

Citation:

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20. If $b_1 \begin{matrix} < \\ > \end{matrix} b_2 = b_3$, everything is much simpler. If the motion of light is given e.g. by a point P of the electric part of the wave-surface, which is not the point of intersection with the X -axis, we find that \mathfrak{D} lies in the plane through P and the X -axis, and touches therefore the meridian through P ; \mathfrak{B} lies in a plane parallel to the YZ -plane and so touches the parallel-ellipse. The reverse takes place when P lies on the magnetic part of the wave-surface. If however, P lies on the X -axis, i. e. in the point where the two parts of the wave-surface touch each other, the ray is the X -axis and the wave-front the YZ -plane, \mathfrak{D} and \mathfrak{B} being now indeterminate in the wave-front (they must, however, be doubly conjugate to each other).

If finally $b_1 = b_2 = b_3$, the two parts of the wave-surface coincide. In this case to every wave-front belongs one ray and vice versa, \mathfrak{D} and \mathfrak{B} being always indeterminate in the wave-front.

Physics. — Mr. PH. KOHNSTAMM and Mr. B. M. VAN DALFSEN:
"Vapour-tensions of mixtures of ether and chloroform".
 (Communicated by Prof. J. D. VAN DER WAALS).

For our determinations of vapour-tensions for mixtures of ether and chloroform we have made use of the dynamical method, i. e. we have determined the boiling-point at a certain pressure. As the methods of the determination of the vapour-tension, and specially the apparatus used by us, will be the subject of an extensive communication by one of us, which will appear before long, it seems superfluous to discuss these two points at length. Yet we will point out, specially to show how far our values are to be trusted, that we found it impossible to attain an accuracy greater than 1 m.m. mercury for dynamical determinations of vapour-tensions of mixtures. The values given are therefore at the utmost only in so far accurate; the errors of some of the observations can even become three or four times the amount. This is specially due to two sources of error, first the hydrostatic pressure of the boiling liquid, the influence of which was already pointed out by Dr. SMITS in the reports of these proceedings¹⁾, and secondly the superheating. We have tried to annul the disturbing

¹⁾ Volume II p. 475.

influence of superheating by several methods viz. those proposed by BECKMANN, SMITS and VON ZAWIDZKI, but none of them seemed to warrant greater accuracy. We refer to the fuller discussion which is to follow for the arguments to support this opinion.

The choice of the substances was determined by theoretical considerations. The following rules follow immediately from the formulae given by VAN DER WAALS¹⁾ for the pressure-curves of mixtures for normal substances if the relation of GALITZINE-BERTHELOT $a_{12} = \sqrt{a_1 a_2}$ holds good, viz. that a minimum pressure cannot occur and that near the border a curve ascending from the border must be concave seen from below. Now it is known of all substances which present a minimum of pressure, that they act chemically upon each other or are anormal in some other respect. Only the mixture ether-chloroform seems to be an exception. But as it is known that these substances may combine by the presence of KOH and that they therefore may exercise some chemical attraction on each other, this contradiction is only apparent. Nor does the literature afford more than one exception to the second rule, viz. the mixture of ether and chloroform examined by GUTHRIE, and for these substances we have most likely not to think of chemical action or anormality from other causes. But the experiments of GUTHRIE do not seem to be very accurate and his curve shows clearly that it was his aim to find so called molecular combinations. On account of the great importance of the matter, for the question is here whether the conduct of a mixture of two substances may be represented only from quantities, characteristic for each of these substances separately, or whether another quantity will appear indicating a mutual influence, it seemed advisable to us, to subject the mixture to a new investigation. We give our results in the table, where x is the molecular proportion of ether, and p the pressure. The temperature is 33°25. (See table p. 158).

These values show clearly that the combination of the two liquids chloroform and ether is not only contrary to the second of the rules given above, as might be expected from the course according to GUTHRIE, but also to the first. For it is evident that this curve shows a minimum, though it is quite on the border. So this curve is remarkable also in this respect, that it adds a second case where

$\left[\frac{dp}{dx_1} \right]_{x_1=0} = 0$ to the one found already by CUNAEUS; a possibility which was doubted from different sides.

¹⁾ Proceedings Vol. III p. 163.

$t = 33^{\circ}25$

x	p
0	276 mM. ¹⁾
0.050	276 »
0.080	276 »
0.203	282 »
0.295	294 »
0.500	355 »
0.588	412 »
0.695	500 »
0.898	657 »
0.955	697 »
1.	731 » ²⁾

It is evident that we shall have to renounce either the relation $a_{12} = \sqrt{a_1 a_2}$ or at least part of the simplifications which lead to the before-mentioned formulae of VAN DER WAALS. The simplifications are: the application 1st of the equation of state in its simplest form, 2nd of the wellknown equations for a_x and b_x , 3rd of the equation

