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**Physics.** — “*The liquid state and the equation of condition.*” By  
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It has been repeatedly pointed out that if we keep the values of the quantities  $a$  and  $b$  of the equation of state constant, this equation indicates the course of the phenomena only qualitatively, but in many cases does not yield numerically accurate results. In particular DANIEL BERTHELOT testing the equation of state at the experimental investigations of AMAGAT, has shown that there occur some curves in the net of isothermals, e. g. those indicating the points for which the value of the product  $pv$  is a minimum, and other curves of the same kind, whose general course is correctly predicted by the equation of state, but whose actual shape and position as determined by the experiments of AMAGAT, shows considerable deviations from the course of those curves as it may be derived from the equation of state.

In consequence of this circumstance the quantities  $a$  and  $b$  have been considered as functions of the temperature and volume. Already CLAUSIUS proposed such a modification for the quantity  $a$ ; for carbonic acid he does not put  $a = \text{constant}$ , but he multiplies it with  $\frac{273}{T}$ . Such a modification seems to be required principally with a view to the course of the saturated vapour tension.

From the beginning I myself have clearly pointed out that, though  $a$  may probably be constant, this cannot be the case with the quantity  $b$ . One of the circumstances which I was convinced that I had shown with the highest degree of certainty as well in the theoretic way as by means of the comparison of the experiments of ANDREWS, was that the quantity  $b$  must decrease when the volume decreases. So for carbonic acid I calculated for  $b$  in the gaseous state at  $13^{\circ}$  the value 0,00242 and in the liquid state a value decreasing to 0,001565. But the law of the variability of  $b$  not being known, I have been often obliged to proceed as if  $b$  were constant. In the following pages I will keep to the suppositions assumed by me from the beginning, namely that  $a$  is constant and that  $b$  varies with the volume; and I will show that if we do so, the considerable deviations disappear for the greater part and that it is possible to assume already now a law for the variability of  $b$  with the volume, from which we may calculate in many cases numerically accurate data even for the liquid state at low temperatures.

To that purpose we shall begin with the discussion of the tension of the saturated vapour over liquids at low temperature. From the conditions for coexisting phases of a simple substance, that namely  $p$ ,  $T$  and the thermodynamic potential are the same in both phases, follows:

$$(pv - \int p dv)_1 = (pv - \int p dv)_2$$

or

$$\left( pv - \frac{a}{v} - RT \int \frac{dv}{v-b} \right)_1 = \left( pv - \frac{a}{v} - RT \int \frac{dv}{v-b} \right)_2$$

If we put  $b = \text{constant}$  i. e.  $b$  independent of the volume, then the latter equation assumes the well known form:

$$\left[ pv - \frac{a}{v} - RT \log(v-b) \right]_1 = \left[ pv - \frac{a}{v} - RT \log(v-b) \right]_2$$

Properly speaking this equation is not suitable for the direct calculation of the coexistence pressure; it must be considered to give a relation between the specific volumes and so also between the densities of the coexisting phases. At lower temperatures, however, for which the vapour phase, which we have indicated by means of the index 2, is rare and may be estimated not to deviate noticeably from the gas-laws, the equation becomes suitable for the calculation of the pressure of the saturated vapour. In this case it assumes the following form:

$$pv_1 - \frac{a}{v_1} - RT \log(v_1 - b) - RT = RT \log \frac{p}{RT}$$

We find after successive deductions which are too simple to require special discussion:

$$\begin{aligned} pv_1 - \frac{a}{b} + \frac{a(v_1 - b)}{lv_1} - \left( p + \frac{a}{v_1^2} \right) (v_1 - b) &= RT \log \frac{p(v_1 - b)}{RT} \\ pb - \frac{a}{b} + \frac{a}{v_1^2 b} (v_1 - b)^2 &= RT \log \frac{p}{p + \frac{a}{v_1^2}} \\ pb - \frac{a}{b} + \frac{v_1 - b}{b} [RT - p(v_1 - b)] &= RT \log \frac{p}{p + \frac{a}{v_1^2}} \\ - p \frac{v_1(v_1 - 2b)}{b} - \frac{a}{b} + \frac{v_1 - b}{b} &= \log \frac{p}{p + \frac{a}{v_1^2}} \end{aligned}$$

Undoubtedly  $p$  may be neglected by the side of  $\frac{a}{v_1^2}$ . Even if  $p$  amounts to one Atmosphere, its value is certainly still smaller than 0.0001<sup>th</sup> part of  $\frac{a}{v_1^2}$ . In the same way  $p \frac{v(v-2b)}{b}$  may undoubtedly be neglected by the side of  $\frac{a}{b}$  or  $pv_1(v_1-2b)$  by the side of  $a$  — and this for the same reason, for  $\frac{a}{v_1(b-v_1)}$  is a quantity of the same order as  $\frac{a}{v_1^2}$ .

So the equation may be simplified to:

$$\log \frac{p}{\frac{a}{v_1^2}} = -\frac{\frac{a}{b}}{RT} + \frac{v_1-b}{b} \dots \dots \dots (1)$$

For the limiting case, when  $v_1$  may be equated to  $b$ , we get:

$$\log \frac{p}{\frac{a}{b^2}} = -\frac{\frac{a}{b}}{RT}$$

If we introduce the critical data, namely:

$$pv = \frac{1}{27} \frac{a}{b^2} \text{ and } RT_k = \frac{8}{27} \frac{a}{b},$$

then we get the following equation for the calculation of  $p$ .

$$-\log \frac{p}{p_k} = \frac{27}{8} \frac{T_k}{T} - \log 27$$

or, as  $\log 27$  is equal to 3,3 and may therefore be nearly equated to  $\frac{27}{8}$  we get with a high degree of approximation:

$$-\log \frac{p}{p_k} = 3,375 \frac{T_k - T}{T}$$

This last equation is nearly equal to that derived by prof. KAMERLINGH ONNES by means of a graphical method from the equation of state with  $a$  and  $b$  constant, namely:

$$-\log \frac{p}{p_k} = 3,4 \left( \frac{T_k - T}{T} \right)^1$$

KAMERLINGH ONNES found this equation to hold in approximation up to the critical temperature, here we could only derive it for low

<sup>1)</sup> Arch. Néerl. Livre Jub. dédié à H. A. LORENTZ. p. 676.

temperatures. If in equation (1) we do not immediately introduce  $v_1 = b$ , we may write it as follows:

$$\log \frac{p}{\frac{a}{b^2} \left( \frac{b}{v_1} \right)^2} = - \frac{\frac{a}{b}}{RT} + \frac{v_1 - b}{b}$$

or

$$\log \frac{p}{\frac{a}{b^2}} = - \frac{\frac{a}{b}}{RT} + \frac{v_1 - b}{b} - 2 \log \frac{v_1}{b}.$$

For values of  $v_1$  only slightly greater than  $b$  we may write  $\frac{v_1 - b}{b}$  for  $\log \frac{v_1}{b}$ . So we get:

$$- \log \frac{p}{p_k} = \frac{27}{8} \frac{T_k}{T} + \frac{v_1 - b}{b} - \log 27.$$

The value of  $\frac{v_1 - b}{b}$  varies with the temperature and starts with the value zero for  $T = 0^\circ$ . It may be calculated from:

$$\frac{a}{v_1^2} (v_1 - b) = RT.$$

This last equation may be written as follows:

$$\frac{8}{27} \frac{T}{T_k} = \frac{\left( \frac{v_1}{b} - 1 \right)}{\left( \frac{v_1}{b} \right)^2}.$$

With  $\frac{T}{T_k} = \frac{15}{32}$  we find for  $\frac{v_1 - b}{b}$  the value  $\frac{1}{5}$  and with  $\frac{T}{T_k} = 0,54$  the value  $\frac{1}{4}$ . With  $\frac{T}{T_k} = \frac{1}{2}$  the value of  $\frac{v_1 - b}{b}$  is equal to 0,2125.

