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Physics. — *"On the system hexane-water."* By Dr. F. E. C. Scheffer.
(Communicated by Prof. J. D. van der Waals).

1. In the 17th contribution [1]) to the theory of binary mixtures
Prof. van der Waals has demonstrated that the phenomena which
occur when the concentration of the vapour phase with three-phase
pressure lies between that of the two coexisting liquid phases, may
be derived from the course of the plaitpoint curve already drawn
in fig. 43 of the 14th contribution [2]). In this T-x projection the
plaitpoint line exhibits two minima and one maximum; the minimum
P_{ab} and the maximum P_{cd} are heterogeneous double plaitpoints,
hence they lie in the covered region, and correspond to cusps in the
P-T projection. The other minimum indicated in fig. 43 by Q_2, is
a homogeneous double plaitpoint, and may occur both in the stable
and in the covered region. Further two points are found on the
plaitpoint curve which indicate the highest, resp. the lowest temperature
at which three-phase equilibrium can occur. These two points, the
critical endpoints, which indicate stable states, must lie on the
branches AP_{cd}, resp. BP_{ab} in fig. 43.

Whereas the different situation of the lower critical endpoint on
the branch BP_{ab} does not bring about an essential modification in
the phenomena, three possibilities present themselves with regard to
the situation of the higher critical endpoint, which give rise to the
distinction of three different cases; the endpoint of the three-phase
pressure can namely either lie on the leftside (Type 1), or on the
rightside (Type 3) of the minimum on the plaitpoint line, or it can
just coincide with it (Type 2). The last case, to which fig. 43
corresponds, may be considered as the transition between the two
preceding ones.

We have an example of type 3 in the system ether-water.

For the peculiarities which present themselves for this system I
may refer to my publication in these Proceedings [3]) and to Prof.
van der Waals' 21th contribution [4]).

The chance of the occurrence of type 2 seems naturally very
slight; yet it is very well possible that further investigation will
make us acquainted with a system for which the distance between
the minimum of the plaitpoint line and the endpoint of the three-

[1]) These Proc. Vol. XIV p. 655.
[2]) These Proc. Vol. XI p. 816.
[3]) These Proc. Vol. XV p. 380.
[4]) These Proc. Vol. XV p. 602.

phase line is so small that it is smaller than the errors of observation. Then we shall be compelled to class such a system with type 2. And that the chance to such a situation may not be so slight as might be supposed at first sight, appears from my investigation of the system ether-water, where two such transitions are found. In this system the distance between the points Q_2 and A (see fig. 43 of Prof. VAN DER WAALS' 14th contribution) is so small that I could not possibly decide whether the minimum of the plaitpoint curve occurs in the figure, lies on the axis, or would be found just outside the figure. Besides, it appeared that in the critical endpoint the slopes in the P-T projection of the three-phase line and the plaitpoint curve differed so little that practically we have to do with a transition case here too.

Of type 1 no example was known as yet. In the 17th contribution Prof. VAN DER WAALS has only shortly alluded to this case, and in fig. 51 he has given a P-T projection which corresponds with this case, but omitted a full discussion, particularly also because this case is attended with great complications. I have, however, now succeeded in finding an example of this type in the system hexane-water, the particularities of which I wish to describe in the following pages.

2. Without further purification the vapour pressure line was determined with KAHLBAUM's synthetically prepared hexane, and the three-phase line with a great quantity of water (47 mol. $^o/_o$ H_2O). For the filling of the test-tube, just as for the following investigation, the apparatus was used which I described in my paper on the system ether-water [1]. The following values were found for the hexane $t_k = 235,3$, $P_k = 30,1$ atm., for the critical endpoint $t_k = 222,3$, $P_k = 51,95$. It appeared from these data that the three-phase pressure lies higher than the vapour tension of the two components (at the same temperature), and that therefore most probably the concentration of the vapour lies between that of the coexisting liquid phases. Whether, however, we had to do here with type 1 or 3, could not be decided from these observations.

Before proceeding to an accurate investigation I purified the hexane in the following way. A fractionation of the hexane yielded a fairly large middle fraction of the boiling point 68.9° (range 0.1); $t_k = 234.55$; $P_k = 30.1$. Accordingly only the critical temperature had been appreciably changed by this fractionation.

