Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

the region of convergence being the same as for the expansion of $1 : 1 - x$.

For a test we may make the substition $x = -1$; we shall find

$$\frac{1}{2} = 0.5000 = 1\text{-}0.5785\text{+}0.1214\text{-}0.0436 + 0.0065\text{-}0.0042 + \ldots$$
$$= 0.5016 + \ldots,$$

$$bg\,tg\,(-1) = -0.7854 = -0.5785 - 0.2133 - 0.0323 +$$
$$+ 0.0266 + 0.0195 + \ldots = -0.7820 + \ldots,$$

$$\frac{1}{\sqrt{2}} = 0.7070 = 1 - 0.2892 + 0.0189 - 0.0164 - 0.0015 -$$
$$- 0.0022 + \ldots = 0.7096 + \ldots.$$

Phycics. — Prof. J. D. VAN DER WAALS on: *"The equation of state and the theory of cyclic motion."* II. (Continued from page 528).

Before we are able to calculate the equation for the equilibrium and the entropy and the specific heat of a substance with triatomic molecules, we. must first know the mode of motion. If the motion should be such, that the first atom is placed exactly in the centre of gravity, and consequently only the two other atoms move, such a molecule must be regarded as a diatomic one, and the equation of the equilibrium will be again equal to:

$$\left(p + \frac{dP_v}{dv} + \frac{dP_b}{db}\right)(b - b_0) = RT.$$

But the value represented by b_0 will include besides the space of the moving atoms, also the space occupied by the stationary atom.

If the motion of the three atoms relative to their centre of gravity should be such that the distance of one of them quite determines the place of the two others, as would be the case when they move along three lines, which enclose constant angles, and if the case is therefore to be considered as a vibrating system with one degree of freedom, then such a molecule must be treated in our considerations as a diatomic one.
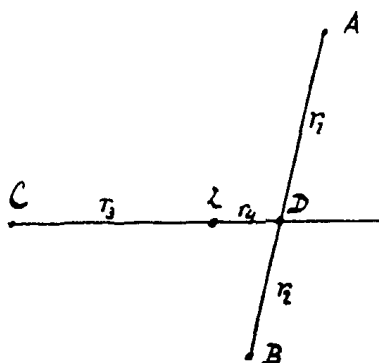
Only if thé motion of two of the three atoms relative to each other is such, that it is independent of the motion of the third atom relative to the centre of gravity of the two first-mentioned, the molecule may be called a triatomic molecule also from our point of view, and we shall find a greater specific heat and a modified equation of state.

Let Z in the figure be the centre of gravity of the molecule, and A, B and C indicate the instantaneous position of the three atoms. If D is the centre of gravity of A and B, then the points C, Z and D must of course lie on the same straight line. Let us take the distances $DA = r_1$, $DB = r_2$, $CZ = r_3$ and $DZ = r_4$. Let us now imagine the motion of the atoms to be such that A and B move along their connecting line, and that at the same time, but independent of this, C and D approach each other. Then the vis viva of the first motion may be represented by :

$$B_1 (r_1 - r_{01})^2 \dot{s}_1{}^2 + B_2 (r_2 - r_{02})^2 \dot{s}_2{}^2$$

and that of the second motion by :

$$C_3 (r_3 - r_{03})^2 \dot{s}_3{}^2 + C_4 (r_4 - r_{04})^2 \dot{s}_4{}^2.$$

Then $A (v - b)^{2/3} \dot{s}^2$ added to the sum of these quantities represents the whole vis viva.

From this we deduce for the equation of the equilibrium:

$$\frac{dL}{db} + p + \frac{dP_v}{dv} = 2 \left\{ \frac{L_1}{r_1 - r_{01}} \frac{dr_1}{db} + \frac{L_2}{r_2 - r_{02}} \frac{dr_2}{db} + \frac{L_3}{r_3 - r_{03}} \frac{dr_3}{db} + \frac{L_4}{r_4 - r_{04}} \frac{dr_4}{db} \right\}$$