The quantity  $\frac{v_1 - b}{b}$  varying with the temperature, the term  $\frac{27}{8} \frac{T}{T_k}$  does not represent the total variation of  $\beta$  with the temperature, but the difference is small. We might calculate the value of  $\frac{T}{p} \frac{dp}{dT}$  from the above equation, but it is simpler to calculate this quantity from the following equation:

$$T \left( \frac{\partial p}{\partial T} \right)_v - p = \left( \frac{\partial \epsilon}{\partial v} \right)_T$$

For coexisting phases this equation becomes:

$$T \frac{dp}{dT} - p = \frac{\varepsilon_2 - \varepsilon_1}{v_2 - v_1}$$

or

$$T \frac{dp}{dT} - p = \frac{\frac{a}{v_1} - \frac{a}{v_2}}{v_2 - v_1} = \frac{a}{v_1 v_2} \dots \dots \dots (2)$$

For low temperatures this yields:

$$\frac{T}{p} \frac{dp}{dT} - 1 = \frac{\frac{a}{v_1}}{RT} = \frac{\frac{a}{b}}{RT} - \frac{\frac{a(v_1 - b)}{v_1 b}}{RT}$$

or

$$\frac{T}{p} \frac{dp}{dT} - 1 = \frac{\frac{a}{b}}{RT} - \frac{v_1}{b}$$

or

$$\frac{T}{p} \frac{dp}{dT} = \frac{27 T_k}{8 T} - \frac{v_1 - b}{b}$$

For  $T = T_k$  equation (2) yields:

$$\left( \frac{T}{p} \frac{dp}{dT} \right)_k = 4.$$

For the highest temperature, therefore, at which the pressure curve occurs, the coefficient with which  $\frac{T_k}{T}$  must be multiplied in order to yield

the value of  $\frac{T}{p} \frac{dp}{dT}$ , does not differ much from that for the lowest temperature at which the liquid may exist without solidification.

Here we have one of the striking instances, how the equation of state with constant  $a$  and  $b$  may represent the general course of a quantity just as it is found in reality, though the numerical value differs considerably. For the real course of the vapour tension is at least in approximation represented by the formula:

$$- \log \frac{p}{p_k} = f \frac{T_k - T}{T},$$

but the value of  $f$  is not 4 or somewhat less — but for a great many substances a value is found which does not differ much from 7.

Before discussing this point further, we shall calculate some other quantities whose values for the liquid state for low temperatures follow from the equation of state when we keep  $a$  and  $b$  constant.

Let us take again  $p$  to be so small that we may write

$$\frac{a}{v^2}(v-b) = RT.$$

From this we may deduce:

$$1 = \left( \frac{T}{v} \frac{dv}{dT} \right)_{p=0} \times \left\{ \frac{v}{v-b} - 2 \right\} \dots \dots \dots (3)$$

For  $\frac{T}{T_k} = 0,585$  (Ether at  $0^\circ$ )  $\frac{v}{v-b}$  is equal to 4,7 as appears from:

$$\frac{8}{27} \frac{T}{T_k} = \frac{\left( \frac{v}{b} - 1 \right)}{\left( \frac{v}{b} \right)^2}.$$

With this value  $\frac{v}{v-b} = 4,7$  we find:

$$\frac{T}{v} \left( \frac{dv}{dT} \right)_{p=0} = \frac{1}{2,7}.$$

So we find for the coefficient of dilatation under low pressure and at this temperature which is so low that we may neglect the pressure, the value:

$$\frac{1}{v} \left( \frac{dv}{dT} \right)_{p=0} = \frac{0,00367}{2,7} = 0,00136.$$

Comparing this value with that which the experiment has yielded and which we may put at 0,001513, we see that it may be used at least as an approximated value.

The above equation (3) yields for  $\frac{1}{v} \left( \frac{dv}{dT} \right)_{p=0}$  with  $v = 2b$  an infinite value and so  $\frac{T}{T_k} = \frac{27}{32}$ . This quite agrees with the circumstance that the isothermal for  $\frac{T}{T_k} = \frac{27}{32}$  touches the  $V$ -axis and it warns us that equation (3) cannot yield any but approximated values for much lower values of  $T$ .

For the coefficient of compressibility  $\beta$  namely  $-\left( \frac{dv}{v dp} \right)_T$  in that same liquid state we find

$$-v_1 \left( \frac{dp}{dv_1} \right)_T = \frac{RTv_1}{(v_1-b)^2} - \frac{2a}{v_1^2} = \frac{a}{v_1^2} \left( \frac{v_1}{v_1-b} - 2 \right)$$

or

$$\frac{1}{\beta} = 27 p_k \left( \frac{b}{v_1} \right)^2 \left( \frac{v_1}{v_1-b} - 2 \right).$$

With the aid of the above data and putting  $p_k=37,5$  atmospheres we find:

$$\beta = 0.0006 \text{ (nearly).}$$

The experiment has yielded no more than about 0,00016 for this value. So we have found it so many times too large, that for this quantity the equation of state with constant  $a$  and  $b$  cannot be considered to hold good even in approximation.

From the well known equation:

$$\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_v \left(\frac{\partial p}{\partial v}\right)_T = -1$$

follows

$$\frac{T}{v} \left(\frac{\partial v}{\partial T}\right)_p \left(-v \frac{\partial p}{\partial v T}\right) = T \left(\frac{\partial p}{\partial T}\right)_v$$

and therefore

$$\frac{T}{v} \left(\frac{dv}{dT}\right)_p \times \frac{1}{\beta} = \frac{a}{v^2} \text{ 1)}$$

With the values mentioned above and yielded by the experiment we should therefore have for ether at  $0^\circ$ :

$$\frac{273 \times 0,001513}{0,00016} = 27 \times 37,5 \left(\frac{b}{v}\right)^2$$

or

$$2,5 = \left(\frac{b}{v}\right)^2.$$

According to this equation  $v$  should be smaller than  $b$  which would be absurd, if  $b$  does not vary with the volume.

If we calculate the value of  $b$  from  $\frac{RT_k}{8p_k}$  then we find for ether  $b=0,0057$  circa; in reality the liquid volume appears to be smaller than  $b$ . Dividing namely the molecular liquid volume by the normal molecular gas volume we find about 0,0047 <sup>2)</sup>. From this appears convincingly that the variability of  $b$  exists in reality and that therefore an equation of state in which this variability is not taken into account, cannot possibly yield the data of the liquid state.

Let us return to the equation:

$$-\log \frac{p_k}{p} = f \frac{T_k - T}{T},$$

which holds good at least approximately, as is confirmed by the experiments, if we take for  $f$  a value which is about twice as great as would follow from the equation of state if we keep  $a$  and  $b$  con-

<sup>1)</sup> Continuität 2nd Edition, p. 171.

<sup>2)</sup> Continuität 2nd Edition, p. 172.



stant. What modification must the equation of state be subjected to in order to account for this twice greater value? CLAUSIUS answered this question by supposing  $a$  to be a function of the temperature e. g. by substituting  $a \frac{273}{T}$  for it.

When we consider the question superficially, the difficulty seems to be solved. But it is only seemingly so. At  $T = T_k$  this modification really causes  $f$  to assume the value 7 — but this supposition has consequences which for lower temperatures are contrary to the experiment. If we calculate the value of

$$T \frac{dp}{dT} - p = \frac{\varepsilon_2 - \varepsilon_1}{v_2 - v_1},$$

as on page 4 and if we take into account that  $\varepsilon = -2 \frac{a}{v} \frac{273}{T}$  we find

$$\frac{Tdp}{pdT} - 1 = \frac{2 \frac{a}{v_1} \frac{273}{T}}{RT}.$$

For lower temperatures we will put  $v_1 = b$  and we deduce approximately :

$$\frac{Tdp}{pdT} = 2 \frac{a}{b} \frac{273}{RT^2}$$

or <sup>1)</sup>

$$\frac{T}{p} \frac{dp}{dT} = 2 \times \frac{27}{8} \left( \frac{T_k}{T} \right)^2.$$

For  $\frac{T}{T_k} = \frac{1}{2}$  we find then for  $\frac{T}{p} \frac{dp}{dT}$  a value which is not twice as great as that which follows from a constant value of  $a$ , but a value which is four times as great.

