

Citation:

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The points of intersection of these curve with C_1 which are not situated at the same time on $x_1x_2 + x_3^2 = 0$ lie on the conic ξ_2 ,

$$3y_3(x_1x_2 + x_3^2) = 2(y_2x_1 + y_1x_2 + 2y_3x_3)x_3.$$

So the tangential points of the four tangents out of any point of the double tangent lie on a conic through the cusps.

For $y_3 = 0$, so $y_1 : y_2 = b_2 : -b_1$ (the point H) we find as it ought to be

$$(b_1x_1 - b_2x_2)x_3 = 0.$$

The conics ξ_2 form evidently a pencil of which two basepoints lie on h , the remaining two in O_1 and O_2 .

7. The curve of HESSE of C_4 has as equation.

$$6x_1^3x_2^3 + 18(b_1x_1 + b_2x_2)x_1^2x_2^2x_3 + (18c + 32)x_1^2x_2^2x_3^2 + \\ + 60(b_1x_1 + b_2x_2)x_1x_2x_3^3 + (36b_1b_2 + 24c - 8)x_1x_2x_3^4 + \\ + 9(b_1x_1 + b_2x_2)^2x_3^4 + 18(b_1x_1 + b_2x_2)x_3^5 + (18b_1b_2 + c)x_3^6 = 0.$$

By combination with the equation of C_4 we find that the points of intersection of the two curves not lying in the cusps are situated on the curve

$$12(b_1x_1 + b_2x_2)x_1x_2 + (18b_1b_2 - 18c - 30)x_1x_2x_3 - 27(b_1x_1 + b_2x_2)^2x_3 - \\ - (54c + 22)(b_1x_1 + b_2x_2)x_3^2 + (18b_1b_2 - 19c - 18c^2)x_3^3 = 0.$$

So the eight points of inflexion of the C_4 are situated on a cubic curve passing through the cusps and the point H .

The polarcurve of the point $O_3 = k_1k_2$ consists of $x_3 = 0$ and the conic

$$2x_1x_2 + 3b_1x_1x_3 + 3b_2x_2x_3 + 2cx_3^2 = 0,$$

passing through the cusps and through the points of contact of the four tangents which meet in the point of concurrence of the cuspidal tangents.

It is easy to see that O_3 and H are the only points for which the polarcurve degenerates.

Chemistry. — “On the system hydrogen bromide and bromine.”

By Dr. E. H. BÜCHNER and Dr. B. J. KARSTEN. (Communicated by Prof. A. F. HOLLEMAN).

The research, a report of which is given here, was undertaken in connection with a remark from Prof. HOLLEMAN, that the existence of compounds of the type HBr_n has been assumed several times in order to explain the mechanism of reactions in organic chemistry. In order to test the validity of this assumption it was thought desirable to ascertain, in the first place, whether pure bromine and

hydrogen bromide are capable of forming a compound. As in binary systems the safest conclusions as to the existence or non-existence of a compound may be drawn from the course of the melting point curves we have attempted to determine the melting point figure of the system HBr-Br.

It soon became evident that, at atmospheric pressure, the hydrogen bromide instantly escaped from the mixtures so that we were compelled to use sealed tubes. The experiments were now carried out as follows: A quantity of specially purified bromine was weighed in a glass tube a part of which was drawn out; the tube was now connected to a HBr-generating apparatus and placed in a bath of solid carbon dioxide and alcohol. As soon as a sufficient quantity of HBr had condensed the tube was sealed and reweighed. The hydrogen bromide which was prepared from bromine, phosphorus and water was dried by passing it through two U-tubes containing P_2O_5 , whilst care was also taken that no moisture could enter the tube during the condensation. The tube was now fixed in a frame of copper wire and suspended in a rectangular wooden case, the long sides of which consisted of glass panes; in order to get a better isolation a second pane was fixed to each of these. Inside this case was placed a mixture of calcium chloride and ice for the higher temperatures whilst for the lower ones down to -50° solid carbon dioxide and alcohol were used. For still lower temperatures this apparatus is unsuitable and the ordinary vacuum vessels were used; these, however, suffer from the disadvantage that, unlike in the other apparatus, the tubes cannot be shaken properly without lifting them out. Anyhow, in all cases we allowed the temperature of both to rise very slowly and the reading of the thermometer was taken at the moment that the last crystals fused. If only care be taken that the bath is kept constant at a trifling lower temperature for some time and that the tube and the bath are well stirred we may assume that the temperature of the mixture is practically the same as that of the bath. The observations were made with an "Anschütz" thermometer down to -40° and a BAUDIN toluene thermometer for the lower temperatures; each determination was repeated a few times and the subjoined figures represent the mean result.

