

Citation:

Kohnstamm, Ph., On vapour-pressure lines of binary system with widely divergent values of the vapour-pressures of the components, in:
KNAW, Proceedings, 15 I, 1912, 1912, pp. 96-113

be possible to characterize anthropologically the different races of men by indicating the differences in the character and the intensity of the processes of transformation.

And if the vertebral column should be chosen for such an investigation, an opinion about the degree of organisation attained would certainly not rest on too narrow a basis, as the vertebral column is in contact with many organs that surround it, and actively or passively participate in its transformation.

Physics. — “*On vapour-pressure lines of binary systems with widely divergent values of the vapour-pressures of the components.*”
(In connection with experiments of Mr. KATZ). By Prof. PH. KOHNSTAMM. (Communicated by Prof. VAN DER WAALS).

§ 1. *General character of the vapour-pressure lines derived from the differential quotients.* The theory of the p, x -lines of binary mixtures was developed by VAN DER WAALS in Verslagen Kon. Ak. v. Wet. (3) 8 p. 409 and These Proc. III p. 163 (See also Cont. II p. 120 et seq.) on the supposition that the quantity μ'_{x_1} occurring there may

be represented by $-\frac{d\frac{a_x}{b_x}}{dx}$, and so is only dependent on the critical temperature of the mixture taken as homogeneous. VAN DER WAALS showed later on that a further approximation may be obtained by the introduction of the quantity p_c , the vapour-pressure of the mixture taken as homogeneous. Then:

$$\mu'_{x_1} = \frac{dp_c}{dx}$$

while:

$$-l \frac{p_c}{p_k} = f\left(\frac{T_k}{T} - 1\right).$$

In a recently published paper¹⁾ I showed that a number of particularities of the vapour-pressure lines follow from these equations. Since then Mr. KATZ's investigations²⁾ and the results communicated

obtained was $\frac{3}{2}R$. It was mentioned during the discussion at the Conseil SOLVAY, Nov. 1911 that Professor KAMERLINGH ONNES and myself had undertaken an investigation of γ_{Λ^0} by KUNDT's method for hydrogen at temperatures down to that of liquid hydrogen, but this investigation has not yet been completed.

¹⁾ Zschr. f. phys. Ch. 75 p. 527.

²⁾ These Proc. Vol. XIII p. 958.

in a paper by Mr. TIMMERMANS and myself ³⁾ have drawn my attention to some other conclusions from the formulae derived l. c. particularly with regard to systems the components of which differ much in vapour pressure. I shall deal with this in the following pages.

Let us first give the formulae which we shall want. A p, x_1 -line will ascend or descend with increase of x_1 according as $\frac{dp_c}{dx}$ is positive or negative. Let us call the substance with the larger value of b the second component ($x = 1$), and put:

$$b_2 = nb_1 \quad a_2 = k^2 a_1 \quad a_{1,2}^2 = l^2 a_1 a_2$$

$$\frac{b_{1,2} - b_1}{b_1} = g \quad \frac{b_2 - b_{1,2}}{b_2} = h \quad m_1 = \frac{T}{T_{k_1}} \quad m_2 = \frac{T}{T_{k_2}}$$

then

$$\left(\frac{dlp_c}{dx}\right)_{x=0} = -\frac{2f}{m_1}(kl-1-g) + 2(kl-1-2g) \quad . \quad . \quad (1)$$

$$\left(\frac{dlp_c}{dx}\right)_{x=1} = -\frac{2f}{m_2}\left(1-h-\frac{l}{k}\right) + 2\left(1-2h-\frac{l}{k}\right) \quad . \quad . \quad (2)$$

The question whether the p, x_1 -line is concave or convex downward at the border, depends on the sign of $\frac{d^2lp_c}{dx^2}$ in this way that $\frac{d^2p}{dx_1^2}$ will have the same sign as $\frac{d^2lp_c}{dx^2}$ for a line that ascends from the border, or if it descends so long as $x_2 > \frac{1}{2}x_1$ resp. $1-x_2 > \frac{1}{2}(1-x_1)$. If $x_2 < \frac{1}{2}x_1$ resp. $1-x_2 < \frac{1}{2}(1-x_1)$, the vapour-pressure line is convex when $\frac{d^2lp_c}{dx^2}$ is negative, and concave when $\frac{d^2lp_c}{dx^2}$ is positive. Also the stability or unstability of the liquid phases depends on this quantity. We are, namely, on the verge of stability when:

$$1 + x_1(1-x_1)\frac{d^2lp_c}{dx^2} = 0$$

So we are certain to be in the stable region everywhere where $\frac{d^2lp_c}{dx^2}$ is positive; if on the other hand $\frac{d^2lp_c}{dx^2}$ has a large negative value, then (for not too small value of $x(1-x)$) we shall be in the unstable region, i.e. unmixing will take place. Expressed in the quantities defined just now we find for the required value at the two borders:

³⁾ These Proc. Vol. XIII p. 865.

$$\left(\frac{d^2lp_c}{dx^2}\right)_{x=0} = -\frac{f}{m_1} \left\{ 2 + 8g^2 + 8g - \frac{d^2b}{b_1 dx^2} + 2k^2 - lk(4 + 8g) \right\} +$$

$$+ 4lk - 4l^2k^2 + 8g^2 + 2k^2 - 2 - 2 \frac{d^2b}{b_1 dx^2} \dots \dots \dots (3)$$

$$\left(\frac{d^2lp_c}{dx^2}\right)_{x=1} = -\frac{f}{m_2} \left\{ 2 + 8h^2 - 8h - \frac{d^2b}{b_2 dx^2} + \frac{2}{k^2} - \frac{l}{k}(4 - 8h) \right\} +$$

$$+ \frac{4l}{k} - \frac{4l^2}{k^2} + 8h^2 + \frac{2}{k^2} - 2 - 2 \frac{d^2b}{b_2 dx^2} \dots \dots \dots (4)$$

