

Citation:

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Chemistry. — "*Three-phases in chloralalcoholate and aniline-hydrochloride*". By Prof. H. W. BAKHUIS ROOZEBOOM.

It is now 20 years since the study of the dissociation phenomena of various solid compounds of water and gases enabled me to find experimentally the peculiar form of that three-phase line which shows the connection between temperature and pressure for binary mixtures in which occurs a solid compound in presence of solution and vapour. The general significance of that line was deduced, thermodynamically, by VAN DER WAALS and the frequency of its occurrence was proved afterwards by the study of many other systems.

That this three-phase line is so frequently noticed in practice in the study of dissociable compounds is due to the circumstance that, in the majority of the most commonly occurring cases, the volatility of the two components or of one of them, is so small, that at the least dissociation of the compound both liquid and vapour occur in its presence.

In the later investigations, which have led to a more complete survey of the many equilibria which are possible between solid liquid and gaseous phases, pressure measurements have been somewhat discarded. When, however, the survey, as to the connection of all these equilibria in binary mixtures got more and more completed and could be shown in a representation in space on three axes of concentration, temperature and pressure, the want was felt to determine for some equilibria, theoretically and also experimentally, the connection between temperature and pressure, in order to fill up the existing voids.

Of late, the course and the connection of several p, t -lines, have been again studied by VAN DER WAALS, SMITS and myself either qualitatively or qualitative-quantitatively.

To the lines, which formerly had hardly been studied, belonged the equilibria lines which are followed, when, with a constant volume, the compound is exposed to change of temperature in presence of vapour only. They can be readily determined experimentally only when the volatility of the least volatile component is not too small. STORTENBEKER at one time made an attempt at this in his investigation of the compounds of iodine with chlorine, but did not succeed in obtaining satisfactory data.

In the second place it was desirable to find some experimental confirmation for the peculiar form of the three-phase line of a compound, recently deduced by SMITS for the case in which a

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minimum occurs in the pressure of the liquid mixtures of its components.

Mr. LEOPOLD has now succeeded in giving experimental contributions in regard to both questions, by means of a series of very accurately conducted researches where chloralalcoholate and anilinehydrochloride occur as solid compounds.

Solid compounds which yield two perceptibly volatile components (such as PCl_5 , $\text{NH}_3 \cdot \text{H}_2\text{S}$, $\text{PH}_3 \cdot \text{HCl}$, $\text{CO}_2 \cdot 2 \text{NH}_3$ etc.) have been investigated previously, but either merely as to their condition of dissociation in the gaseous form, or as to the equilibrium of solid in presence of gaseous mixtures of different concentration at constant temperature; but liquids occur only at higher pressures, so that the course of the three-phase lines had never been studied.

These two compounds were selected because in their melting points neither temperature nor pressure were too high. Moreover, the difference in volatility of the two components in the first example (chloral + alcohol) was much smaller than in the second (aniline + hydrogen chloride). It was also safe to conclude from the data of both compounds that the liquid mixtures of their components would show a minimum pressure.

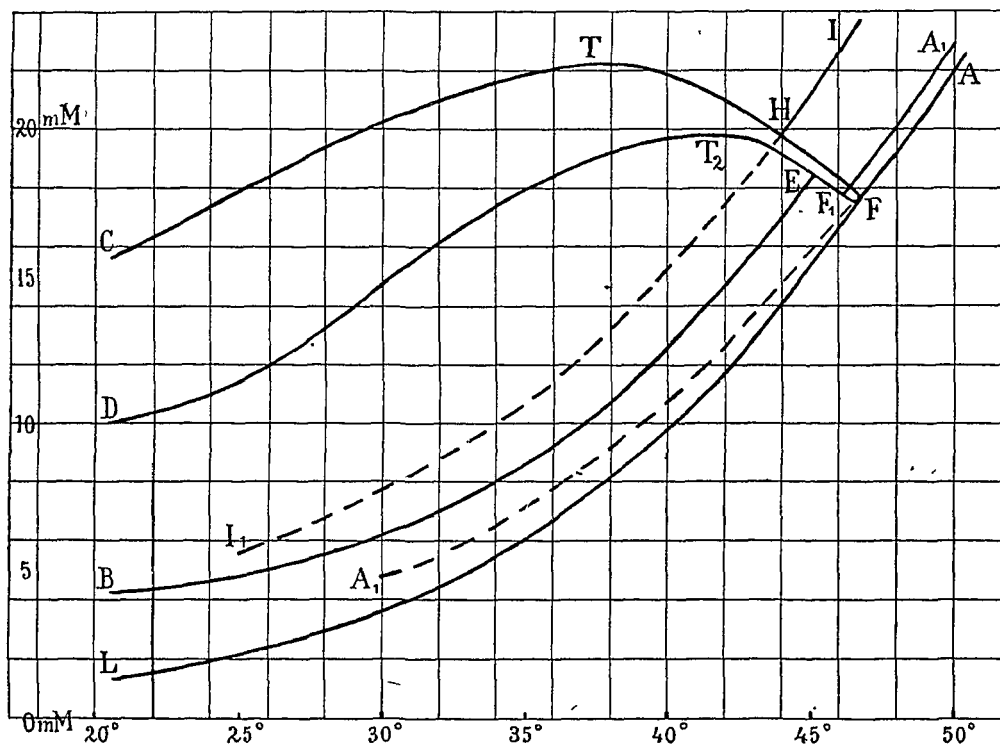


Fig. 1.

