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Physics. *"On the shape of the three-phase-line solid-liquid-vapour for a binary mixture."* By Dr. PH. KOHNSTAMM. (Communicated by Prof. J. D. VAN DER WAALS.)

Already for a considerable time I have been engaged in arranging Prof. VAN DER WAALS' thermodynamic lectures, and having arrived at the discussion of the three phase line solid-liquid-vapour, and the metastable and unstable equilibria solid-fluid which are in connection with it, I have formed on some points a different opinion from that laid down in the literature known to me on this subject. It does not seem unprofitable to me to shortly discuss the points of deviation in this and the following communication.

The first concerns the shape of the three phase line solid-liquid-vapour when the solid substance is one of the components, viz. the least volatile one. We find given for this that this line must always possess a pressure maximum [1]), and that it must also possess a temperature maximum [2]) when the solid substance, — as is usual, — melts with expansion of volume. The latter remark is the generalisation of a supposition, advanced by VAN DER WAALS [3]) with respect to the line for ether and anthraquinone. These considerations, however, hold only for definite assumptions on the extent of the difference of volatility of the two components. This appears immediately from the differential equation of the three phase line given by VAN DER WAALS [4]):

$$\frac{dp}{dT} = \frac{\eta_v - \eta_s - \frac{x_v}{x_l}(\eta_l - \eta_s)}{v_v - v_s - \frac{x_v}{x_l}(v_l - v_s)} \quad . \quad . \quad . \quad . \quad (1)$$

in which η, x and v denote resp. entropy, concentration and volume of the coexisting phases, the index v, l and s denoting that resp. the vapour, liquid and solid phase is meant. x_s does not occur, because we assume, that the solid phase is the first component itself so $x_s = 0$. The pressure maximum will now occur in the line when the numerator, the temperature maximum when the denominator can become zero. Now $\eta_v - \eta_s > \eta_l - \eta_s$ and $v_v - v_s > v_l - v_s$; the two cases are therefore only possible when $x_v > x_l$, i.e. when the vapour is richer in the component which does not form the solid phase,

1) BAKHUIS ROOZEBOOM. Die heterogenen Gleichgewichte II. p. 331.
2) SMITS. These Proc. VIII, p. 196; Zeitsch. phys. Ch. LIV, p. 498.
3) These Proc. VI, p. 243.
4) Verslag Kon. Akademie V, p. 490.

(for in the equation is put $x_s = 0$) than the liquid. Or in other words, as we said above, the points sought can only present themselves in the three phase line with the least volatile component as solid substance[1]). However, whether those points *will* occur, depends on the value which $lim \left(\frac{x_v}{x_l}\right)_{x=0}$ will get. If this value may be put = infinite, we get for $x = 0$:

$$\frac{dp}{dT} = \frac{\eta_l - \eta_s}{v_l - v_s}$$

so equal to the slope of the melting-point curve. So we must have both pressure and temperature maximum, at least when the solid substance expands on melting. This was the purport of the above cited remark of VAN DER WAALS about ether and anthraquinone; if however $\left(\frac{x_v}{x_l}\right)_{x=0}$ may not be put infinite, this conclusion is no longer valid; it then depends on the value which:

$$v_v - v_s - \frac{x_v}{x_l}(v_l - v_s)$$

assumes for $x = 0$ whether there exists a temperature maximum or not; if the difference in volatility, so $\frac{x_v}{x_l}$, should not be so large, that this expression becomes negative at the limit, the maximum does not occur, even when $v_s > v_l$.