Now we arrive at a surprising result when we apply this formula to systems whose molecules differ much in size. If e.g. b_2 is = 100 b_1 , then $\frac{b_2}{b_1}$ becomes = 22.4 according to the well-known formula of LORENTZ; so $g = 21,4$ and $h = 0.776$. If we further suppose $k = 20$, so that $T_{k_2} = 4T_{k_1}$, $\rho_{k_2} = \frac{1}{25} \rho_{k_1}$, and $m_2 = \frac{1}{4} m_1$, equations (1) and (2) become:

$$\left(\frac{dlp_c}{dx}\right)_{x=0} = -\frac{2f}{m_1} (kl - 22.4) + 2(kl - 43.8) \dots \dots \dots (1a)$$

$$\left(\frac{dlp_c}{dx}\right)_{x=1} = -\frac{2f}{m_2} \left(0.224 - \frac{l}{k}\right) - 2\left(0.552 + \frac{l}{k}\right) \dots \dots \dots (2a)$$

So we find $l = 1.04$ for the value of l which makes $\left(\frac{dlp_c}{dx}\right)_{x=0}$ equal to 0 for a temperature $m_1 = \frac{1}{2}$ and the supposition $f = 7$; for smaller values of l $\left(\frac{dlp_c}{dx}\right)_{x=0}$ is then positive at this temperature, for larger values negative. Equation (2a) shows further that for values of $l < 4$ the p, x -line ends descending for the second component. So $\frac{dp}{dx}$ has the same sign on both sides for $l = 1.05$. But between a region of non-miscibility will be found. For with the values mentioned equation (3) passes into:

$$\left(\frac{d^2lp_c}{dx^2}\right)_{x=0} = -14 \{ 4525 - 3504 l \} + 80 l - 1600 l^2 + 4237 \dots \dots \dots (3a)$$

With a value of l in the neighbourhood of 1 the lefthand member becomes of the order 10^{-1} ; so the curve is at first concave down-

ward, but already for a value of x of the order 0.0001 unstable states are reached. On the other hand equation (4) passes into:

$$\left(\frac{d^2lp_c}{dx^2}\right)_{x=1} = -56\{-0.507 + 0.1104l\} + 0.2l - 0.01l^2 + 0.581 \quad (4a)$$

and so this value becomes (with l about 1) of the order +20. So on the righthand side the p, x -line will be concave downward, and we shall have to get very far from the border before meeting with a region of unmixing.

If we put $b_2 = 1000b$ instead of $b_2 = 100b$, we get the equations:

$$\left(\frac{dlp_c}{dx}\right)_{x=0} = -\frac{2f}{m_1}(kl-166) + 2(kl-331) \quad \dots \quad (1b)$$

$$\left(\frac{dlp_c}{dx}\right)_{x=1} = -\frac{2f}{m_2}\left(0.166 - \frac{l}{k}\right) - 2\left(0.668 + \frac{l}{k}\right) \quad \dots \quad (2b)$$

$$\left(\frac{d^2lp_c}{dx^2}\right)_{x=0} = -\frac{f}{m_1}(217800 + 2k^2 - 1324lk) + 4lk - 4l^2k^2 + 2k^2 + 215000. \quad (3b)$$

$$\left(\frac{d^2lp_c}{dx^2}\right)_{x=1} = -\frac{f}{m_2}\left\{0.45 + \frac{2}{k^2} + 2.67\frac{l}{k}\right\} + 4\frac{l}{k} - 4\frac{l^2}{k^2} + \frac{2}{k^2} + 0.89. \quad (4b)$$

and if we now suppose $k = 63$, so that again $T_{k_2} = 4T_{k_1}$, all our conclusions remain of force, and the peculiarities which we pointed out (insolubility on the side of the small molecule etc.) are still more pronounced. And also values of $\frac{b_2}{b_1}$ considerably smaller than 100 still yield the same results.

Summarising them we must say that for the systems considered with a value of about $l = 1$ the p, x_1 -line begins at the side of the small molecules slightly ascending concave downward, that, however, already with exceedingly small concentration a region of unmixing is reached, which lies very asymmetrically in the lefthand side of the figure, and that the p, x_1 -line after having left this region of unmixing, continually descending and finally convex downward reaches the line for the second component.

§ 2. *The experimental results of Mr. KATZ.*

Now it is very remarkable, that this course entirely agrees with that of the vapour-pressure lines determined by Mr. KATZ for the majority of "swelling" bodies, those with limited imbibition power. Here too on the side of water an exceedingly small line (generally so small that it cannot even be determined experimentally) is found for the solution of the swelling substance in water, and on the other

side of this very asymmetrically situated region of unmixing just such a line as was described just now.