Then the hexane was heated with reflux by the side of sodium

[1] These Proc Vol. XV p. 382, 383 and fig. 1.

for 30 hours, then shaken with a sulphuric acid-nitric acid mixture, washed three times with a solution of potassium hydroxide, four times with water, dried on potassium hydroxide, and then fractionated. Repeated fractionation, the last time on phosphorus pentoxide yielded a large fraction, which distilled over within a range of 0°05. Boiling point 69.0°. For the hexane purified in this way we found:

$$t_k = 234.6 \quad ; \quad P_k = 30.15.$$

The range of pressure for isothermal condensation, determined about 10 degrees below the critical temperature, amounted to from 0.1 to 0.2 atmosphere.

By means of this hexane the critical endpoint was determined with a pretty considerable quantity of water. (47 mol. $^o/_o$ H_2O). This experiment yielded:

$$t_k = 222,05 \quad ; \quad P_k = 52,05.$$

These values differ but little from those which were obtained with the impure hexane. So the stable part of the plaitpoint curve on the hexane side extends over a range of **21,9** atm. and **12°,55**.

3. In order to investigate the mixtures with a great quantity of hexane, I have, starting from pure hexane, prepared mixtures with increasing quantity of water, till 1 reached the critical endpoint. Of these mixtures I have determined the initial and the final condensations of the hexane layer. I have had to relinquish the thought of a determination of the disappearance or appearance of the waterlayer here as in my investigation of the system ether-water, as a slight quantity of water again becomes invisible here. Besides, we could dispense with these determinations as well now as on the former occasion, as their knowledge is not required for an insight into the phenomena. For if there is no layer rich in water by the side of the vapour and the liquid rich in hexane the pressure deviates from the three-phase pressure; if there is one, the pressure gets on the three-phase line which is equal for all the mixtures, and reversely from the fact that the found pressure deviates or does not deviate from the three-phase line, determined with excess of water, we may conclude whether we have to do with a two-phase or with a three-phase equilibrium. Besides, in the observation of one or more points of the three-phase curve, which was possible for almost all the mixtures if only the temperature be low enough, I had a criterion of the purity of the mixtures The observations of these three-phase pressures have been given in the subjoined table 1, and deviate

nowhere appreciably from the three-phase pressure of the mixture with great quantity of water.

In fig. 1 the P-T projection is given of the vapour pressure lines of the components, that of the hexane by AB, that of the water by CD The critical point B of the hexane here happens to lie in the immediate neighbourhood of the waterline, so that the volatility of the two components at the critical point of hexane is equally great. The vapour tension line CD of the water must be thought prolonged towards higher temperature as far as the critical point of water, which according to the latest determinations from the Deutsche Reichsanstalt lies at 374° and 217.5 atm. [1]) The three-phase line is indicated by EF; hence it lies appreciably higher than the vapour tension lines of both components.

On the plaitpoint line BF the critical points are given of eight mixtures; in each of these plaitpoints the liquid and the vapour branch of the sections for constant concentration meet. As a rule only a small number of points of the vapour branch have been determined, because at low temperature the volume would have to be more considerably increased than the test-tube allowed. The further continuation of the vapour branches towards lower temperature might be realized by a slighter filling of the test tube, but this would at the same time increase the error in the concentration of the mixtures. The examined mixtures all contain a great excess of hexane; the water-content varies between 0 and 27 mol. percentages, but if one considers that the molecular weight of hexane is almost five times as great as that of water, and that hence the greatest quantity of water only amounted to a little more than seven percentages by weight, and not even so many percentages of volume, because the specific weight of hexane is smaller than water, it appears that if the error in the concentration is to be small, a great filling is required. In this investigation just as in my investigation concerning the system ether-water, a Cailletet tube with widened upper end has rendered excellent services. The mixture that contained the smallest quantity of water (2,3 mol. percent.), contained 3,4 mgr. of water to about 700 mgr. of hexane; when a Cailletet tube of the common shape had been used, the total filling could at most have been a fifth part.

For the mixtures from 5 to 8 (8 inclusive) the phenomenon of the isothermal retrograde condensation could be clearly realized, as in fact will also be clear from fig. 1. In the neighbourhood of the

