

connected with the frictions presenting themselves, i. e. these values will be independent of the initial condition. At the same time the two clocks will show a different rate ¹⁾, of which clocks one therefore will have to sustain the rapid principal oscillation, the other the intermediate one. Periodic transference of energy will then take place.

Probably it will not be easy to realize this condition, characterizing itself particularly by the fact, that one of the clocks goes considerably faster than would be the case when placed independently ²⁾. The initial conditions will then have to be chosen in such a manner that from the very beginning one oscillation will predominate for one clock, the other for the other clock. And this will become all the more difficult as c_1 and c_2 become more and more equal, therefore according as the two clocks become more and more alike and are suspended in a more symmetric way. For, so much smaller will, according to what was mentioned in note (2) p. 453 be the difference in proportion of the amplitudes α_1 and α_2 at each of the oscillations. ³⁾

17. Finally we wish to point out how we must represent to our-

¹⁾ So this differs again from what ELLICOTT observed in his last experiments, so that these cannot be regarded as the realisation of this case, though they have the transferences of energy in common with it. However, between the fact of those transferences and the assurance that both clocks have entirely the same rate exists a contradiction, as we have already seen, which is not to be solved. Indeed, those transferences can be explained by interference only, so they require the cooperation of two oscillations of different periods; but these oscillations must both be sustained if the state is really to continue indefinitely, and then each of them by one of the motive works where the oscillation referred to will predominate the other one. See also the last note.

To me it seems most probable that with ELLICOTT the transferences of energy existed only at first indicating the *temporary* presence of the rapid principal oscillation. ELLICOTT's wording is not emphatically against this conviction.

²⁾ The difference from case *A* is of course only quantitative. In both cases the clocks go faster than when placed independently, but in case *C* the acceleration of the quickest clock becomes much greater than that of the less rapid one (see § 13). A gradual transition presents itself then, and the case of ELLICOTT was probably situated on that transition-line.

³⁾ The idea that perhaps each of the motive works might be able to take over one principal oscillation and the other in turns had to be set aside after a closer investigation. If we compose in the well-known graphical way two oscillations of unequal amplitudes and of periods of oscillation differing but little, it is evident that the motive work will go alternately somewhat quicker and somewhat slower than will correspond to the period of oscillation of the greatest amplitude, but this can never go so far that the rate of the smaller amplitude is taken over, not even for a short time.

selves the transition of case *A* into case *C*. In case *A* in which the rate of the clocks differs greatly, the manner of motion which is most difficult to realize in case *C*, namely the one, where the clocks have each their own rates, is the normal one. Yet the two other manners of motion also are possible, i. e. those where exclusively *one* of the principal oscillations appears; however in these cases, the pendulum of the least active of the two clocks will still perform a slight oscillation though not sufficient to set its motive work in motion.

If now starting from case *A* we reach case *C*, i. e. if the rate of the clocks is taken more and more equal, the state of motion with mutually different rate of the clocks becomes continually more difficult to realize, finally perhaps impossible; whilst for the two other possible manners of motion the pendulum of the second clock too keeps performing greater and greater deviations till these deviations are finally sufficient to set its motive work also in motion, so that both clocks go quite alike, either with the rate belonging to the rapid principal oscillation or, what is more easily realized, with that or the intermediate one.

Chemistry. — “*The different branches of the three-phase lines for solid, liquid, vapour in binary systems in which a compound occurs.*” By Prof. H. W. BAKHUIS ROOZEBOOM.

(Communicated in the Meeting of October 28, 1905)

A chemical compound, formed from two components, need not to be regarded as a third component, when this compound is somewhat dissociated, at least when it passes into the liquid or gaseous state. Instead of the triple point we then get a series of triple points, the three-phase line, indicating the co-related values of temperature and pressure at which the compound can exist in presence of liquid and vapour of varying compositions ¹⁾ This was advanced for the first time in 1885 by VAN DER WAALS. The equation for that line was deduced by him ²⁾ and shortly afterwards ³⁾ applied by me in a few instances where it was always admitted that the vapour tension of the liquid mixtures gradually diminished from the side of the most volatile (*A*) towards that of the least volatile component (*B*).