No doubt we are not justified in concluding from this agreement that the substances to which Mr. KATZ's figures refer, satisfy all the conditions that we had to put in order to be able to arrive at our conclusions; to apply the law of corresponding states to casein and haemoglobin must certainly be called a very bold generalisation, even apart from the other suppositions on which our formulae are founded. Still I thought this agreement striking enough to justify a closer investigation for the solution of the question in how far the experimental particularities found by Mr. KATZ would have to be expected in virtue of the simplest theory for a mixture of two perfectly normal components, when the ratio between the size of the molecules, b_2/b_1 , becomes very great. Mr. KATZ was so kind as to summarize the results of his measurements for me as follows:

1. If we draw the water-vapour tension of the swelling substance as function of the molecular percentage (VAN DER WAALS'S p, x -curve), we get a line which (cf. fig. 1, which represents the line for inulin in proper proportions¹⁾):

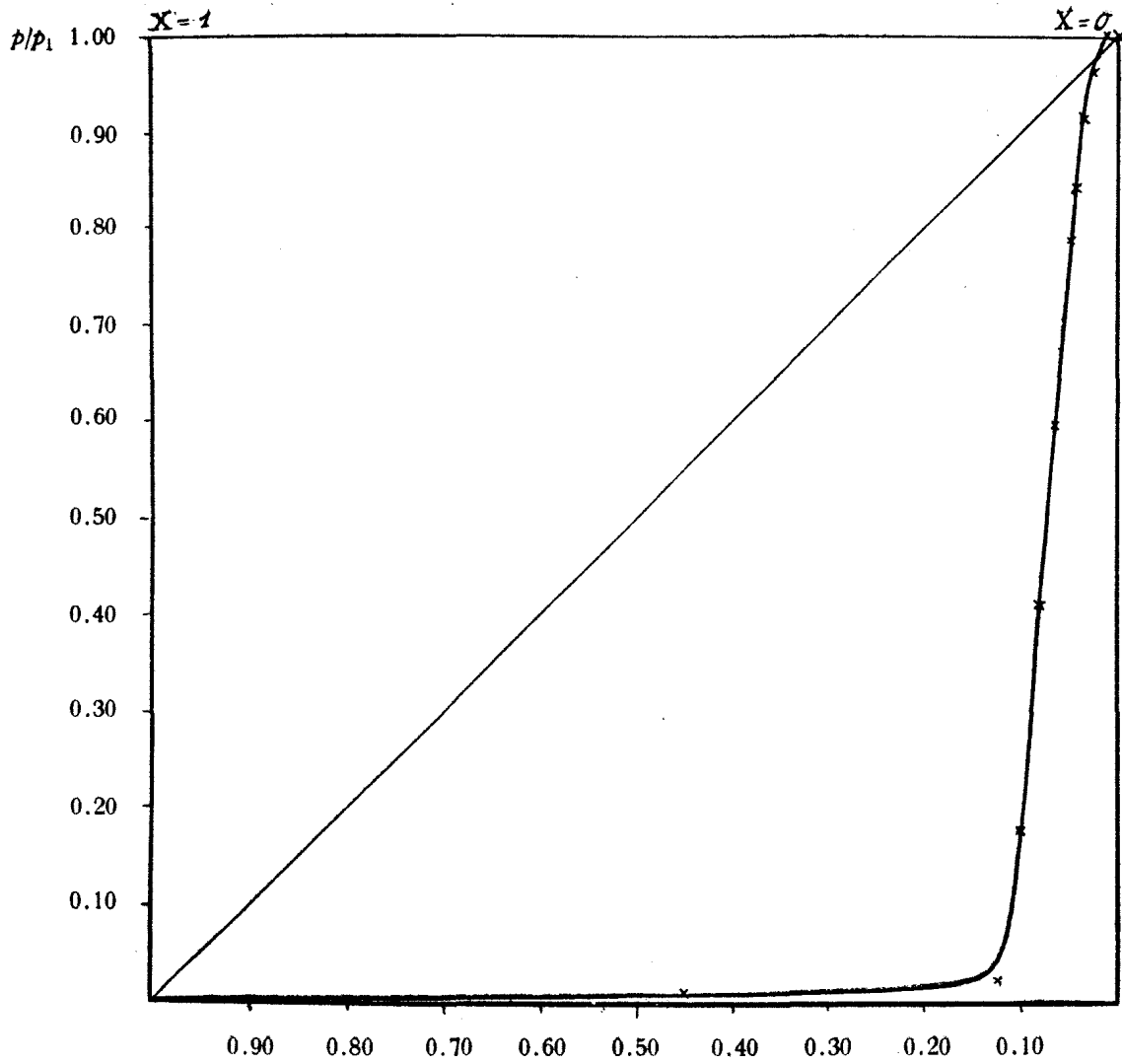
a. lies for not very small values of x (pure water) under the value which the vapour tension would have if VAN 'T HOFF'S law $p = p_1 (1 - x)$ held for all concentrations.

b. begins almost horizontally for x about 1, and does not begin to rise abruptly until past $x = 1/2$.

c. turns its convex side downward for x about 1, then gets a point of inflection (for smaller x), and finally turns its concave side downward for very small value of x .

d. presents an excentrically situated region of unmixing for very small x , so excentrically as has not been observed anywhere else as yet. Pretty well pure water $x = 0.00001$ coexists with $x = 0.002$ or 0.006. The lines for casein (albumen) and inulin (polysaccharide) may serve as an example. For both substances the minimum molecular weights have been taken (casein = 4000, inulin = 1800) in all these calculations. If higher values are used, the above-mentioned properties are even more pronounced.

¹⁾ In this figure of Mr. KATZ the component with the smaller molecule (water), has, however, been thought on the right hand, whereas in the text it has been assumed, where the contrary has not been expressly stated, that the molecular weight increases from left to right.



