

Citation:

J.J. van Laar, On the different forms and transformations of the boundary curves in the case of partial miscibility of two liquids, in:

KNAW, Proceedings, 7, 1904-1905, Amsterdam, 1905, pp. 636-646

Chemistry. -- "On the different forms and transformations of the boundary-curves in the case of partial miscibility of two liquids." By J. J. VAN LAAR. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM.

(Communicated in the meeting of March 25, 1905).

1. In a preceding communication¹⁾ I showed, that when one of the two components of a binary mixture is *anomalous*, the T, x -representation of the spinodal curve, and consequently also that of the connodal curve, the so-called saturation- or boundary-curve $x=f(T)$, can assume different forms, which are indicated there. It depends principally only on the value of the *critical pressure* of the normal component, with regard to that of the anomalous component, which of the different forms may occur with a definite system of substances.

An affirmation of the theory, developed by me, that is to say of the cases and transformations deduced by me from the general equations, is found in the circumstance, that these cases and transformations may be realised *in quite the same succession with one and the same substance*, and this by *external pressure*. In the same way as with *different* normal substances as second component the form drawn in fig. 7 l.c., presents itself at relatively *low* critical pressures (with regard to that of the anomalous component), and that of fig. 2 l.c. at relatively *high* critical pressures — the form of fig. 7 may be realised at relatively *low* external pressure, and that of fig. 2 at relatively *high* external pressure, whereas at intermediate pressures all the transitional cases again will return in just the same succession.

2. For that purpose we but have to look at the p, T -diagram of the critical curve for ethane and methylalcohol, as projected by KUENEN²⁾ in consequence of his experimental determinations (compare fig. 1). We see, namely, immediately from the form of the curve, departing from C_2 (the higher critical temperature, that of CH_3OH), which indicates the pressures, at which for different temperatures the two coexistent phases coincide, and above which we have consequently perfect homogeneity, that according to the value of the pressure *one* critical point a may occur (at the pressures 1 and 2), *two* viz. a and b, c (at 3), *three*, viz. a, b and c (at 4), again *two*, that is to say (a, b) and c (at 5), and finally again *one*, viz. c (at 6). (also compare fig. 2).

¹⁾ These Proceedings of 28 Jan. 1905.

²⁾ Phil. Mag. (6) 6, 637—653, specially p. 641 (1903).

All this is rendered still more conspicuous, when we project a *space*-representation, in connexion with fig. 1 and of some successive p, x -sections. In fig. 1 D_1 and D_2 represent the vapour pressure-curves of the two components; ΔM is the threephase pressure-curve, which terminates abruptly in M , where the gaseous phase 3 coincides with the liquid phase 1 (which consists for the greater part of ethane), because it meets there the critical curve $C_1 C_2$, that is to say the curve of the plaitpoints P . Beyond M there is coexistence only between the *fluid* phase 3,1 and the phase 2, which consists principally of alcohol. It is the equilibrium between these latter phases, of which in fig. 2 the T, x -representation is projected at different pressures. (The dotted boundary-curve 0 corresponds with a pressure inferior to the critical pressure of the second component, and superior to that of the first one). The T, x -representation of fig. 3 corresponds, at the (variable) threephase-pressure, with the threephase-equilibrium unto M . In fig. 4 the indicated *space*-representation is drawn, which will be clear now without the least difficulty¹). For the different higher pressures the corresponding T, x -sections are drawn in that representation.

Remark. From C_2 (see fig. 1) to the maximum at 126° , where a and b coincide, and also from the minimum at 26° , where b and c coincide, to the lowest temperatures, increase of pressure will *lower* the critical temperature Q , and these critical points will be *upper* critical points in the T, x -sections at constant pressure (see fig. 2). On the other hand, from the maximum at 126° to the minimum at 26° increase of pressure will *raise* the critical temperature, and the designed critical points will be *lower* critical points.

That increase of pressure *favours* the mixing, as is clear from fig. 1 and from the p, x -representations — as well in the case of an upper critical point, as of that of a lower one — is also in agreement with the T, x -representation of fig. 2. For in the case of an *upper* critical point (see also fig. 5) a point A , situated *within* the boundary-curve will come — when the pressure is increased, by which T_0 will be removed to the lower point T_1 (for $\frac{dT}{dp}$ is *negative*, as we saw above) — *without* the new boundary-curve. And the same will be obviously the case for a *lower* critical point, where $\frac{dT}{dp}$ is *positive*.