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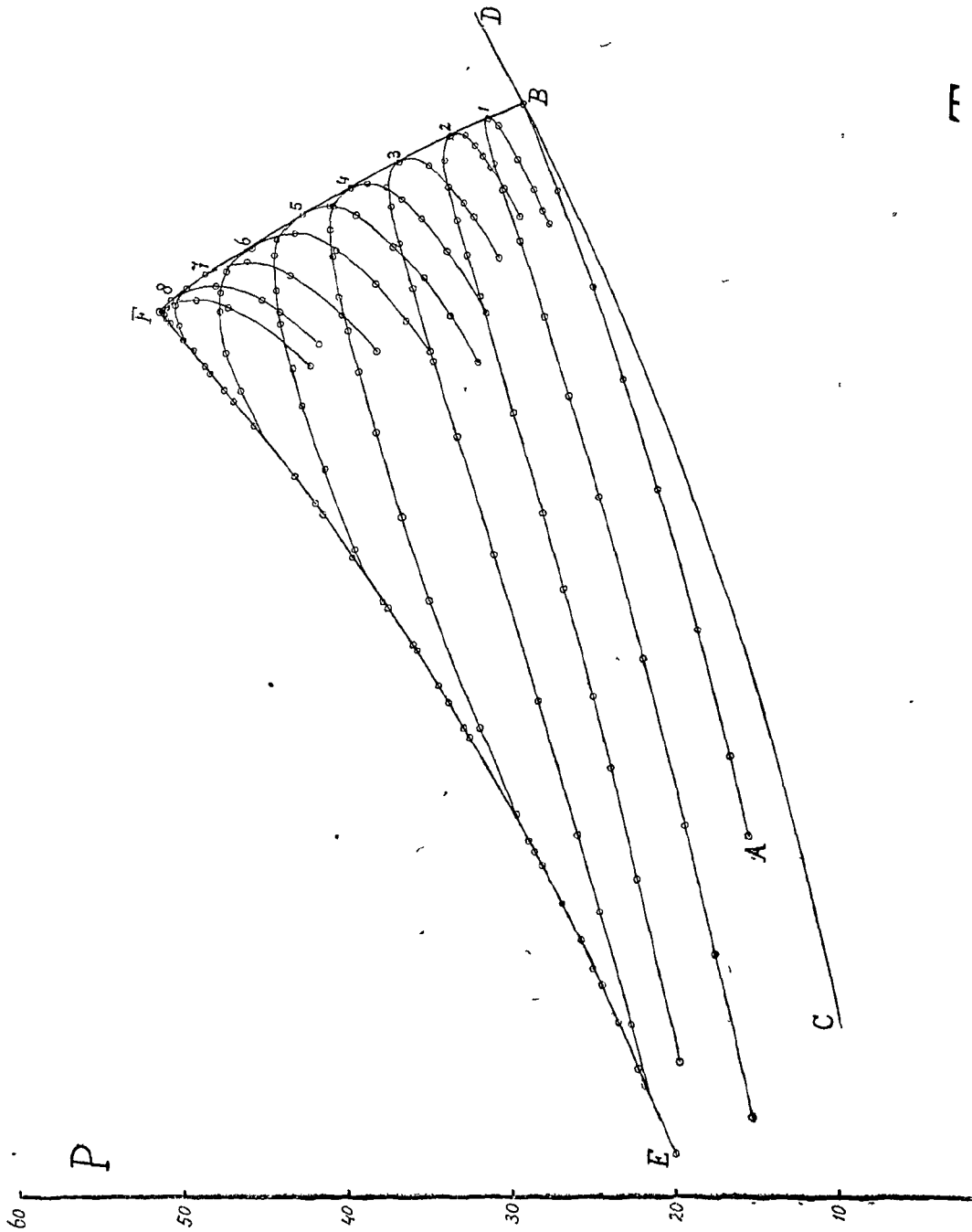[1]) LANDOLT BÖRNSTEIN-ROTH, Tables p 447.

Fig. 1.

critical endpoint the vapour branch of a ninth mixture is found in the P-T-figure, the water-content of which was somewhat greater than corresponds to the critical endpoint, and the critical point of which accordingly coincides with F, and no longer lies on the stable vapour branch.

The distance between this concentration and that of the critical endpoint, however, is so small that the vapour branch still terminates on the three-phase line in the immediate neighbourhood of the critical endpoint. With still greater water-content the point of intersection of vapour branch and three-phase line moves to lower temperature, and then the vertical tangent will disappear from the stable part of the vapour branch, and this will put an end to the retrogade phenomenon; I have, however, not continued the investigation of this, as it was perfectly needless for the insight into the phenomena.

I have realized the intersection between the liquid branch and the three-phase line for the mixtures from 3 to 8 inclusive; below these points of intersection these mixtures yield the three-phase pressures which are equal for all concentrations, and hence the criterion of purity which I mentioned in the beginning of this paragraph. I have not prolonged the liquid branches of the mixtures 1 and 2 so far that the above-mentioned intersection takes place, as this intersection takes place outside the temperature range investigated by me.