<i>Inulin</i>		<i>Casein</i>	
<i>x</i>	<i>p/p₁</i>	<i>x</i>	<i>p/p₁</i>
0.007	1	0.004	1
0.024	0.962	0.014	0.962
0.034	0.914	0.018	0.917
0.041 ^s	0.853	0.021	0.853
0.049	0.788	0.024	0.788
0.063	0.596	0.031	0.596
0.079	0.410	0.041	0.410
0.100	0.176	0.062	0.176
0.125	0.022	0.178	0.022
0.45	0.01	0.29	0.01

2. The heat of mixing (generation of heat when 1 gr. of dry substance absorbs i gr. of water) is *strongly positive*, and is very well rendered by a hyperbola:

$$W = \frac{Ai}{B+i}.$$

3. The volume contraction c by the mixing (in cm^3 . when 1 gr. of dry substance absorbs i gr. of water) is strongly positive, and follows a line which closely resembles a hyperbola.

4. If we compute $\frac{c}{i}$ for small i 's (*lim.* $i = 0$), we find that this quotient is of the same order of magnitude for the most different swelling substances viz. between 10 and 25×10^{-4} , and that this quotient is of the same order of magnitude as for mixtures of sulphuric acid, phosphoric acid, and glycerin with water.

The analogy of the latter substances with the swelling substances is the more striking, because they present all the properties described under 1 (a , b , and c), under 2 and under 3 exactly as for the swelling substances. There is only one difference: they are miscible in all proportions, whereas some swelling bodies exhibit the characteristically excentric region of unmixing described under 1 d . Other swelling substances have an unlimited power of imbibition, but behave for the rest as described above. So this difference will not be essential.

Limited or unlimited miscibility, it seems, may depend on small factors, as closely allied substances may belong to different types. Further quantitatively there exists this difference that for the swelling substances the vapour pressure line begins to ascend much less steeply, the lines for the volume contraction and for the heat of mixing on the other hand much more steeply than in the usual case. We may express the latter also in this way that for swelling substances the quantity b in the equation of the hyperbola for the volume contraction $c = \frac{ai}{b+i}$ is remarkably small, just as the quantity B in the formula of the heat of mixing.

§ 3. *The integral equation of the vapour pressure line.* Let us begin our investigation with the vapour pressure lines. To investigate whether they agree with the experimentally determined ones also with respect to the peculiarities not yet treated in § 1, it is easier to use the integral relation between p and x instead of the differential

relation used there. We find for this ¹⁾, when the vapour pressure of the second component may be neglected which is certainly the case here:

$$p = p_1 (1 - x) e^{-\left\{ \log p_1 - \left(\log p_c - x \frac{d \log p_c}{dx} \right) \right\}} = p_1 (1 - x) y$$

So everywhere, where the exponent of e is positive, the vapour pressure line lies below the straight line which would represent the vapour pressure when the law of VAN 'T HOFF held for all concentrations. When this exponent is negative the real vapour pressure lies below this straight line. If we now apply VAN DER WAALS'S formula for p_c , and if we assume as above $b_2 = 100 b_1$, $b_{12} = 22,4 b_1$, $a_2 = 100 a_1$, $a_{12} = 20 a_1$, we get: $y = 10^{-4}$ for $x = 0.5$ and $y = 0.25$ for $x = 0.2$. So we really see the same course as given under a, b , and c). But on these suppositions the region of unmixing is not so narrow as is required in d . For y becomes $= 2.5$ for $x = 0.1$, and as for absolutely stable states the vapour pressure in the mixture cannot be greater than the sum of the vapour pressures of the components ³⁾, we must be in the region of unmixing already here.

If, however, we take $a_2 = 1000 a_1$ and $a_{12} = 25 a_1$, we get $y = 0.1$ for $x = 0.1$ and $y = 1.22$ for $x = 0.01$. If $\frac{b_2}{b_1}$ is still greater than 100, we may even find much narrower regions of unmixing: Thus e.g. $y = 0.95$ for $x = 0.01$ with $\frac{b_2}{b_1} = 1000$ and the corresponding $\frac{b_{12}}{b_1} = 166$, while a_2 is put $= 10000 a_1$ and $a_{12} = 105 a_1$. That there exists still a region of unmixing, however, appears from the value $y = 1,04$ for $x = 0.001$. If a_{12} is taken somewhat greater still, the region of unmixing disappears.

¹⁾ Compare the second volume of the Lehrbuch der Thermodynamik, which will shortly appear, p. 178.

²⁾ That a point of inflection must occur follows from the fact that the vapour-pressure line is turned convex downward at first, and then concave downward in the region of unmixing, as it has a maximum there. No general rule can, however, be derived as to whether this point of inflection will still lie in the absolutely stable, or in the metastable region. In virtue of the very slight breadth of the plait, however, which leads us to expect that we are already quite close to the maximum of the vapour-pressure line on the verge of unmixing it may be considered as exceedingly probable that the point of inflection still falls in the absolutely stable region.

³⁾ Cf. the footnote p. 111.