¹ This *space*-representation (without the T, x -sections) has been already projected independently by Mr. BÜCHNER; but is not inserted in his communication. (These Proceedings of 28 Jan. 1905).

To the considered type also belongs $\text{SO}_2 + \text{H}_2\text{O}$, $\text{C}_2\text{H}_6 + \text{H}_2\text{O}$, and equally *ether* and *water*. This latter mixture only with this difference, that the composition of the vapour-phase is here continually *between* that of the two liquid phases (see fig. 3^a). KUENEN¹⁾ found, that at 201° the vapour-phase coincides with that liquid phase, which consists for the greater part of ether. The three-phase-pressure is then 52 atm. (At C_1 we have $T_1 = 195^\circ$, $p_1 = 38$ atm.).

The p, x -diagrams would now show a *maximum-vapourpressure*, if the two liquid phases 1 and 2 could become identical. In connexion with this the three-phase-pressure will be *higher* (here only some mM) than the vapourpressures of each of the components, and it follows immediately from fig. 1, that the critical curve C_1C_2 , or rather C_1M , will at first run back from C_1 , that is to say will present a *minimum* critical temperature. In the case of $\text{C}_2\text{H}_6 + \text{CH}_3\text{OH}$, where the composition of the vapour-phase is *without* that of the liquid layers, the three-phase-pressure will always be *between* the vapourpressures of the components.

3. Now, as to the representation of the so-called transversal- and longitudinal plait on the ψ -surface at different temperatures (in its projection on the v, x -surface) in the case of $\text{C}_2\text{H}_6 + \text{CH}_3\text{OH}$, it will be obvious, that the critical point Q , considered above, of the longitudinal plait always lies at the side of the *small* volumes. For increase of pressure finally favours (see above) the mixing.

The successive transformations of the transversal- and of the longitudinal plaits are further represented *schematically*, in agreement with the p, x -sections, in fig. 6. The longitudinal plait, occurring here, is regarded by VAN DER WAALS²⁾ — and this equally in the case to be considered presently — as a *transformed* transversal plait. Many questions however, connected with these plaits, lose — as has been remarked already by VAN DER WAALS³⁾ — much of their weight, and become of *secondary* interest, as soon as we succeed *in connecting with other properties* of the components of the mixture the often so complicated transformations, which may occur at the different plaits. And to do this an attempt is made in my preceding communication. There I showed, that the *ordinary* theory of the association is capable of representing the different possible forms of the boundary-curves qualitatively, and in many cases even quantitatively.

4. We will now consider the *second* of the *three* principal types,

¹⁾ Z. f. Ph. Ch. 28, 342—365, specially p. 352 (1899).

²⁾ These Proceedings 7, p. 467 (1899).

³⁾ Id. 25 Oct. 1902, p. 399.

indicated in a recent communication of BAKHUIS ROOZEBOOM and BUCHNER¹⁾, the *first* of which is amply considered above.

Fig. 7 gives the p, T -representation of it; fig. 8 the T, x -diagram of some sections at constant pressure (the dotted boundary-curves are relative to pressures between that of M'' and C_2 , and to that below M').

The series of p, x -diagrams, and also the space-representation (also projected already by BUCHNER) are omitted here. We find that case with mixtures of *ethane* and *ethyl-, propyl-, isopropyl- and normal butylalcohol*, all examined by KUENEN²⁾.! Also *triethylamine + water*, and some other mixtures³⁾ with a *lower* critical point (this lies at $18^{\circ},3$ C in the last mentioned case) belong to that type. Indeed, it is obvious from fig. 8 and from the p, x -diagrams, that M' is at present a lower critical point, contrary to M in fig. 1, which was an upper critical point. For, whereas in M (fig. 1) the three-phase-pressure *ends*, this pressure *commences* in M' . Farther however, in M'' , the gaseous phase coincides again with the first liquid phase (rich in ethane) (because the three-phase-pressure-curve $M'M''$ anew meets the critical curve C_1C_2), after which the further course is the same as with the preceding type. The T, x -representation with variable three-phase-pressure, that is to say between M' and M'' (fig. 9a), is in agreement with it.