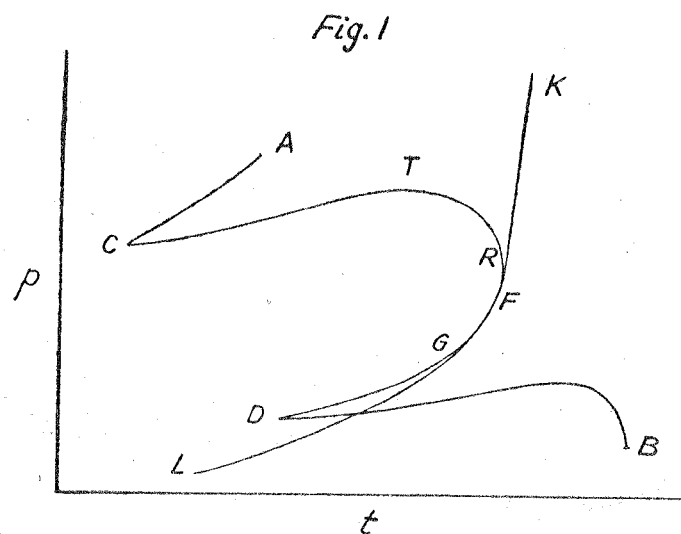
In the first considerations as to the course of the three-phase line

¹⁾ There exist several other three-phase lines which are not considered here.

²⁾ Verslag Kon. Akad. 28 Febr. 1885.

³⁾ Rec. Tr. Chim. 5, 334 (1886)

and the parts which could be realised in different binary systems, the line was generally divided by me into two branches according as the coexisting liquid contained more *A* or more *B* than the compound.



In figure 1 branch 1: *CTRF* represents liquids with more *A* and branch 2: *FD* liquids with more *B*.

At the commencement, special attention was called to the important fact that in the first branch a maximum pressure occurs at *T* where the heat of transformation of the three phases passes through zero. Less attention was paid to the fact that the maximum temperature *R* does not completely coincide with the point *F*, where the composition of the liquid becomes the same as that of the compound, but is situated either on branch 1, if the compound expands when melting, or on branch 2 if the reverse is the case; this may be best understood if one remembers that the melting point line of the compound *FK* meets the three-phase line in the point *F*. Although indicated in the first publication of VAN DER WAALS and in my more extended paper¹⁾ this point remained in the background because, practically, the difference in temperature between *F* and *R* is very small. Afterwards²⁾, VAN DER WAALS worked it out more carefully and only recently SMITS³⁾ has fully considered the peculiarities of the *p, x*-figures between *F* and *R*, after these had become important

¹⁾ Rec. 5, 339, 340, 356, 1886.

²⁾ Verslag Kon. Akad. April 1897.

³⁾ These Proc. June 1905.

from the point of view of the hidden equilibria which continuously connect with each other the lines of the liquids and vapours coexisting with the solid phase.

In the systems which formerly came most to the front, the difference in volatility between the two components was so large — such as with water and salts — that on the whole three-phase line no vapour occurred which had the same composition as the compound.

If however, the difference in volatility is less pronounced, a case may occur where the equality in composition between vapour and compound is attained somewhere. VAN DER WAALS foresaw that possibility in 1885, but not until 1897 did he point out how such a point, occurring on the three-phase line below the point *F*, indicates the maximum temperature at which the compound may still evaporate in its entirety, and how in that point the subliming line of the compound meets the three-phase line. Such a point is indicated in fig. 1 by *G*, the subliming line by *GL*.

It was, however, thought very desirable to elucidate the manner in which, in such a case, the equilibria solid-vapour, solid-liquid and liquid-vapour join each other on the three-phase line by a representation in which is also shown the change of the concentrations of liquid and vapour along the three-phase line of the compound with increasing temperature.

Dr. SMITS¹⁾ recently gave a representation of this by working out a connected series *p, x*-sections of a spacial figure, which in the case of a binary compound takes the place of my spacial figure, where only the components occur as solid phases.