The equation :

$$\left[ pv - \int pdv \right]_1 = \left[ pv = \int pdv \right]_2$$

yields for this value of  $a$  :

$$- \log \frac{p}{p_k} = 2 \times \frac{27}{8} \left( \frac{T_k}{T} \right)^2 - \log \left( 27 \frac{T_k}{T} \right) + 1.$$

In order to agree with  $f \left( \frac{T_k}{T} - 1 \right)$  the positive term of the right-hand member of this equation should have the form  $2 \times \frac{27}{8} \frac{T_k}{T}$ ; and the negative term should not be  $\log 2 \times 27$ , but  $\log 27^2$ .

<sup>1)</sup> Continuität, p. 171.

The imperfect agreement between the real course of the vapour tension and that derived from the equation of state with  $a$  and  $b$  constant, has induced us to assume that  $a$  is a function of the temperature. It appears however that this agreement is not satisfactorily established by the modification proposed by CLAUSIUS. It will therefore be of no use to proceed further in this way — specially because this modification in itself is certainly insufficient to account for the fact that liquid volumes occur which are even smaller than  $b$ .

If we had not supposed  $a$  to increase so quickly with decreasing temperature as agrees with  $a \frac{T_k}{T}$ ; if we had chosen  $ae^{1-\frac{T}{T_k}}$  for instance, then the greater part of the above difficulties would have vanished.

We should then have found:

$$\frac{T}{p} \frac{dp}{dT} - 1 = \left(1 + \frac{T}{T_k}\right) \frac{ae^{1-\frac{T}{T_k}}}{RTv_1}$$

The expression  $\left(1 + \frac{T}{T_k}\right)e^{1-\frac{T}{T_k}}$  is equal to 2 at  $T = T_k$  and at  $T = 0$  it would have increased to  $e = 2,728$  etc.; so the increase is relatively small. But the term which should be found equal to  $\log 27^2$ , would also have remained far below the required value. For this reason it seems desirable to me to inquire, in how far the variability of  $b$  alone can account for the course of the vapour tension.

As I dared not expect that the variability of  $b$  could explain the course of the vapour tension as it is found experimentally, and in any case not being able to calculate this variability, I have often looked for other causes, which might increase the value of the factor  $f$  from  $\frac{27}{8}$  to about twice that value. The quantity  $\frac{a}{v}$  representing the amount with which the energy of the substance in rare gaseous condition surpasses that of the same substance in liquid condition, and this quantity seeming — from the value of  $\frac{Tdp}{pdT}$  — to be only half of what it should be, I have thought that the transformation of liquid into vapour ought perhaps to be regarded as to consist of two transformations. These two transformations would be: that of liquid into vapour and that of complex molecules into simple gasmolecules. If this really happened then the liquid state would essentially differ from the gaseous state even for substances which we consider to be

normal. We should then have reason to speak of "molécules liquidogènes" and "molécules gazogènes". It would then, however, be required that the following equalities happened to be satisfied. In the first place the two transformations would require the same amount of energy; and in the second place the number of "molécules liquidogènes" in the liquid state <sup>1)</sup> at every temperature would have to be proportional with the value of  $\frac{p(v_2-v_1)}{T}$ . The following equation would then hold:

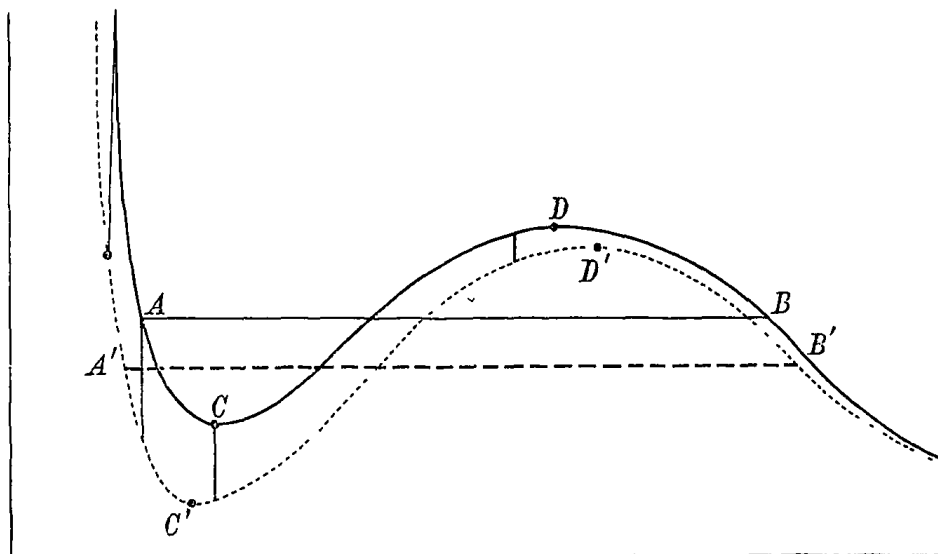
$$\frac{Tdp}{pdT} - 1 = \frac{\frac{a}{v_1} - \frac{a}{v_2} + (x_2-x_1)E}{p(v_2-v_1)} = \frac{a}{v_1v_2p} + \frac{(x_2-x_1)\varepsilon}{p(v_2-v_1)}$$

Not succeeding in deducing this course of the amount of the liquidogène molecules from the thermodynamic rules and in accounting for the above mentioned accidental equalities I have relinquished this idea, the more so as this supposition is unable to explain the fact that the liquid volume can decrease below  $b$ .

If we ask what kind of modification is required in the equation of state with constant  $a$  and  $b$  in order to obtain a smaller vapour tension, we may answer that question as follows. Every modification which lowers the pression with an amount which is larger according as the volume is smaller, satisfies the requirement mentioned. In the following figure the traced curve represents the isothermal for constant  $a$  and  $b$ ; the straight line  $AB$ , which has been constructed according to the well known rule indicates the coexisting phases, and the points  $C$  and  $D$  represent the phases with minimum pressure and maximum pressure. The dotted curve has been constructed in such a way that for very large volumes it coincides sensibly with the traced curve, but for smaller volumes it lies lower, and the distance is the greater according as the volume is smaller. Then the point  $D'$  has shifted towards the right and the point  $C'$  towards the left. For in the point exactly below  $D$  as well as in the point exactly below  $C$  the value of  $\frac{dp}{dv}$  for the dotted curve is positive;

these points lie therefore on the unstable part of the modified isothermal and the limits of the unstable region are farther apart. But it is also evident — and this is of primary interest — that if for the modified isothermal we trace again the straight line of the coexisting phases according to the well know rule, this line will lie lower than the line  $AB$ . The area of the figure above  $AB$

<sup>1)</sup> Diminished with that number in the gaseous state.



has decreased, that of the figure below  $AB$  has increased in consequence of the modification. The line  $A'B'$  must therefore be traced noticeably lower in order to get again equal areas.  $B'$  will of course lie on the right of  $B$ , and we may also expect that  $A'$  will lie on the left of  $A$ .

We have, however, put the question in too general terms; for our purpose it should have been put as follows: what modification in the quantities  $a$  and  $b$  makes the vapour pressure at a temperature which is an equal fraction of  $T_k$ , decrease below the amount which we find for it, keeping  $a$  and  $b$  constant — and it would even be still more accurate not to speak of the absolute value of the pressure, but of the fraction  $\frac{p}{p_k}$ .