The investigations which have served for the construction of figure 1, are collected in table 1. The vapour tension line of the hexane, the three-phase line determined by means of a mixture with about 47 mol. percent. of water, besides the observations obtained with the nine above-mentioned mixtures, are found there. In the table the critical data are given in bold type, above them the values of the liquid branch, below them those of the vapour branch are given.

4. I have constructed the T-x projection of the critical line in fig. 2 by the aid of these data, this projection appears to deviate only very little from a straight line. In the same figure are also given the points of intersection of the liquid branches of the sections for constant concentration of the above-mentioned mixtures with the three-phase line. These points of intersection indicate the states where liquid rich in hexane exists by the side of a very small quantity of vapour and of liquid rich in water, and so the locus of these points of intersection yields a liquid branch of the three-phase region. In the critical endpoint this branch passes with a horizontal tangent

into the vapour branch which extends towards higher water concen-, trations and is not drawn in the figure. In an analogous way the $P\text{-}x$ projection of the plaitpoint curve and of the liquid branch of
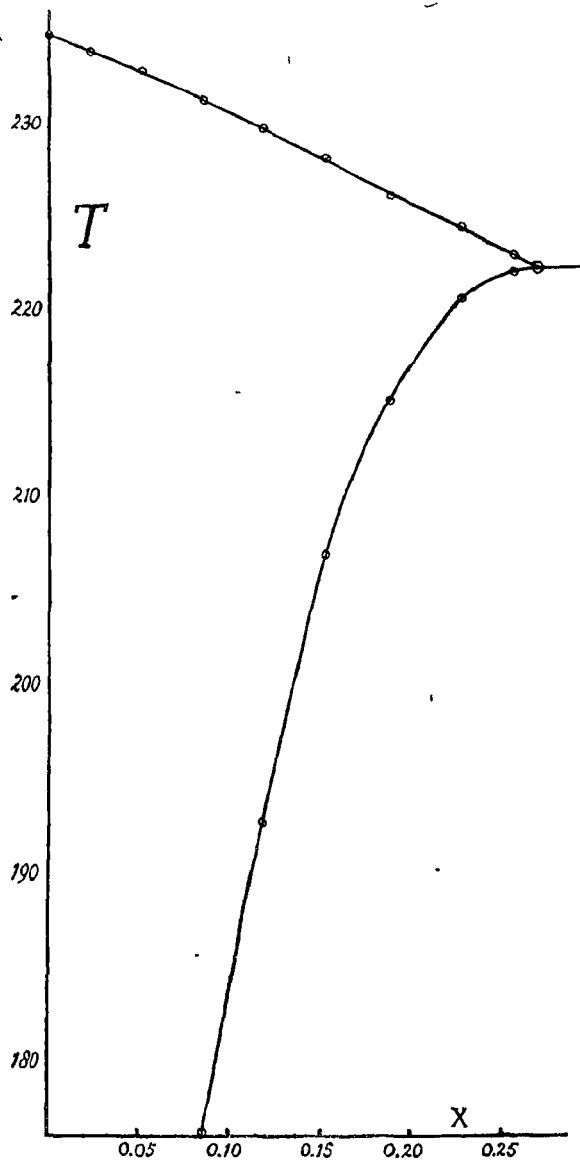

Fig. 2.

the three-phase region is indicated in fig. 3. It appears again that both lines have a perfectly regular course; the projection of the plaitpoint line has a feeble curvature; it is concave seen from below; here too the liquid branch of the three phase equilibria is connected with the not drawn vapour branch by means of a horizontal tangent.

TABLE 1.