Let us call the increase of volume in consequence of the existence of the first motion:

$$b_1 - b_{01} = S_1 (r_1 - r_{01}) + S_2 (r_2 - r_{02})$$

and in consequence of the existence of the second motion:

$$b_2 - b_{02} = S_3 (r_3 - r_{03}) + S_4 (r_4 - r_{04}).$$

The way in which in these expressions r_1 and r_2 depend on each

other, is known, just as that of r_3 and r_4; r_1 and r_3 however must be considered to be independent of each other at any moment. The sum of b_1-b_{01} and b_2-b_{02} is the quantity which we may consider as the increase of volume of the molecule, and so:

$$b-b_{01} = (b_1-b_{01}) + (b_2-b_{02}).$$

On account of the independence of the two atomic motions, we get therefore two equations of the equilibrium:

$$\frac{dL}{db_1} + p + \frac{dP_v}{dv} = \frac{2(L_1 + L_2)}{b_1-b_{01}}$$

and

$$\frac{dL}{db_2} + p + \frac{dP_v}{dv} = \frac{2(L_3 + L_4)}{b_2-b_{02}}$$

the former applying to the direction in the molecule which connects A and B, the latter for the direction which connects C and D. In other words, the molecule has two directions, according to which it can possess a different degree of compressibility. A form for the potential energy, which does not take these different properties in different directions into account, is therefore insufficient. The thermodynamic deduction of the equation of the equilibrium is therefore wrongly simplified by assuming the quantity P_b, and we should act more in accordance with the difference in properties in the two directions by introducing two quantities P_{b1} and P_{b2}. By means of them we may write then:

$$\left(p + \frac{dP_v}{dv} + \frac{dP_{b1}}{db_1}\right)(b_1-b_{01}) = 2(L_1 + L_2) \eqsim RT$$

and

$$\left(p + \frac{dP_v}{dv} + \frac{dP_{b2}}{db_2}\right)(b_2-b_{02}) = 2(L_3 + L_4) = RT.$$

If we calculate in the same way as is done for diatomic molecules on page 523, the value of dQ, we find for triatomic molecules, the atoms of which move in the way described:

$$dQ = L_0 \, d \log [(v-b)^{2/3} L_0] + (L_1 + L_2) \, d \log [(b_1-b_{01})^2 (L_1 + L_2)] +$$

$$+ (L_3 + L_4) \, d \log [(b_2-b_{02})^2 L_3 + L_4)].$$

If we put $\dfrac{L_1 + L_2}{L_0} = \dfrac{1}{3} = \dfrac{L_3 + L_4}{L_0}$, we get:

$$\eta = R\{log\,(v-b)\,T^{1/2} + log\,(b_1-b_{01})\,T^{1/3} + log\,(b_2-b_{02})\,T^{1/2}\}$$

and therefore for the value of the specific heat at $v = \infty$:

$$C_v = R\left\{{}^3/_2 + {}^1/_2 + {}^1/_2 + \frac{Td\,(b_1-b_{01})}{(b_1-b_{01})\,dT} + \frac{Td\,(b_2-b_{02})}{(b_2-b_{02})\,dT}\right\}.$$

If we take for P_{b1} the form : $P_{b1} = \frac{1}{2}\,\alpha_1\,(b_1-b_{01})^2$ and in the same way for P_{b2} the form: $P_{b2} = \frac{1}{2}\,\alpha_2\,(b_2-b_{02})^2$, we find, supposing α_1 and α_2 independent of the temperature, from the equations of the equilibrium for which $v = \infty$, so from

$$\alpha_1\,(b_1-b_{01})^2 = RT$$

and

$$\alpha_2\,(b_2-b_{02})^2 = RT$$

both $\dfrac{Td\,(b_1-b_{01})}{(b_1-b_{01})\,dT}$ and $\dfrac{Td\,(b_2-b_{02})}{(b_2-b_{02})\,dT}$ equal to $\frac{1}{2}$, and we get:

$$C_v = \frac{7}{2}R \text{ and } C_p = \frac{9}{2}\,R,$$

and consequently

$$\frac{C_p}{C_v} = 1 + \frac{2}{7} = 1{,}2857.$$

For carbonic acid values for this relation are given varying from 1,274 to 1,322 [1]). For N_2O the values vary from 1,267 to 1,327. For SO_2 we find the values from 1,238 to 1,262.