The modifications in  $a$  and  $b$  should then be such, — if we base our considerations on the preceding figure — that in consequence of the modifications themselves the values of  $T_k$  and  $p_k$  either do not change at all or very slightly.

If we make  $a$  a function of the temperature we have to compare the following two equations:

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

and

$$p = \frac{RT}{v-b} - \frac{aT_k}{Tv^2}$$

Both equations yield  $RT_k = \frac{8}{27} \frac{a}{b}$  and  $p_k = \frac{1}{27} \frac{a}{b^2}$  i. e. the same values for  $T_k$  and  $p_k$  if  $a$  and  $b$  have the same values in both

equations. The value of  $p$  — the values of  $T$  and  $v$  being the same for both curves — for the modified isothermal is smaller than that for the isothermal with constant  $a$  and  $b$ , and the difference is greater according as the volume is smaller. According to the figure discussed  $\frac{p}{p_k}$  — the value of  $\frac{T}{T_k}$  being the same for both curves — will therefore have a smaller value for the modified isothermal than for the unmodified one. A value of  $a$  increasing with decreasing value of  $v$  would have the same effect. But I have not discussed a modification of this kind, at least not elaborately, because I had concluded already before (see “Livre Jub. dédié à LORENTZ” p. 407) that the value of the coefficient of compressibility in liquid state can only be explained by assuming a molecular pressure of the form  $\frac{a}{v^2}$ . The supposition of complex molecules in the liquid state would involve a modification of the kinetic pressure to  $\frac{RT}{v-b} \varphi(vT)$ , where  $\varphi(v, T)$  must increase with decreasing value of  $v$ . Also this supposition would lead to a smaller value of  $\frac{p}{p_k}$  for the same value of  $\frac{T}{T_k}$ . This is namely certainly true, if the greater complexity has disappeared in the critical state, and if therefore the values of  $T_k$  and  $p_k$  are unmodified; probably it will also be the case if still some complex molecules occur even in the critical state. But whether this is so or not can only be settled by a direct closer investigation, and for this case the property of the drawn figure alone is not decisive. I have, however, already shown above, that we cannot regard this circumstance as the probable cause of the considerable difference between the real value of the vapour pressure and that calculated from the equation of state with constant  $a$  and  $b$ . So we have no choice but to return to my original point of view of 30 years ago and to suppose  $b$  to be variable, so that the value of  $b$  decreases with decreasing volume. It is clear that a variability of this kind causes the kinetic pressure  $\frac{RT}{v-b}$  to be smaller than we should find it with constant  $b$ , and the more so according as  $b$  is smaller. Moreover it is possible in this way to account for the fact, that liquid volumes occur smaller than the value which  $b$  has for very large volumes and which I shall henceforth denote by  $b_g$ . Or I may more accurately say that I do not return to that point of view, for properly speaking I have never left it. As the law of the variability was not known, I could

not develop the consequences of this decreasing value of  $b$  — but it appears already in my paper on “The equation of state and the theory of cyclic motions” and in the paper in the “Livre Jub. dédié à LORENTZ” quoted above that I still regarded the question from the same point of view.

My first supposition concerning the cause of the decrease of  $b$  with the volume was not that the smaller value of  $b$  corresponded to smaller volume of the molecules.  $b_g$  being equal to four times the molecular volume, I supposed smaller values of  $b$  to be lower multiples of this volume. In this way of considering the question the decrease of  $b$  does not indicate a real decrease of the volume of the molecules. We will therefore call it a quasi-decrease.

It can scarcely be doubted that such a quasi-decrease of the volume of the molecules exists. In his “Vorlesungen” BOLTZMANN started from the fundamental supposition that the state of equilibrium i.e. the state of maximum-entropy is at the same time the “most probable state”; in doing which he was obliged to take into account the chance that two distance spheres partially coincide. And comparing the expression which he found in this way for the maximum-entropy with the expression  $R \int \frac{dv}{v-b}$  (i. e. the entropy in the state of equilibrium according to the equation of state) it was possible for him to determine the values of some of the coefficients of the expression:

$$b = b_g \left\{ 1 - \alpha \left( \frac{b_g}{v} \right) + \beta \left( \frac{b_g}{v} \right)^2 \dots \right\}.$$

This method is indirect. I myself had tried to find these coefficients by investigating directly the influence of the coincidence of the distance spheres on the value of the pressure. According to these two different methods different values for the coefficients were found. My son has afterwards pointed out (see these Proceedings 1902) that also according to the direct method a value of  $\alpha$  equal to that calculated by BOLTZMANN is found, if we form another conception of the influence on the pressure than I had formed and since then I am inclined to adopt the coefficients calculated according to the method of BOLTZMANN as accurate.

But these values apply only to spherical molecules and only in the case of monatomic gases we may suppose molecules with such a shape. It is not impossible that for complex molecules these coefficients will be found to be much smaller. Moreover for the determination of  $\int \frac{dv}{v-b}$  knowledge of all the coefficients is required — and

we cannot expect that the calculations required for this purpose will soon be performed. Even the determination of  $\beta$  required an enormous amount of work — compare the calculations of VAN LAAR.

For complex molecules another reason is possible for decrease of  $b$  with decreasing volume. The molecules might really become smaller under high kinetic pressure i.e. in the case of high density. If the atoms move within the molecule — and we can hardly doubt that they do so — they require free space. And it is highly probable, we may even say it is certain, that this space will diminish when the pressure which they exercise on one another, is increased. The mechanism of the molecules however being totally unknown it is impossible to decide a priori whether this decrease of the volume of the molecules will have a noticeable effect on the course of the isothermal. In my application of the theory of cyclic motions on the equation of state I have tried to give the formula which would represent such a real decrease of the volume of the molecules with diminishing volume. VAN LAAR has tested this formula to AMAGAT'S observations on hydrogen, — and though new difficulties have arisen, the agreement is such that we may use the given formula at any rate as an approximated formula for the dependency of  $b$  on  $v$ . I will apply the formula, which may have a different form in different cases, in the following form:

$$\frac{b-b_0}{v-b} = 1 - \left( \frac{b-b_0}{b_g-b_0} \right)^2 \cdot \cdot \cdot \cdot \cdot \cdot \quad (4)$$

The symbols  $b_g$  and  $b_0$  in this formula denote the limiting values for  $b$ , the first for infinitely large volume, the second for the smallest volume in which the substance can be contained. For more particulars I refer to my paper on "The equation of state and the theory of cyclic motions." VAN LAAR concluded from his investigation that agreement is only to be obtained if  $b_0$  decreases with  $T$ , a result which I myself had already obtained applying the formula for carbonic acid (Arch. Néerl. Serie II, Tome IV, pag. 267). If this is really the case and if it appears to be also true after we have modified the formula in some way or other compatible with the manner in which it is derived, then the following difference exists between the course of  $b$  with  $v$  when ascribed to a quasi-diminishing and when ascribed to a real diminishing of the volume of the molecules: in the first case  $b$  is independent of  $T$ , in the second case however it does depend on  $T$ . The fact that  $\left( \frac{dp}{dt} \right)_v$  is not perfectly constant seems to plead for the latter supposition.

For the present, however, I leave these questions and difficulties out of consideration, and I confine myself to showing that a formula of the form (4) can really make the considerable differences disappear which we have met with till now. The more so as this formula appears to be adapted for the derivation of general consequences, which follow from the decrease of  $b$  with  $v$ . I leave therefore a possible dependency of  $b_0$  on  $T$  out of consideration. Moreover in applying the formula I will suppose  $b_g = 2b_0$ . I choose one — in some respect arbitrarily — from all the forms which I have found to be possible (compare also my paper in the Arch. Néerl. “Livre Jub. dédié à Bosscha). The numerous calculations required in order to investigate in how far modifications are necessary and possible in order to make the agreement with the experiments more perfect, may perhaps be performed later.