A good example may be found in STORTENBEKER's²⁾ research on the system chlorine + iodine. There it is found that both the compounds *JCl* and *JCl₃* yield at their melting point a vapour containing more *Cl*, but at a lower temperature they have a point on their three-phase line where the vapour becomes the same as the compound. STORTENBEKER had noticed this fact during his research, but had not followed the matter up. After I had completed in 1896 my *p, t, x*-figure for binary mixtures, I also projected the spacial representation for this case, and I had then already come to the view, by graphical methods, that the point *G* is the highest temperature at which a compound can exist near vapour of equal composition.

BANCROFT³⁾, in consequence of VAN DER WAALS' publication, tried to elucidate the case of *JCl* by a representation of partial pressures,

¹⁾ These Proc. June 1905.

²⁾ Rec. Trav. Chim. 7. 183. 1888.

³⁾ Journ. Phys. Chemistry 3. 72. 1899.

which appears to me less suitable, to survey the connection of the phase-equilibria. The representation now worked out by SMITS (see his communication fig. 4) is a p, x -projection of my own spacial figure with p, t, x as coordinates which, however, had not yet been published.

This representation is well suited to explain at once which are the transformations which take place on the different parts of the three-phase line, owing to change in pressure or temperature, and finally lead to the disappearance of one of the three phases.

Those transformations are dominated first of all by the connection of the compositions of the three-phases.

From the figure it will be seen at once that, if we indicate the solid compound by S , the coexisting liquid by L , and the vapour by G , the order of the compositions of the phases commencing with one richest in the volatile component A , is as follows:

on branch $CTRF$: GLS

„ „ FG : GSL

„ „ GD : SGL .

The only transformation which can take place between three phases is such that one is converted into two others, or reversely. That one must then necessarily be the middlemost in composition, consequently successively L, S, G .

The most rational division of the three-phase line is obtained when this takes place according to the transformation which occurs between the phases, and we will, therefore, call in future the branches on which L, S or G are the middle-bodies, the branches 1, 2, 3.

The transformation of 1 into 2, therefore, takes place in the point F where $S = L$, that of 2 into 3 in the point G where $S = G$.

If now we observe in what direction that transformation takes place, for instance on applying heat, we have

on branch 2 : $S \rightarrow G + L$

„ „ 3 : $S + L \rightarrow G$

on the other hand on branch 1 we have:

on the part TRF : $S + G \rightarrow L$ branch Ia

„ „ „ CT : $L \rightarrow S + G$ „ Ib

whilst in the point T itself, both transformations are without heat effect. The reversal of the direction of the transformation causes retrograde phenomena, on increasing or lowering the temperature.

A reversal of the direction of the transformation caused by a change in pressure also takes place on either side of the point F on branch 1, or on branch 2 if the compound melts with contraction,

and in this way retrograde phenomena by variation in pressure become possible.

On the branches 2 and 3 a reversal of the direction of the transformation caused by heat supply is as a rule not probable, as this always consists in the evaporation of the solid matter, coupled with melting of the same, or evaporation of the liquid, processes which generally want a supply of heat¹⁾. The readiness of the reversal on branch 1 is, therefore, closely connected with the fact that the liquid phase is here the middle body.

If we consider in an analogous manner the character of the three-phase line on which the most volatile component A occurs as solid phase, the order of the phases is here SGL , therefore the line AC represents branch 3; in the point A , G and L become simultaneously equal to S ; consequently, there exists no branch corresponding with branch 2 of the compound. On the three-phase line DB where the least volatile component B is the solid phase, the order is GLS , therefore DB corresponds with branch 1.

In the previously studied binary compounds the volatility of the one component was so much smaller than that of the other, that on the three-phase line only the branches 1 and 2 were noticed; if the second constituent is sufficiently volatile branch 3 may be met²⁾ with as in the case of JCl and JCl_2 .

Such is the state of affairs in the case that the vapour tension of the liquid mixtures gradually decreases from 100% A to 100% B .

