

Citation:

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phase line $fm_1'd$ for $C + FeC_2 + L$, and so this latter three-phase line, which starts from the metastable quadruple point f , becomes stable at k , and then after having reached a maximum, it runs to the quadruple point d . So the point k is also a quadruple point, where besides the two mentioned three-phase lines, two others meet viz. the three-phase line for $FeC + FeC_2 + L$ and that for $C + FeC + FeC_2$. It is clear that the situation could also have been such that the three-phase line for $C + FeC + L$ possessed a stable maximum, but this does not give rise to essential modifications. If we examine a combination of twice the type of fig. 5, the case is less remarkable.

Anorganic Chemical Laboratory

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Physics. — “*On the system ether-water.*” By Dr. F. E. C. SCHEFFER.
(Communicated by Prof. J. D. VAN DER WAALS).

1. In his Thesis for the doctorate (1912) Dr. REEDERS described a number of experiments which were undertaken with a view to the experimental realisation of the phenomenon of double retrograde condensation, which had been predicted by Prof. VAN DER WAALS. Both the systems which were used for this investigation, carbonic acid and urethane, resp. carbonic acid and nitrobenzene exhibited three-phase pressures, which at the same temperature, were lower than the vapour pressures of the carbonic acid. In neither of the systems the direct observation of the said phenomenon has been possible. In my opinion Dr. REEDERS justly ascribes the failure of this observation to the fact that the difference in volatility of the components of both systems is so great that the vapour phase under three-phase pressure practically consists of pure carbonic acid, and consequently the quantity of the liquid layer, poor in carbonic acid, which is formed during the retrograde condensation, is so small that it escapes observation. The critical points of the upper layer lie for both systems at concentrations which are smaller than 2 mol. percentages of the least volatile substance, and hence the concentration which is to present the double retrograde condensation contains still less of the second component.

When Dr. REEDERS told me his results a long time before the publication of his Thesis for the Doctorate, it did not seem impossible to me that a system, in which the volatility of the components

differs less, might offer a greater chance to the realisation of the said phenomenon. Such systems, however, are pretty rare. For "normal" substances such a behaviour will probably seldom occur. The system ether-water, on the other hand, which as appears from KUENEN'S observations, possesses three-phase equilibria which extend to the critical neighbourhood of the ether, satisfies the requirement that the vapour under three-phase pressure contains an appreciable quantity of the least volatile component, in casu the water, the vapour tension of the water amounting to about 14 atms. at the critical temperature of ether (critical pressure 36 atms.). That this system differs from those used by REEDERS in this that the three-phase pressure lies higher than the pressure of saturation of the two components at the same temperature need not interfere with the appearance of the phenomenon. Therefore I carried out some experiments about a year ago with a view of examining whether double retrograde condensation can be observed in the system ether-water. However, this system too appeared unsuitable for the observation. It is true that the critical point of the upper layer lies at a concentration of about 30 mol. % water, and that it is therefore not so one-sided as for the mentioned systems of carbonic acid, but an altogether different difficulty prevents the observation, viz. the invisibility of the lower layer for comparatively small quantities. So after some futile attempts I discontinued the observations with this system. Hence a direct observation of the phenomenon in question has not succeeded as yet, and will, it seems to me, be always attended with great experimental difficulties.

2. Of late attention has been drawn to the system ether-water in consequence of an investigation by Prof. VAN DER WAALS. In his 17th contribution to the theory of binary mixtures VAN DER WAALS discusses this system fully as an example of that series of systems for which under three-phase pressure the concentration of the vapour phase lies between that of the two coexisting liquids. As far as the system ether-water is concerned, this investigation led to a number of conclusions, some of which could be experimentally tested through the investigations mentioned in § 1, as was already stated by Prof. VAN DER WAALS in the cited paper. As it was, however, of importance to examine this system more closely with a view to the remaining conclusions, I have taken up again the interrupted investigation. In the following pages I intend to discuss the results obtained for so far as they are necessary as a test of the above-mentioned conclusions.