Before stating our results we just wish to explain, that, strictly speaking, we do not determine a melting point curve by means of the method described, for a vapour phase is also existent in the tubes which deviates considerably in composition from the liquid, and exists perhaps under a relatively high pressure. And from the weighings we know only the total concentration, and not that of

the liquid phase alone. From some calculations, however, it appears that the composition of the liquid corresponds fairly well with the total-composition ¹⁾, so that the curve representing our results graphically does not differ much from the projection on the t, x -plane of the liquid-branch of the three-phase line, when we call to mind the p, t, x model in space of BAKHUIS ROOZEBOOM. In any case, the conclusions as to the existence of compounds which we can draw from the course of the curve, remain unaltered.

In the subjoined table our figures are united whilst in the annexed drawing they are represented graphically; it should be observed that the composition is expressed in mol. percentage of Br_2 .

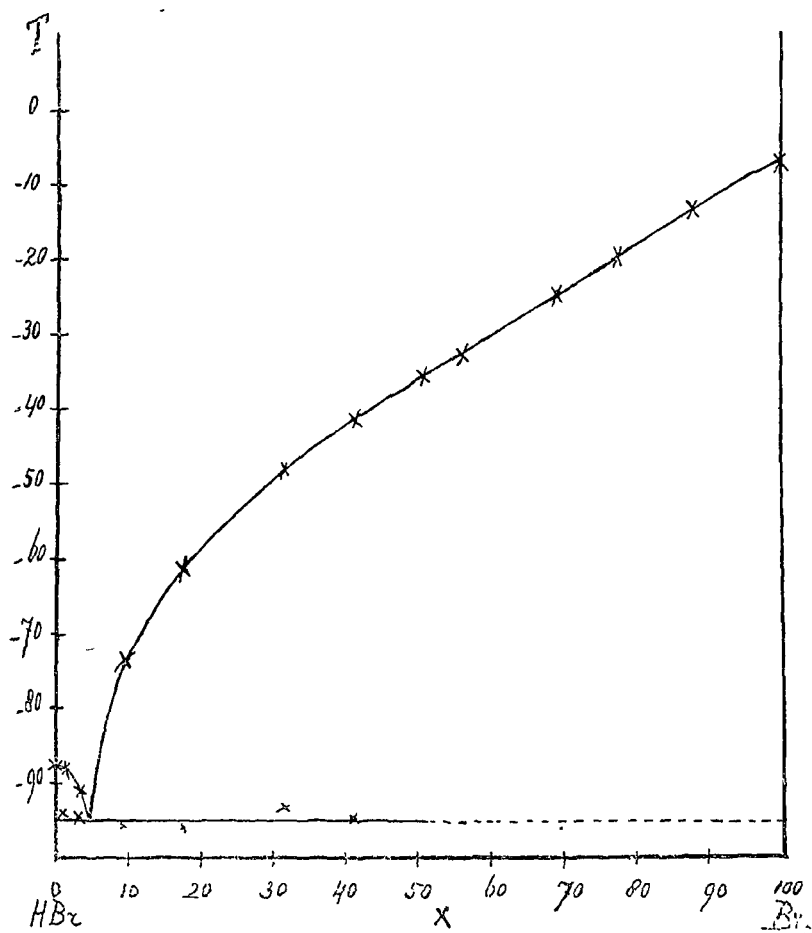
Composition in mol. % Br_2 .	End melting point.	Initial melting point
0.0	— 87.3°	
1.2	— 88	— 94°
3.3	— 91	— 95
9.6	— 73.5	— 95.5
17.4	— 61.5	— 96
31.6	— 48	— 93
41.0	— 41.5	— 95
50.5	— 35.5	
55.8	— 32.5	
69.0	— 24.5	
77.6	— 19.6	
87.7	— 13.4	