If now, however, a minimum or a maximum occurs in the vapour tensions the possibility may arise that, somewhere on the three-phase line of a compound, the liquid and vapour phases, which coexist with the solid phase, become equal in composition; and the question arises what significance this fact possesses for the division of the three-phase line.

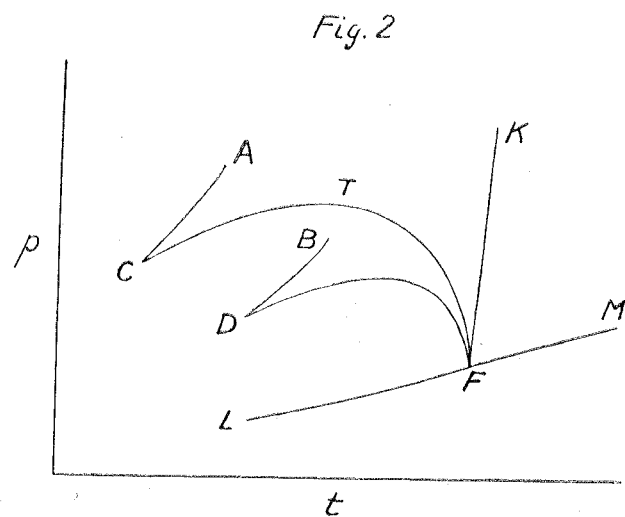
In his communication cited Dr. SMITS has for the first time given the three-phase lines for both cases and also the p, x -projections of the appertaining spacial figure but has not further investigated the character of the different parts of the three-phase line.

Let us first take the case that a minimum occurs in the $p-x$ -lines for liquid-vapour. If the compound in liquid and gaseous state was

¹⁾ The special cases where reversal might take place will not be considered here.

²⁾ If branch 3 is wanting because on branch 2, S nowhere becomes equal to G , there is still a possibility that this occurs somewhere on the three-phase line which the compound with the least volatile component as solid phase and vapour gives below the point D . This we cannot further enter into.

not at all dissociated, that minimum would coincide with the composition of the compound.



The three-phase lines would then appear about as shown in Fig. 2. Instead of one continuous line for the compound, there would be two branches sharply meeting in F , CF and DF , both exhibiting the character of branch 1, and therefore the order GLS of the three phases, and both becoming tangent in F , to the melting point line.

The sharp meeting in F is caused by the fact that there is no continuity between liquids or vapours containing an excess of A or of B , if the compound itself on its transformation into liquid or vapour, that is in F , remains totally undissociated and therefore contains no trace of A or B in the free state. In this case F is a triple point for the compound.

In case of the least trace of dissociation we, however, get continuity and the branches CF and DF unite to one three-phase line of the compound, which therefore assumes the general form deduced by SMITS, and is represented in fig. 3. The minimum in the vapour and liquid line now, however, shifts towards a composition differing from that of the compound, generally all the more as the volatility of A and B differs more and the dissociation is greater. Unless special influences¹⁾ decidedly modify the partial pressures of the components in the liquid phase, the minimum will generally be situated at the side of B . From the p, x -representation deduced for this case by SMITS, it will be easily seen that, proceeding along

¹⁾ Such as the existence of several compounds.

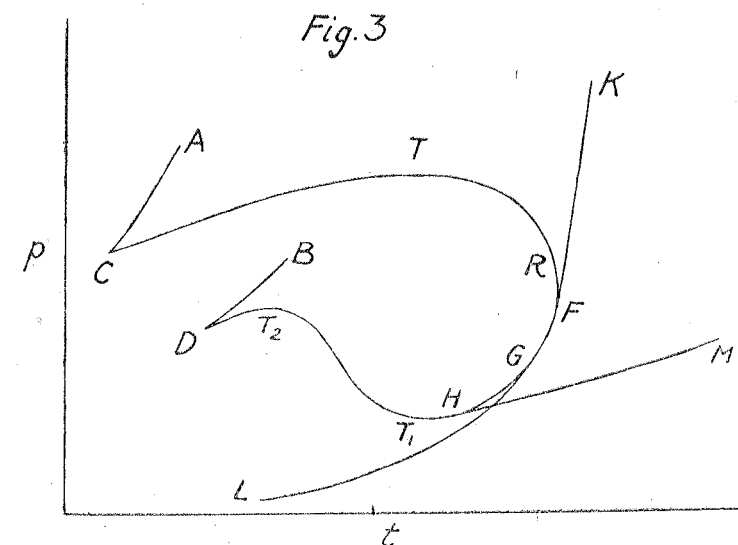
branch CF of the three-phase line and continuing over FD , the order in which two of the three phases become equal in composition is as follows:

$$\text{point } F: \quad L = S$$

$$\text{point } G: \quad G = S$$

$$\text{point } H: \quad L = G.$$

From this it follows firstly that, if somewhere on the three-phase line of the compound liquid and vapour become identical (point H), there is certainly also a point G where vapour and solid become equal, as G is situated between H and F .



Let us now consider the character of the different parts of the three-phase line. From C to H , the state of affairs is just the same as in Fig. 1. CF is, therefore, again branch 1 with the order GLS for the composition of the phases, FG branch 2 with the order GSL and GH branch 3 with the order SGL .

Whilst however in Fig. 1 the character of branch 3 continued up to D , a change occurs at H because $L = G$. It is easy to deduce from Dr. SMITS's p, x -figure that the continuation HD of the three-phase line again exhibits the character of branch 1, the order of the phases is just as on CTF : GLS , with this difference that G is now the richest in the component B whilst on branch CTF the vapour was richest in A . Because in H the compositions of L and G become equal, a transformation in that point of the three-phase line

only occurs between those two and, therefore, the tangent HM to the three-phase line must be the line indicating the p, t values for the series of liquids and vapours having equal composition.

Just as in F occurs as tangent to the three phase line the melting point line EK , which is the extreme limitation of the equilibria between solid and liquid, and in G the subliming line GL , which is the extreme limitation for the equilibria solid and vapour, the tangent in H is the line HM , which is the boiling point line of the liquids with a constant boiling point, and also the extreme limitation for the equilibria liquid-vapour ¹⁾.

The points F , G and H are, therefore, points of strictly related significance; they are the points where the order of the phases suddenly changes.

Let us now further consider branch HD . In fig. 3 occurs a point of maximum pressure T_2 and of minimum pressure T_1 . The first point is quite comparable with the maximum T in the branch CTE , the part DT_2 is again Ib on which, on heating, the transformation $L \rightarrow S + G$ takes place, the part $T_2 T_1$ is branch Ia , to which belongs the reverse transformation, whilst in T_2 itself the heat of transformation passes through zero.

Owing to the continuous connection of $DT_2 T_1$ to HG , we necessarily get a small rising part $T_1 H$ of branch 1, after the line has passed through a minimum T . The possibility of this minimum may be explained as follows:

Just beyond T_2 , the amount of heat necessary to convert $S + G$ into L can at first increase, because L and G both approach in composition to S , so that the quantity of G concerned in the said transformation diminishes with regard to S . But as we approach on the three-phase line the point H , L and G approach each other more than they approach S (for point H , where $L = G$, is reached sooner than G , where $S = G$); consequently the ratio of the phases G/S , which transform themselves in L , becomes again larger and the heat required for this again smaller until it finally becomes zero at T_1 and beyond this point negative, in other words the transformation again becomes $L \rightarrow S + G$; the small part $T_1 H$ again represents Ib and keeps on doing so up to the point H where the transformation in branch 3 takes place.

As the minimum T_1 does not coincide with the point H where $L = G$, a small modification must be made in the p, x -projection of

¹⁾ In the figure the lines HM and LG intersect. In the spacial figure this is however, a crossing.

the spacial figure given by Dr. SMITS in his fig. 5. His three-phase strip, which I will rather call two-phase strip because it is formed by the