3. Preparation of the mixtures, method of observation.

Commercial ether (*Pharmacopoeia Néerlandica*) was twice shaken with strong sulphuric acid, and dried first on sodium sulphate, then on sodium. It was preserved in this condition; for the preparation of every mixture part of this stock was distilled. As second component distilled water was used. For the preparation of the mixtures use

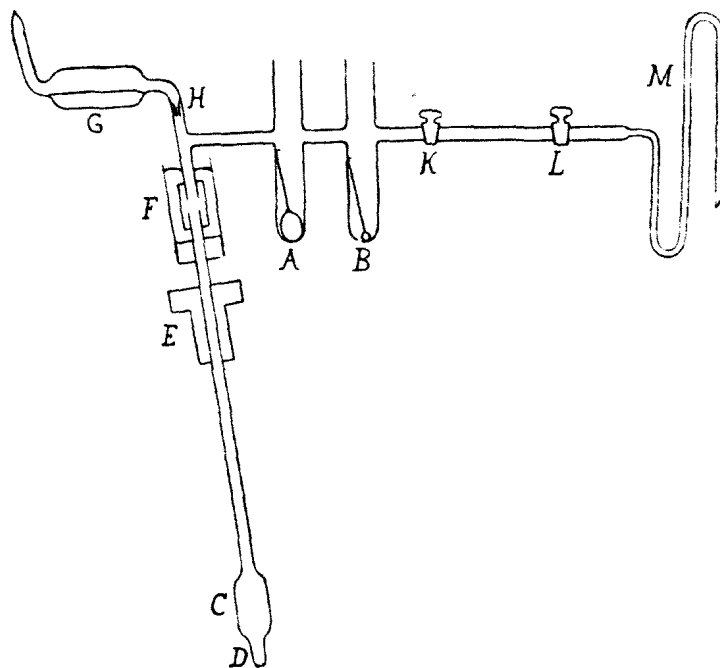


Fig. 1.

was made of the apparatus represented in fig. 1. Each of the components was weighed in a small thin-walled glass bulb provided with a capillary stem, and put in the tubes *A* and *B*, which were then fused to at their tops. The Cailletet test tube of combustion glass *ED* was connected with the filling apparatus in reversed position by means of a rubber tube surrounded by a mercury joint. Near its end *D* the tube is widened to enlarge the volume, which enabled us to perform the experiments with a comparatively large quantity of substance. This was necessary, because exclusively concentrations on the ether side were examined for this investigation; if a Cailletet tube of the ordinary shape had been used the quantity of water used would have been too small for accurate observations.

The part of the apparatus represented in fig. 1 was connected by means of the glass spiral *M* with two tubes with cocoa-nut carbon, a Geissler tube, and a water-jet pump, which served to

bring about a sufficient vacuum¹⁾. When the whole apparatus had been exhausted, the bulb with water was broken by cooling with carbonic acid alcohol, that with ether by heating, and the contents of both were condensed in *C* and *D* by means of liquid air. The air dissolved in the liquid in the bulbs could then be removed by the cocoa-nut carbon. Then the mercury which had been boiled in vacuo was conveyed from *G* in small drops through the constriction *H* into the Cailletet tube, which was then screwed into the pressure cylindre in the known way after having been separated from the filling apparatus at *F*.

In some experiments the stem of the bulb filled with water was put into the opening of the plug of cock *K*, and broken after the evacuation of the apparatus by rotation of *K*. This method of working proved very convenient for the realisation of concentrations of definite amount. Then there was no necessity for the bulb to be filled so far with water as is necessary for bursting in consequence of solidification and the weighing of a definite quantity of substance was rendered a great deal easier thereby.

At last the Cailletet tube was surrounded with a jacket, in which nitrobenzene was electrically heated till it boiled under varying pressures²⁾.