| Hexane		Three-phase line		(1) x = 0.023		(2) x = 0.052		(3) x = 0.086		(4) x = 0.118		(5) x = 0.153		(6) x = 0.189		(7) x = 0.228		(8) x = 0.257		(9) x = 0.277	
t	p	t	p	t	p	t	p	t	p	t	p	t	p	t	p	t	p	t	p	t	p
191.2	15.7	177.4	22 3	174.6	15.4	177.8	19.8	172.4	20.0	180.2	23.55	190.85	29.2	182.4	24.6	189.4	28.3	202.4	36.35	187.2	27.1
195.9	16.9	183.3	25.15	184.25	17.7	188.6	22.5	180.0	22.8	185.0	25.9	196.95	32.8	200.0	34.75	216.8	47.4	220.4	50.55	222.2	52.1
203.4	19.0	190.2	28.8	191.8	19.6	195.2	24.2	186 7	24.8	192.45	29.9	202.1	36.0	207.6	40.1	218.85	49.2	221.4	51.35	222.4	51.6
211.75	21.5	199.05	34.2	201.65	22.3	199.4	25.35	191.2	26.2	197.5	32.2	208.1	39.95	210.8	42.4	219.8	49.8	221.65	51.55	222.8	49.7
218.2	23.75	204.6	37.9	211.25	25.2	205.8	27 2	199.1	28.65	205.05	35.4	212.8	41.9	212.4	43.7	221.2	50.8	221.95	51.7	222.35	47.8
223.7	25.65	205.0	38.2	217.2	27.05	210.3	28.55	207.8	31 45	210.0	37.1	216.6	43.3	217.45	47.0	222.45	51.0	222.75	51.3	218.9	42.9
229.4	27.9	210.15	42.0	221.9	28.6	216 2	30.4	214.8	33.8	215.0	38.75	218.75	43.9	219.6	47.9	223.45	50.4	223.6	48.5		
234.6	30.15	215.4	46.2	226.4	30.15	223.1	32.5	219.25	35.3	218.6	39.85	221.35	44.7	222.1	48.3	224.25	49.3	222.8	45.8		
		222.05	52.05	229.4	31.2	225.5	33.3	223.5	36.6	221.0	40.55	223.35	44.95	223.2	48.3	225.1	46.7	222.1	44.7		
				231.0	31.8	227.6	33.95	226.2	37.45	223.05	41.1	225.45	45.1	224.5	47.95	224.35	44.15	220.2	42.3		
				233.65	32.2	229.6	34.45	228.4	37.95	225.4	41.5	226.4	44.95	225.9	46.4	222.0	40.9				
				233.25	31.55	231.15	34.8	231 05	37.5	227.0	41 7	226.95	44.6	226.8	43.9	219.8	38.75				
				231.2	30.4	232.65	34.35	230.85	35.7	228.4	41.5	227.9	43.4	225.8	41.35						
				229.4	29.3	232.6	33.45	228.6	33.55	229.5	40.45	228.4	41.75	223.8	38.95						
				228.2	28.8	232.05	32.9	227.8	32.95	229.8	39.5	227.85	40.1	221.6	37.0						
				227.4	28.35	231.4	32.4	225.4	31.4	229.55	38.3	226.4	37.8	219.8	35.5						
						230.8	31.9			228.8	37 35	224.2	35.95								
						229.5	31.1			227.65	36.05	221.95	34.2								
						227.85	30.15			225.75	34.5	219 2	32.6								
										222.15	32.1										

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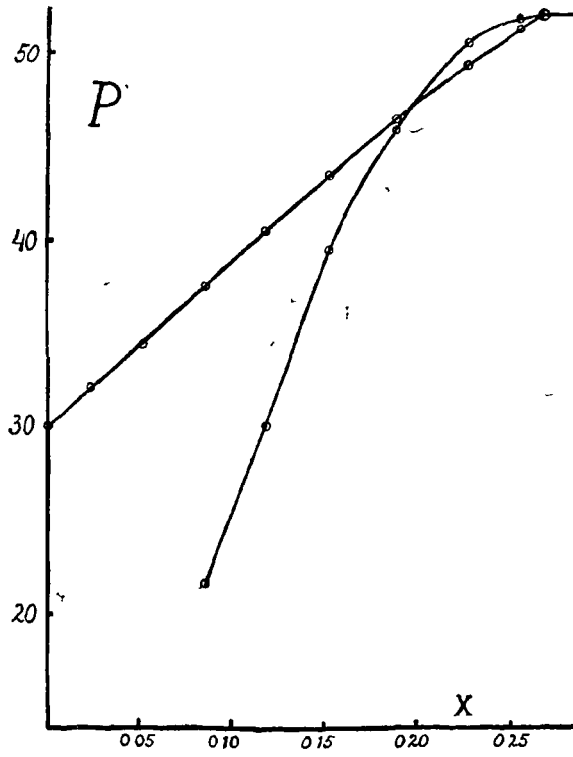
Fig. 3.
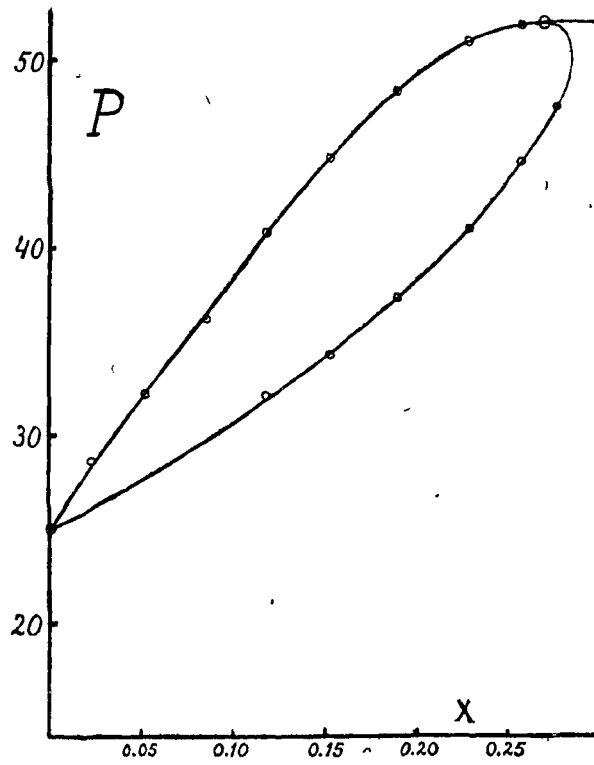
Fig. 4.

