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will be obtained in case of a quick cooling — independent of the situation of the heating-temperature.

The velocity of cooling as mentioned in Case III—V, is supposed to be such that the liquid finds no occasion to alter its mixing-proportion α/β acquired at a higher temperature. Should the velocity of cooling be less, this only results in the differences between the first acquired congealing-point and point *II* being smaller than in a case of very quick cooling. The deviations remain however in the same direction.

It is therefore possible to determine with perfect accuracy the apparently curious phenomena of congelation, with a knowledge of the lines *GF*, *FD* and *FE*. On the other hand it would be possible, from observation of the congealing temperatures, after the substance α or β having gone through a sharply defined way, to conclude to the situation of different points of these lines, consequently to determine their direction, if this were not possible along other ways.

The phenomena described here, may appear not only in tautomeric substances, but in all substances which in the liquid state, give two modifications that are apt to transformation.

Consequently many optic isomers that show equilibrium at higher temperatures, come under this head. There however the matter can often become complicated, it being possible that after the transformation of the *d* or the *l*-form, the racemic form deposits in the solid condition. It is however easy to take this into account.

Physics. — „*Variation of volume and of pressure in mixing*”.
By Prof. J. D. VAN DER WAALS.

The supposition of Mr. AMAGAT (C. R. 11 Juillet 1898), that in a mixture every gas can be considered to occupy the volume which it would occupy separately under the same pressure and at the same temperature, comes to the same thing as supposing, that mixing under a constant pressure does not cause variation of volume, and that there would be no question of either positive or negative contraction. As at great densities (of liquids), mixing is generally accompanied by contraction, the thesis, also in case of slight densities, can only be meant as an approximation. For slight densities this thesis can be tested by means of the characteristic equation of a mixture.

For a molecular quantity of a mixture, consisting of $m_1(1-x)$ and m_2x unities of mass, the equation holds:

$$pv = MRT \frac{v}{v-b_x} - \frac{a_x}{v}$$

or by approximation

$$pv = MRT - \frac{1}{v} (a_x - b_x MRT) \dots \dots \dots (1)$$

For each of the components

$$pv_1 = MRT - \frac{1}{v_1} (a_1 - b_1 MRT) \dots \dots \dots (2)$$

would hold for a molecular quantity, and

$$pv_2 = MRT - \frac{1}{v_2} (a_2 - b_2 MRT) \dots \dots \dots (3)$$

If we put $v = v_1(1-x) + v_2x + \Delta v$, and take into consideration

$$\text{that } a_x = a_1(1-x)^2 + 2a_{12}x(1-x) + a_2x^2$$

$$\text{and } b_x = b_1(1-x)^2 + 2b_{12}x(1-x) + b_2x^2$$

we get

$$p\Delta v = -\frac{1}{v} (a_x - b_x MRT) + \frac{(1-x)(a_1 - b_1 MRT)}{v_1} + \frac{x(a_2 - b_2 MRT)}{v_2}$$

by subtracting the sum of $(1-x)$ times equation (2) and x times equation (3) from equation (1).

As pv as well as pv_1 and pv_2 are equal to MRT by approximation, we may put

$$MRT \Delta v = \{a_1(1-x) + a_2x - [a_1(1-x)^2 + 2a_{12}x(1-x) + a_2x^2]\}$$

$$- MRT \{b_1(1-x) + b_2x - [b_1(1-x)^2 + 2b_{12}x(1-x) + b_2x^2]\}$$

or

$$MRT \Delta v = -x(1-x) \{ [2a_{12} - a_1 - a_2] - [2b_{12} - b_1 - b_2] MRT \}$$

or

$$\Delta_v = x(1-x) \left\{ \frac{a_1 + a_2 - 2a_{12}}{MRT} - (b_1 + b_2 - 2b_{12}) \right\} . . (4)$$