4. Discussion of the results.

In the cited paper the shape of the plaitpoint curve in its T, x -, and its P, T -projection was examined by Prof. VAN DER WAALS. It then appeared that after some modification fig. 43 of the series of contributions mentioned can account for the phenomena which appear

¹⁾ Cf. e.g. These Proc. XIII p. 831 and fig. 1 on p. 830.

²⁾ To obtain constant temperatures I made use of a steam-jacket, which is different from the one generally used. A wide tube is provided with a smaller one on either side which are closed with rubber stoppers prepared for high temperatures. On the constriction at the bottom rests an inner tube, which ends about 10 cm from the upper constriction. The stopper on the bottom side has one perforation for the Cailletet tube, which is entirely inside the inner tube, two for the supply of the electric current, and an aperture through which a tube is put for sucking up and letting out the boiling liquid. The heating is effected by means of a nickeline wire adjusted in the inner tube and wound spirally. The boiling liquid rises in the inner tube, condenses in the upper part of the outer tube, and flows down in it. In the inner tube two branch apertures have been made close to the bottom to keep the liquid at the same level inside and outside the inner tube. A glass tube through the stopper at the upper end brings about the connection with water jet pump, manometer, pressure regulator etc. If we proceed in this way there is no difficulty whatever in keeping the temperature constant for any length of time.

in the system ether-water. In fig. 43 the case has been drawn that the three-phase line would just terminate at the minimum critical temperature; in the 17th contribution, however, it is pointed out that this end-point of the three-phase line, which we will designate by the name of "critical endpoint" in our further considerations, may occur both on the branch AQ_2 and on the branch Q_2P_{cd} .

Hence we shall have to distinguish three cases as regards the relative situation of the critical end-point and the minimum critical temperature, viz.:

1. If the critical end-point lies on the branch AQ_2 , the critical line in its P, T -projection will have the shape as has been drawn in fig. 51 of the paper that has already been cited several times. Then the minimum critical temperature is found in the metastable region, and cannot be experimentally realized except by the appearance of phenomena of retardation.

2. If the three-phase line terminates exactly in the point Q_2 (fig. 43), the minimum critical temperature would occur just on the boundary of metastable and stable phases, and so it could be demonstrated by experiment. The P, T -projection for this case has been represented in fig. 50.

3. If lastly the three-phase line terminates on the branch Q_2P_{cd} , the critical end-point lies on the righthand of the minimum critical temperature. Accordingly the latter, if really present, will lie in the stable region, and might be found experimentally. If, however, it is not present, it might be imagined to lie outside the figure, and the plaitpoint curve on the side of the ether would have to exhibit the tendency to this minimum. At last as transition case we might still suppose that the minimum critical temperature would just coincide with the critical point of ether, and that therefore it could just be still demonstrated. As far as the P, T -projection is concerned, the presence or absence of the minimum critical temperature would have to manifest itself in a strong negative rise with vertical tangent, resp. in a very strong positive rise on the ether side.

From the above-cited experiments by KUENEN it may be already inferred that the system ether-water is a case as mentioned under 3. The critical temperature of the upper layer lies, namely, at higher temperature than the critical temperature of pure ether. So the critical end-point lies on the ascending branch in the T, x -projection.

In the cited treatise case 3 has therefore been fully examined, and Prof. VAN DER WAAALS arrives at the conclusion that it is possible that the three-phase line before terminating on the critical line, first

intersects it in its P, T -projection. With regard to this last case again three cases may be distinguished. We may, namely, imagine that the three-phase line without previous intersection terminates on the critical line, that intersection takes place before this end-point (see fig. 48), and thirdly that the intersection takes place exactly in the end-point, i.e. that in the critical end-point the three-phase line touches the critical line (fig. 49). This last case is again to be considered as the transition case between the two first-mentioned ones.