In this calculation of the specific heat both of diatomic and of triatomic molecules, we have taken P_b as independent of the temperature, and on the supposition that $P_b = \frac{1}{2}\,\alpha\,(b - b_0)^2$, we have found a contribution to C_v of the same amount, as if there were in each case one degree of freedom more for the atomic motion than we assumed. If we had taken α as depending on the temperature, we should have found another amount for this contribution to C, which we may regard as a kind of potential energy. Specially if we

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1) See O. E. Meyer: Die kinetische Theorie der Gase. 1877 pag. 91.

put α as proportional to the temperature, this contribution to C_v is equal to zero, as is evident without further calculation, if we put for the equation of the equilibrium at $v = \infty$:

$$\alpha' T (b - b_0)^2 = RT.$$

If we want to make the calculated value of C_v agree with the above mentioned, we have to assume every time one degree of freedom more for the atomic motion, than we put above. For the diatomic molecules we have then to assume besides the radial motion a motion normal to the radius vector. For the triatomic molecules we have then to assume besides the motions already assumed, still other motions, e.g. such a one that the line which connects A and B, leaves the plane of the figure, and that the line which connects C and D rotates in the plane of the figure.

Accordingly on the supposition that α is proportional to T, we find the potential energy of the molecule (i. e. the amount with which the total energy exceeds the vis viva) equal to zero, as appears from:

$$\varepsilon = F(T) + P_v - T \left(\frac{dP_v}{dT}\right)_v + P_b - T \left(\frac{dP_b}{dT}\right)_b.$$

For then $T \left(\frac{dP_b}{dT}\right)_b$ is always equal to P_b.

But it was not chiefly the calculation of the specific heat of the complex molecules, which induced me to this investigation. And though I am of opinion that its true knowledge is urgently required for getting an insight into the way in which atoms are grouped in the molecule and move relatively to each other, and though I think that through its value we shall often be able to take a decision, when other methods for the determination of the formula for the structure of the molecule fail, there is as yet still too little experimental material at hand to test different ideas which might suggest themselves. The prevailing opinion, that $\frac{C_p}{C_v}$ must decrease with the number of atoms, may be true in general, still there are remarkable exceptions. So the value of $\frac{C_p}{C_v}$ for NH_3 found experimentally is not in accordance with what we should expect for a tetratomic molecule. It points more to a molecule in which not four, but only three atoms move with respect to the centre of

gravity. This leads to the idea that the atom N is placed in the centre of gravity of the three atoms H and does not take part in the atomic motion.

But let us now return to what I consider as the principal part of this investigation, viz. the two equations of equilibrium:

$$\left(p + \frac{dP_v}{dv} + \frac{dP_{b1}}{db_1}\right)(b_1 - b_{01}) = RT$$

and

$$\left(p + \frac{dP_v}{dv} + \frac{dP_{b2}}{db_2}\right)(b_2 - b_{02}) = RT.$$

There are two cases in which we might substitute one single equation of state for these two equations.

1st if $\frac{dP_{b1}}{db_1}$ could be taken as very great with respect to $\frac{dP_{b2}}{db_2}$, or rather if we assume $P_{b1} = \frac{1}{2}\alpha_1(b_1 - b_{01})^2$ and $P_{b2} = \frac{1}{2}\alpha_2(b_2 - b_{02})^2$ α_1 as being very great with respect to α_2. In this case $b_1 - b_{01}$ is small with respect to $b_2 - b_{02}$ and $b_2 - b_{02}$ may be equated to $b - b_0$. The equation of state becomes then:

$$\left\{p + \frac{dP_v}{dv} + \alpha_2(b - b_0)\right\}(b - b_0) = RT,$$

just as for a diatomic molecule.

2nd if $\alpha_1 = \alpha_2$. Then is $b_1 - b_{01} = b_2 - b_{02} = \frac{1}{2}(b - b_0)$, and we get:

$$\left\{p + \frac{dP_v}{dv} + \frac{\alpha_2}{2}(b - b_0)\right\}(b - b_0) = 2RT.$$

For the suppositions as to the value of α_1 and α_2 which lie between these two limiting cases, there remain two separate equations, but as an approximation it may be admissible to put in all cases:

$$\left\{p + \frac{dP_v}{dv} + \alpha(b - b_0)\right\}(b - b_0) = fRT,$$

if f has a value between 1 and 2.