From this equation (4) follows: 1°. that the absolute value of the variation of volume at a given temperature is independent of the pressure, under which the mixture takes place, of course only as long as it does not surpass the limit, below which the calculations mentioned are sufficient approximations; 2°. that the maximum value of this volume variation is found for $x = \frac{1}{2}$; so if the substances to be mixed have the same volume. For air, which is composed of oxygen and nitrogen, the volumecontraction will amount to no more than $\frac{16}{25}$ of the value, found when equal volumes of oxygen and nitrogen are mixed. The quantities must, of course, be chosen in such a way, that in both cases the total volume of the components is the same; 3°. that it depends on the value of the expression:

$$\frac{a_1 + a_2 - 2a_{12}}{1 + \alpha t} - (b_1 + b_2 - 2b_{12}) (5)$$

whether negative or positive contraction takes place.

As in the characteristic equation the volume, occupied by the molecular quantity under the pressure of one atmosphere and at 0°, has been taken as unity of volume, the quantity Δ_v is also expressed in that unity.

It is true that the unity of volume in the three equations (1), (2) and (3) is not absolutely the same, on account of their different degree of deviation from the law of BOYLE, but the influence of this fact may be neglected in these calculations, as the deviation it causes, is a small quantity of higher order.

If we proceed to the discussion of the expression (5), we see in the first place that $b_1 + b_2 - 2b_{12} = 0$ comes to the same thing as assuming the co-volume of a mixture equal to the sum of the co-volumes of the components.

The circumstance, that it is easier to arrange arbitrarily formed bodies, which take up together a certain volume, in a given space, when the bodies are different in size, than when they are all of the same size, makes it probable, that the co-volume of a mixture of molecules of different sizes will be smaller than 4 times the real volume. In the deduction of the characteristic equation, in which, however, the molecules are thought as spheres, this has been proved,

and $\frac{3}{2} (\sqrt{b_2} - \sqrt{b_1})^2 (\sqrt{b_2} + \sqrt{b_1})^{-1}$ has been found for the value of $b_1 + b_2 - 2b_{12}$, an expression which is always positive. On the other hand, this expression, which is equal to 0, when $b_1 = b_2$, and which is positive, as well when $b_1 > b_2$ as when $b_1 < b_2$, shows that for a small difference in size the value of $b_1 + b_2 - 2b_{12}$ is very small. If we might neglect it, it would only depend on the sign of $2a_{12} - a_1 - a_2$, whether mixture would cause contraction or not.

When $2a_{12} - a_1 - a_2$ is positive, mixing is favoured by the molecular forces. For if we suppose the two gases before the mixing separated by a mathematic surface, $\frac{a_1}{v_1^2}$ and $\frac{a_2}{v_2^2}$ are the forces which

oppose mixture, and $\frac{2a_{12}}{v_1 v_2}$ is the force, which draws the two substances through the bounding surface. In this case we may put $v_1 = v_2$, and the sign of $2a_{12} - a_1 - a_2$ proves to be decisive.

In general we are justified in expecting, that when mixing is favoured by the molecular forces, and when in consequence of the mixing a smaller molecular volume must be subtracted from the external volume, both circumstances cause positive contraction (negative value of Δ_v).

If $(a_1 + a_2 - 2a_{12})$ and $(b_1 + b_2 - 2b_{12})$ are both positive, a temperature exists, below which Δ_v is positive and above which Δ_v is negative, just as is the case for the deviation from the law of BOYLE for a simple substance. But in general we may expect that $-\Delta_v$ (volume contraction) will be small and that the thesis of Mr. AMAGAT will hold true with a high degree of approximation, at least in all cases, in which the properties of the components differ little. In the first place because $a_1 + a_2 - 2a_{12}$ and $b_1 + b_2 - 2b_{12}$ are both equal to 0, if the substances are the same, and we may therefore put, that when the difference is small, the value of these quantities will be small, compared to each of the terms, of which they consist, e.g. $a_1 + a_2 - 2a_{12}$ is small as compared with a_1 or a_2 , and $b_1 + b_2 - 2b_{12}$ is small as compared with b_1 or b_2 . Secondly on account of the factor $x(1-x)$; for air this factor amounts to no more than $\frac{4}{25}$.