It appears that, as little as with the preceding type, there exists here a properly-said upper critical point. For in both cases 1 and 3 coincide, when the three-phase-pressure comes to an end, and not 1 and 2 (see fig. 3a and 9a). The vapour-phase becomes identical with the upper liquid layer and vanishes, but then there remain still two phases, the lower liquid layer 2 and the fluid phase 1,3. These however always pass into each other with further increase of the temperature, as is plainly indicated by the space-representations (see e. g. fig. 4), at the vapour-pressure-curve of the second component at $x_{13} = x_2 = 1$ (also compare the dotted boundary-curves in fig. 2 and 8). So, if we begin with a mixture of a definite composition, then *with increase of temperature we come finally* beyond the boundary-curve 1,3 at the moment, that the liquid layer 2 has entirely vanished. So we have demonstrated more exactly at the same time what I have said in my preceding communication, namely that the existence of a lower critical point involves necessarily that of a higher upper one. It is however not, as we have seen, a *critical* point proper.

¹⁾ Id. 28 Jan. 1905, p. 531—537.

²⁾ Z. f. Ph. Ch. 28, p. 358—363 (1899).

³⁾ Among others β -collidine, and the bases of the pyridine- and chinoline-series with H_2O .

From the series of p, x -diagrams we might still see, that the boundary-curve of the two liquid phases with the plaitpoint Q below the temperature, where 1 and 2 coincide (in M'), does not come *within* the boundary-curve vapour-liquid, as KUENEN ¹⁾ thinks, but has *entirely vanished*. In fact, there is no reason to suppose, that in M' decrease of pressure should cause again permanent separation (if that state were realisable), as apparently KUENEN thought that he had "undoubtedly" to expect with mixtures of triethylamine and water ²⁾. What he has observed in another case with propane and methylalcohol³⁾, must be ascribed in my opinion to this, that the expansion just above the (upper) critical point has caused the temperature to fall a little, so that he came on the (metastable) part of the two liquid curves, which lies below the threephase-pressure. But when the cusp was reached, the metastable equilibrium became immediately stable, and by further expansion homogeneous liquid and vapour reappeared.

Because increase of pressure in this case too favours the mixing, as appears from fig. 7 and from the p, x -diagrams, the plait on the ψ -surface will have turned its plaitpoint Q also to the side of the *small* volumes. Fig. 10 gives a schematical representation of the successive transformations of the two plaits, or rather of the transversal plait, for we can regard again with VAN DER WAALS the longitudinal plait as a transformed transversal one.

In fig. 7 we see, that increase of pressure raises the critical points Q , at least in the beginning, if the curve $M'C_2$ should present a maximum; and from the p, x -diagrams, that these critical points will be again in that case *lower* critical points, just as in fig. 1 between the minimum and the maximum in the curve of the critical points Q .

Equally in the case of the second general type the threephase-pressure may be either *between* the vapourpressures of the two components, as in the case of C_2H_6 and the mentioned alcohols, in which case the composition of the vapour-phase will be *not between* that of the liquids — or may be *higher* than that of the components. Then there is again a *maximum*-vapourpressure after the coinciding of the two liquid phases below the lower critical point, and the composition of the vapourphase is *between* that of the liquid layers⁴⁾.

¹⁾ Phil. Mag. l. c. p. 645.

²⁾ Id. p. 652.

³⁾ Id. p. 646.

⁴⁾ That at the coinciding of the two liquid phases 1 and 2 in M' the vapour-phase does not necessarily coincide with 1 and 2, has been already remarked by KUENEN, and still earlier has been deduced by me theoretically for an analogous case

(see fig. 9b). It is a matter of course, that in fig. 7 the critical curve C_1C_2 , or rather C_1M' , again turns back in that case, consequently presents a *minimum*; equally the critical curve $M'C_2$ will not seemingly cut C_1C_2 between C_1 and M'' in this case, but remain on the left of C_1 . This case occurs e. g. with mixtures of *water* and *triethylamine*, where in consequence of the almost complete unmiscibility of the two components above the lower critical point the threephase-pressure will be but very little smaller than the *sum* of the vapourpressures of the two components. So KUENEN found, that at 93° C. the threephase-pressure was 142,6 cm., whereas the vapourpressures of triethylamine and water were resp. nearly 86 c.m. and 58,6 cm., consequently together 144,6 cm.