We shall presently return to these results, but we may now already state that with suitable values of a_{12} and a_1 really vapour pressure lines are obtained which perfectly agree in type with the experimentally determined ones. It deserves notice that this result is in the first place the consequence of the great value which $\frac{d^2b}{dx^2}$ assumes according to our suppositions (great value of $\frac{b_2}{b_1}$ and validity of LORENTZ's formula for b_{12}). If we take b as linear function of x , as is often permissible for small values of $\frac{b_2}{b_1}$ nothing remains of these results. The obtained vapour-pressure lines are namely characterised by this that μ''_x is strongly positive for values of x near 1, which leads to the strongly convex px -line, whereas near $x=0$ μ''_x is strongly negative, which circumstance gives rise to the region of unmixing. If, however, we take b as linearly dependent on x , change of sign of μ''_x becomes impossible¹⁾. This quantity must have the same sign throughout the whole breadth of the figure; then we can have unmixing with negative value of μ''_x , but then the vapour pressure line ends also concave downwards on the side of the slight vapour pressures. This is accompanied by an extension of the region of unmixing over the full width of the figure as in the case of mercury-water. When the vapour-pressure line ends concave downward, however, on the side of the small vapour pressures, μ''_x must be positive, and then unmixing is impossible. And this holds whatever values one may choose for a_2 and a_{12} . Only for very large values of $\frac{d^2b}{dx^2}$ as they follow from the formula of LORENTZ. for great values of $\frac{b_2}{b_1}$ a region of unmixing can occur in a px -line which is convex on the other side. *Whether* this region of unmixing then occurs, and how wide it will be, will depend on the a 's, and more particularly on the ratio of $\frac{a_{12}}{a_1}$. We have seen this already in the foregoing discussion, and we shall find confirmed in what follows that only a very small change of this quantity is required to make a mixture with an exceedingly narrow region of unmixing on the side of the small molecule pass into a system that is miscible over its full breadth. This is in accordance with Mr. KATZ's remark "limited or unlimited miscibility, it seems, may depend on small factors, as closely allied

¹⁾ Cont. II, p. 152.

substances may belong to different types". Of course it would be entirely premature now that we are still altogether ignorant about the causes that govern the value of the quantity $\frac{a_{12}}{a_1}$ even for the best known systems, to pronounce an opinion about the question why for some systems the value is such that a very narrow region of unmixing appears, whereas for others there exists complete miscibility. Even quite apart from the fact that it does indeed follow from what precedes and what follows that the experimental peculiarities found by Mr. KATZ can all appear for perfectly normal substances, but that it does not follow by any means, of course, that not all kinds of other circumstances might be found for the systems investigated by him, which do not affect the general character of the lines, but might have a very considerable influence on the numerical values of the quantities to be calculated. For this reason I have abstained from endeavours to find the numerical values of a 's and b 's, and have confined myself to the general course of the investigated lines.

§ 4. *The volume-contraction.* Further on we shall return to the vapour-pressure lines, but for a reason which will soon become clear, we shall first speak about the volume contraction. According to Mr. KATZ it may be represented by a hyperbola:

$$c = \frac{ai}{b+i}$$

in which c is the contraction in cm^3 when 1 gr. of dry substance absorbs i gr. of water. What does the theory of the normal mixtures teach us about this quantity? If we may assume that the temperature has been chosen so low that we may put the limiting volume b for the liquid volume, the increase of volume Δv in consequence of the mixing of $M_1(1-x)$ gr. of water and M_2x gr. of dry substance becomes:

$$\Delta v = b_x - b_1(1-x) - b_2x = -x(1-x)(b_1 + b_2 - 2b_{12}) \quad (5)$$

From this we must derive the relation between c and i . Now evidently:

$$c = -\frac{\Delta v}{M_2x}$$

follows from the definitions, c and Δv taken for the same concentration.

If we further mix 1 gr. of dry substance and i gr. of water resp. M_2 with M_1 i gr., the number of molecules are evidently in the ratio $1 : \frac{M_2}{M_1}i$ so:

$$x = \frac{1}{1 + \frac{M_2 i}{M_1}} = \frac{M_1}{M_1 + M_2 i} \quad \dots \quad (6)$$

and

$$1 - x = \frac{M_2 i}{M_1 + M_2 i}$$

So equation (5) becomes :

$$c = \frac{i}{M_1 + M_2 i} (b_1 + b_2 - 2b_{1,2})$$

so really a hyperbola.

Also the second above mentioned peculiarity of the c, i -lines that the quantity b in the equation of the hyperbola becomes much smaller than is usually the case, is found confirmed here. For $\frac{M_1}{M_2}$ is found for this quantity.

The heat of mixing. Mr. KATZ has already pointed out¹⁾, that the hyperbola found by him is in accordance with a formula given by VAN DER WAALS in the *Théorie Moléculaire*. But this formula was derived on the supposition of linear dependence of b on x ($b_1 + b_2 = 2b_{1,2}$) and we saw already that both the experimental vapour pressure and volume contraction lines and the theory exclude this supposition in our case. If we, however, again assume the supposition, on which the said formula of VAN DER WAALS is also founded, that viz. the potential energy of a mixture may be represented by $-\frac{a_x}{b_x}$, we find for the increase of the potential energy or the absorbed quantity of heat when $M_2 x$ gr. of dry substance is mixed with $M_1 (1-x)$ gr. of water :

$$A = \frac{x(1-x)}{b} \left\{ 2a_1 \frac{b_{1,2}}{b_1} + a_2 \frac{b_1}{b_2} - 2a_{1,2} - a_1 - x \left(\frac{a_2}{b_2} - \frac{a_1}{b_1} \right) (b_2 + b_1 - 2b_{1,2}) \right\} \quad (7)$$

Between A and the quantity W used by Mr. KATZ the relation $W = -\frac{A}{M_2 x}$ exists again, and of course, equation (6) holds again.

So it appears that we do not get a hyperbola for W , but a curve of higher degree than the second.

In how far this involves a deviation from the experimental data, we shall examine presently ; first we must see what conclusion may be derived from the limiting ratio $\frac{c}{W}$ for very small values of i .