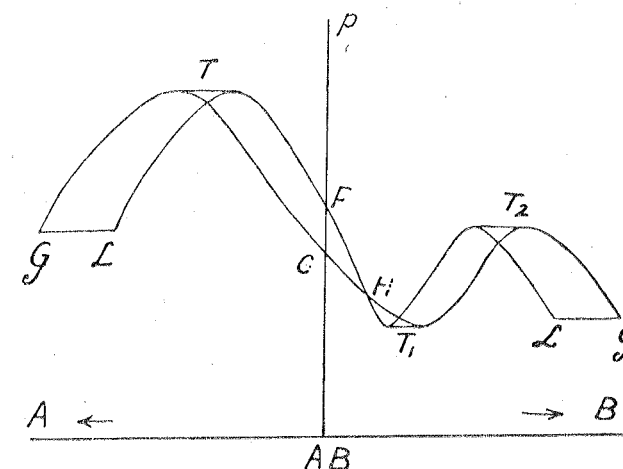


Fig. 4

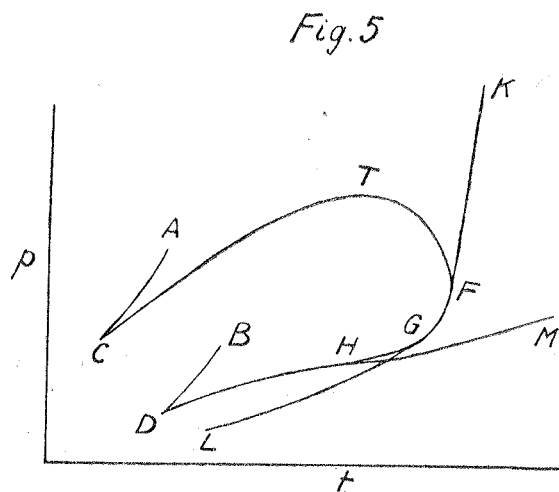
lines indicating the liquid and vapour existing by the side of the compound, assumes the form of fig. 4, in which the particular points of the three-phase line fig. 3 with which this figure corresponds are indicated by the same letters. The line is extended so far that it also includes the maxima T and T_2 , and so shows in which respects it differs from the case corresponding with fig. 2, and of which the strips have been indicated by SMITS in his fig. 2.

If the minimum in the liquid-gas surfaces should be very little pronounced, another type of the three-phase line may be expected, which is represented in fig. 5 in which both minimum and maximum have disappeared in branch HD , the whole line having the character of branch Ib .

In fig. 4 this would result that beyond the point H vapour and liquid lines keep on a downward course, which may be the case if the composition of L and G , which coexist with the compound, shifts but little with the temperature so that the increase in pressure which would occur owing to the shifting towards the side of B is more than compensated by the decrease in pressure caused by the fall in temperature.

Up to the present not a single example has been studied where a three-phase line of the type fig. 3 or 5 made its appearance. Still it is not difficult to see that both must frequently exist in the case of dissociable compounds with sufficient volatility of the two com-

ponents. Examples will be found in the compounds of NH_3 or amines with volatile acids as HCl , HBr , H_2S , HCN or organic acids as formic acid, acetic acid, in chloral hydrate or alcoholate, etc.



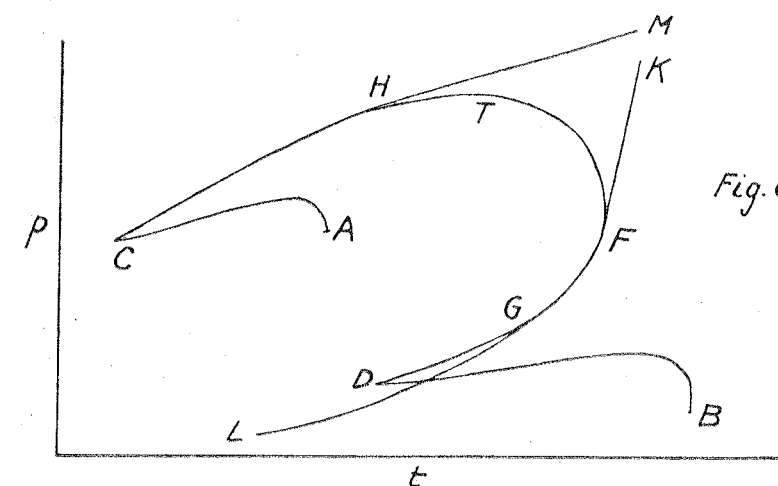
When the compound becomes less dissociated, fig. 3 will assume more the character of fig. 2. To this belongs, perhaps methylamine hydrochloride. As the dissociation becomes greater and the volatility of B differs more from A , the point H , where $L = G$, will be further removed from F . In the case of amine salts of organic acids it is already known that the liquid with a constant boiling point lies much closer to the acid-side than the compound.