A. *The tension of the saturated vapour.*

Let us begin with the calculation of the pressure of the saturated vapour at low temperatures and let us to that purpose write the equation expressing that the thermo-dynamic potential has the same value in coexisting phases, in the following form:

$$\left[ pv - \frac{a}{v} - RT \int \frac{d(v-b)}{v-b} - RT \int \frac{db}{v-b} \right]_1 = \left[ \dots \dots \dots \right]_2$$

of

$$\left[ pv - \frac{a}{v} - RT \log(v-b) - RT \int \frac{db}{v-b} \right]_1 = \left[ \dots \dots \dots \right]_2$$

In my paper “De kinetische beteekenis der thermodynamische potentiaal” I have already pointed out the signification of the term  $RT \int \frac{db}{v-b}$ ; it represents namely the amount of work performed by the kinetic pressure on the molecule when this passes in a reversible way from the condition of the first phase into that of the second phase and when its volume is therefore enlarged either fictitiously or as we now take it to be, really. We may calculate this term if we assume the chosen form for  $b$  and this is one of the reasons why I adhere to the idea of a real increase of the molecular volume. But though its value may depend upon the particular form which we have assumed for  $b$ , it will certainly have a positive value for every law of variability of  $b$  with  $v$  which we may choose.

Let us for the calculation of  $\int \frac{db}{v-b}$  denote  $\frac{b-b_0}{b_g-b_0}$  by  $z$ , then we



have  $db = (b_g - b_0) dz$  and according to the form of formula (4) chosen for  $b$ :

$$\frac{b_g - b_0}{v - b} = \frac{1 - z^2}{z},$$

in consequence of which  $\int \frac{db}{v - b}$  passes into  $\int \frac{1 - z^2}{z} dz = \log z - \frac{1}{2} z^2$ .

Substituting into the expression for the thermodynamic potential we get:

$$pv - \frac{a}{v} - RT \log(v - b) - RT \log \frac{b - b_0}{b_g - b_0} - \frac{1}{2} RT \left( \frac{b - b_0}{b_g - b_0} \right)^2$$

If we suppose the temperature to be low, the second phase is a rare gas phase and we have:

$$pv = RT, \log(v - b) = - \log \frac{p}{RT} \text{ and } \frac{b - b_0}{b_g - b_0} = 1.$$

In consequence of this we get:

$$pv_1 - \frac{a}{v_1} - RT \log(v_1 - b_1) - RT \log \frac{b_1 - b_0}{b_g - b_0} - \frac{1}{2} RT \left( \frac{b_1 - b_0}{b_g - b_0} \right)^2 = RT + RT \log \frac{p}{RT} - \frac{1}{2} RT$$

or

$$pv_1 - \frac{a}{v_1} - RT - RT \log \frac{b_1 - b_0}{b_g - b_0} + \frac{1}{2} RT \frac{b_1 - b_0}{v_1 - b_1} = RT \log \frac{p(v_1 - b_1)}{RT}$$

or

$$pb_1 - \frac{a}{b_1} + RT \frac{v_1 - b_1}{b_1} - \frac{p(v_1 - b_1)^2}{b_1} - RT \log \frac{b_1 - b_0}{b_g - b_0} + \frac{1}{2} RT \frac{b_1 - b_0}{v_1 - b_1} = RT \log \frac{p}{p + \frac{a}{v_1^2}}$$

As yet we have not applied any approximation for the liquid condition.

If in the first member we collect the terms containing  $p$ , we may write them as follows:

$$- p \frac{v_1^2 - 2b_1 v_1}{b_1}.$$

The value of  $v_1$  in the liquid condition being only slightly larger than  $2b_1$ , the value of this expression remains below  $pb_1$  and it may certainly be neglected; if in the second member we neglect also  $p$  compared with  $\frac{a}{v_1^2}$ , then we may write the equation for the calculation of the vapour pressure at low temperatures as follows:

$$\log \frac{p}{a} = - \frac{\frac{a}{b_1}}{RT} + \frac{v_1 - b_1}{b_1} - \log \frac{b_1 - b_0}{b_g - b_0} + \frac{1}{2} \frac{b_1 - b_0}{v_1 - b_1} \quad \dots \quad (5)$$

In order to draw attention to the principle circumstances, we shall assume for the present that the following equations also hold in the case that  $b$  is variable :

$$RT_k = \frac{8}{27} \frac{a}{b_g}$$

and

$$p_k = \frac{1}{27} \frac{a}{b_g^2}$$

Equation (5) may then be written in this form :

$$\log \frac{p}{27 p_k \left(\frac{b_g}{v_1}\right)^2} = -\frac{27}{8} \frac{T_k b_g}{T b_1} + \frac{v_1 \cdot b_1}{b_1} \log \frac{b_1 - b_0}{b_g - b_0} + \frac{1}{2} \frac{b_1 - b_0}{v_1 - b_1}$$

A comparison of this equation with :

$$-\log \frac{p}{p_k} = f\left(\frac{T_k}{T} - 1\right),$$

shows that it is possible to satisfy the condition that the coefficient of  $\frac{T_k}{T}$  approaches to 7 by equating  $\frac{b_g}{b_1}$  to 2, i.e. by assuming that the molecules in volumes equal to the volume of liquids at low temperatures are only half as large as those in the gaseous condition. But the agreement in the value of the coefficient of  $\frac{T_k}{T}$  does not suffice for establishing agreement between the calculated value and that of the formula which at low temperatures is followed by the vapour tension, though it be only in large features. For this purpose it is required that

$$\left[ \log 27 \left(\frac{b_g}{v_1}\right)^2 \frac{b_g - b_0}{b_1 - b_0} \right] + \frac{1}{2} \frac{b_1 - b_0}{v_1 - b_1} + \frac{v_1 - b_1}{b_1}$$

differs only slightly from 7.

We must return to the equation of state in order to be able to determine the value of this expression, and we must investigate its consequences for the case that  $p$  may be neglected compared with

$\frac{a}{v^2}$ . So we must return to :

$$\frac{a}{v_1^2} (v_1 - b_1) = RT = \frac{8}{27} \frac{a}{b_g} \frac{T}{T_k}$$

If we express  $b_1$  and  $v_1$  in the quantity  $z$ , we get :

$$b_1 = b_0 + z(b_g - b_0)$$

and

$$v_1 - b_1 = \frac{1 - z^2}{z} (b_g - b_0)$$

or

$$v_1 = b_0 + \left( z + \frac{1-z^2}{z} \right) (b_g - b_0)$$

Substituting these values and putting  $b_g = n b_0$  we get the equation:

$$\frac{8}{27} \frac{T}{T_k} = \frac{n(n-1) \frac{z}{1-z^2}}{\left\{ 1 + \left( z + \frac{z}{1-z^2} \right) (n-1) \right\}^2}$$

If we put $n = 2$ , then we get	$z = \frac{1}{4}$	for	$\frac{T}{T_k} = 0,8$
	$z = \frac{1}{5}$	„	$\frac{T}{T_k} = 0,7$
	$z = \frac{1}{6}$	„	$\frac{T}{T_k} = 0,65$
	$z = \frac{1}{7}$	„	$\frac{T}{T_k} = 0,615$ .

For very small values of  $z$  we may neglect  $z^2$  compared to unity and we may calculate the value of  $z$  from the approximated equation:

$$\frac{8}{27} \frac{T}{T_k} = \frac{2z}{(1+2z)^2}$$

which equation yields the value of  $z = \frac{1}{9}$  for  $\frac{T}{T_k} = \frac{1}{2}$ . For such

small values of  $z$  we have  $\frac{b_1 - b_0}{v_1 - b_1} = 1$ ,  $\frac{v_1 - b_1}{b_1} = \frac{z}{1+z}$  and  $\frac{v_1}{b_1} = \frac{1+2z}{1+z}$ .