¹⁾ l. c. p. 970.

determined by Mr. KATZ, so values of x which are nearly equal to 1. With such values of x the terms multiplied by $(b_2 + b_1 - 2b_{12})$ now predominate on the lefthand side; so we find for the required ratio:

$$\frac{A}{\Delta v} = \frac{\frac{a_2}{b_2} - \frac{a_1}{b_1}}{b_2}$$

If this expression is to be independent of the order of magnitude of b_2 , we must conclude that in general a increases proportionally with b^2 for increasing values of b , so that $\frac{a}{b^2}$ remains of the same order of magnitude.

Also with a proportional to b the coefficients $\frac{A}{\Delta v}$ would remain equal, they all being zero then. This supposition does not call for any further discussion, also because the critical temperature rapidly rises for all known bodies with great increase of b , whereas the critical pressure remains of the same order of magnitude.

§ 5. *Supposition that $\frac{a}{b^2}$ is of the same order of magnitude for the components.* So we should have to conclude from this that we have assumed the increase of a for certain increase of b too small in § 1 and 3. And now the question should be solved whether what was found above for the vapour-pressure line continues to hold also with the now supposed great increase of a . For this purpose I once more examined the course of the vapour-pressure line with the aid of the above formula, now on the suppositions $b_2 = 100 b_1$, $b_{12} = 22.4 b_1$, $a_2 = 10000 a_1$. For $a_{12} = 150$ we find then that the region of unmixing has quite disappeared; with $a_{12} = 140$ on the other hand we find $y = 1.03$ for $x = 0.01$. So if we take x slightly higher, we shall find exactly the required width of the region of unmixing already with $\frac{b_2}{b_1} = 100$. So all Mr. KATZ's results mentioned under 1, 3, and 4 can be derived from our theory.

So it finally remains the question in how far the result under 2 is incompatible with the simplest theory developed here. If we take the last mentioned example, viz. $b_2 = 100 b_1$, $b_{12} = 22.4 b_1$, $a_2 = 10000 a_1$ and $a_{12} = 140 a_1$, we find for the heat of mixing the expression:

$$A = - \frac{x(1-x)}{b_x} (136.2 + 5563.8x) \dots \dots \dots (7a)$$

This is in conflict with the hyperbolical line $W = \frac{Ai}{B+i}$, for this leads to an expression of the form :

$$A = -\frac{x(1-x)}{C+Dx} \dots \dots \dots (8)$$

For a course from $x=0$ to $x=1$ equations of these two types can certainly not perfectly accurately agree ; it is, however, the question in how far they deviate within the region in which the observations lie ($x=0.1$ to $x=0.4$). If now for $x=0.1, 0.2, 0.3, 0.4$ we calculate the value of the expression $\frac{b_x}{136.2 + 5563.8x}$, and if we divide the result by the value for $x=0.4$, we find :

0.7342, 0.8223, 0.9110 and 1.0000

these values do not ascend linearly, but they differ from the purely linearly ascending ones :

0.7336, 0.8223, 0.9110, 0.9997

everywhere less than 1‰, the experimental errors certainly amounting to a few percentages. So it is clear that the discrepancies which exist between a formula of the type (7) and of the type (8), are much too small in the considered region to allow of an experimental decision. We must conclude that a formula of type (7) represents the experimental data as well as a formula of type (8)¹⁾. Farther reaching conclusions are of course excluded, as we already remarked

¹⁾ Perhaps we may go still further and say that in the general case a formula as (7) represents the experimental relations *better* than (8). For according to the latter formula the total heat of mixing W and also the differential heat of mixing $\frac{dW}{di}$ must always retain the same sign, while on the other hand for certain values of the a 's and b 's a reversal of sign is possible according to formula (7). And this change of sign of $\frac{dW}{di}$, which can never take place for a hyperbolical formula, seems indeed to appear in reality in some cases e.g. for inulin, as appears from the subjoined table.

i	W in Cal.
0	0
0.052	11.8
0.095	16.7
0.116	19.0
0.223	22.4
0.293	23.0
1.05	21.8

It is also in connection with this deviation of the theoretically required formula

above, by the absence of accurate numerical values of all the a 's, b 's, and even the molecular weights.

So summarizing we must say that *all* the experimentally found particularities can appear exactly in the same way for mixtures of perfectly normal substances which behave according to the simplest theory.

§ 6. *Deviation from the law of VAN 'T HOFF even in case of extreme dilution.* There is another particularity in connection with the absence or presence of unmixing, to which it may be desirable to draw attention. I mean departures from the well-known vapour-pressure formula of VAN 'T HOFF for extreme dilutions

$$\frac{dp}{p dx_1} = -1.$$

This formula, which may be expressed geometrically by saying that the vapour-pressure line ¹⁾ in its limiting direction points to the opposite angle (direction AB in figure 3), is considered of general validity for systems whose components differ widely in volatility. And indeed if we understand by this latter condition that $\frac{x_2}{x_1} = 0$, at the limiting value,

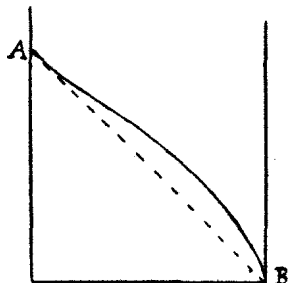


Fig. 3.

from a hyperbola that the property mentioned in the last lines of § 2 can be cal.