Our equation cannot be tested at the values which Mr. AMAGAT gives for air of the ordinary temperature and which begin at a

¹⁾ Théorie Moléc. Arch. Néel. Tom. XXIV.

pressure of 100 atm., as the equation is not sufficiently approximative, and because Mr. AMAGAT himself comes to the conclusion, that the deviation found does not exceed the possible errors of observation. It were desirable that similar experiments were made with equal volumes of substances which differ much in physical properties. In testing, the equation (4) should be replaced by another which would hold with a higher degree of approximation. If the volumes v_1 , v_2 and v show a marked difference, the term $a_1 + a_2 - 2 a_{12}$ should be replaced by:

$$v_1 v_2 \left\{ \frac{a_1}{v_1^2} + \frac{a_2}{v_2^2} - \frac{2 a_{12}}{v_1 v_2} \right\}$$

an expression, which at a feeble density may be considered as equal to $a_1 + a_2 - 2 a_{12}$, but which approaches

$$b_1 b_2 \left(\frac{a_1}{b_1^2} + \frac{a_2}{b_2^2} - 2 \frac{a_{12}}{b_1 b_2} \right) .$$

if the density increases.

We have no right to expect, that the value of Δ_v will remain perfectly constant at various degrees of density (which would follow from the approximative equation), and at any rate the reservation is to be made, that always either two gas-phases or two liquid-phases are to be mixed. We may however expect, that the value of Δ_v will keep within certain finite limits, and that therefore, that which may seem large as compared to two small volumes (liquid volumes), may be neglected if compared with very large gas volumes.

Mr. KUENEN (Dissertation 1892, Leyden) has made observations, from which the quantity Δ_v may be determined for mixtures of CO_2 and CH_2Cl and has found it positive. It is to be regretted, that he has not tried to determine the value of Δ_v , but that he gives the increase of pressure, which is to be applied, in order to reduce the volume of the mixture to the sum of the volumes of the components. Intricate calculations are necessary for finding our result confirmed, namely that Δ_v is not 0, but that it has a value of the same order of greatness all through the course of the isotherme. If he had restricted himself to the determination of Δ_v , he would undoubtedly have come to the conclusion, that Δ_v is quasi-constant, and he might have given an approximative rule, which I now feel obliged to ascribe to Mr. AMAGAT, though AMAGAT's rule $\Delta_v = 0$ must be replaced by Δ_v is nearly constant.

I shall not carry out the intricate calculations, which would be necessary to calculate Δ_v from Mr. KUENEN's observations of the increase of pressures, but I shall restrict myself to an approximation, sufficient to conclude that the different values of Δ_v in Mr. KUENEN's experiments must have been quantities of the same order.

From

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

follows

$$-\frac{dp}{dv} = \frac{MRT}{(v-b)^2} - \frac{2a}{v^3}$$

and

$$-MRT \frac{dp}{dv} = p^2 - \frac{a(a-2bMRT)}{v^4}$$

by approximation.

So we can calculate the quantity Δ_v from $\Delta_v = \frac{(1 + \alpha t) (\Delta_p)'}{p^2}$.

Variation of pressure in mixing.