We will assume that for all temperatures below  $0,6 T_k$  the vapour phase may be considered to have a sufficient degree of rarefaction for following the gaslaws; therefore we may assume  $z$  to have a value below  $\frac{1}{7}$ . If we choose  $z = \frac{1}{8}$ , then we find for  $\left( \frac{b_g}{v_1} \right)^2$  the

value  $4 \left( \frac{b_g}{v_1} \right)^2 = 4 \left( \frac{1}{1+2z} \right)$  or  $\frac{4 \times 16}{25} = 2,56$ . With this value we have:

$$\log 27 \left( \frac{b_g}{v_1} \right)^2 \frac{b_g - b_0}{b_1 - b_0} + \frac{1}{2} \frac{b_1 - b_0}{v_1 - b_1} + \frac{v_1 - b_1}{b_1} = \log 27 \times 20,5 + \frac{1}{2} + 0,11.$$

It is true that this value is smaller than  $\log 27^2$ , but it approaches sufficiently to that value. The fact that it is smaller than  $\log 27^2$  is in perfect agreement with the circumstance that for the quantity  $f$  in the formula  $-\log \frac{p}{p_k} = f \frac{T_k - T}{T}$  according to the experiments at low

temperatures a higher value must be chosen in order to establish agreement. For a higher value of  $f$  yields the same result as a not higher value of  $f$  in  $f \frac{T_k}{T}$ , from which a smaller quantity is subtracted.

It might appear that the dependency of  $p$  on  $T$  is strongly increased by the difference between the values of  $z$  for different temperatures. The following relation however always holds good if  $b$  is independent of  $T$ :

$$\frac{T}{p} \frac{dp}{dT} - 1 = \frac{a}{RT}$$

and therefore (see p. 127)

$$\frac{T}{p} \frac{dp}{dT} = \frac{a}{RT} - \frac{v_1 - b_1}{b_1}$$

or

$$\frac{T}{p} \frac{dp}{dT} = \frac{27 T_k b_0}{8 T b_1} - \frac{v_1 - b_1}{b_1}$$

In the supposition made here, this is equal to

$$\frac{T}{p} \frac{dp}{dT} = \frac{27 T_k}{4 T} \frac{z}{1+z} - \frac{z}{1+z}$$

which expression does not vary much with  $z$ , if  $z$  remains small.

Yet we find the value of  $\frac{T}{p} \frac{dp}{dT}$  at low temperatures for most substances to be somewhat higher than is indicated by this formula. We should in fact have found a higher value if we had assumed  $b_0 > 2b_1$ . If therefore we had only to deal with the formula for the vapour tension, then it would be rational to investigate the consequences of the suppositions:  $n = 2 \frac{1}{4}$  or  $n = 2 \frac{1}{2}$ . Other experimental quantities however follow less perfectly the formula chosen for  $b$ , if we give  $n$  these values. Therefore I will confine myself to the investigation of the consequences of the equation chosen for  $b$  with  $n = 2$ .

I think the following theoretical observation to be of some importance, even if we disregard the question whether we have established a perfect, numerically accurate agreement with the experiments, by assuming the quantity  $b$  only to be variable, and even this variability to be independent of  $T$ . The pressures in two coexisting phases which lie at a great distance from the critical conditions satisfy, if

we suppose the volume of the molecules to be invariable, the following approximated equation

$$\log \frac{p}{M} = - \frac{\frac{a}{b}}{RT}.$$

In this formula  $M$  denotes the pressure of the liquid phase i. e. the molecular pressure, and  $\frac{a}{b}$  the heat required for the transformation.

The following approximated equation holds for molecules of variable volume:

$$\log \frac{p}{Mk} = - \frac{\frac{a}{b_1}}{RT},$$

where again  $\frac{a}{b_1}$  denotes the heat required for the transformation, which is greater if the molecules in the liquid phase are smaller, as well in the case that this diminishing of the volume is real, as in the case that it is only fictitious. Again the molecular pressure is also higher. But the molecular pressure is now provided with the factor  $K$ . If it is a real diminishing then the signification of this factor can be sharply defined. The factor is in this case at least approximately equal to  $\frac{b_g - b_0}{b_1 - b_0}$ , its signification can be derived from the following equations, (comp. my paper: "The equation of state and the Theory of cyclic Motions"):

$$\left\{ M + \left( \frac{\partial P_b}{\partial b} \right)_{b=b_1} \right\} (b_1 - b_0) = RT$$

$$\left( \frac{\partial P_b}{\partial b} \right)_{b=b_g} (b_g - b_0) = RT$$

So we find for it:

$$\frac{b_g - b_0}{b_1 - b_0} = \frac{M + \left( \frac{\partial P_b}{\partial b} \right)_{b=b_1}}{\left( \frac{\partial P_b}{\partial b} \right)_{b=b_g}}.$$

The quantity  $\left( \frac{\partial P_b}{\partial b} \right)$  in this equation represents the atomic forces, which keep the molecule intact or at least contribute to the causes which keep the molecule intact. Making use of this value of  $K$  we find:

$$\log \frac{p}{M} \frac{\left(\frac{\partial P_b}{\partial b}\right)_{b=b_g}}{M + \left(\frac{\partial P_b}{\partial b}\right)_{b=b_l}} = -\frac{a}{RT} \dots \dots \dots (6)$$

The first member of this equation contains the logarithm of the product of two ratios, namely the ratio of the inwardly directed forces which keep the molecules — considered as separate systems — inside the vapour and the liquid phase, and the ratio of the inwardly directed forces which keep these systems in both phases intact. In the case that it is a quasi-decrease it is impossible to indicate the signification of  $K$  in such a precise manner; but the quantity  $\int \frac{db}{v-b}$  differing also in this case from zero, the above considerations show with certainty that the quantity  $K$  exists also in this case. The question whether it will be larger or smaller can only be decided by a comparison of the course of  $b$  with  $v$  in the supposition of a quasi decrease with that in the supposition of a real diminishing.

The term  $\frac{1}{2} \frac{b-b_0}{v-b}$  has been neglected in equation (6). This equation applies only for low temperatures, and for those temperatures the term in question is equal to  $\frac{1}{2}$  according to the formula given for  $b$ . It is remarkable that also many other suppositions concerning the nature of the forces which keep the molecules intact, different from those suppositions which have led to the form chosen for  $b$ , yield the same equation (6), every time however only after neglection of a relatively small quantity in whose kinetic interpretation I have not yet succeeded. We obtain equation (6) when we assume, 1<sup>st</sup> that the molecule may be regarded to be a binary system consisting of two atoms or of two closely connected groups of atoms, which we shall call radicals, 2<sup>nd</sup> that these parts move relatively to each other, and 3<sup>rd</sup> that the amplitudes of these motions are of the same order as the dimensions of the atoms. If the parts are radicals, other motions take place inside those radicals, but the amplitudes of these motions are so small that they have no noticeable effect on the volume of the radicals. We have represented the forces which the atoms or radicals exercise on one another by  $\alpha(b-b_0)$ , so in the gaseous state by  $\alpha(b_g-b_0)$ . So, as we have derived the equation:

$$\alpha(b_g-b_0)^2 = RT$$

and as  $b_g-b_0$  is constant,  $\alpha$  must be proportional with the temperature, — and I must acknowledge that it is difficult to image a mechanism

for the molecule in which the forces between the two parts of which it is thought to consist, satisfy the conditions, that they are proportional with the distance, and at the same time increase proportionally with  $T$ . Perhaps we get a more comprehensive conception of a molecule, if we ascribe the forces which keep the atoms together in the molecule not to a mutual attraction of the atoms, but to the action of the general medium by which the atoms are surrounded. The molecules of a gas are free to move inside the space in which they are included and they are kept inside that space only by the action of the walls; in the same way it might be that the atoms of a molecule were free to move inside a certain space — the volume of the molecule — and that they are only prevented from separating by an enclosure of ether. Still assuming that  $b_g - b_0$  has for all temperatures the same value, we should be again obliged to conclude that the forces which keep the molecule intact are proportional with the temperature, but this conclusion would now be much less incomprehensible. According to these suppositions it is also rational to assume that the force required to split up the molecule into two atoms is the same for all temperatures. So we should obtain the formula.