5. To enable us to decide which of the possible cases discussed in the preceding paragraph presents itself in the system ether-water, the P, T -projections of the plaitpoint line and the three-phase line had to be experimentally determined. For it is possible to derive from the situation of the plaitpoint line whether or no a minimum critical temperature occurs (vertical tangent), and from the relative situation of the said lines a conclusion may be drawn as to whether or no an intersection occurs. So the determination of the P, T -projections of the two lines might suffice; the three-phase line can be determined by means of one mixture, provided it do not possess a concentration that lies too much on one side. For the determination of the critical line the T_k and P_k found for different mixtures should be combined together to one line. So for every mixture practically nothing but the critical phenomenon need be observed, and of a single one the three-phase line in the neighbourhood of the critical end-point.

However, I have not been satisfied with this. To obtain as much certainty as possible I have observed part of the three- and two-phase equilibria of every mixture. The great advantage yielded by these observations, is the following. If a mixture should contain a slight quantity of admixtures, and the presence of air is the most probable, this mixture would bring about an error in T_k and P_k , and so it might furnish a point which might cause the course of the critical line to deviate from the correct one. In the determination of the three-phase pressure, which must show the same value for all the mixtures used, we have, however, a criterion of purity. With none of the mixture, for which this test could be applied, a deviation was found exceeding 0,1 atmosphere.

But besides this, the observation of the two-phase equilibria furnished another advantage. We want to decide, among others, whether intersection takes place between the three-phase line and the critical curve. If we now put the case that this intersection really occurs, the part of the critical line between the point of intersection in question and

the critical end-point lies at higher pressure than the three-phase line. So two-phase equilibria must be possible at these temperatures between liquid rich in ether and vapour at pressures higher than the three-phase pressure. If, therefore, only one point of end-condensation of the ether layer was found to lie higher than the three-phase pressure at the same temperature, the intersection would have been proved. So we see that in the observation of the two-phase equilibria we may find a second decision on the presence or absence of the point of intersection in question.

Now what concerns the observation of the two-phase equilibria we have already seen in § 1, that the liquid which is rich in water is sometimes not observable in the mixtures. This, however, does not

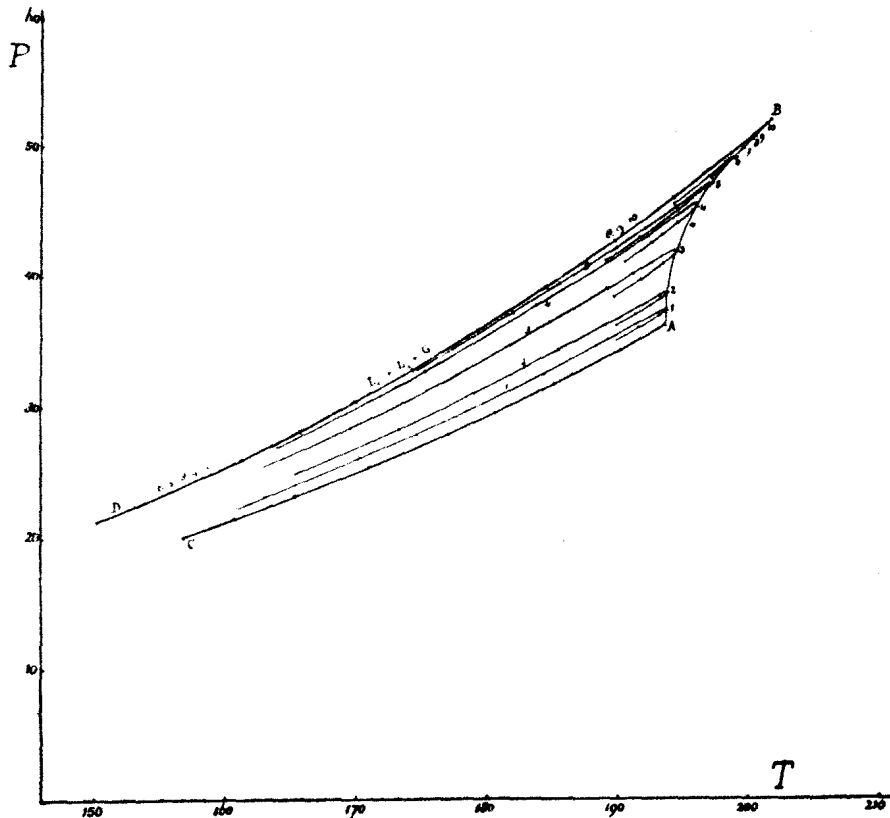


Fig. 2.