Atmosph.	Mixture.	T. 433.0	403.0	373.0	343.0
10	$\frac{3}{4}$	10.06	10.07	10.08	10.08
	$\frac{1}{2}$	10.04	10.05	10.07	10.10
	$\frac{1}{4}$	—	10.06	10.07	10.09
30	$\frac{3}{4}$	30.67	30.85	31.20	—
	$\frac{1}{2}$	30.56	30.81	31.25	—
	$\frac{1}{4}$	—	30.78	31.06	—
50	$\frac{3}{4}$	52.4	54.4	—	—
	$\frac{1}{2}$	52.1	54.3	—	—
	$\frac{1}{4}$	—	53.1	—	—

If we take $T = 403^\circ$ and $x = \frac{3}{4}$, as an example from Mr. KUENEN's table, which I have reproduced here, we find at

$$p = 10 \dots \Delta_v = 0,0010$$

$$p = 30 \quad \Delta_v = 0,0014$$

$$p = 50 \quad \Delta_v = 0,0026$$

Also from Mr. KUENEN's values, about which he himself remarks, that they show but little regularity, we get the impression, that the exact determination touches the limit of the errors of observation.

From the observation at 433° we find if $x = \frac{3}{4}$

$$p = 10 \quad \Delta_v = 0,00095$$

$$p = 30 \quad \Delta_v = 0,00118$$

$$p = 50 \quad \Delta_v = 0,00152$$

According to the formula (4) Δ_v must be smaller at a higher temperature, which is also confirmed by the calculated values; for the rest the increase is not so quick at 433° as at 403° . But I repeat, what I said before, that though the approximative formula gives a constant value for Δ_v , we want more accurate formulae, to indicate the real course.

Let us compare, in order to judge about the degree of approximation, with which the thesis of Mr. AMAGAT holds true, the calculated quantity Δ_v with the value of Δ_p . By Δ_p we represent the difference between the pressure of a mixture and that pressure, which we should find if the law of DALTON held good.

If we take in a volume v first $1 - x$ molecules of the first substance and if we call p_1 the pressure, after that x molecules of the second substance, with the pressure p_2 ; and finally a mixture with pressure p , then $\Delta_p = p - (p_1 + p_2)$.

In the first case the molecular volume is $\frac{v}{1-x}$; in the second case $\frac{v}{x}$, and for the mixture v . So we have the three following equations :

$$p = \frac{MRT}{v-b_x} - \frac{a_x}{v^2}$$

$$p_1 = \frac{MRT(1-x)}{v-b_1(1-x)} - \frac{a_1(1-x)^2}{v^2}$$

and

$$p_2 = \frac{MRTx}{v-b_2x} - \frac{a_2x^2}{v^2}$$

and from this by approximation

$$\Delta_p = p - (p_1 + p_2) = \frac{2MRTb_{12}x(1-x) - 2a_{12}x(1-x)}{v^2}$$

or

$$\Delta_p = 2 \frac{(1 + \alpha t)b_{12} - a_{12}}{v^2} x(1-x).$$

If we first restrict ourselves, when discussing the value of Δ_p , to this approximative formula, which is sufficiently accurate under a small pressure, we see 1°. that Δ_p varies greatly with the density, that it is even proportional to the square of the density; 2°. that Δ_p depends on the composition of the mixture in the same way as Δ_v , and 3°. that the sign of Δ_p depends on the sign of $(1 + \alpha t)b_{12} - a_{12}$. This expression cannot be considered as small, and does by no means disappear, when the two components are the same.

In this case $b_{12} = b_1$ and $a_{12} = a_1$ and the value of Δ_p is also of the same order as the deviation of the pressure in the investigation of the law of BOYLE, and varies also inversely as the square of the volume. Also for Δ_p there is a temperature, at which it is 0, just as is the case with $p - p^1$, if p^1 is the pressure according to the law of BOYLE and p the observed pressure. Below this temperature Δ_p is negative, above it, on the contrary it is positive. The agreement of the course of Δ_p with that of $p - p^1$, when the volume gradually decreases, is nearly perfect.

When the volume is continually decreasing, a maximum value for $p - p^1$ is found in those cases, in which this difference is negative for a large volume, and in this case a volume may be

reached, at which $p - p'$ has descended again to 0, reversing its sign when the volume is still more diminished. The same holds true for Δ_p ¹⁾.