$$\frac{b-b_0}{v-b} = 1 - \frac{b-b_0}{b_g-b_0}$$

With this equation we have:

$$\int_b^{b_g} \frac{db}{v-b} = \int_b^{b_g} db \left\{ \frac{1}{b-b_0} - \frac{1}{b_g-b_0} \right\} = \log \frac{b_g-b_0}{b-b_0} - \frac{b-b_0}{v-b}$$

The term which must be subtracted from  $\log \frac{b_g-b_0}{b-b_0}$  has now twice the value it had before, but the chief term has remained unchanged. In my further investigation, however, I will continue with the discussion of equation (4), because my chief aim is only to investigate the principle consequences of the nearly certainly existing diminution of  $b$ , independent of the question whether this diminution is real or only fictitious; and in doing so I will confine myself to a certain conception of the molecule — that which leads to equation (4) — as an instance.

B. *The coefficient of dilatation and the coefficient of compressibility of liquids.*

Let us again assume the temperature to be so low that  $p$  may be neglected compared with  $\frac{a}{v^2}$  and that we therefore have:

$$\frac{a}{v^2} (v-b) = RT.$$

The value for  $\frac{1}{v} \left( \frac{dv}{dT} \right)_p$  which we may calculate from this equation applies only to the pressure  $p = 0$ , and is therefore not the same as would be found for another constant pressure; neither is it that which corresponds to the points of the border curve. For very low temperatures the difference will probably be small. For higher temperatures the differences might be considerable; and for the temperature which is so high that the isothermal in its lowest point touches the  $v$ -axis, in which case  $\frac{1}{v} \left( \frac{dv}{dT} \right)_p = \infty$ , it would even be absurd to suppose the two values to be mutually equal.

An accurate calculation of the value of  $\frac{1}{v} \left( \frac{dv}{dT} \right)_{p=0}$  yields according to the relations chosen above:

$$\frac{T \left( \frac{dv}{dT} \right)_{p=0}}{v} = \frac{(n-1)z \left\{ 1 + \frac{1}{1-z^2} + \frac{2z^2}{(1-z^2)^2} \right\}}{1 - (n-1) \left[ z + \frac{z}{1-z^2} \right] - 4(n-1)z \frac{z^2}{(1-z^2)^2}}.$$

We will put  $n = 1$  and the following approximated relation:

$$\frac{T \left( \frac{dv}{dT} \right)_{p=0}}{v} = \frac{2z}{1-2z}.$$

With  $z = \frac{1}{7}$  (see p. 140) this yields 0,4 for the value of  $T\alpha_v$  or  $\alpha_v = \frac{0,4}{273}$  (for ether) = 0,00146. Our assumptions therefore appear to lead to a value for the coefficient of dilatation which does not deviate much from the experimental value.

If we had taken the form  $a e^{1 - \frac{T}{T_k}}$  for  $a$ , then the corresponding value of  $z$  would have been  $\frac{1}{13,5}$  and we should have had:

$$\frac{T \left( \frac{dv}{dT} \right)_p}{v} = \left( 1 + \frac{T}{T_k} \right) \frac{2z}{1-2z},$$

which is only about  $\frac{3}{4}$  of the true value. From this we conclude that the assumption that our relations are satisfied and that at the

same time  $a$  has the form  $a e^{1 - \frac{T}{T_k}}$  leads to inaccurate results.



We might also write a value for  $\left(-\frac{v dp}{dv}\right)$  or  $\frac{1}{\beta}$ , but we will calculate the coefficient only indirectly from:

$$\frac{T}{v} \left(\frac{dv}{dT}\right)_p \left(-v \frac{dp}{dv_T}\right) = \frac{a}{v^2}$$

or

$$0,413 \times 6000 = 27 p_k \left(\frac{b_g}{v}\right)^2$$

or with approximation:

$$1,6 = \frac{z}{1+2z},$$

which agrees with  $z = \frac{1}{8}$ .

The value of  $\beta$  calculated according to our relations may therefore be considered to be at any rate approximately accurate.

Yet it remains strange that for the liquid volume itself a calculation according to our suppositions yields a value which is much too small.

According to a table in Cont. I 2<sup>nd</sup> p. 172 the liquid volume for temperatures which do not differ much from  $\frac{1}{2} T_k$  is equal to  $0,8 b_0$ .

Even if we take into account that  $b_0 < b_g$  we cannot diminish the factor  $0,8$  to less than  $0,7$ .

We have then the equation

$$0,7 b_g = b_0 (1 + 2z)$$

or

$$0,7 n = 1 + 2z.$$

With  $n = 2$ , this yields  $z = \frac{1}{5}$ , which does not agree with the value  $\frac{1}{7}$ , which we must assume for  $z$ , as we saw above. I have

not yet been able to investigate, what modification must be made in the relation assumed for  $b$ ; e. g. to put  $n = 1,8$  or to suppose  $b_0$  really to be smaller at low temperatures. If we suppose  $b_0$  to be a function of the temperature, then the calculations become very intricate and difficulties of another kind arise. Therefore I prefer to regard the above considerations as conducing to point out that everything shows that  $b$  must really increase with  $v$ .

Let us investigate what consequences of general nature follow from this variability of  $b$ . In the first place we observe that the three real values of  $v$  for given temperature and given pressure cannot be calculated any more by means of an equation of the third degree. The equation of state namely may assume a very intricate form if

we substitute in it the expression for  $b$  which we get by solving the equation which expresses the variability of  $b$  with  $v$  and  $T$  — the possibility of a dependency of  $b$  on  $T$  being admitted. We shall represent the solution of this equation by

$$b = \varphi(v, T).$$

But the general course has remained the same; e.g. the fact that for temperatures below the critical temperature a maximum and a minimum pressure occurs. The critical temperature is that for which this maximum and this minimum pressure coincide and the critical point may again be calculated from the three equations:

$$p = F(v, T),$$

$$\left(\frac{dp}{dv}\right)_T = 0$$

and  $\left(\frac{d^2p}{dv^2}\right)_T = 0$

If therefore we could exclude all disturbing influences, if we could neglect phenomena of capillarity and adsorption, if we could neutralize gravity, if we could keep the temperature absolutely constant throughout the space occupied by the substance, if we could perform the experiments with perfectly pure substances without the slightest trace of admixtures and if we could suppose that the equilibrium is established instantaneously, then we should have coexistence of two homogeneous phases of well defined properties for all temperatures below the critical one, and exactly at the critical temperature only one homogeneous phase of well defined properties would exist.

But the requirements enumerated here can never be fulfilled. Already below the critical temperature deviations occur. The straight line representing the evaporation parallel with the  $v$ -axis has probably never been realised as yet in connection with the circumstance that nobody has as yet experimented with a perfectly pure substance. The boiling point always varies when the distillation is continued, chiefly if we observe near the critical temperature. If in a closed vessel we heat a substance which is separated into a liquid and a vapour phase, then the properties of the liquid phase may be varied by shaking the vessel (EVERSHEIM. Phys. Zeitschr. 15<sup>th</sup> June 1903), probably in connection with the circumstance that the liquid expanding during the heating is internally cooled in consequence of the expansion and the evaporation and reaches the surrounding temperature only very slowly by conduction; and also in connection with the always occurring impurities. If further the substance is subjected to gravity, then neither vapour phase nor liquid phase is homogeneous. To

every horizontal layer corresponds another density according to the formula of hydrostatics:

$$dp = - \rho g dh.$$

For temperatures far below the critical one this circumstance is of little importance; for the critical temperature itself, however, the influence of gravity is considerable. If we write namely the formula of hydrostatics in the following form:

$$\frac{1}{\rho} \frac{dp}{dh} = -g,$$

then we see that  $\frac{dp}{dh} = 0$  or  $\frac{dh}{d\rho} = \infty$  at that point of the height of the

vessel where the critical phase really occurs, i. e. where  $\frac{d\rho}{dh} = 0$ .