The question whether such a maximum will occur in many systems, cannot be answered with certainty for the present. For this many data would be required, which we have not at our disposal as yet; it is, however, possible to show the probability that only in very extreme cases the volability of the components will be so diversified, that a temperature maximum is to be expected. For this maximum to be just present, viz. in the triple point of the solid component, it is evidently required that:

$$\frac{x_v}{x_l} \frac{v_l - v_s}{v_v - v_s} = 1.$$

Now the first datum we should want, would be the variation of volume during melting. It seems, however, that only a few data have been collected for this; I have found some in WINKELMANN'S "Hand-

1) If has of course been tacitly assumed here, that there is no maximum vapour pressure; in that case the points in question could be found in *both* three phase lines.

buch" [1]), and in BAKHUIS ROOZEBOOM [2]); LANDOLT tables do not give anything on this subject. The values indicated at the places mentioned confirm that the percentage of these expansions is not very considerable, which was a priori to be expected; they amount for the highest cases to little more than 10% and for most substances they are considerably lower. So if we take 10% as basis, we shall find for by far the majority of the cases a too great, so for our proof a too unfavourable value. If we introduce this value, we get as condition (neglecting v_l by the side of v_v):

$$\frac{x_v}{x_l}\frac{v_l}{v_v} = 10.$$

So we must now try and get a rough estimation of the relation between liquid and vapour volume in the triple point. If at the triple point the vapour tension was of the order of an atmosphere, this ratio would be about of the order of magnitude 1000. Now, however, the vapour tension is always very considerably lower; almost for every substance the melting point lies very considerably below the boiling point. If we now assume that the triple point lies at about $^1/_2\, T_k$, we find the order of the vapour tension from the well known formula:

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

With $f = 7$ and $T = {}^1/_2\, T_k$ this gives $log \frac{p_c}{p_k} = -7$ or $p_c = \frac{p_k}{1000}$. If we put p_k at 100 atms.[3]), p_c becomes of the order of 0.1 atm. So we may safely say that in general v_l/v_v will be smaller than 0.0001. For a temperature maximum it is, therefore, necessary, that at least:

$$\frac{x_v}{x_l} = 10^5 \text{ or } l.\, nat \frac{x_v}{x_l} = 11.5.$$

Now according to a formula which has been repeatedly derived by VAN DER WAALS [4]), for low temperatures (a condition which in this case is certainly fulfilled) the equation:

$$log.\, \frac{x_l}{1-x_l}\,\frac{1-x_v}{x_v} = \left(\frac{f}{m} - 1\right)\frac{dT_k}{T_k\, dx} + \frac{1}{b}\,\frac{db}{dx},$$

[1]) II p. 612 2nd p. 775.

[2]) l. c. I p. 89.

[3]) In the table of LANDOLT and BÖRNSTEIN only two substances occur, ammoniac and water which have a higher p_k; the majority by far is considerably lower, particularly that of the little volatile substances which we have in view.

[4]) See e.g. These Proc. VII, p. 159.

holds, or for the limit, where $\frac{1-x_v}{1-x_l}=1$.

$$log.\frac{x}{x_v}=\left(\frac{f}{m}-1\right)\frac{dT_k}{T_k\,dx}+\frac{1}{b}\frac{db}{dx}\quad\ldots\ldots\quad(2)$$

It is clear that everything will depend on the first term here, because the second would not amount to more than -1 in the utmost case, i.e. when the b of the other component would be zero. Moreover it might even be possible that the second term was positive, it would hence decrease the value of the second member.

The greatest difficulty for our calculation lies now in our ignorance of with the variability of T_k with x, or more strictly in this that for this variability not one fixed rule is to be given, because in every special case it will depend on the special properties of the mixture in question, viz. on the quantity a_{12}, a quantity which does not admit of being expressed [1]) in the characteristic quantities of the components, at least for the present. It is, therefore, certainly not permissible to try and derive results for all kinds of systems. But it is only our purpose to determine the course of T_k for those cases, in which the components differ exceedingly much in volatility, and for those cases it is perhaps not too inaccurate a supposition to assume for the present that the line which represents T_k as function of x, does not deviate too much from a straight one. [2]) On this supposition then we may write $\frac{T_{k_2}-T_{k_1}}{T_{k_1}}$ for $\frac{1}{T_k}\frac{dT_k}{dx}$. As now $\frac{f}{m}=14$, as we already supposed, $\frac{T_{k_2}-T_{k_1}}{T_{k_1}}$ must not descend considerably below