For carbonic acid I had expected f to be little different from 2 — and with this value for f I have tested this equation of state of b to the series of values for this quantity which occur in the Chapter

"Experiments of ANDREWS" in the first part of Continuity etc., in order to see whether the observed variability of b might be explained in this way. For the calculation of this series of values for b I had assumed, that $\dfrac{dP_v}{dv}$ is equal to $\dfrac{a}{v^2}$, for a I had put the value of 0.00874. It has afterwards been doubted whether the molecular pressure is expressed perfectly accurately by this simple value. Nevertheless this form has always seemed the only rational one to me, and the accuracy, with which by means of this form the coefficient of compressibility can be calculated, as I have shown in the paper, which has been inserted in the volume of the Archives Néerlandaises dedicated to Prof. LORENTZ [1]), has confirmed this opinion.

It is not to be expected that I should have hit upon the exact value of a, and in fact there is reason to assume, that a must be about 3 percent lower, as will be shown presently. From this follows that the series of values for b is not perfectly accurate either.

But as $\Delta_b = \dfrac{\Delta a}{RT} \dfrac{(v-b)^2}{v^2}$, the error in b, which at $v = \infty$ equal to $\dfrac{\Delta a}{RT}$, will continually become smaller with decreasing volume, and become zero for the limiting volume; and as the value of b, as will appear presently, also decreases from a certain limiting value at $v = \infty$ to zero, it will have decreased approximately in the same proportion. Consequently the series of the given value may serve as a test for the given equation. The constants occurring in the equation will, however, get a value somewhat different from what they would have if they were derived from a perfectly correct series of values for b.

It is obvious that whatever formula we may take for the molecular pressure, we shall find a certain course in the value b, of such a nature that if we on the other hand presume this series of values of b, we can trace back every particular of the course of the pressure curve. It is only the question whether the course of the values found for b is such as we have a priori cause to expect. Now the series of values of b first fulfils the condition that for large volumes b does not sensibly differ and seems constant. Not before we get volumes of the order of b (formerly I had thought volumes of $2b$),

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[1]) Dr. G. BAKKER informs me, that he made such a calculation of the coefficient of compressibility already 14 years ago. It appeared from some pages of a M.S. sent to me that he had calculated β for ether at $25°$ as equal to 0,000179.

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does this value decrease sensibly. And it seemed then to me a strong proof of the accuracy of the values chosen for the molecular pressure, that this condition was fulfilled in the values found for b. The proof becomes much stronger if we can show that the values found for b quite answer to a before calculated formula for this value. The endeavours for finding such a formula for b, made by BOLTZMANN, JAGER, VAN LAAR, myself and several other investigators, have as yet always been based on the supposition, that the molecules are rigid bodies of a spherical shape. The endeavours have failed. Not only do they require hopelessly elaborate calculations, but I have had to convince myself that the calculated values of the coefficients found for such an equation cannot be in accordance with the observations. Now that I have found that for complex molecules of whatever shape, we find the same form for the equation of state of the substance as for a substance composed of simple molecules, I have thought that I might give up the rigidity and the spherical form of the molecules, and I have wished to try whether the compressibility of the molecules might be able to explain the decrease of b with the decrease of the volume. In the following pages I shall communicate the result, obtained in that investigation. Whether we have quite to reject the correctness of the considerations, on which the earlier attemps at the calculation of the variability of b are based, I shall not make bold to decide. I have only tried whether the equation:

$$\left\{ p + \frac{a}{v^2} + \alpha\,(b - b_0) \right\} (b - b_0) = f\,RT$$

represents the value of b found at every value of v.

This formula gives a value of b which changes exceedingly little, if the value of v is great, and which decreases strongly for small values of v.