5. It is worth remarking, that the region of the threephase-pressure continually shrinks the more we ascend to *higher alcohols* (KUENEN). In the case of $C_2H_6 + C_2H_5OH$ the temperatures in M' and M'' were resp. 31°,9 (46 atm.) and 40°,7 (55 atm.); in that of $C_2H_6 + C_3H_7OH$ these are 38°,7 and 41°,7; in that of $C_2H_6 +$ isopropylalcohol? and ± 44°; in that of *n*-butylalcohol 38°,1 and 39°,8 (55 atm.). Finally with isoamylalcohol three phases were no longer realisable, so that the critical points Q coincide there with the critical points P , one continuous critical curve being formed from C_1 to C_2 (General type III).

In agreement with this is the fact, that the anomaly of the alcohols decreases, as these are higher. In fact, we approach then more and more the case of mixtures of *normal* substances, where only at *very low* temperatures (see my preceding communication) a formation of two liquid layers can present itself. KUENEN found indeed, that $C_2H_6 +$ ether mix in all proportions, whereas $C_2H_6 + H_2O$ again present a threephase-equilibrium.

The influence of the fact that the *alcohol* is higher is also sensible in the case of mixtures of CS_2 and different alcohols. So we find for the upper critical points of CS_2 with CH_3OH , C_2H_5OH , C_3H_7OH and C_4H_9OH successively +40°,5 (ROTHMUND), -10°,6 (KUENEN) -52° (K.) and -80° (K.).

Equally the influence of the hydrocarbon was examined by KUENEN. While, as we saw above, the separation between type I and II in the case of $C_2H_6 +$ different alcohols was between CH_3OH and

(equilibrium between two solid phases and one liquid phase). This will obviously also be the case with an upper critical point, as appeared from the experiments of SCHREINEMAKERS with *water* and *phenol*. We will return to this question in § 8.

C_2H_5OH , and that between II and III between *n*-butyl- and isoamylalcohol, the separation between I and III in the case of $CH_3OH +$ different hydrocarbons is lying now between C_2H_6 and C_3H_8 . Propane and the following hydrocarbons + CH_3OH belong consequently, just as $C_2H_6 +$ isoamylalcohol, and the greater part of the mixtures with an *upper* critical point, examined by GUTHRIE, ALEXEJEW and ROTHMUND, to the *third* general type, which we will briefly consider now.

6. The *third* general type is principally characterised by this, that the threephasepressure-curve meets *no* longer the critical curve $C_1 C_2$, but has come to an end already before (fig. 11). This third type may proceed either from the second type (see fig. 7), the threephasepressure-curve $M' M''$ shrinking more and more, and finally vanishing, as is the case with the transition from $C_2H_6 + C_4H_{10}OH$ to $C_2H_6 + C_5H_{11}OH$ (see above) — or from the first type, when ΔM ends already before $C_1 C_2$. In the first case (e.g. with $C_2H_6 + C_5H_{11}OH$, $C_2H_6 +$ ether) there exists no threephase-equilibrium at all — or it should be at very low temperatures, which even may be expected according to the theory (see my preceding communication), so that the question arises, whether also in the case of fig. 7 there exists at low temperatures a new threephasepressure-curve, and we will return to that question at the end of this communication — in the second case there exists a threephase-pressure from the beginning, which vanishes at a definite temperature (*upper* critical point). To this latter case belong the mixtures of CH_3OH with C_3H_8 , etc., $H_2O + CO_2$, $CS_2 +$ different alcohols (KUENEN), and also the greater part of the mixtures formerly examined (see above).

But in the case of this third type there exists still another difference. Firstly the threephasepressure-curve again may lie either between or without the vapourpressure-curves of the two components, with all the consequences, connected with it in the p, x -diagrams, etc. (see above). As to the mixtures of CH_3OH with C_3H_8 , C_5H_{12} , C_6H_{14} , with all these is found (KUENEN, l. c.), that the threephasepressure is *higher* than the vapourpressures of the hydrocarbons, contrary to $C_2H_6 + CH_3OH$, which belongs to type I, where the threephasepressure is lower than that the vapourpressure of C_2H_6 . Equally with phenol and water (SCHREINEMAKERS, v. D. LEE), $H_2O + CS_2$ (REGNAULT) — where, according to the exceedingly small miscibility, the threephase-pressure is again a little smaller than the sum of the vapourpressures of the components — $H_2O + Br_2$ (BAKHUIS ROOZEBOOM), $H_2O +$ isobutylalcohol (KONOWALOW), $CS_2 + CH_3OH$ and C_2H_5OH (KUENEN), $H_2O +$ aniline (KUENEN), etc. we find everywhere the three-