[1]) The equation of GALITZINE-BERTHELOT $a_{12}^2=a_1\,a_2$, which I rejected as general rule already on a former occasion on account of the properties of the mixture ether-choroform (These Proc. IV, p. 159), can certainly not be accepted as such. Not only is it easy to mention other examples which are incompatible with this rule (see e.g. QUINT, Thesis for the doctorate p. 44; GERRITS, Thesis for the doctorate, p. 68); but besides, — and perhaps this must be considered as a still more serious objection — by assuming this equation we wilfully break up the unity of the isopiestic figure (v. D. WAALS, Proc. of this meeting p. 627) by pronouncing its middle region on the left of the asymptote to be impossible, whereas the left and right regions are considered as real. For if $a_{12}=\sqrt{a_1a_2}$ it is never possible that $da/dx=0$ for whatever system; and this takes exactly place in the middle region. I had overlooked this in the paper mentioned; Prof. VAN DER WAALS has since drawn my attention to it. The already mentioned system of QUINT gives an example of the occurrence of this case $\frac{da}{dx}=0$; a_{12} is there smaller than even the smallest of the two a's.

[2]) Cf. VAN DER WAALS, These Proc. VIII, p. 272.

0.9, that $log. \frac{x_v}{x_l}$ may not become smaller than the required value 11.5, or in other words, for the maximum in temperature to be reached, the critical temperature of one component must be about ten times as high as that of the other. A system, in which hydrogen occurs, will most likely show the temperature maximum when the other component has its critical point above 0° C., but already when the more volatile component is nitrogen or oxygen, we shall be more restricted in the choice of the other component. For then the latter must have its critical point at about 1000° C. resp. 1250° C. If ether were the more volatile component, this temperature would almost amount to 4500° C.

This conclusion is hardly affected when we put the temperature of the melting point not at $^1/_2$, but at $^1/_3$ of the critical temperature, as it really is for a number of substances whose critical temperature and melting temperature are known. It is true that this considerably increases the second member of equation (2), and so $\frac{x_v}{x_l}$, but in the same ratio $\frac{v_v}{v_l}$ increases too, so that the quotient remains about unchanged. This is most easily seen when the condition on which a temperature maximum occurs, is written:

$$\frac{x_l}{x_v}\frac{v_v}{v_l} < 0.1 \text{ or } log. \frac{x_l}{x_v} + log.\, v_v - log.\, v_l < log.\, 0.1.$$

Now for $log. \frac{x_l}{x_v}$ we may introduce the value from the equation[1]):

$$log. \frac{x_l}{1-x_l}\frac{1-x_v}{x_v} = \left(\frac{f}{T}\frac{dT_k}{dx} - \frac{1}{p_k}\frac{dp_k}{dx}\right),$$

and write for $log.\, v_v$:

$$log.\, v_v = log. \frac{MRT}{p_c} = log.\, MRT + f\left(\frac{T_k}{T} - 1\right) - log.\, p_k,$$

so that the condition becomes:

$$\frac{m}{f}\left\{1 + \frac{dT_k}{T_k dx}\right\} - \frac{1}{p_k}\frac{dp_k}{dx} - log.\, p_k - log.\, v_l - f + log.\, MRT < log.\, 0.1.$$

So an increase of T will only affect the first term and the term $log.\, MRT$, and the logarithmic change of the latter will certainly amount to less than the change of the former. This now increases when T becomes smaller, hence when at $T = {}^1/_2\, T_k$ the inequality

[1]) These Proc. VII, p. 559.

is not satisfied, this will certainly not be the case for $T = {}^1/_3\, T_k$.