The drawing, as will be noticed, does not leave the least doubt; bromine and hydrogen bromide do not form a single solid compound. It has not yet been decided whether the solid phases which are deposited, consist of pure bromine and pure hydrogen bromide or of mixed crystals; in the latter case there is a discontinuous series as at about -95° a eutectic point was observed.

Some experiments on the composition of the liquid and vapour phases at a pressure of one atm. render it highly probable that a compound of the type HBr_n does not occur in the liquid or the

¹⁾ Only in the case of one tube — 77.6 % Br_2 — the deviation might amount to about 2 %, at least under a pressure of 5 Atm.; with the others it amounts to at most $\frac{1}{2}$ %.

vapour. Moreover, the fact that in our tubes the pressure exceeded 1 atm. showed that at 1 atm. solid bromine (or the mixed crystals) would be in equilibrium with a gas-phase which contains much more HBr; from this we deduced that the liquid- and the vapour branches of the t, x -curve for constant pressure (the boiling point line) are much diverged. We tried to prove this by passing gaseous hydrogen bromide through bromine at 0° and analysing both the liquid and



the gas. The bromine was placed in a tube furnished at the bottom with a tap by means of which the solution saturated with HBr could be removed. The hydrogen bromide which had bubbled through the bromine was passed through a tube furnished with stopcocks at both ends, from which it finally emerged in a flask over water. After the gas had passed for some time so that it might be taken for granted that the bromine was saturated and the tube completely

filled with the vapour which was in equilibrium with the liquid the two stopcocks were closed. After introducing aqueous sodium hydroxide by gently opening one of the stopcocks until all HBr and Br had been absorbed, the solution was introduced into a measuring flask and diluted to the mark. An aliquot portion was then titrated at once with KJ and $\text{Na}_2\text{S}_2\text{O}_8$, and in another portion the bromine was all converted into bromide by means of H_2O_2 , and then titrated according to VOLHARD with AgNO_3 and NH_4CNS . In this way we found the free bromine and the total bromine from which the relation $\text{HBr} : \text{Br}_2$ may be calculated. In a similar manner the composition of the liquid was determined. At 0° we found for the liquid 8 mol. % of HBr and 92 % of Br_2 ; for the vapour 87 % of HBr and 13 % of Br_2 ¹⁾.

This result renders the existence of a compound in the vapour highly improbable, for if a compound occurs in a binary system in the fluid phases an inward bend is noticed in the p, x - or t, x -curves; the liquid- and the vapour branch approach each other more or less according to the degree of dissociation of the compound. Judging from our observations there can be no question of something of the kind taking place in our case.

We beg to say just a few words as to the significance of these results in connection with the supposition mentioned above. Although we have proved that HBr and Br_2 in a pure state do not form a compound it cannot be denied that facts may be disclosed which plead for the existence of such compounds in solvents. But those facts only relate to solutions which possess electrical conductivity power and in which we must assume a powerful action of the solvent on the dissolved matters: in our case splitting into H' - and Br' -ions. One might certainly imagine that the Br' -ion has a tendency to take up Br_2 and to pass into Br'_2 -ion without this necessitating the existence of a *compound* HBr_3 , but in non-conductive solutions the idea of the existence of compounds HBr_n should, in our opinion, be rejected.

Amsterdam, December 1908.

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¹⁾ These experiments are being continued.