

Citation:

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be the case, a plait, which appears as a longitudinal plait, but which has its plaitpoint on the side of the small volumes, as in the observations of KUENEN and ROBSON, is not a longitudinal plait, but a somewhat modified transverse plait. If then in the liquid state complete mixture does not take place under all circumstances, the phenomenon is to be ascribed to other causes than in case of a real longitudinal plait.

If further investigations confirm what has been said, we should have to find the cause in this case in the fact that at least one of the substances is abnormal.

Physics. — “*On variation of volume and of pressure*”. III. By Prof. J. D. VAN DER WAALS.

In order to be able to judge about the extent of the variation of volume and of pressure in mixtures of two substances, it will be necessary, to find for the different proportions of mixing the pressures at which the number of the molecules is the same for the two substances, if the volume and the temperature are also the same. If there were no deviations from the law of BOYLE, the pressures required would be equal. Assume that for a mixture the characteristic equation is :

$$\left(p + \frac{a_x}{v^2} \right) (v - b_x) = MRT ,$$

at a given temperature the 2nd member of this equation has a constant value for mixtures with the same number of molecules, and so we may find the pressure which satisfies the preceding condition in solving the value of p from this equation, if the value of v is constant. Take as unity of pressure 1 atmosphere and as unity of volume, the volume occupied by a molecular quantity of the mixture under that pressure. The value of the second member is then

$$(1 + a_x) (1 - b_x) (1 + \alpha t) ,$$

for which we may write with a sufficient degree of approximation

$$(1 + a_x - b_x) (1 + \alpha t) .$$

If we write p_0 for the value of the pressure taken as unity, and

$(v_0)_x$, for the volume occupied by a molecular quantity at 0° , the characteristic equation is

$$\left[p + a_x p_0 \frac{(v_0)_x^2}{v^2} \right] \left[1 - b_x (v_0)_x \right] = p_0 (v_0)_x (1 + a_x) (1 - b_x) (1 + \alpha t),$$

from which we deduce that the conditions that in 1 cM³. the same number of molecules be found are, that we have different mixtures with the same value for v , the same value for t and that we have that value of p , for which the first member and therefore also the second, is the same. The simple result is that the quantity of the different mixtures is to be chosen in such a way that $(v_0)_x (1 + a_x) (1 - b_x)$ has the same value for them all.

As $p_0 (v_0)_x (1 + a_x) (1 - b_x) (1 + \alpha t)$ is the limiting value of the product pv , the preceding condition is also fulfilled, when this limiting value is the same for the different mixtures.

In the two preceding proceedings of the Academy Mr. J. VERSCHAFFELT has published observations about mixtures of carbonic acid and hydrogen. In order to determine the volumes, which contain an equal number of molecules, the observer has followed a course which agrees with the determination of $(v_0)_x (1 + a_x) (1 - b_x)$. He is of opinion that the investigation of the limiting value of pv would not serve the purpose. I think that this conclusion must be drawn from his remark p. 332. „From the point of view” etc.

Be this as it may, I shall prove that both ways may be followed. At the same time I shall investigate, in how far his observations agree with my characteristic equation. But first a remark about the accurate form of the characteristic equation, or rather about the value of the quantities a_x and b_x .

I have always taken for them the following expressions:

$$a_x = a_1 (1-x)^2 + 2 a_{12} x (1-x) + a_2 x^2$$

$$\text{and } b_x = b_1 (1-x)^2 + 2 b_{12} x (1-x) + b_2 x^2.$$

It is easy to see that if we want to be perfectly accurate we must put:

$$a_x (v_0)_x^2 = a_1 (v_0)_1^2 (1-x)^2 + 2 a_{12} (v_0)_1 (v_0)_2 x (1-x) + a_2 (v_0)_2^2 x^2$$

$$\text{and } b_1 (v_0)_x = b_1 (v_0)_1 (1-x)^2 + 2 b_{12} \sqrt{(v_0)_1 (v_0)_2} x (1-x) + b_2 (v_0)_2 x^2.$$

If we were allowed to equate $(v_0)_1$, $(v_0)_2$ and $(v_0)_x$, there would

be no difference between the two values of a_x and b_x ; and at any rate the difference will be scarcely noticeable, if the observations on the mixtures do not reach the highest degree of accuracy. But to know the accurate form is necessary in the first place for the sake of perfect accuracy of the theoretical considerations, and in the second place in his observations Mr. VERSCHAFFELT seems to have aimed at and perhaps reached that high degree of accuracy, at which differences between the two sets of values of a_x and b_x might be of influence.