Still, it would be too hazardous to assert that it has now been incontestably proved that e.g. for the system ether-anthraquinone no temperature maximum *can* occur. For we have had to make use of the supposition that T_k depends linearly on x, and though this supposition may possess some degree of probability for critical temperatures that differ much, it is just with substances which — as ether and anthraquinone-lie closer together, that there is some ground for expecting a deviation from the straight line. Only very few experimental data are at our disposal. As such may e. g. be used the determinations on the increase of the plaitpoint temperature by addition of little volatile substances, made by SMITS, CENTNERSZWER and BÜCHNER. For by means of the formula given by VAN DER WAALS[1])

$$\frac{dT}{Tdx_0} = \frac{dT_k}{T_k dx} + \frac{49}{45}\left\{\frac{dT_k}{T_k dx} - \frac{1}{7}\frac{dp_k}{p_k dx}\right\}^2 \quad . \quad . \quad . \quad . \quad (3)$$

in which we need only pay regard to the principal terms (those with T_k), we may calculate the value of $\frac{dT_k}{T_k dx}$ from those directly measured. If we now calculate by the aid of the thus found value of $\frac{dT_k}{T_k dx}$ and the supposition of rectilinearity, T_{k_2}, i. e. the value of T_k for the admixed substance, we find the data collected in the following table. (P. 645).

From this appears that the values calculated in this way at least for some substances, and particularly for anthraquinone according to the determination by SMITS, are not inconsiderably lower than double the melting point temperature. It may, therefore, be considered highly probable that these lines are convex seen from below, and so the absolute value of $\frac{dT_k}{T_k dx}$ will be larger than might be expected from the supposition of rectilinearity. With our imperfect knowledge of the further course of the plaitpoint line, and hence à fortiori of the line for T_k an estimation as to this will, naturally, remain very uncertain; but yet it seems to me that something about this may be ascertained in the following way. We have on the side of the ether:

$$\left(\frac{dT_k}{T_k dx}\right)_{x=0} = \left(\frac{da}{adx} - \frac{db}{bdx}\right)_{x=0},$$

[1]) These Proc. VII, p. 272 and 296.

Second component	First component	Observer	T_k calculated	Double the melting-point temperature
Anthraquinone	Ether	SMITS	932°	1120°
"	SO_2	CENTNERSZWER	1032	1120
Resorcin	"	"	903	960
Camphor	"	"	790	900
Naphthaline	"	"	770	700
"	CO_2	BUCHNER	640	700
Paradichloro benzene	"	"	670	650
Paradibromo benzene	"	"	690	720
Bromoform	"	"	640	560
Orthochloronitro benz.	"	"	760	610

BUCHNER's values have been borrowed from his thesis for the doctorate (Amsterdam 1905); those of CENTNERSZWER from a table by VAN LAAR (These Proc. VIII, p. 151); that of SMITS has been calculated from his determination: plaitpoint at 203° and $x = 0.015$, (These Proc. VII, p. 179).

and so when introducing for a the quadratic and for b the linear function:

$$\left(\frac{dT_k}{T_k dx}\right)_{x=0} = \frac{2a_{12} - 2a_1}{a_1} - \frac{b_2 - b_1}{b_1} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Now it will not be too hazardous an estimation, when — keeping in view that the formula for ether is $C_4H_{10}O$ and for anthraquinone $C_{14}H_8O_2$ —, we put the size of the anthraquinone molecule at about two or three times that of the ether molecule; so $b_2 = 2b_1$ à $3b_1$. If we introduce this value and the value of $\frac{dT_k}{T_k dx}$, calculated by the aid of equation (3), into equation (4), we obtain a value for a_{12}. Assuming that the value of T_k for anthraquinone is $2 \times 560° = 1120°$, we can find an a_2 from the ratio of the critical temperatures of ether and anthraquinone, and the a for ether; and with these quantities we can finally calculate the $\frac{dT_k}{T_k dx}$ on the anthraquinone side from:

$$\left(\frac{dT_k}{T_k dx}\right)_{x=1} = \frac{2a_2 - 2a_{12}}{a_2} - \frac{b_1 - b_2}{b_2}.$$