The second inteisection of these lines occurring in this figure is of course quite incidental, i.e. the point of intersection has no special physical signification.

Finally I have given in fig. 4 the P-x section for the temperature of .the critical endpoint. In this section the initial and the final condensations of the hexane layer are found, the liquid branch is again in connection with the vapour branch in the critical endpoint; the retrograde portion of the vapour branch is only narrow. The above-mentioned ninth mixture has served to determine the point of the vapour branch which lies at higher water concentration than the critical endpoint.

5. When we now review the results yielded by this investigation, it appears that this system really belongs to the type which we denoted by 1 in § 1; in the T-x projection the critical line, namely, descends, proceeding from the hexane side towards greater water concentration. a minimum temperature is, however, not reached, as the endpoint of the three-phase line appears before that time. Hence the minimum that was to be expected lies in the covered region. It is, however, remarkable that the T-x-projection does not betray the tendency towards this minimum; if there is question of a curvature, it would sooner have the opposite sign. And an analogous particularity also presents itself in the P-T projection; the curvature of this projection would theoretically have to be expected so, that the tendency to the reaching of a vertical tangent is expressed; the curvature lies here, however, certainly to the other side. So in connection with the theoretical considerations we should have to conclude here to the existence of a point of inflection in the plaitpoint line in the covered region.

6. When comparing the pressures of the threephase equilibrium with the vapour tensions of the two components, we come to the remarkable conclusion *that the three-phase pressure is higher than the sum of the vapour tensions of the components at the same temperature*. This conclusion appears from table 2, in which the difference between the three-phase pressure and the sum of the vapour pressures for some temperatures are given.

The difference of pressure appears to increase with the, temperature, so that it has reached its greatest value of a little more than three atmospheres at the critical endpoint.

These facts seem astonishing at first sight, because one is naturally inclined to consider the vapours of the two components and

TABLE 2.

Tempera-ture	Three-phase pressure	Hexane-pressure	Water pressure	Difference
195	31.6	16.7	13.8	1.1
200	34.8	18.0	15.3	1.5
210	41.8	20.9	18.8	2.1
220	50.2	24.3	22.9	3.0
222.05	52.05	25.0	23.8	3.25

the three-phase vapour as rarefied gases. If this is the case, it may be derived from the laws of the rarefied gases by a thermodynamic way that the three-phase pressure is necessarily smaller than the sum of the vapour tensions of the two components. For the proof we refer to the second part - of the Thermodynamik of VAN DER WAALS-KOHNSTAMM (p. 476). The conclusions stated there: "Denn der Partialdruck einer Komponente in einer absolut stabilen Phase kann niemals grosser sein als der Sättigungsdruck der reinen Komponente" and "Für alle absolut stabilen Phasen ist also der Partialdruck kleiner als der Sattigungsdruck; auch wenn der Dreiphasendruck höher liegt als die beiden Sättigungsdrucke, wird er also dennoch immer kleiner sein als die Summe dieser beiden Tensionen" refer therefore only to equilibria of real gasphases, i e. gases, which do not possess an appreciable surface tension. If, however, the gas phases depart from the rarefied gas laws, so if the phases have surface layers, the quantities a , a_2 and a_{12} resp. b_1, b_2, and possibly also b_{12} play a part, and the above-mentioned proof is no longer valid.