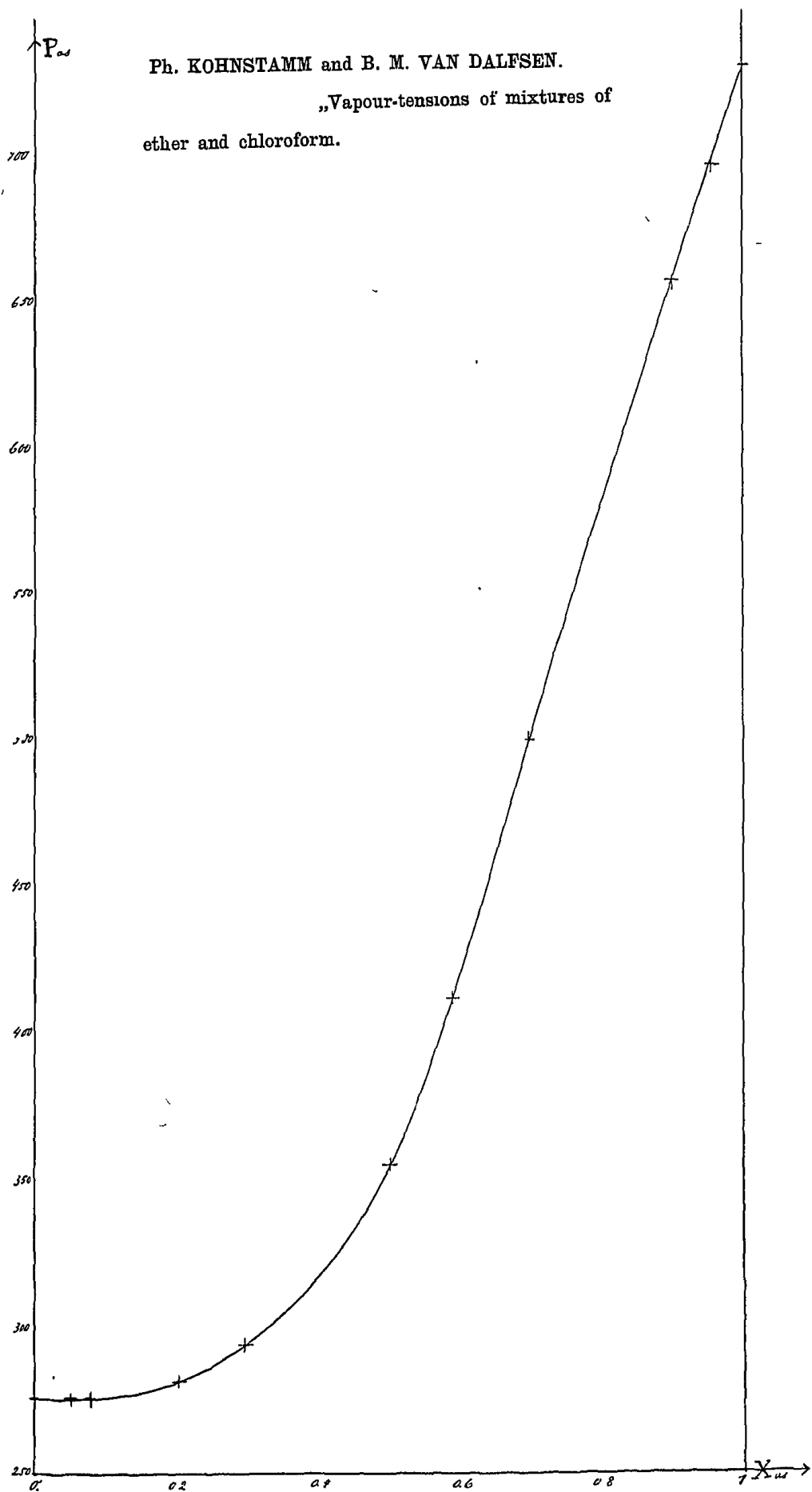
$\mu''_x = - \frac{d \frac{a_x}{b_x}}{dx_1}$. These simplifications are certainly not all quite correct, but it seems nevertheless not probable, that a more accurate formula would give such considerable correction-terms, that through them alone the strongly positive value of $\left[\frac{d^2 p}{dx_1^2} \right]_{x_1=0}$ might be explained.

For the present it seems therefore most advisable to give up the

1) For chloroform we know only the determinations for vapour-tensions of REGNAULT. According to v. ZAWIDZKI however, his values must be inaccurate, as he had no pure chloroform at his disposal.

2) At 30° RAMSAY and YOUNG found for ether 647.92; BATELLI 648.21. At the same temperature our observations give 649 mm. So the deviations are not greater than our probable error.

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„Vapour-tensions of mixtures of
ether and chloroform.



relation of GALITZINE-BERTHELOT, though the matter can really not be decided before the theory has proceeded so far that it will determine the value of the correction-terms more accurately.

Finally it is noteworthy that seen from below the given curve on the right side is concave, though very slightly ¹⁾. So it has an inflection-point.

From the theory of VAN DER WAALS the appearance of such inflection-points under some circumstances was to be expected ²⁾; OSTWALD, on the other hand, denied their possibility. So our results confirm the before-mentioned theory, as the experiments of RAOULT ³⁾ on mixtures of ether and very slightly volatile substances did before ⁴⁾.

Yet we wish to state this latter point with some reserve. When determining the points $x = 0.955$ and 0.898 , a difficulty was added to those already mentioned viz. that through the very considerable sloping of the p_x -curve the composition of the mixture when boiling, had a tendency to change in consequence of the extraction of the more volatile ether by distillation; the more so as, these experiments being made only lately, our coolingwater was considerably warmer than in previous experiments made in February and March. The reason why we think that we are justified in considering these two points as accurate is only that they as well as the previously determined point for $x = 0.695$ lead to the same result ⁵⁾. We hope, however, to return to this point afterwards.

¹⁾ This particularity is far less obvious in the subjoined representation on a reduced scale than in the original drawing.

²⁾ l c. p. 170.

³⁾ Zeitschrift f. phys. Chem. 2. p. 353.

⁴⁾ Zeitschrift f. phys. Chem. 36, p. 60.

⁵⁾ Comp. note on the preceding page.

(August 6, 1901).