Starting from $b_2 = 2b_1$ we find in this way $\left(\frac{dT_k}{T_k dx}\right)_{x=1} = 0.66$; with $b_2 = 2.5$: 0.65 and with $b_2 = 3\,b_1$: 0.64. The error which we committed in our choice of b_2, will, therefore, bring about no considerable modification in the result; it would, indeed, be considerably modified if the critical point of anthraquinone should prove to lie considerably higher than 1120°. This is not in contradiction with our former remark that it is of little importance whether the reduced temperature is $^1/_2$ or $^1/_3$ at the triple point; for this we started from the supposition of the linear dependence, whereas here we have abandoned this supposition, and calculate this dependence from the experimental data. So according to the course of reasoning followed here the a_{12} is given by the experiment, and the smaller value of m would now result in a higher value of a_2 at given b_1, b_2 and a_{12}. If our estimation may be considered as not too inaccurate, we may conclude that the deviation from rectilinearity does increase the value of $\left(\frac{dT_k}{T_k dx}\right)_{x=1}$, but by no means in the degree which would be required to reach the critical value 0.9. (The value derived from the supposition of rectilinearity is 0,58).

Though the foregoing calculations teach us hardly anything positive, they fix first of all our attention on the great desirability of more data concerning the values of the quantities a and b of very little volatile substances; for it appears again that the whole behaviour of all the systems in which such substances appear, is controlled by these quantities, and it would exactly be of great importance for the theory of mixtures, if its results could be tested by such cases where the properties of the two components differ strongly. It is true that it will not be easy to determine the critical point of such substances in the usual way, but we should have gained already much if we could obtain an estimation of the critical temperature by calculation of the a and b from the deviations from the law of Boyle in rarefied gas state, so still some hundreds of degrees below the critical point.

And further I think that after the foregoing I may be allowed to draw this conclusion, that the appearance of a temperature maximum in the three phase line, far from being the general case, will be confined to mixtures of very exceptional nature.

Much more frequently than a temperature maximum will a pressure maximum occur. It appears from equation (1) that this will always be the case, when the expression:

$$(\eta_v - \eta_s) - \frac{x_v}{x_l}(\eta_l - \eta_s)$$

may become negative. Now it is true that we cannot properly say that $\eta_v - \eta_s$ is a heat of sublimation and $\eta_l - \eta_s$ a latent heat of melting, because the η's do not refer to the same concentration, but we may say that $\eta_v - \eta_s$ is of the order of magnitude of a heat of sublimation, $\eta_l - \eta_s$ of the order of a latent heat of melting. Or in other words $\eta_v - \eta_s$ will be about 7 or 8 times $\eta_l - \eta_s$. So in all cases where $\left(\frac{x_v}{x_l}\right)_{x=0} < 7$ the pressure maximum in the three phase line will also fail. Here too the necessary data are wanting to ascertain whether there are many systems for which the $\frac{x_v}{x_l}$ at the triple point will descend to this amount. For, determinations of vapour tension or direct determinations of the required ratio have been nearly always carried out at considerably higher temperature [1]), and for the calculation by the aid of the just used formula the necessary data fail here too; besides, it would be doubtful whether the formula would be accurate enough, now that we have to deal with such small amounts. But — quite apart from the existence of mixtures with minimum vapour pressure — the existence of a system like ether-chloroform [2]) where on the chloroform side x_v becomes almost equal to x_l, already proves, that such systems exist.