7. It appears from the determinations of § 3 that the water-content of the liquids rich in hexane increases pretty considerably on approach to the critical endpoint. Though it was not indispensable for the purpose of this investigation to know the concentration of the liquids rich in water of the three-phase equilibrium, I have yet carried out some experiments with a view of getting to know these concentrations. It then appeared that the quantity of hexane occurring in the liquids rich in water, is particularly small. With a mixture of 0.06 mol. perc. of hexane it was still possible for me to follow the three-phase line throughout the investigated temperature range. The hexane content of the water-layer is therefore decidedly smaller than 0.06 mol. perc.

So in this water layer we' meet with a solution in which the hexane occurs in "gas concentration". If we now question what osmotic pressure would occur when we bring this hexane-water layer (in three-phase equilibrium) into contact with pure water by means of a membrane only permeable to water, we can therefore easily calculate this pressure by the aid of VAN 'T HOFF's laws on the osmotic pressure. In the three-phase layer rich in water less than 0.06 gram-molecule of hexane is found to 100 gram-molecules of water. A hundred gram-molecules of pure water have a volume of $1,8 \times 1,195$ liters under their own vapour pressure at 220°, as the specific volume of water at this temperature amounts to 1,195. Now the pressure on this water layer at 220° is not the saturated vapour pressure of water (22,9 atm.), but the three-phase pressure (50,2 atm.). So we should have to take the compressibility of water into account at the said temperature. As, however, the water is here still very far from the critical temperature, the compressibility is probably slight here, and roughly we may estimate the volume at 1.8×1.195 liters $= 2.15$ liters. A gram-molecule of hexane, therefore, is found in more than $\frac{2.15}{0.06}$ liters $= 36$ liters.

At 0° C. and one atmosphere one gram-molecule of gas occupies a volume of 22,41 liters, so at 220° C. one of $\frac{27.3 + 220}{273}$ 22.41 l. $=$ 40.5 l. Hence the osmotic pressure of the hexane is smaller than $\frac{40,5}{36}$ or about 1.1 atmospheres.

So the three-phase mixture with a pressure of 50.2 atm. would be osmotically in equilibrium with water of $50.2 - 1.1 = 49.1$ atm.

If, therefore, the pressure of the pure water is lower than 49.1 atm., water from the three-phase mixture will pass through the membrane, and so when we bring the three-phase mixture into contact with water under its saturated vapour pressure (22.9 atm.), water passes through the membrane. Hence we should get here unmixing, so splitting up of the hexane-water mixture in the components.

One might surmise a contradiction here to the second law of thermodynamics. For if one considers that hexane and water both under their own vapour pressure, spontaneously mix under formation of the three-phase mixture, and that the three-phase mixture on the other hand cedes water to water under its own vapour pressure through a semi-permeable membrane, one might conclude to a conflict with the second law. But of course this is only seemingly so.

In case of osmotic equilibrium the thermodynamic potential of the water is equal on both sides of the wall. If water under vapour pressure is brought into contact with the three-phase mixture, un-mixing will take place as appears from the above calculation; so the thermodynamic potential of the water in the three-phase mixture is greater than the thermodynamic potential of the water under vapour-pressure.

Reversely if in a vessel water by the side of vapour is made to mix with hexane by the side of vapour, we shall have to conclude to a rise of the thermodynamic potential of the water.

In order to examine whether the same thing is also the case for hexane, we must be able to calculate the ósmotic pressure of the three-phase mixture with respect to a wall permeable to hexane. This, however, is impossible, as the fluid phase contains about 27 mol. percent. of water at the critical endpoint, and can, therefore, no longer be considered as dilute solution. It is, however, possible to find out something about the value of the osmotic pressure of the binary equilibria in which dilute solutions of water take part. When, for instance, the P-x section for the critical endpoint (fig. 4) is considered, it appears that a liquid with 2 mol. percent. of water possesses an external pressure of 28 atm., if it coexists with vapour. This solution contains one gram-molecule of water to 49 gram-molecules of hexane. The specific volume of hexane at 222° amounts to 2,69 according to 'Young. Now at this temperature the hexane is not far from the critical temperature, and we must, accordingly, expect a pretty great compressibility. If the compressibility. were zero, the volume of one gram-molecule of water would amount to 49 $\times$ 86 $\times$ 2,69 c. c. or about 11,3 l. As now one gram-molecule of gas occupies a volume of 40,6 l. at this temperature under the pressure of one atmosphere, the osmotic pressure of the mixture with respect to a membrane permeable to hexane would amount to about 3,6 atmospheres. The difference in external pressure between the mixture and the pure hexane under the vapour pressure is, however, three atmospheres. So we, conclude that in the experiment in which the two-phase mixture (2 mol. $^0_0$ of water in the liquid) is brought into contact with hexane under the vapour-pressure by means of a membrane only permeable to hexane, hexane will pass to the two-phase mixture. The compressibility does not affect this conclusion, as the osmotic pressure is still increased in conse-quence of the compressibility, and the qualitative result can, there-fore, not be modified by it.