Let us now proceed to investigate in how far Mr. VERSCHAFFELT has succeeded in determining the volumes which contain an equal number of molecules under a pressure of 1 atmosphere.

He puts for this :

$$y = 0,99931 + 0,006 (1-x)^2 .$$

From this formula we obtain the value 0,99931 for hydrogen ($x = 1$), the value 1,0053 for carbonic acid ($x = 0$) and the value 1,00081 for $x = \frac{1}{2}$. By means of these three values, taken from observations, he has calculated his formula, assuming that y might be put under the form $a + bx + cx^2$.

According to the theory the factor, with which $(v_0)_x$ is to be multiplied in order to obtain the volume, which contains the same number of molecules, must be equal to:

$$(1 + a_x) (1 - b_x) = 1 + a_x - b_x .$$

If we take the latter form, viz $(1 + a_x - b_x)$, we make already use of an approximation. But even with this approximation we find:

$$y = 1 + (1 + a_x - b_x)^2 \left[\frac{a_1 (1-x)^2}{(1 + a_1 - b_1)^2} + 2a_{12} \frac{x(1-x)}{(1 + a_1 - b_1)(1 + a_2 - b_2)} + a_2 \frac{x^2}{(1 + a_2 - b_2)^2} \right] - (1 + a_x - b_x) \left[\frac{b_1 (1-x)^2}{1 + a_1 - b_1} + 2b_{12} \frac{x(1-x)}{\sqrt{(1 + a_1 - b_1)(1 + a_2 - b_2)}} + b_2 \frac{x^2}{1 + a_2 - b_2} \right] ,$$

so that we must make use of another approximation to get a form like $y = a + bx + cx^2$. All this may cause deviations, but the error which is committed by assuming this form, will remain but insignificant. My objection to the formula:

$$y = 0,99931 + 0,006 (1-x)^2$$

has another ground. Mr. VERSCHAFFELT himself remarks, that if he had made use of other experimental data to determine the values of a , b and c , he would have found the following formula:

$$y = 0,9995 + 0,00136 (1-x) + 0,0056 (1-x)^2.$$

But he uses the former — and now I shall show that the latter agrees to a great extent with what his own experiments teach, and that the former certainly cannot be true.

When two gases are mixed in different proportions — and one of the gases (carbonic acid) deviates in one direction from the law of BOYLE, whereas the other gas (hydrogen) does so in the other direction, we may expect the existence of a mixture, which follows the law of BOYLE. What may be brought about by change of temperature in case of a simple gas, occurs here by change of the mixing proportion. For such a mixture $y = 1$. From the formula

$$1 = 0,99931 + 0,006 (1-x)^2$$

follows $x = \pm \frac{2}{3}$. From the formula

$$1 = 0,9995 + 0,00136 (1-x) + 0,0056 (1-x)^2$$

follows $x = 0,8$.

Mr. VERSCHAFFELT has made observations for $x = 0,7963$ and $x = 0,6445$. The products pv for $x = 0,7963$ are respectively

$$1,0740, \quad 1,0756, \quad 1,0764, \quad 1,0749, \quad 1,0748.$$

At $v = 0,02$ pv has still the value of 1,0750, and not before $v = 0,01$ it has reached the value of 1,0960.

From these values of pv we may conclude that the mixture has nearly that composition, in which it would follow the law of BOYLE in great volumes. From the long series of larger volumes, in which actually constancy of this product has been found, we might deduce, that the mixture deviates still in the direction of carbonic acid — and that therefore x should have a somewhat greater value in order to form a mixture, which follows the law of BOYLE only in very large volumes, but yet shows an increasing product from the beginning.

If we take the value of pv that belongs to the mixture, in which $x = 0,6445$, we find:

$$1,0431, \quad 1,0425, \quad 1,0413, \quad 1,0411, \quad 1,0413, \quad 1,041,$$

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while at $v=0,002$ the product is diminished to 1,036 and at $v=0,01$ it descends still more down to 1,021. From the former series of values we might still be in doubt whether this mixture also possibly follows the law of BOYLE, but the value at $v=0,01$, which has perceptibly decreased, decides, and shows convincingly, that this mixture still deviates in the direction of carbonic acid. My conclusion is therefore that for the mixture for which $y=1$ the value of x cannot descend below 0,8.