If therefore we construct a graphical representation of the successive densities, laying out the height as abscissa and the density as the ordinate, then we get a continually descending curve. In the beginning its concave side is turned downwards; at a certain point the tangent is vertical and the curve has a point of inflexion; farther the convex side is turned downwards. In the neighbourhood of the critical phase we find therefore a rapid change in the density.

The equation of state can only account for the *state of equilibrium* described above as it deals only with states of equilibrium. Another question is how that equilibrium is established and whether it is established in a longer or shorter time according to the method of investigation.

It has been observed several times in these latter years that the state of equilibrium of a quantity of a substance which is contained in a closed vessel slowly heated to the critical temperature, requires so long a time before it has been reached that some investigators have concluded that the liquid consists of other molecules than the vapour. DE HEEN, GALITZINE, TRAUBE and others speak therefore of "molecules liquidogènes" and "molecules gasogènes". Some of them suppose the "molécules liquidogènes" to be more complex, others suppose them to be only smaller. This latter supposition agrees with the ideas I have expressed in my "The equation of state and the theory of cyclic motions." And for an explanation of the fact that the equilibrium is so slowly established, these investigators refer to the slow diffusion of the heterogeneous molecules.

To this fact they refer however wrongly. The kinetic theory accounts satisfactorily for the slowness of the diffusion and has even enabled us to calculate the coefficient of diffusion for mixtures of

heterogeneous molecules which cannot pass into one another. Here however we are dealing with molecules which can pass into each other. And if in such a case the establishing of the equilibrium requires a long time, then we must account for the fact that in this case more-atomic molecules only slowly conform their size to the varied circumstances, though in other cases they can bring their internal motions so quickly into harmony with, for instance, a variation of the temperature.

I therefore think it not to be proved, that the increase of  $b$  being either a real or a quasi-increase, requires a noticeable time to be brought about, till the real constancy of the temperature throughout the closed vessel and the perfect purity of the substance has been proved, which as yet is not the case.

It must be granted that the summit of the boundary curve is broadened and flattened by the variability of  $b$  and that the critical isothermal may be estimated to have a larger part which is nearly parallel with the  $v$ -axis. And this causes considerable differences of density to follow from small differences of pressure. But if no causes even for small differences of pressure can be pointed out, then the occurrence of differences of density larger than those that follow from the action of gravity cannot even be called *phenomena of retardation*, these latter being also a kind of phenomena of equilibrium.

Another observation of general nature before I conclude at least for the present these considerations on the influence of the variability of  $b$ . This variability accounts for the possibility of deviations from the law of corresponding states. If the way in which  $b$  varies with the volume is different for different substances i.e. in consequence of a different ratio of  $b_g$  and  $b_v$ , then the general course remains the same, but the isothermals become different in details. I have even begun to doubt whether the behaviour of substances containing the radical OH in the molecule — acids, alcohols, water etc., which in gaseous state present no association to double molecules and which are often indicated by the name of abnormal substances — which behaviour deviates so markedly from that of other substances, must really be ascribed to association of the molecules in the liquid state.

In connection with equation (6) (see p. 143) the question arises: Is the quantity which I have denoted by  $\frac{\partial T_b}{\partial b}$  for these substances perhaps small? Is the easy substitution of one of the components perhaps an indication of a feeble connection of the parts of the compound which involves a strong variability of the size of the molecule. The so called

abnormal substances would then be those whose molecules can undergo large variations in size. More suchlike questions arise — but I will no further discuss them without a closer investigation.

#### POSTSCRIPTUM.

When the above paper was printed I received a kind letter from Dr. GUSTAV TEICHNER, who informs me that he has sent me one of his tubes filled with  $\text{CCl}_4$  in which he has succeeded in strikingly showing the large differences in density at the critical temperature by means of floating glass spheres whose specific gravity has been determined accurately. He himself however acknowledges emphatically: "dass diese Erscheinungen insofern keine Gleichgewichtszustände vorstellen, als die Phasen in Berührung mit einander sich ausserst langsam (beim Rühren sofort) zu einer homogenen Mischung vereinigen."

The equation of state deals only with states of equilibrium as I have observed already before. Discussing these anomalies as I have done in this paper, I treated questions which properly speaking lie outside my subject. I have mentioned them, because I also expected for a moment that the variability of  $b$  assumed by me, might account for the slowly establishing of the state of equilibrium. But this is only the case if we assume, that the molecule does not immediately assume the size which agrees with the value of  $T$  and  $v$  — and this seems after all to be improbable to me, though I acknowledge that molecular transformations occur which proceed slowly. The expectation of Dr. TEICHNER, that the theory would lead to two really homogeneous phases is inaccurate in consequence of the action of gravity — as has been shown already before i. a. by GOUY. Not the phenomenon itself as it is seen, is anomalous, only the differences of the density are anomalously large. It is true that Dr. TEICHNER writes to me that he has ascertained that the temperature was constant but even a difference of temperature of  $\frac{1}{100}$  degree yields a very considerable difference in density. For densities which are larger than the critical one we have:

$$\frac{T}{p} \frac{dp}{dT} > \xi$$

$\xi \frac{p}{T}$  being comparable to unity. If therefore in a point the temperature is  $\frac{1}{100}$  degree too low, a diminishing of the pressure with

an amount of about  $\frac{1}{100}$  atmosphere will keep such a phase in equilibrium, at least as far as the pressure is concerned. And a cause which accounts for a difference of pressure of about  $\frac{1}{100}$  atmosphere accounts also for considerable differences in density as the critical isothermal runs nearly horizontally in the neighbourhood of the critical point.

A return to the time when we thought to explain a thing by speaking of solubility and insolubility, seems not to be desirable to me.

**Chemistry.** — “*On the possible forms of the meltingpoint-curve for binary mixtures of isomorphous substances.*” By J. J. VAN LAAR. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

I. The occurrence of so called “*eutectic points*” in *meltingpoint-curves* does not seem to agree with the supposition of *perfect isomorphy* of the two solid components and of their mixtures. This fact has been repeatedly pointed out. It has been assumed that an interruption in the curve representing the solid mixtures (as in fig. 1 of the plate) can only occur for *isodimorphous* substances, and that the series of mixtures in the case of isomorphous substances was necessarily to be uninterrupted (as in fig. 2).

Lately STORTENBEKER <sup>1)</sup> expressed again the same idea and this induced me to subject the question to a closer investigation. In the following paper I hope to show that an interruption in the series of the mixtures can very well occur even for *perfectly isomorphous* substances. In order to do this we must keep in view that — especially in the *solid* condition — *unstable* phases may occur, and that in all occurring cases it is possible to trace the meltingpoint-curve *continuously through the eutectic point*. Only the stable conditions which generally lie above the eutectic point are liable to be realized, so the series of the mixtures is interrupted only *practically*.

Prof. BAKHUIS ROOZEBOOM has expressed the idea of prolonging the meltingpoint-curve beyond the eutectic point already before; the way however in which we must think this to be performed is indicated inaccurately in the figure of an earlier paper of STORTENBEKER <sup>2)</sup>.

<sup>1)</sup> Ueber Lücken in der Mischungsreihe bei isomorphen Substanzen, Zeitschrift für Ph. Ch. **43**, 629 (1903).

<sup>2)</sup> Ueber die Löslichkeit von hydratierten Mischkrystallen, Z. f. Ph. Ch. **17**, 645 (1895).