In order to show this, the approximative value of equation (5) does not suffice. A more accurate value of Δ_p is:

$$\Delta_p = 2x(1-x) \left\{ b_{12} (1+a_x) (1-b_x) \frac{(v-f) (1+\alpha t)}{(v-b_x) [v-b_1(1-x)] (v-b_2x)} - \frac{a_{12}}{v^2} \right\},$$

if we represent by f the quantity

$$(b_1 + b_2) x (1-x) + \frac{[b_2x - b_1(1-x)]^2}{2 b_{12}}.$$

If we calculate $p - p'$, we find

$$p - p' = \frac{(1+a) (1-b) b (1+\alpha t)}{v (v-b)} - \frac{a}{v^2}.$$

If $a > (1+a) (1-b) b (1+\alpha t)$, $p - p'$ is negative, when the volume is large, but positive when

$$v < \frac{b}{1 - \frac{b}{a} (1+a) (1-b) (1-\alpha t)}$$

Δ_p has, it is true, a more intricate form than $p - p'$. But this is more in appearance than in reality.

If $a_{12} > b_{12} (1+a_x) (1-b_x) (1+\alpha t)$, Δ_p is negative, when the volume is large, but positive when v does not differ much from b_x . It has in reality no significance that the sign would be again reversed for other values of v also, e. g. between b_x and $b_1(1-x)$, because in a volume smaller than b_x the mixture could not take place.

A series of values for Δ_p , which Mr. KUENEN gives from his observations on mixtures of CO_2 and CH_3Cl and which we reproduce here, may be used to test the properties of Δ_p pointed out here.

¹⁾ These results have already been deduced by MARGULES from the observations of ANDREWS. Wien Sitz. Ber. 1889, Band XCVIII, Seite 885. See also B. GALITZINE. Wied. Ann. Band XLI.

Deviation from the law of DALTON.

Vol.	T 433.0		403.3		373.0		343.0	
	<i>p.</i>	Δ	<i>p.</i>	Δ	<i>p.</i>	Δ	<i>p.</i>	Δ
0 015	$\frac{3}{4}$	74.43 -5.9	62.8	-6.8	50.0	-8.9 ^s	35.7	-11.7
	$\frac{1}{2}$	81.14 -9.1	71.3	-9.9	60.0	-11.9	48.8	-13.2
	$\frac{1}{4}$	—	78.5	-7.4	68.3	-8.8	57.7	-10.4
0 030	$\frac{3}{4}$	44.5 -1.6	39.7	-2.0	34.5	-2.6	28.93	-3.35
	$\frac{1}{2}$	46.2 -2.9	41.8	-3.2	37.0	-3.7	32.31	-4.10
	$\frac{1}{4}$	—	43.9	-2.1	39.5	-2.5	34.94	-2.96
0 045	$\frac{3}{4}$	31.58 -0.78	28.59	-0.96	25.46	-1.22	22.13	-1.55
	$\frac{1}{2}$	32.30 -1.38	29.50	-1.52	26.55	-1.78	23.62	-1.95
	$\frac{1}{4}$	—	30.50	-0.93	27.69	-1.16	24.83	-1.36
0 060	$\frac{3}{4}$	24.46 -0.46	22.30	-0.56	20.06	-0.70	17.72	-0.90
	$\frac{1}{2}$	24.83 -0.81	22.79	-0.89	20.66	-1.04	18.55	-1.14
	$\frac{1}{4}$	—	23.35	-0.55	21.30	-0.66	19.23	-0.78

$$\Delta = p - (p_1 + p_2).$$

In the approximative equation (5) the value of Δ_p does not vary, when we interchange x and $1 - x$. In the more accurate equation this is no longer perfectly true, but the asymmetry is only perceptible for very small volumes.