affect the decision in question. For every mixture I determined the initial and the final condensations of the ether layer in the neighbourhood of the critical temperature. If in one of the two a layer is present, visible or invisible, which is rich in water, the pressure must be the same as the three-phase pressure. Now it follows from

Ether		Three-phase line		(1) $x = 0.024$		(2) $x = 0.051$		(3) $x = 0.118$		(4) $x = 0.1925$	
t	p	t	p	t	p	t	p	t	p	t	p
156.9	20.0	150.3	21.2	160.75	22.2	165.5	24.9	163.1	25.5	164.15	26.95
160.9	21.45	155.9	23.5	165.5	24.0	173.45	28.3	169.7	28.4	175.45	32.7
165.5	23.1	161.5	26.0	170.5	26.05	179.35	31.15	177.9	32.5	184.1	37.65
171.1	25.3	165.9	28.1	174.85	27.9	185.7	34.3	185.1	36.4	192.7	43.05
177.3	27.9	170.15	30.45	180.2	30.4	189.3	36.1	189.55	38.9	196.5	45.55
180.8	29.55	174.5	32.8	184.6	32.55	193.55	38.4	191.5	40.05	196.4	45.3
185.3	31.7	179.55	35.75	189.5	35.0	194.1	38.6	193.0	40.95	196.15	45.0
190.5	34.2	184.85	39.1	191.75	36.2	193.7	38.2	194.7	41.9	194.95	44.0
193.9	36.1	190.15	42.65	192.7	36.7	192.85	37.65	194.85	41.9	193.75	43.2
		194.7	45.9	193.3	37.0	191.7	36.95	193.85	40.95	193.0	42.55
		199.1	49.2	194.0	37.3	190.2	36.1	192.1	39.65	190.9	41.0
		202.2	51.8	193.5	36.9			190.05	38.3		
				191.9	35.9						
				190.15	35.0						
(5) $x = 0.226$		(6) $x = 0.260$		(7) $x = 0.275$		(8) $x = 0.298$		(9) $x = 0.300$		(10) $x = 0.316$	
t	p	t	p	t	p	t	p	t	p	t	p
164.2	27.2	176.7	33.9	157.9	24.3	178.7	35.15	176.7	33.9	163.1	26.8
174.9	32.8	185.0	39.0	169.1	29.8	186.75	40.3	188.1	41.15	182.5	37.6
182.3	37.2	189.9	42.1	185.7	39.6	194.35	45.5	191.5	43.55	186.9	40.4
185.9	39.35	194.7	45.45	189.3	42.0	198.3	48.4	195.65	46.5	193.9	45.25
190.35	42.15	198.75	48.4	192.5	44.2	200.8	50.4	200.1	49.95	196.9	47.55
192.5	43.65	199.35	48.9	195.1	46.0	199.5	49.3	201.0	50.65	199.15	49.3
194.85	45.2	197.6	47.5	200.1	49.7	197.1	47.4	200.2	49.95	201.9	51.55
197.6	47.1	194.05	44.85	198.65	48.5	193.45	44.75	198.65	48.75	200.55	50.35
197.35	46.9	189.85	41.8	195.1	45.8	189.55	42.0	195.8	46.6	198.85	49.0
195.6	45.5			192.7	44.05			193.25	44.7		
192.05	42.85			190.0	42.2			191.4	43.4		
189.4	41.1										