phase-pressure higher than the vapourpressures of each of the components. Only of $\text{H}_2\text{O} + \text{SO}_2$ (BAKHUIS ROOZEBOOM), and of some systems more ($\text{S} + \text{Xylol}$ and Toluol , $\text{CO}_2 + \text{H}_2\text{O}$) we know with certainty, that the threephase-pressure is between the vapourpressures of the two components.

There exists, however, still another, important difference. Whereas in the case of type I (fig. 1) the critical curve QC_2 presents alternately positive and negative $\frac{dT}{dp}$, and in that of type II (fig. 7) $\frac{dT}{dp}$ is of course positive in the beginning in M' (indeed, the point Q just appears in M') — in the case of type III the initial course of MQ may be as well to the left as to the right.

Is this course to the *left*, that is to say is $\frac{dT}{dp}$ negative, then — just as in fig. 1 between C_2 and the maximum and between the minimum and the lowest temperatures — increase of pressure will *lower* again the critical temperature in the case of these upper critical points, and the plait on the ψ -surface in its v, x -projection will again have turned the plaitpoint Q to the side of the *small* volumes. (This is equally the case with $\text{C}_2\text{H}_6 + \text{isoamylalcohol}$, where no threephase-equilibrium could be stated, but where the plaitpoint Q , which has become here identical with P , has removed strongly to the x -axis, just as in the case of mixtures of C_2H_6 and the *lower* alcohols). We find this e. g. with $\text{C}_3\text{H}_8 + \text{CH}_3\text{OH}$.

But when the initial course of MQ is to the *right*, as in the case of $\text{C}_6\text{H}_{12} + \text{CH}_3\text{OH}$, $\text{C}_6\text{H}_{14} + \text{CH}_3\text{OH}$, and of phenol and water, then increase of pressure will *raise* the point Q , and the mentioned plait will now have turned the plaitpoint Q for the first time to the side of the *large* volumes.

The question, whether the longitudinal plait, as in the case of phenol and water, will present still a second plaitpoint at very small volumes, consequently at very high pressures — in other terms, whether the coexistent liquid phases, after diverging initially, will reapproach afterwards in composition, has not yet been answered theoretically with certainty. It however appears to me, that where in the case of $\text{C}_3\text{H}_8 + \text{CH}_3\text{OH}$ the plait has turned the plaitpoint Q to the side of the *small* volumes, whereas C_6H_{12} and C_6H_{14} , equally with CH_3OH , have turned this point to the side of the *large* volumes, there must exist a *continuous* transition between the two kinds of longitudinal plaits, and that also the latter (as long as it has not yet detached itself from the liquid curve of the transversal plait, that is to say below the upper critical point) must be regarded

as an appendix of the transversal plait. Only when the longitudinal plait has detached itself entirely from the liquid curve of the transversal plait above the critical temperature of mixing, it can be regarded in my opinion as a *separate* plait by the side of the transversal one. This is in full agreement with what we find e. g. for the boundary-curves in the T, x -representation (see fig. 2).

As long as the two parts of the boundary-curve, for instance N^o. 2, are not yet separated, we can hardly speak of two boundary-curves: it remains one continuous boundary-curve; only beyond the transitional case N^o. 3, e. g. N^o. 4, we have a right to speak of two isolated boundary-curves.

As to the values of the different critical temperatures, we still mention, that with $C_3H_8 + CH_3OH$ the upper critical point was found at 21° C., with $C_6H_{12} + id.$ at 19°, 5, and with $C_6H_{14} + id.$ at circa 40°. With $C_6H_{14} + C_2H_5OH$ the latter temperature immediately falls down to — 65°.