Let us begin with modifying the equation somewhat. Let us viz. introduce the limiting value of b for $v = \infty$. Let us represent it by b_g. It is calculated from:

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

If we write for $p + \dfrac{a}{v^2}$ its value viz. $\dfrac{RT}{v - b}$, we get:

$$\frac{b - b_0}{v - b} = f \left\{ 1 - \left(\frac{b - b_0}{b_g - b_0} \right)^2 \right\}.$$

Let us take the series of values of v and b for $t = 35°.5$ and for $t = 32°.5$, which temperatures differ so little that the same values may be assigned to the constants, and let us put $b_g = 0.0026$. Then two more constants occur in the equation, viz. f and b_0. For both we have some indication as to their value. For f we might take 2, and for b_0 (the smallest possible value which b can assume) I had thought that I might conclude to a value of $\frac{1}{4} b_g$ according to the earlier view of the cause of the variability. As f is much easier to calculate than b_0, which can only be found by solving an equation of the third degree, I took for b_0 the value 0.00065. For the value of f we find then, beginning with the smallest volume:

$$f = 2.114, \quad f = 2.08, \quad f = 2.175, \quad f = 2.14 \text{ etc.}$$

Then I increased b_0 a little, viz. so much that it became $0.0007 = \frac{1}{3,7} b_g$, and then we find with $f = 2$:

	calculated	found
$b = 0,001798$	$v = 0,002622$	$0,002629$
$b = 0,00184$	$v = 0,002731$	$0,00275$
$b = 0,00195$	$v = 0,003050$	$0,003026$
$b = 0,0020$	$v = 0,003213$	$0,00321$

For the great values of v, b draws so near to the limiting values, that here the list of values of b, which increase and decrease irregularly, are of no importance.

Only the value of v which is given for $b = 0,00234$ does not agree, but it would perfectly agree if we might put $b = 0,002295$.

As I observed above, if the course of the value of b is represented perfectly correctly by the equation, the isothermal calculated by the aid of it will have to possess all the peculiarities of the isothermal determined experimentally. So the value of v, for which $\frac{dp}{dv}$ and $\frac{d^2p}{dv^2}$ are equal to zero, will have to coincide with the critical volume and in the same way the value of $\frac{p_k v_k}{R T_k}$ will have to possess for that volume the value which the experiment has determined for it.

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Now if b is kept constant, the equation of state has shown such large differences between the calculated and the experimental values of v_k and $\frac{p_k v_k}{RT_k}$, that it is advisable to examine whether the variability of b according to the given formula can annihilate these differences.

For the determination of the critical point we have now the following equations:

$$p + \frac{a}{v^2} = \frac{RT}{v-b} \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

$$\frac{2a}{v^3} = \frac{RT}{(v-b)^2}\left(1 - \frac{db}{dv}\right) \quad \ldots \quad \ldots \quad (2)$$

$$\frac{3}{v} = \frac{2\left(1 - \frac{db}{dv}\right)}{v-b} + \frac{\frac{d^2 b}{dv^2}}{1 - \frac{db}{dv}} \quad \ldots \quad (3)$$

The last of these equations, in which neither p nor T occurs, will have to serve as a determination of v_k, and that in connection with:

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

Let us write (3) in the form:

$$\frac{3(v-b)}{2v} = 1 - \frac{db}{dv} + \frac{v-b}{2}\frac{\frac{d^2 b}{dv^2}}{1 - \frac{db}{dv}} \quad \ldots \quad \ldots \quad (5)$$

For the determination of the critical volume we have therefore to choose such a value for v, that the values for b, $\frac{db}{dv}$ and $\frac{d^2 b}{dv^2}$, which according to (4) belong to it, satisfy (5).

From (4) we find:

$$\frac{db}{dv} = \frac{1}{1 + 2\left\{\left(\frac{v-b}{b-b_0}\right)^2 + \left(\frac{v-b}{b_g-b_0}\right)^2\right\}} \quad \ldots \quad \ldots \quad (6)$$

and

$$\frac{v-b}{2}\frac{\dfrac{d^2b}{dv^2}}{1-\dfrac{db}{dv}}=-\frac{db}{dv}\frac{2\left\{\left(\dfrac{v-b}{b-b_0}\right)^2+\left(\dfrac{v-b}{b_g-b_0}\right)^2-\left(\dfrac{v-b}{b-b_0}\right)^3\dfrac{\dfrac{db}{dv}}{1-\dfrac{db}{dv}}\right\}}{1+2\left\{\left(\dfrac{v-b}{b-b_0}\right)^2+\left(\dfrac{v-b}{b_g-b_0}\right)^2\right\}}.\quad(7)$$

Such a value for v satisfying (5) can only be found by repeated approximation. For this it is useful to get to know the course of b, $\dfrac{db}{dv}$

and $\dfrac{v-b}{2}\dfrac{\dfrac{d^2b}{dv^2}}{1-\dfrac{db}{dv}}$.