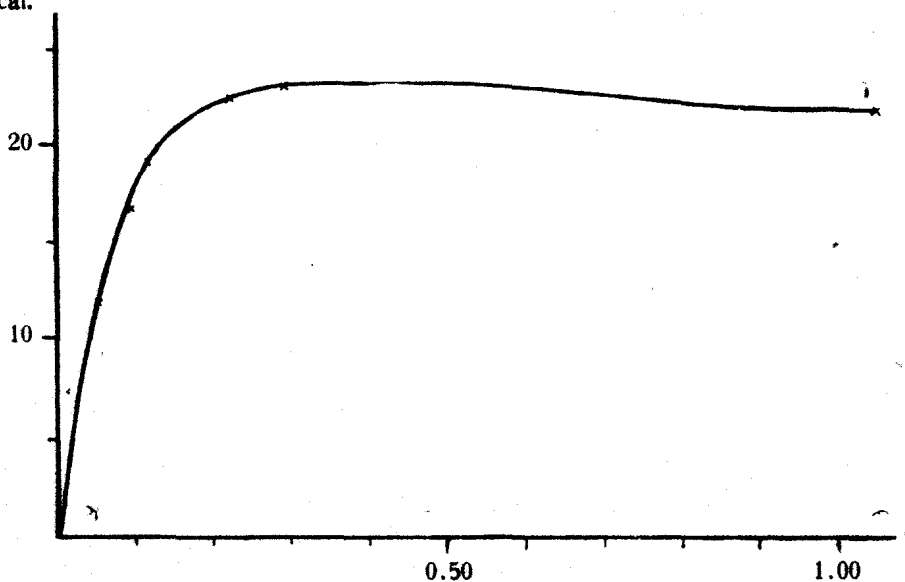


Fig. 2.

proved in a simple way for the volume contraction, but not for the heat of mixing.

¹⁾ Of course the *total* vapour-pressure line is meant here. For the partial vapour

i. e. that the ratio of the concentration of the second component in the vapour and in the liquid is very small, this rule can be perfectly rigorously derived for the limiting value purely thermodynamically in the wellknown way. Purely thermodynamically, because we have then only to do with the logarithmic part of the thermodynamic functions, and need not know anything more about the system. But this definition of "difference in volatility" is not the only possible one, and not the only one that naturally suggests itself. We might as well, perhaps better, understand by this idea, that one pure component has a very much lower vapour-pressure than the other at a definite temperature. And these two definitions by no means always coincide. Let us e. g. take a system for which the equations 1—4 hold. On the supposition $f=7$ and $T_{k_2}=4T_{k_1}$ it follows that the quantity p_2/p_1 is of the order 10^{-18} at a temperature of $1/2 T_{k_1}$. So there seems, indeed, to be every reason to say that the second component is much less volatile than the first. Yet by no means $\lim. \frac{x_2}{x_1} = 0$. On the contrary, if we put $l=1$, it follows from the above that the p_1x_1 -line begins ascending, so $x_2 > x_1$; in the beginning the second component is present in the vapour in greater quantity than in the liquid, and VAN 'T HOFF's law by no means holds any longer even for the extremest dilutions. Exactly the same thing applies for other values of $\frac{b_2}{b_1}$. So we must supplement the condition for the validity of VAN 'T HOFF's law also for the extremest dilutions as follows, that the components differ greatly in vapour-pressure, and that *there be no region of unmixing in the neighbourhood*. For if this were not the case we should already soon get a vapour in which the partial pressure of the second component would be greater than the total pressure of the component at the chosen temperature, and this is not possible for absolutely stable states¹⁾. So where the rule of VAN 'T HOFF does not hold with great difference in vapour pressure, this will be in the closest connection with this

pressure lines on the side of their component it *always* holds that they point to the opposite angle with their initial direction, as immediately follows by differentiation of the equation on p. 103.

1) We used this thesis already above to conclude to the existence of unmixing. It may be proved as follows. It follows from the differential equations of the two partial vapour-pressure lines (Cont. II, p. 163) that they will possess a maximum or a minimum only on the borders of the stable and unstable region. So if there is no unmixing, the partial vapour-pressure line of the first component is always descending, that of the second always ascending. If there is a region of unmixing,

that the liquid phase becomes unstable and unmixing appears already at very slight concentrations. So we shall have to expect that VAN 'T HOFF'S law does hold for substances with unlimited imbibition power. And our formulae prove in harmony with this. As we namely saw it is required e.g. in the case $b_2 = 100 b_1$ and l not far from 1 that $\frac{a_2}{a_1}$ does not lie far below 35. Then, however, we find for $\frac{d\pi_c}{dx}$ about -380 , and so $\lim_{x_1} \frac{x_2}{x_1}$ of the order 10^{-150} . On the other hand for substances with limited imbibition power VAN 'T HOFF'S law may hold, but this is by no means necessary, or even probable, and we shall undoubtedly have to take this circumstance into account in attempts to derive the molecular weight of these substances from the properties of their solutions.