This last point was ascertained first of all by a determination of the boiling point lines, in which a maximum must occur. In both cases this was found to exist and to be situated at the side of the least volatile component, respectively chloral or aniline.

The investigation of the three-phase lines showed first of all that these possess the expected form in which two maxima and one minimum of pressure occur.

In the first system (Fig 1) CFD is the three-phase line, T and T₂ are the respective maxima for the vapour pressure of solutions with excess of either alcohol or chloral and saturated with chloralalcoholate; the minimum is situated very close to the melting point F.

In the second system (anilinehydrochloride Fig. 2) the first maximum, in presence of excess of HCl is situated at such an elevated

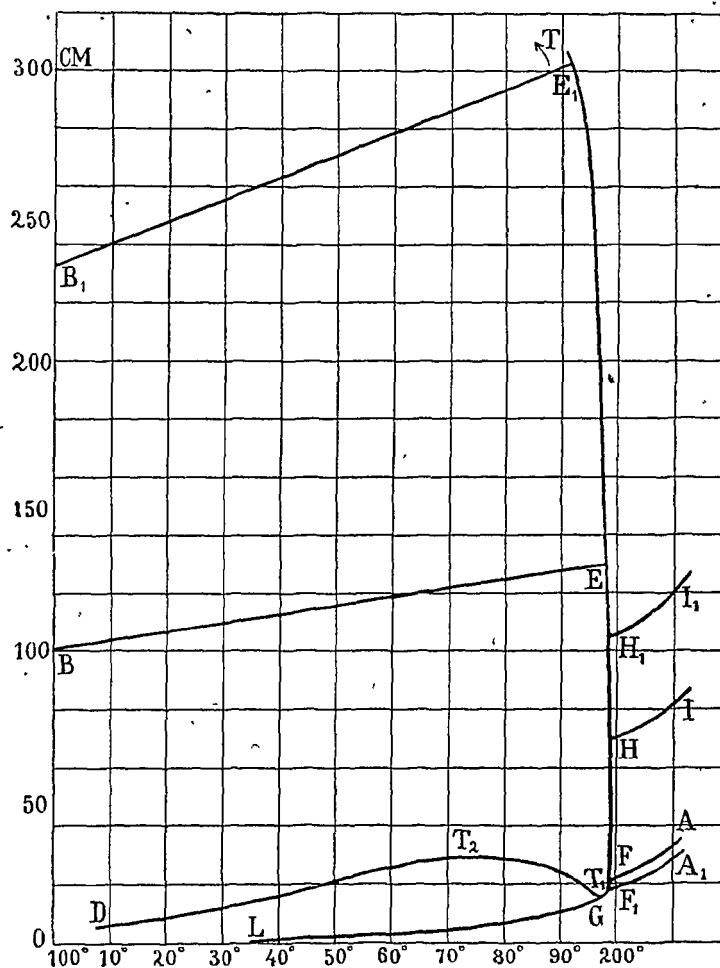


Fig. 2.

pressure that this has not been determined, the second T_2 at a moderate pressure is situated at the side of the aniline. The minimum T_1 is situated at the same side and is removed further from the melting point than in Fig. 1.

	T_1 minimum	F melting point
p	16 cM.	22.5 cM.
t	197°	199°2

The determination of these lines and also that of the equilibria-lines for compound + vapour or liquid + vapour which also occur in both figures can only take place on either side of point F , for in measuring the pressures, we can only have in the apparatus a larger, or smaller, excess of either component. Moreover, it is possible to fill the apparatus with the compound in a dry and pure condition. In the case of the compounds employed, this was attained by preparing very pure crystals by repeated sublimation in vacuo.

In the second example, the sublimation line LG of aniline hydrochloride was thus determined. On this line then follows the piece GF of the three-phase line, because beyond G , no vapour can exist which has the same composition as the compound, except in the presence of some excess of HCl , so that a little liquid is formed with a slight excess of aniline. If, however, the apparatus is properly filled with the compound so that there remains but little space for the vapour then the three-phase line G may be traced to very near the melting point F , where one passes on to the line FA , for the equilibrium of the fused compound with its vapour.

