeta} d\tilde{\xi}_1 d\eta_1 d\tilde{\zeta}_1$  in the region of the  $\tilde{\xi} \dots \tilde{\zeta}_1$  corresponds a volume

$$\left| \frac{d(\xi' \dots \zeta'_1)}{d(\tilde{\xi} \dots \tilde{\zeta}_1)} \right| d\tilde{\xi} d\eta d\tilde{\zeta} d\tilde{\xi}_1 d\eta_1 d\tilde{\zeta}_1$$

in the region of the  $\xi' \dots \zeta'_1$ , or also that the first mentioned extension, occupied by the representing points in the space of 6 dimensions before the collision, will give rise to the second extension after the collision. We can, therefore very well compare these expressions inter se, without integration, if only the second expression is not interchanged with  $d\tilde{\xi}' d\eta' d\tilde{\zeta}' d\tilde{\xi}'_1 d\eta'_1 d\tilde{\zeta}'_1$ , i. e. the volume element obtained by dividing the extension after the collision in another way.

We now suppose the points of velocity before the collision to be situated in two cylinders, the axes of which are parallel to the normal of collision. The bases of the cylinders are  $dO dO_1$  and the heights  $d\delta$  and  $d\delta_1$ . The extension occupied by the combinations of the points of velocity is evidently equal to the product of the contents of the cylinders:  $dO dO_1 d\delta d\delta_1$ . In case of collision the components of the velocities perpendicular to the normal remain unchanged, so the points of velocity are shifted in the cylinders in the direction of the axis, so that  $\delta$  becomes  $\delta'$ , and  $\delta_1$  becomes  $\delta'_1$ . Between these quantities exist the relations:  $\delta' = \frac{m\delta + m_1(2\delta_1 - \delta)}{m + m_1}$  and  $\delta'_1 = \frac{m_1\delta_1 + m(2\delta - \delta_1)}{m + m_1}$ , when  $m$  and  $m_1$  denote the masses of the colliding molecules (i.e. the same relations as between the normal initial and final velocities with elastic collision).

If we now wish to calculate the extension after impact we may make use of the fact that  $dO$  and  $dO_1$  have not changed, so that we need only examine what happens to  $d\delta d\delta_1$ , or what extension in the region of the  $\delta' \delta'_1$  corresponds to the extension  $d\delta d\delta_1$  in the region of the  $\delta \delta_1$ .

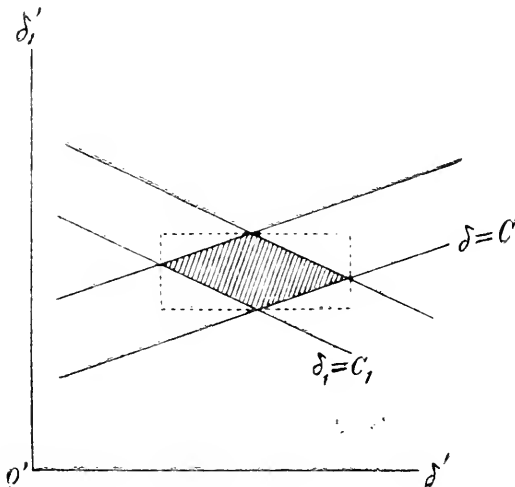
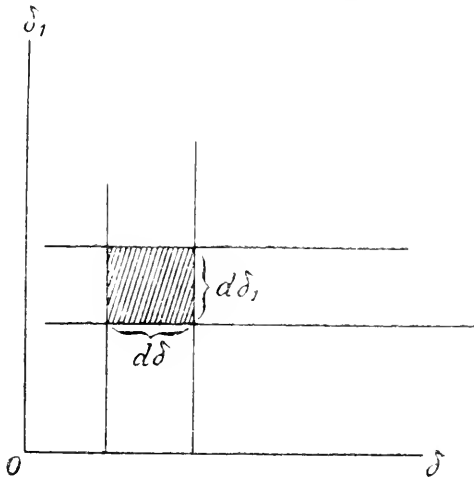
According to the above this is:  $\left| \frac{d(\delta' \delta'_1)}{d(\delta \delta_1)} \right| d\delta d\delta_1$ , and as it follows from the formulae for  $\delta'$  and  $\delta'_1$  that the absolute value of the determinant = 1, the extensions before and after impact are equal. The extension after the collision is, however, not equal to the product of the cylinders in which the points of velocity will be found after the collision. This will be easily seen with the aid of the geometrical representation given by WIND. The extension before impact may be thought as the product of the extension in the space