§ 7. *Other systems with great difference in vapour pressure of the components.* I already pointed out the possibility of such departures from VAN 'T HOFF'S rule in an earlier communication published in These Proceedings, mentioned in the beginning of this paper. What was said there, will have been made sufficiently clear by the foregoing discussion. So I shall only add a few calculations here for systems as the one discussed there (aniline or nitrobenzene with isopentane or hexane). These systems agree in so far with the systems discussed in the foregoing that there exists a very large difference in vapour pressure between the two components, though not nearly so great as in the cases examined by Mr. KATZ, where the second component nowhere shows a measurable vapour pressure. But for the rest the difference is great; whereas in the systems discussed up to now the ratio $\frac{b_2}{b_1}$ reaches very great values, the ratio here is not far from 1,

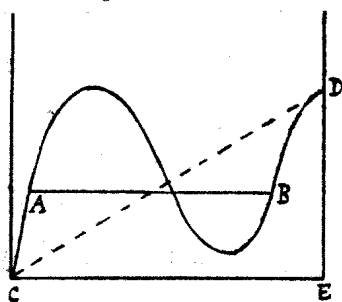


Fig. 4.

the partial vapour pressure of a component in the maximum can of course considerably rise above the value for the component itself (see fig. 4), but then this is always in the metastable or unstable region. For the partial vapour pressures must be the same in the two coexisting liquid phases. So the point A must lie on the same level as B, and as both between A and C, and between B and D the partial vapour pressure line can only be ascending, the partial vapour pressure must be smaller than DE throughout the region of the absolute stable mixtures.

and the substance with the greater vapour pressure has here even the greater molecule. Instead of in the righthand half of the general isobaric figure of VAN DER WAALS we are now in the lefthand part. Accordingly the unmixing found here must not be ascribed to the same cause, the high value of $\frac{b_2}{b_1}$, but (so long as we assume that we have not to do with abnormal systems, and with the systems mentioned we may do so to all probability) to a smaller value of l than generally occurs.

Let us take as an example the system aniline-hexane. b_1 is here 0,006113, $\frac{b_2}{b_1} = 0,007849$, so $b_2 = 1,284$, and $\frac{b_{12}}{b_1} = 1,136$ follows

from the formula of LORENTZ, so $h = 0,1153$, and $\frac{d^2b}{dx_2} = 0,017$.

Further $a_2 = 0,04928$ and $a_1 = 0,05282$, so $k = 0,9659$. If we substitute these values in the equations (2) and (4), we get:

$$\left(\frac{dlp_c}{dx}\right)_{x=1} = -\frac{2f}{m_2}(0,8847 - 1,035l) + 2(0,7694 - 1,035l). \quad (2c)$$

and

$$\left(\frac{d^2lp_c}{dx^2}\right)_{x=1} = -\frac{f}{m_2}(3,31 - 3,19l) + 4,14l - 4,29l^2 + 0,22. \quad (4c)$$

So we get $\left(\frac{d^2lp_c}{dx^2}\right) = -1,2$ for $l=1$ with $f=7$ and $m_2 = \frac{2}{3}$ (T_k hexane = 235° and the temperature of the upper mixing point = $68^\circ,9$). So we have not to expect unmixing, at least in the neighbourhood of the border, nor for greater concentrations, because $\frac{d^2lp_c}{dx^2}$ must at least be -4 to make $1 + x(1-x)\frac{d^2lp_c}{dx^2}$ negative. In agreement with the complete miscibility $\frac{dlp_c}{dx} = 2,62$, and so

$\frac{1-x_2}{1-x_1} = \frac{1}{10}$, and accordingly VAN 'T HOFF's law is fulfilled with pretty close approximation. As soon, however, as l becomes smaller, this is changed. For $l=0.9$ we get $\frac{dlp_c}{dx} = 0.66$, and so $\frac{1-x_2}{1-x_1} > \frac{1}{2}$, and the lowering of the vapour pressure of the second component by addition of the first will therefore amount to only half of what VAN 'T HOFF's rule would require. But as $\frac{d^2lp_c}{dx^2}$ has the

value — 4,08 already now, we see clearly that there is a region of unmixing at hand, and it will already have appeared with some decrease of temperature. For $l = 0,85$ finally $\frac{dlp_c}{dx}$ has already got the negative sign $\left(\frac{dlp_c}{dx} = -0,3\right)$ at the chosen temperature; so the vapour-pressure line does not descend from the side of the most volatile component, but ascends; there is a maximum vapour pressure. But then the value of $\frac{d^2lp_c}{dx^2}$ has fallen to almost —6, and we may expect that even for not very great concentrations unmixing will take place.

The calculations given here, will, I hope, have sufficiently elucidated the thesis which I pronounced in the cited paper that VAN 'T HOFF's rule need not hold, even as a limiting law, for systems whose components differ very much in vapour-pressure, when viz. these substances do not mix in all proportions, or at least a region of unmixing is close at hand. They also set forth again ¹⁾, how much greater the influence is of slight deviations in the value of l from unity, than in those of $\frac{b_2}{b_1}$ or $\frac{a_2}{a_1}$ and that such deviations are able to modify the course of phenomena entirely, so that certainly only a small part of all the possible cases is observed when we start from the supposition that the relation $l = 1$ should be always rigorously fulfilled. On the other hand they also show that in all the systems known to us, we have to do with values of l which are contained within narrow limits, and that we have not a single indication to think values possible for the value of l of the same order as undoubtedly occur for $\frac{b_2}{b_1}$ and also for $\frac{a_2}{a_1}$.

Mathematics. — “On looping coefficients.” By Dr. L. E. J. BROUWER.
(Communicated by Prof. D. J. KORTEWEG.)

(Communicated in the meeting of February 24, 1912).

Let us suppose in Sp_s two non-intersecting simple closed curves k_1 and k_2 , furnished with a sense of circuit. Then k_1 possesses with respect to k_2 a *looping coefficient* answering to the intuitive notion

¹⁾ Cf. the paper in the Zsch. f. phys. Ch. 75 cited in the beginning of this treatise.