With regard to b we point out that at $v=\infty$ the value of b approaches b_g asymptotically, that b decreases continually with v and that v and b assume at the same time the value b_0.

So if we take two axes, a v axis and a b axis, and if we draw the point P_0, for which $v=b_0$ and $b=b_0$, then the line representing b, will ascend trom the point P_0. The initial direction in P_0 is indicated by $\dfrac{db}{dv}=\dfrac{f}{1+f}$ or in our case by $\dfrac{db}{dv}=\dfrac{2}{3}$. The value of $\dfrac{db}{dv}$ is at $v=\infty$ equal to zero, but may become considerable if v is very small, and increase to $^2/_3$. This value of $\dfrac{d^2b}{dv^2}$ is always negative, but in the equation (5) this quantity does not occur separately; it occurs however, in the combination $\dfrac{v-b}{2}\dfrac{\dfrac{d^2b}{dv^2}}{1-\dfrac{db}{dv}}$. It appears from (7) that this expression is negative, and of the order of $\dfrac{db}{dv}$. The factor, with which $\dfrac{db}{dv}$ is to be multiplied in order to get this complex, is equal to 1, if $v=\infty$, and descends to zero with diminishing volume.

It was necessary that $\dfrac{db}{dv}$ is never greater than 1. For if $\dfrac{db}{dv}$ is larger than 1, $\dfrac{dp}{dv}$ is necessarily negative, and then we should get unstable

phases for very small values of v, which is quite opposed to the experiment. With the coefficients found in the earlier attempts at explaining the variability of b, I repeatedly met such unstable phases.

It is obvious that a value for v, satisfying (5) can be found, and probably but a single value, if we pay attention to the fact that the first member varies regularly between the values $\dfrac{3}{2}$ and 0, and the second member between 1 and $\frac{1}{3}$.

But when determining the value of v which satisfies (5), we meet with the difficulty, that we must be able to calculate not only b, but also $\dfrac{db}{dv}$ and $\dfrac{d^2b}{dv^2}$ perfectly from the equations given for them, while a slight change in the value of f and b_0 might cause a very great change in the value of these quantities which is to be calculated. So the equation (5) is not perfectly satisfied, if we take v equal to the observed critical volume. With $b = 216,7$ we calculate $v = 0,004082$, and we find the value of $\dfrac{db}{dv}$ equal to $0,16$ à $0,17$ and for the relation

$$\frac{v-b}{2} \; \frac{\dfrac{d^2b}{dv^2}}{1-\dfrac{db}{dv}} \quad \text{and} \quad \frac{db}{dv} \quad \text{the value } 0.71. \text{ Now (5) may also be written:}$$

$$\cfrac{3\,b}{1+2\left\{\cfrac{db}{dv}-\cfrac{v-b}{2}\; \cfrac{\dfrac{d^2b}{dv^2}}{1-\dfrac{db}{dv}}\right\}} \quad . \quad . \quad . \quad . \quad (8)$$

and calculated with this we do not get back $v = 0,004082$, but $v = 0,00411$. With $b = 0,00223$, we find $v = 0,004406$, so the assumed critical volume, then $\dfrac{db}{dv} = 0,132$ and $-\dfrac{v-b}{2}\; \dfrac{\dfrac{d^2b}{dv^2}}{1-\dfrac{db}{dv}}$ has a value very near $0,1$. Then we find from (8) $v = 0,000457$, so a greater difference between the two values calculated in different ways. But the cause of this may be that the given equation for the determination of b is drawn up to represent the series of values which I have calculated for them by aid of a not quite accurate value of a. And moreover it appears sufficiently from the

deduction of the formula for b that it can only be meant as an approximation.