of four dimensions  $dO dO_1$  and the extension  $d\delta d\delta_1$ , which we may imagine as a rectangle in the region of the  $\delta\delta_1$ , when we project them as two mutually normal coordinates in a plane.

Every point in the rectangle represents therefore a number of combinations of velocities with equal  $\delta$  and  $\delta_1$ . The sides of the rectangle with equations  $\delta = c$  and  $\delta_1 = c_1$ , correspond in the region of the  $\delta'\delta'_1$  with the right lines  $m\delta' + m_1(2\delta'_1 - \delta') = (m + m_1)c$  and  $m_1\delta'_1 + m(2\delta' - \delta'_1) = (m + m_1)c_1$ , so that from the combinations represented by points within the rectangle after the impact others follow represented by points within an oblique parallelogram.

The formula  $\frac{d(\delta'\delta'_1)}{d(\delta\delta_1)} = 1$  expresses that the two figures have the same area. Now the extension after impact is equal to this paral-



logram  $\times dO_1O_1$  or the product of the two cylinders in which points of velocity were found before impact. The product of the cylinders, in which points of velocity are found after impact is equal to the product of  $dO_1O_1$  and the area of the rectangle with sides parallel to the axes  $O'd'$  and  $O'd'_1$  described round the parallelogram under investigation. In this rectangle lie a number of points which have no corresponding points in the first rectangle. Only when  $m = m_1$  rectangle and parallelogram coincide.

Collisions of opposite kind, now, are such for which the combinations of velocity before impact are represented by points of the parallelogram in the plane  $d'O'd'_1$  and after impact by points of the rectangle in the plane  $dO_1d_1$ .

**Physics.** — “Contributions to the knowledge of the  $\psi$ -surface of VAN DER WAALS. XII. On the gas phase sinking in the liquid phase for binary mixtures.” By Prof. H. KAMERLINGH ONNES and Dr. W. H. KEESOM. Communication N<sup>o</sup>. 96<sup>b</sup> from the Physical Laboratory at Leiden.

§ 1. *Introduction.* In what follows we have examined the equilibrium of the gas phase with the liquid phase for binary systems, with which the sinking of the gas phase in the liquid phase may occur.

It lies to hand to treat this problem by the aid of  $\psi$  (free energy)-surfaces for the unity of mass of the mixture (VAN DER WAALS, Continuität II p. 27) for different temperatures construed on the coordinates  $v$  (volume of the unity of mass of the mixture) and  $x$  (quantity of mass of the second component contained in the unity of mass of the mixture).

As VAN DER WAALS (loc. cit.) has already observed, the laws referring to the stability and the coexistence of the phases are the same for these  $\psi$ -surfaces as for the more generally used  $\psi$ -surfaces for the molecular quantity: in particular also the coexisting phases are indicated by the points of contact of the  $\psi$ -surface with a plane which rolls with double contact over the plait in the  $\psi$ -surface. In what follows we have chiefly to consider the projections of the conodal curve and of the conodal tangent-chords on the  $vr$ -plane.

More particular cases as the occurrence of minimum or maximum critical temperature or minimum or maximum pressure of coexistence we shall leave out of account: we shall further confine ourselves to the case that retrograde condensation of the first kind occurs. Moreover we shall restrict ourselves to temperatures, at which the