If the volatility of B decreases very much, fig. 5 may form.

If the line HM lies strongly to the side of B the case might happen that the point H did not occur on the three-phase line of the compound, but on that of the component B . In fig. 3 and 5 branch 3 is represented by the three-phase line ALG as well as by BLG . In the case mentioned, the line BLG starting from B would at first represent branch 3 but after passing the point $L = G$ it would represent branch 1 either $1b$ or later even $1a$. These branches then join on branch 3, the three-phase line of the compound. Of this, no instance is as yet known. In the systems HCl , HBr , HJ and H_2O the ice line runs to very low temperatures, and therefore to very high concentration of HCl etc., but the line HM when running to lower temperatures also runs to a higher acid concentration, so that according to PICKERING's data on the coexisting liquids the minimum in $\text{HCl} - \text{H}_2\text{O}$ would fall on the three-phase line of the third hydrate, in $\text{HJ} - \text{H}_2\text{O}$ on that of the fourth hydrate (both on the side of the solutions richer in water) in $\text{HBr} - \text{H}_2\text{O}$ even just before the melting point

of the fourth hydrate at the side of the solutions richer in HBr — in no case, therefore, on the ice line.

Let us further consider the case where liquid and vapour become equal at a maximum pressure. Here, this point will lie generally on the side of the most volatile component and as the compound becomes more dissociated and the difference in volatility of its components greater, the chances are that the composition of liquid and vapour at which they become equal, differs more from the compound.



From this originates a form of the three-phase line which is in general indicated by Fig. 6. The point H is now shifted to the top branch at the left side of the maximum T in branch 1. The part HC now exhibits the character of branch 3. The line HM , which indicates the maximum pressures of the series of liquids and vapours having an equal composition, is tangent in H to the three-phase line and forms the extreme limitation of the equilibria between liquid and vapour. The three-phase lines for solid A and solid B both exhibit the character of branch 1.

Owing to the non-coincidence of the points H and T a similar correction must be applied to the p, x -projection of the two-phase strip given by Dr. SMITS as has been done by me in Fig. 5 in the case of the minimum.

The type fig. 6 will, presumably, not frequently occur, as a combination between two bodies is as a rule accompanied by a reduction in pressure and therefore, the occurrence of a maximum

pressure in the series of the liquid-vapour equilibria is but little probable. At the moment there only seems an indication that the case occurs with PH_4Cl .

If the line HM is situated much more towards the side of A it might then also happen that the point H did not occur on the three-phase line of the compound, but on that of the compound A , so that branch 3 on this line follows on branch 1 and disappears from the three-phase lines of the compound.

In a future communication I will discuss the boiling phenomena of the saturated solutions corresponding with the said branches of the three-phase lines.

Crystallography. — "On *Diphenylhydrazine*, *Hydrazobenzene* and *Benzylaniline*, and on the miscibility of the last two with *Azobenzene*, *Stilbene* and *Dibenzyl* in the solid state." By Dr. F. M. JAEGER. (Communicated by Prof. BAKHUIS ROOZEBOOM).

(Communicated in the meeting of October 28, 1905).

The following research was undertaken to furnish a new contribution to the knowledge of the relation of the crystal-symmetry of organic compounds and their power of yielding crystallised mixed phases with each other¹⁾. Originally, it only aimed at the investigation of *Hydrazobenzene* and *Benzylaniline* in their connection with the series, investigated by BRUNI, GARELLI, CALZOLARI and GORNI, of *Azobenzene*, *Stilbene*, *Tolane*, *Dibenzyl* and *Benzylideneaniline*, but afterwards, *Diphenylhydrazine*, which is isomeric with *Hydrazobenzene* was also included.