the observations given in figure 2 and table I of pure ether of the three-phase pressure determined with a mixture of about equal quantities by weight, and of some ten mixtures of the concentration given in the table, that not a single end-condensation of the ether layer can be realized which took place at higher pressure than the three-phase pressure. This shows us in an indirect way, what we also see directly from the locus of the plaitpoints, that there is no intersection between plaitpoint line and three-phase line. The relative position of the two lines is, however, such that we are here quite in the neighbourhood of the above-mentioned transition case. The inclination of the two lines in the critical end-point differs so little that we may practically speak of contact here. In the P, T -projection the lines of the initial and final condensation of the ether layer have been indicated by the same numbers as the corresponding mixtures in the adjoined table.¹⁾ It is clear that the mixtures 6, 7, 8, 9, and 10 in the neighbourhood of 160° have yielded the three-phase line as end-condensation. In ascending order this was the case up to higher and higher temperature. For the mixtures 1 to 5 the end-condensation pressure was lower than the three-phase pressure over the whole range of temperature; hence there was no question of the occurrence of three-phase equilibria with these mixtures. The intersection of the line of the end-condensations and the three-phase line must be looked for here at lower temperature.

It is, moreover, clear, from figure 2 that the critical line at the critical point A of the ether rapidly proceeds to higher pressure, as Prof. VAN DER WAAALS anticipated. Whether the inclination is infinitely great or very great in the direct neighbourhood of T_k of ether, could not be ascertained. Also in this respect we may again speak of a transition case for this system. For we cannot state with certainty whether the minimum critical temperature lies in the figure or on the axis, or whether it would lie just outside the figure. The last seems, however, the most probable from the given observations.

When the plaitpoint line is considered in its other projections, it appears that in the T, x -projection the inclination on the ether side is very slight, almost zero, and that it continually increases up to the critical end-point on increasing concentration. In the graphical representation the P, x -projection appears to deviate very little from a straight line.

¹⁾ In the table the critical data have been given in bold type, above them we find the values of the end-, below them those of the begin-condensations of the ether layer.

If we finally consider the relative situation of the phases on the three-phase line, it appears from what precedes that the vapour phase lies between the coexisting liquids up to the highest temperature, that the vapour branch, however, closely approaches the branch of the liquid rich in ether already before the critical end-point. It is in agreement with this that a P,x -section brought through the P,T,x -surface e.g. for the critical temperature of ether yields two curves which show decreasing values of $\frac{dP}{dx}$ starting from the critical pressure of ether, that the intersection with the three-phase line, however, appears just before the maximum pressure is reached, at which the concentrations of liquid and vapour would become the same.

So in the system ether-water the minimum critical temperature predicted by Prof. VAN DER WAALS lies in the immediate neighbourhood of the axis, and the remarkable point of intersection at the critical end-point.

I intend to repeat this investigation for another system hoping that I shall be able to demonstrate both peculiarities experimentally when the situation is a less one-sided one.

Anorg. Chem. Laboratory of the University.

Amsterdam, Sept. 13 1912.

Chemistry. — “*On quadruple points and the continuities of the three-phase lines.*” By Dr. F. E. C. SCHEFFER. (Communicated by Prof. J. D. VAN DER WAALS).

1, In a previous paper¹⁾ I examined the continuous connection of the three-phase lines, which occur in BAKHUIS ROOZEBOOM's spacial figure on the most simple suppositions. It then appeared that the three-phase lines $S_A + S_B + L$ and $S_A + S_B + G$ pass continuously into each other, and that in the P,T -projection this transition takes place by means of a partly metastable, partly unstable curve with two cusps, in both of which two three-phase branches touch. I have now extended this investigation to the other quadruple points which can occur in binary systems; I have, however, postponed the publication of it for a long time, because the phenomena which present themselves in the most interesting case, are much more complicated than in the above mentioned case, and a full description would require a great many intricate figures. Without treating the cases

¹⁾ These Proc. 1910, p. 158.