We have here, therefore, the first experimental confirmation of the normal succession of the p, t -lines when those are determined with a pure compound which dissociates more or less.

Theoretically, the minimum T_1 in the three-phaseline must be situated at the left of the terminal point G of the sublimationline. The difference here, although small, is yet perfectly distinct:

	T_1	G
p	16 cM.	16.5 cM.
t	197°	198°

In the case of chloralalcoholate the points T_1 and G both coincide so nearly with F that this point is practically undistinguishable from the triple point of a non-dissociating compound, both LF and FA , or their metastable prolongation FA' appear to intersect in F . Moreover, the investigation of the melting point line proved that chloralalcoholate in a melted condition is but little dissociated.

In both compounds the p, t -lines have also been determined with excess of chloral or aniline. A very small quantity of these suffices to cause the occurrence of liquid in presence of the compound at temperatures far below the melting point and we then move on the lowest branch of the three-phaseline.

In the case of a slight excess of chloral (Fig. 1) this was followed from D over T_2 to F_1 just a little below the melting point, and from there one passed on to the liquid-vapour line F_1A_1 , which was situated a little above FA .

In the case of a slight excess of aniline the piece $DT_2T_1GF_1$ could be similarly followed (Fig. 2). In this occurred the minimum T_1 , whilst the piece GF_1 coincided entirely with the corresponding part of GF , which had already been determined in the experiment with the pure compound. Just below F the compound had disappeared entirely and one passed on to the liquid-vapour line F_1A_1 , which, unlike that in Fig. 1, was situated below FA .

If the excess of the component is very trifling, liquid is formed only at higher temperatures of the three-phaseline, and below this temperature a sublimationline is determined, with excess of the component in the vapour, which line must, therefore, be situated higher than the pure sublimationline.

With chloralalcoholate a similar line BE (Fig 1) was determined, situated decidedly above LF . At E , liquid occurred and a portion of the three-phaseline EF was followed up to a point situated so closely to F that the liquid-vapourline, which was then followed, was situated scarcely above FA .

The excess of chloral was, therefore, exceedingly small, but in spite of this, BE was situated distinctly above LF . The position of BE depends, in a large measure, on the gas-volume above the solid compound, as this determines the extra pressure of the excess of the component, which is totally contained in the same; so long as no liquid occurs. It appeared, in fact, to be an extremely difficult matter to prepare chloralalcoholate in such a state of purity that it exhibited the lowest imaginable sublimationline LF , which meets the three-phaseline in F .

Similar sublimation lines may also occur with mixtures containing excess of alcohol. But also in this case, even with a very small excess of alcohol we shall retain liquid even at low temperatures and, therefore, obtain branch CTF of the three-phaseline. Such happens, for instance, always when we use crystals of the compound which have been crystallised from excess of alcohol. They then contain sufficient mother-liquor.

We then notice the peculiar phenomenon that the compound is apparently quite solid till close to the melting point and we find for the vapour pressure the curve CTF , whilst the superfused liquid gives the vapour pressureline FA_1 which is situated much lower. RAMSAY has found this previously without being able to give an explanation, as the situation of the three-phaseline was unknown at that period.

In the case of anilinehydrochloride, it was not difficult, on account of the great volatility of HCl , to determine sublimationlines when an excess of this component was present. In Fig. 2 two such lines are determined BE and B_1E_1 . From E_1 the three-phaseline was followed over the piece E_1H_1 afterwards the liquid-vapourline H_1I_1 . From E also successively EH and HI . With a still smaller excess of hydrogen chloride we should have stopped even nearer to F on the three-phaseline.

In the case of chloralalcoholate we noticed also the phenomenon that a solid substance which dissociates after fusion may, when heated not too slowly, be heated above its meltingpoint, a case lately observed by DAY and ALLEN on melting complex silicates, but which had also been noticed with the simply constituted chloralhydrate.

An instance of the third type of a three-phaseline where the maximum and minimum have disappeared in the lower branch of the three-phase line has not been noticed as yet.

The two types now found will, however, be noticed frequently with other dissociable compounds such as those mentioned above, and therefore enable us to better understand the general behaviour of such substances.

Physics. — "*On the polarisation of Röntgen rays.*" By Prof. H. HAGA.

In vol. 204 of the Phil. Trans. Royal Soc. of London p. 467, 1905 BARKLA communicates experiments which he considers as a decisive proof that the rays emitted by a RÖNTGEN bulb are partially polarised, in agreement with a prediction of BLONDLOT founded upon the way in which these rays are generated.

In these experiments BARKLA examined the secondary rays emitted by air or by some solids: paper, aluminium, copper, tin, by means of the rate of discharge of electroscopes. In two directions perpendicular to one another and both of them perpendicular to the direction of the primary rays, he found a maximum and a minimum for the action of the secondary rays emitted by air, paper and aluminium.