Mr. KUENEN finds, at $T = 403^{\circ},3$

if $v = 0,06$	and $x = \frac{1}{4}$	$\Delta_p = -0,55$ Atm.
	$x = \frac{3}{4}$	$\Delta_p = -0,56$ »
if $v = 0,045$	and $x = \frac{1}{4}$	$\Delta_p = -0,93$ »
	$x = \frac{3}{4}$	$\Delta_p = -0,96$ »
if $v = 0,03$	and $x = \frac{1}{4}$	$\Delta_p = -2,1$ »
	$x = \frac{3}{4}$	$\Delta_p = -2,0$ »
if $v = 0,015$	and $x = \frac{1}{4}$	$\Delta_p = -7,4$ »
	$x = \frac{3}{4}$	$\Delta_p = -6,8$ »

At lower temperatures the agreement is less perfect than is the case for the three first mentioned volumes in the above table; but

in general more perfect than in the case of the last volume. The rule that Δ_p is proportional to $x(1-x)$ involves that for $x = \frac{1}{2}$ a value must be found that is $\frac{1}{3}$ times larger than that for $x = \frac{1}{4}$ or $\frac{3}{4}$. From Mr. KUENEN's value a greater proportion is generally found for it. At $T = 403^{\circ},3$ the proportion found in the case of the four before-mentioned volumes is $\frac{0,89}{0,555}$, $\frac{1,52}{0,954}$, $\frac{3,2}{2,05}$ and $\frac{9,9}{7,1}$; so values varying between 1,6 and 1,4.

At $T = 373^{\circ}$, the values found were $\frac{11,9}{8,875}$, $\frac{3,7}{2,55}$, $\frac{1,78}{1,19}$ and $\frac{1,04}{0,68}$; so they are varying between 1,5 and 1,35.

But at $T = 343^{\circ}$, we may consider the proportions found as equal to $\frac{1}{3}$.

According to the remarks, deduced from equation (6), the dependence of Δ_p on the volume must be expected less great than proportional to the squares of the density. This may be considered as being confirmed by the values, given by Mr. KUENEN. So Mr. KUENEN finds, if $v = 0,6$ $\Delta_p = 0,81$ and if $v = 0,03$ $\Delta_p = 2,9$ and if $v = 0,045$ $\Delta_p = 1,38$ etc.

The dependence on the temperature, for which according to equation (5)

$$(-\Delta_p)_{T_2} - (-\Delta_p)_{T_1} = 2 \frac{\alpha b_{12} (T_1 - T_2)}{v^2} x(1-x)$$

would hold, and according to which formula for the same value of x and v the differences of the observed values of Δ_p would be proportional to the differences of temperature, is not confirmed by KUENEN's figures. But in all this we must not overlook the fact that the Δ_p 's are already differences of observed quantities and not the observed quantities themselves, while $\{(-\Delta_p)_{T_2} - (-\Delta_p)_{T_1}\}$ are again differences from these differences. It is therefore to be regretted, that there are so few observations, which may be used for this investigation, and specially that Mr. AMAGAT has not been able to continue his investigation of the mixture CO_2 and N_2 ¹⁾.

If we try to calculate a value for α_{12} from the observed value of Δ_p , e. g. from the observation with $v = 0,06$, $x = \frac{3}{4}$, $T = 373$, which gives $\Delta_p = -0,7$, this can of course, only be done by

¹⁾ C. R. Acad. des Sciences. 11 Juillet 1898.

assuming a value for $b_{1,2}$. If we assume 0,0024, a value which lies between $b_1 = 0,0020$ and $b_2 = 0,0029$, while an error in this value will have comparatively little influence on the value of $a_{1,2}$, we find

$$a_{1,2} = 0,7 \times 0,0036 \times \frac{2}{3} + 0,00328 = 0,010 .$$

From Mr. KUENEN's values for the variation of pressure ($-\Delta_p$), we find the following value for $a_{1,2}$, which has been calculated by means of the approximative equation.