Diphenylhydrazine.

$(\text{C}_6\text{H}_5)_2\text{N}-\text{NH}_2$; melting point: 44°C .

This compound, which I obtained through the kindness of Prof. S. HOOGWERFF of Delft, crystallises from ligroine in the form of colourless, large, lustrous crystals, which exhibit a rather varying aspect. On exposure to light they rapidly assume a brown colour.

¹⁾ Compare F. M. JAEGER, These Proc. VII. p. 658.

Triclino-pinacoidal.

$$a : b : c = 0,7698 : 1 : 0,5986.$$

$$\begin{array}{ll} A = 89^\circ 13\frac{1}{2}' & \alpha = 89^\circ 24' \\ B = 137^\circ 28' & \beta = 137^\circ 28\frac{1}{2}' \\ C = 89^\circ 29' & \gamma = 90^\circ 4\frac{1}{2}' \end{array}$$

The approach to *monoclinic* symmetry is very plain.

Forms observed: $b = \{010\}$, broad and lustrous; $m = \{110\}$, somewhat narrower and reflecting less sharply; $p = \{1\bar{1}0\}$, very lustrous and broad; $c = \{001\}$, well developed and yielding fairly sharp reflexes; $o = \{\bar{1}\bar{1}1\}$, very lustrous and well developed. The crystals are mostly flattened towards p , or they may be developed isometrically with a slight elongation along the c -axis. It is peculiar that in the vertical zone the co-related parallel planes of the forms m , p and b are generally very unevenly developed. Perhaps we may have here a new example of the presence of an acentric crystal; the nature of the surface of the parallel planes is also often different on a plane and its corresponding contreplane.

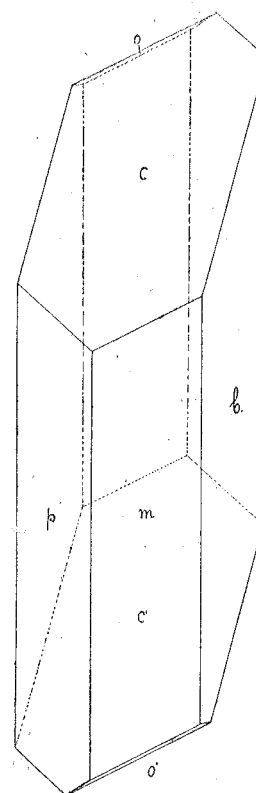


Fig. 1.

(Diphenylhydrazine). Etched figures could not be obtained.

No distinct plane of cleavage.

	Measured:	Calculated:
$b' : p = (0\bar{1}0) : (1\bar{1}0) =$	$* 62^\circ 6'$	—
$b : m = (010) : (110) =$	$* 62^\circ 54\frac{1}{2}'$	—
$b' : c = (0\bar{1}0) : (001) =$	$* 89^\circ 13\frac{1}{2}'$	—
$p : c = (1\bar{1}0) : (001) =$	$* 48^\circ 53'$	—
$o : m' = (\bar{1}\bar{1}1) : (\bar{1}\bar{1}0) =$	$* 73^\circ 38'$	—
$m : c = (110) : (001) =$	$49^\circ 24'$	$49^\circ 28'$
$o : c = (\bar{1}\bar{1}1) : (001) =$	$56^\circ 54'$	$56^\circ 54'$
$p : o = (1\bar{1}0) : (\bar{1}\bar{1}1) =$	$78^\circ 42'$	$78^\circ 36'$
$o : b' = (\bar{1}\bar{1}1) : (0\bar{1}0) =$	$58^\circ 45\frac{1}{2}'$	$58^\circ 43'$
$p : m = (1\bar{1}0) : (110) =$	$54^\circ 59\frac{1}{2}'$	$54^\circ 59\frac{1}{2}'$

In the vertical zone the situation of the optical elasticity axes was almost parallel to the direction of the c -axis; but on b the angle of inclination amounted to about 10° , on m only about 1° . An axial image could not be observed.