If this behaviour continues to exist for greater concentrations, the

three-phåse mixture separated by a membrane from pure hexane would absorb hexane, but separated from the pure water it would expel water. So the thermodynamic potential of the water in the three-phase mixture is greater than that of pure water; that of hexane would be smaller than that of pure hexane on the said assumption. If hexane and water is brought together each under its own vapour-pressure, three-phase equilibrium sets naturally in. In this a rise occurs in the thermodynamic potential of the water.

The thermodynamic potential of one component in a binary mixture is indicated by:

$$M_1\mu_1 = Z - x\left(\frac{dZ}{dx}\right)_{pT}.$$

If in a pure substance A a little of a second substance B is dissolved, the thermodynamic potential of A is changed by an amount:

$$dM_1\mu_1 = \left(\frac{dZ}{dp}\right)_{xT}dp - x\left(\frac{d^2Z}{dx^2}\right)_{pT}dx - x\left(\frac{d^2Z}{dxdp}\right)_{T}dp$$

or

$$dM_1\mu_1 = \left(v - x\left(\frac{dv}{dx}\right)_{pT}\right)dp - x\left(\frac{d^2Z}{dx^2}\right)_{pT}dx.$$

For a dilute solution this value becomes:

$$dM_1\mu_1 = vdp - MRT\,dx.$$

This value is zero for osmotic equilibrium and the osmotic pressure is indicated by:

$$dp_0 = \frac{MRT}{v}dx \quad \ldots \ldots \ldots \ldots (1)$$

If now the change of the external pressure is considered when a little of B is dissolved in A under the vapour-pressure in such a way that the obtained solution is again under its own vapour pressure, then:

$$v_{21}\,dp = (x_2 - x_1)\left(\frac{d^2Z}{dx_1^2}\right)_{pT}dx_1.$$

Hence the change in external pressure amounts to :

$$dp = \frac{x_2 - x_1}{v_{21}}\left(\frac{d^2Z}{dx_1^2}\right)_{pT}dx_1.$$

For dilute solutions the gas volume v_2 may be substituted for v_{21}, if the temperature does not lie in the neighbourhood of the critical temperature; hence:

$$dp = \frac{x_2 - x_1}{v_2 x_1}MRT\,dx_1 \quad \ldots \ldots \ldots \ldots (2)$$

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If then the expressions (1) and (2), are compared, it appears that the value of dp can be greater or smaller than dp_0. For the same solution dx is namely $= dx_1$. Hence if $\dfrac{x_2 - x_1}{x_1} > \dfrac{v_2}{v}$ the change in external pressure will be greater than the osmotic pressure; if $\dfrac{x_2 - x_1}{x_1} < \dfrac{v_2}{v}$ the osmotic pressure will increase more rapidly than the pressure along the liquid binodal. In the first case the thermodynamic potential A will be greater in the mixture than in the pure state; in the second case it will be smaller. The former is the case for the dilute solutions of hexane in water; the latter for dilute solutions of water in hexane.

The case, therefore, which presents itself on the waterside will evidently in general be found when the liquid branch in the P-x section rises very rapidly in pressure with increase of x, i.e. much more rapidly than the corresponding gas binodal. Then the value of $\dfrac{x_2 - x_1}{x_1}$ can be greater than the quotient of vapour- and liquid volume. The discussed phenomenon will, accordingly, be met with in several cases. Solutions of gases sparingly soluble in water, e.g. hydrogen, will certainly present the same phenomenon.

Anorg. Chem. Laboratory of the University of Amsterdam.

Physiology. — *"Variations of state in gelatin-solutions."* By L. Arisz. (Communicated by Prof. H. Zwaardemaker)

In a previous communication [1] a number of experiments were discussed from which it appeared that a gelatin-solution undergoes a change by a variation of temperature, in consequence of which the intensity of the Tyndall-phenomenon assumes another value under for the rest equal conditions. The following formula has been given by Lord Rayleigh for the intensity of the Tyndall-phenomenon:

$$I = f\left(\frac{v^2}{\lambda^4 r^2}\right)$$

$v =$ size of the particles
$r =$ distance of the particles
$\lambda =$ wavelength

As particles to which the dispersion must be attributed the gelatin

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[1] These Proc. XVI p. 331.