$T = 343$	$v = 0,06$	$v = 0,045$	$v = 0,03$
$x = \frac{1}{4}$	0,0105	0,0117	0,0101
$x = \frac{1}{2}$	0,0112	0,0109	0,0104
$x = \frac{3}{4}$	0,0116	0,0114	0,0110
$T = 373$			
$x = \frac{1}{4}$	0,0096	0,01086	0,0100
$x = \frac{1}{2}$	0,0096	0,0104	0,0097
$x = \frac{3}{4}$	0,0093	0,0099	0,0095
$T = 403,3$			
$x = \frac{1}{4}$	0,0088	0,0086	0,0086
$x = \frac{1}{2}$	0,0099	0,0097	0,0093
$x = \frac{3}{4}$	0,0089	0,0087	0,0084

For the calculation of $a_{1,2}$ from the results at $v = 0,015$, given by Mr. KUENEN, the approximative equation is no longer sufficiently accurate.

For these values of $a_{1,2}$ we see the same not yet explained phenomenon, generally observed for the values of a_1 and a_2 , namely that they increase at lower temperatures. The advantage of the equation which has served to calculate them, is that it is independent of possible changes, which might have occurred in the values of a_1 and a_2 through change of temperature. So the accurate determination of $-\Delta_p$ is as yet the best means of supplying at least one relation between $a_{1,2}$ and $b_{1,2}$. The variability of $a_{1,2}$ with the temperature, would therefore be no reason to doubt of the values found for $a_{1,2}$. There is, however, another circumstance, which makes

me doubt; and that is, that according to the results obtained by me formerly (Verslag Kon. Akad. 27 Nov. 1897) $a_1 + a_2 - 2 a_{1,2}$ would be negative for CO_2 and $\text{CH}_3 \text{Cl}$ or $a_{1,2} > \frac{a_1 + a_2}{2}$, and this would require a greater value for $a_{1,2}$ than would be found from Mr. KUENEN's values for $-\Delta_p$. In order that $a_{1,2} > \frac{a_1 + a_2}{2}$ should hold good, e. g. at $T = 343^\circ$, $a_{1,2}$ would have to be greater than 0.00126, while from the calculation of $-\Delta_p$, $a_{1,2}$ is found to be at the utmost 0,0116. That from Mr. KUENEN's observations $a_{1,2} < \frac{a_1 + a_2}{2}$ follows, is confirmed by the observation, that mixing of CO_2 and $\text{CH}_3 \text{Cl}$ gives increase of volume.

If this is really the case, it would prove that I ought to have expressed myself with still greater reserve than I did in my: "Approximative rule for the course of the plait-curve of a mixture" ¹⁾. Though I have drawn the attention to the fact, that the real plait-curve will deviate from the curves drawn, yet I had thought, that the deviations would not be so great, as to make the different types no longer to be distinguished. Yet so great a deviation really occurred in this case.

If we look back on the two rules discussed here: $\Delta_v = 0$ and $\Delta_p = 0$, we are induced to qualify the first rule as an approximative law. Throughout the course of the isotherme, from an infinite volume down to the smallest possible volume of the substance, there may be deviation, but the deviation remains within finite limits. The second rule holds perfectly good for infinite rarefaction, but it would be utterly impossible to apply it also to liquid volumes. Such a law may be qualified as a *loi-limite*. Considered from this point of view, the law of BOYLE too is not an approximative law, but only a *loi-limite*.

Chemistry. — Prof. VAN BEMMELEN reads a paper of Dr. F. A.

H. SCHREINEMAKERS on: „*Equilibriums in systems of three components. Change of the mixing-temperature of binary mixtures by the addition of a third component.*”

Among the different systems composed of the components A , B and C we suppose the case, that in two of the binary systems f. i. $A-B$ and $A-C$ two liquid phases can appear, but not in the system $B-C$. An example of this we find f. i. in the system formed of:

¹⁾ Verslag Kon. Akad. Nov. 1897.