If we put in future for $\dfrac{db}{dv}$ as it is in the critical point α, and β

for $-\dfrac{v-b}{2}\dfrac{\dfrac{d^2b}{dv^2}}{1-\dfrac{db}{dv}}$, then:

$$v_k = \frac{3b_k}{1 + 2(\alpha + \beta)}$$

$$RT_k = \frac{8}{27}\frac{a}{b_k}\frac{(1 - \alpha - \beta)^2[1 + 2(\alpha + \beta)]}{1 - \alpha}$$

$$p_k = \frac{1}{27}\frac{a}{b_k^2}\Big[1 + 2(\alpha + \beta)\Big]^2\Big[4\frac{1 - \alpha - \beta}{1 - \alpha} - 3\Big]$$

If α and β are equal to 0, then we find the known values which have been calculated on the supposition of constant value of b.

Let us take $\alpha = 0{,}138$ and $\beta = 0{,}1$, which in the proximity of the critical point of carbonic acid is not exaggerated. From the series of values of b a value for $\dfrac{db}{dv} = \dfrac{1}{5}$ is even calculated, if v is between $0{,}00496$ and $0{,}00321$.

Then we find a very great difference in the critical volume, and the factor b_k descends even to $2{,}03$ — to which must be added that b_k is smaller than b_g and may be put at about $0{,}86\ b_g$.

But RT_k and p_k are comparatively little influenced by this value of α and β. The factor with which $\dfrac{8}{27}\dfrac{a}{b_k}$ is to be multiplied, descends by it only from 1 to $1 - \dfrac{1}{170}$. And the factor, with which $\dfrac{1}{27}\dfrac{a}{b_k^2}$ is to be multiplied in order to find p_k, rises from 1 to $\dfrac{7}{6}$. Therefore the value of $\dfrac{p_k\ v_k}{RT_k}$ will be smaller than is found on the supposition of constant b and that approximately in the same proportion, as is the case with v_k, which is in perfect accordance with the experiment.

For the value of $\Big(\dfrac{pv}{RT}\Big)_k$ we find the expression:

$$\left(\frac{pv}{RT}\right)_k = \frac{3}{2}\frac{1}{1-\alpha-\beta} - \frac{9}{8}\frac{1-\alpha}{(1-\alpha-\beta)^2},$$

which leads to the wellknown value $^3/_8$, if α and β are 0 and descends to $\frac{1}{3,4}$ with the given value of α and β. From the determinations of VERSCHAFFELT we derive for this value $\frac{1}{3,56}$.

(To be continued.)

Physiology. — Dr. J. BRAND : "*Researches on the secretion and composition of bile in living men*". (Communicated by Prof. B. J. STOKVIS.)

Nine cases of cholecystotomy, performed in the surgical wards of the Binnen-Gasthuis at Amsterdam in the years 1896—1899, afforded the occasion, to examine in the first place the rapidity of the flow of human bile. The secretion is a continuous one, sinking during the night, and showing its minimum in the early hours of the morning. After awakening the flow is rising generally fastly and attains a maximum a few hours after midday. In the evening the flow of bile presents a second maximum, which is much smaller than the first. These maxima probably depend on the taking of meals. The quantity of bile produced in 24 hours may be as great as 1100 cc (so that it comes near the quantity of urine produced in the same time), the smallest quantity found was 500 cc. There was no difference in the concentration of the bile at different times of the day. The quantity of the produced bile is very little influenced by the body-weight ; it is chiefly depending on metabolism, which is exactly measured by the quantity of the essential substances of the bile. The amount of solid matters in freely along the bile-ducts flowing human bile (bile of the liver) attains 1.41 pCt. ; in bile, stored up in the gall-bladder, it can be as high as 20 pCt. The colour of human bile is a bright golden yellow one, and the amount of the colouring matter : the bilirubin is rather low : 0.06 pCt. Human bile contains besides bilirubine urobilinogen or properly speaking reduced urobiline in rather large quantities as a constant compound, and probably also very small quantities of haemato-porphyrine, which is almost never absent