In such a mixture the product $pv=(1+\alpha t)$, or ($t=18^\circ$) $pv=1,06606$. For this value we found above 1,074. This would lead to the conclusion that if Mr. VERSCHAFFELT equates the volume to 0,03, it is in reality no more than 0,02983. As a similar difference is also found for the following volumes, it would point to the fact that he has taken the unity of volume in this mixture $\pm \frac{1}{2}$ pCt. too large, an error which surpasses the amount of the above discussed corrections. If we would not acknowledge this error, we should have to take as the mixture for which $pv=1+\alpha t$ one for which x is smaller, which is contradicted by the experiments on compression, as has been shown before.

Put 35,80 as the value of the pressure, which a gas would exercise, if it should follow the law of BOYLE. For every series of observations if the volume $x=0,02983$, we find in Table XII, p. 334 indicated the pressure which is to be subtracted from 35,8, to find the influence of the deviations.

If we put

$$(35,8 - p) = \frac{a_x - b_x(1 + \alpha t)}{v^2},$$

the value of $a_x - b_x(1 + \alpha t)$ may be calculated for every mixture from this approximated equation. If we calculate $a_1 - b_1(1 + \alpha t)$ (for carbonic acid) we find 0,00614 and $-0,000454$ for $a_2 - b_2(1 + \alpha t)$ (hydrogen). By means of these values we may determine the constants for $y = a + bx + cx^2$, if we make also use of the circumstance that the value of $y=1$ is to be found for $x=0,8$. Then we find:

$$y = 0,999546 + 0,001189(1-x) + 0,005405(1-x)^2,$$

an equation which closely resembles that one, which Mr. VERSCHAFFELT thought, that he ought not to make use of, and which yet has been deduced from his own observations only. In the following table we find the value of y for values of $x=0,1, 0,2$ etc.

$x = 0$	$y = 1,00614$
0,1	1,00499
0,2	1,00396
0,3	1,00303
0,4	1,00220
0,5	1,00149
0,6	1,00089
0,7	1,00039
0,8	1
0,9	0,99972
1	0,99954

By application of the approximated formula

$$(35,8 - p) v^2 = a_x - b_x (1 + \alpha t)$$

we find from the series of observations

$x = 0,0995$	$y = 1,00483$
$x = 0,1990$	1,00398
$x = 0,3528$	1,00276
$x = 0,4993$	1,00177
$x = 0,6445$	1,00093
$x = 0,7963$	1
$x = 0,8972$	0,99965

Only at $x = 0,5$ a deviation of importance is found.

For $t = 18^\circ$ we may calculate from

$$a_x - b_x (1 + \alpha t) = -0,000454 + 0,001189 (1-x) + 0,005405 (1-x)^2$$

the value $a_{12} - b_{12} (1 + \alpha t) = 0,0001375$ and

$$a_1 + a_2 - 2 a_{12} - (b_1 + b_2 - 2 b_{12}) (1 + \alpha t) = 0,005404 .$$

According to this value of $a_{12} - b_{12} (1 + \alpha t)$ the deviation¹⁾ from the law of DALTON would be in the usual direction, i. e. in such a way that the pressure of the mixture at larger volumes is smaller than the sum of the separate pressures, whereas at smaller volumes the sign of the deviation is reversed. In consequence of the small value of $a_{12} - b_{12} (1 + \alpha t) = 0,0001375$, the deviation will be but slight. We may examine whether this is confirmed by the observations of Mr. VERSCHAFFELT (table XII), if $x = 1/2$. So for $v = 0,03$

¹⁾ See Proceedings of Nov. 1898.

$p_1 = 28,9$ and $p_2 = 36,31$. If an equal number of molecules of carbonic acid and hydrogen so that $x = 1/2$, are mixed in the same volume $v = 0,03$, the volume contains twice as many molecules, so the same number in $v = 0,015$. For this volume Mr. VERSCHAFFELT finds $p = 65$. The value of $p_1 + p_2 = 65,21$.