In any case to the scheme for the possible course of the two three phase lines in a binary system plotted by BAKHUIS ROOZEBOOM in Fig. 108 of Vol. II of his "Heterogene Gleichgewichte", must be added types VII and VIII, characterized by a succession of sections,

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[1]) Particularly when we notice that the ratio of x_v and x_l would have to be calculated from the formula:

$$\frac{1}{p}\frac{dp}{dx_v} = \frac{x_v - x_l}{x_v(1-x_v)} \quad \text{or} \quad \frac{1}{p}\frac{dp}{dx_l} = \frac{x_v - x_l}{x_l(1-x_l)}$$

and the value obtained will, therefore, strongly vary in consequence of a change of temperature of some ten degrees, which have generally an enormous influence per cent on the pressure in the neighbourhood of the triple point.

[2]) KOHNSTAMM and VAN DALFSEN, These Proc. IV, p. 159. BAKHUIS ROOZEBOOM (l.c. I p. 41) deems it probable that also systems of gases with water and of water with many salts will show a similar shape. However, for such systems whose three phase line for the least volatile substance shows a pressure maximum, at least at temperatures that do not lie too far from the triple point, the shape of the p, x-line will have to deviate considerably from the line drawn there in Figs. 15 and 19, because from that shape would follow $x_v = x_l$.

denoted by 1 . 7 . 4 . 5 and 1 . 7 . 8 . 5 in ROOZEBOOM's nomenclature [1]). Type VII (see Fig. 1), is therefore distinguished from III in this that

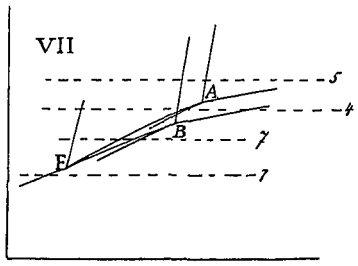

Fig. 1.

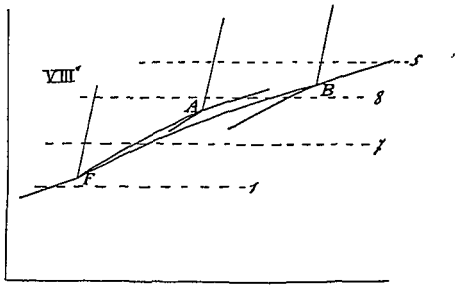

Fig. 2.

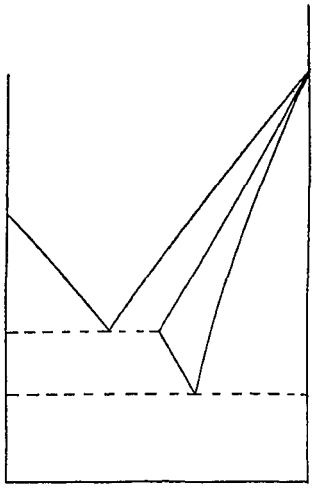

Fig. 3.

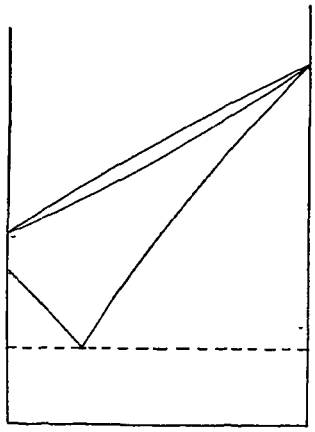

Fig. 4.

section 3 disappears; our Fig. 3 (lacking with ROOZEBOOM) takes its place. Type VIII (see Fig. 2) is distinguished from type V in this that instead of section 6 the section indicated in Fig. 4 appears between 8 and 5.

Physics. — *"On metastable and unstable equilibria solid-fluid."* By Dr. PH. KOHNSTAMM. (Communicated by Prof. J. D. VAN DER WAALS.)

In a preceding communication [2]) I discussed a point on which I could not agree with the existing literature on the equilibria solid-fluid. A second point which will prove to be allied to the preceding one, concerns the course of the curves which are to indicate the

[1]) Loc. cit. p. 392.

[2]) Proceeding of this meeting, p. 639.