In the same way

at $v = 0,028$	$p_1 = 30,58$	$p_2 = 38,97$	$p_1 + p_2 = 69,45$	and at $v = 0,014$	$p = 69,30$
" $v = 0,026$	$p_1 = 32,40$	$p_2 = 42,04$	$p_1 + p_2 = 74,44$	and at $v = 0,013$	$p = 74,20$
" $v = 0,024$	$p_1 = 34,38$	$p_2 = 45,65$	$p_1 + p_2 = 80,03$	and at $v = 0,012$	$p = 80,00$
" $v = 0,022$	$p_1 = 36,55$	$p_2 = 49,94$	$p_1 + p_2 = 86,49$	and at $v = 0,011$	$p = 86,75$
" $v = 0,020$	$p_1 = 39,08$	$p_2 = 55,10$	$p_1 + p_2 = 94,18$	and at $v = 0,010$	$p = 94,40$

So in the case of carbonic acid and hydrogen, the quantity $a_{12} - b_{12}(1 + \alpha t)$ is not large and $(a_1 + a_2 - 2 a_{12}) - (b_1 + b_2 - 2 b_{12})(1 + \alpha t)$ small, but the contrary. The latter may be expected for substances which differ much in physical properties.

In my communications under the same title, in the proceedings of November and December 1898, I have discussed two rules of approximation for mixtures, viz. the law of DALTON and that of AMAGAT. As a third rule of approximation the following rule might be given: In a mixture a substance exercises the pressure that it would exercise if the other molecules were substituted by molecules of its own kind. Let us call the pressure which the first mentioned gas would exercise, if all the molecules were of the same kind p_1 , and that of the second gas p_2 , then this rule of approximation comes to the same as putting

$$p = p_1(1 - x) + p_2 x .$$

From the graphical representation of Mr. VERSCHAFFELT p. 329 it appears that for carbonic acid and hydrogen $p - [p_1(1 - x) + p_2 x]$ is positive.

From the characteristic equation we may deduce for this difference:

$$p - p_1(1 - x) - p_2 x = x(1 - x) \frac{(a_1 + a_2 - 2 a_{12}) - (b_1 + b_2 - 2 b_{12})(1 + \alpha t)}{v^2}$$

for all volumes large enough that we may put $1 + \frac{b}{v}$ for $\frac{v}{v - b}$.

So we see that for large volumes this third rule of approximation is exactly the same as that of AMAGAT.

At a given volume p is a function of x of the second degree and the maximum deviation will be found at $x = 1/2$.

For $v = 0,024$ the following table gives the calculated and the observed values of the pressure.

In the formula $p = p_1(1-x) + p_2x + Ax(1-x)$ we have taken A as equal to 8.

x	0	0,05	0,1	0,2	0,3528	0,5	0,6445	0,8	0,9	1
p calculated	34,38	35,32	36,22	37,91	40,18	42,01	43,47	44,67	45,24	45,65
p observed	34,38	35,53	36,54	38,04	40,12	41,80	43,33	44,80	45,48	45,65

For the value of A which might have been calculated by means of the relation

$$A = \frac{(a_1 + a_2 - 2 a_{12}) - (b_1 + b_2 - 2 b_{12})(1 + \alpha t)}{v^2},$$

we should have found about 9,5, if $\Delta_a - \Delta_b(1 + \alpha t) = 0,005405$ (see p. 395).

The value of p , putting $A = 9,5$, agrees nearly perfectly for small values of x and $1-x$, but in this case the differences are larger again for values of x near $1/2$. From $A = 8$ would follow $\Delta_a - \Delta_b(1 + \alpha t) = 0,00461$ ¹⁾.

From all this follows that absolute agreement between the theory and the observations of Mr. VERSCHAFFELT does not yet exist. But the differences remain below 1 pCt. It would be premature to try to decide as yet whether the differences are to be ascribed to the theory or to the experiments. Yet we may say that in these observations the differences are smaller than in those that I have tested before. And the fact that up to now the differences grow less as the observations grow in accuracy, seems to plead in favour of the theory.

¹⁾ In calculating the coefficient in the equation

$$y = 0,999546 + 0,001189(1-x) + 0,005405(1-x)^2$$

we have made use of the data for carbonic acid and hydrogen, and of the supposition that $y = 1$, if $x = 0,8$.

If we take $y = 1$ for $x = 0,82$, the coefficients become

$$y = 0,999546 + 0,001618(1-x) + 0,00497(1-x)^2.$$

These values of the coefficients seem more probable to me; moreover in this case the values of the two tables on p. 395 agree still better.

With these coefficients is

$$a_{12} - b_{12}(1 + \alpha t) = 0,000355$$

and

$$(a_1 + a_2 - 2 a_{12}) - (b_1 + b_2 - 2 b_{12})(1 + \alpha t) = 0,00197.$$