7. Resuming all that precedes, we have the following summary. (p_3 designs the threephase-pressure, p_1 and p_2 the vapour-pressures of the two components).

$$\begin{array}{l}
 \text{Type I} \\
 \text{(fig. 1).} \\
 \left. \begin{array}{l} p_3 \text{ between } p_1 \text{ and } p_2 \\ p_3 > p_1 \text{ and } p_2 \end{array} \right\} \begin{array}{l} \left\{ \begin{array}{l} C_2H_6 + CH_3OH \\ C_2H_6 + H_2O \\ SO_2 + H_2O \end{array} \right. \\ \underline{\text{Ether} + H_2O} \end{array} \\
 \\
 \text{Type II} \\
 \text{(fig. 7).} \\
 \left. \begin{array}{l} p_3 \text{ between } p_1 \text{ and } p_2 \\ p_3 > p_1 \text{ and } p_2 \end{array} \right\} \begin{array}{l} \left\{ \begin{array}{l} C_2H_6 + C_2H_5OH, C_3H_7OH, \\ \text{iso-id., n. } C_4H_9OH. \end{array} \right. \\ \underline{\text{Triethylamine} + H_2O} \end{array} \\
 \\
 p_3 \text{ between } p_1 \text{ and } p_2 \left\{ \begin{array}{l} CO_2 + H_2O \\ S + \text{Xyloi, Toluol} \end{array} \right. \\
 \\
 \text{Type III} \\
 \text{(fig. 11).} \\
 \left. \begin{array}{l} p_3 > p_1 \text{ and } p_2 \end{array} \right\} \begin{array}{l} \left\{ \begin{array}{l} C_3H_8 + CH_3OH \text{ (} d\rho/dT \text{ -)} \\ C_6H_{12} \text{ and } C_6H_{14} + id. \text{ (} d\rho/dT \text{ +)} \\ C_6H_{14} + C_2H_5OH \\ H_2O + \text{Phenol (} d\rho/dT \text{ +)} \\ H_2O + \text{Aniline; id + isobutylalcohol.} \\ Br_2 + H_2O ; CS_2 + H_2O, CH_3OH, C_2H_5OH, \\ C_3H_7OH, C_4H_9OH. \end{array} \right. \end{array}
 \end{array}$$

8. We saw above, that when the composition of the vapour-phase is *between* that of the two liquids — which is the case, when the threephase-pressure is *higher* than the vapourpressures of each of the components — there must be a *maximum*-vapourpressure *after* the coinciding of the liquid phases 1 and 2. That maximum may however still be present *before* the coinciding of these liquid phases, which is connected with the fact, that this maximum, which appeared originally at lower temperatures as a minimum (see fig. 12) in the metastable region, has become gradually a maximum, and has moved outwards before the coinciding of 1 and 2. The vapour-phase 3, which was lying at lower temperatures always between 1 and 2, as to its composition, remains not necessarily between these till the moment of coinciding of 1 and 2, as was thought formerly, but may have come outwards long before (see also fig. 9*b*). It would be very accidental on the contrary, when 3 coincided in the same time as 1 and 2 to one phase. In the case of *phenol* and *water* SCHREINEMAKERS has in fact shown experimentally this moving outwards¹⁾.

In what manner the moving outwards takes place, has first been clearly shown and considered quantitatively by me²⁾ in a series of figures, and this in the case of coexistence of two solid solutions and one liquid phase, whereas we have here — what of course is quite the same³⁾ — the coexistence of two liquid and one gaseous phase. The figures 9—14, drawn in the indicated communication (which refer to meltingcurves, and consequently are T,x -representations) are to be turned upside down, and the figs. 12, reproduced here, are obtained (fig. 12 of the mentioned communication is omitted). It will be remembered, that the case, which is realised with respect to liquid-vapour with phenol and water, is realised with respect to solid-liquid with $\text{AgNO}_3 + \text{NaNO}_3$ (only the maximum of fig. 14*b* l.c. at D has been already vanished there).

Some months after the publication of my communication KUENEN⁴⁾ came independently of me also to entirely the same view. What is described on the pages 471 and 472 of his communication, is quite identical with that, which I have described and represented on the pages 184—186 of the designed communication.

Z. f. Ph. Ch. 35, p. 462—470 (1900).

²⁾ K. A. v. W. 27 June 1903.

³⁾ The calculations were based on the equation of state of VAN DER WAALS, so that the results of it are à fortiori applicable in the case of two liquid phases and one gaseous phase.

⁴⁾ K. A. v. W. 31 Oct. 1903.

9. Now, that we have sufficiently characterised the three general types, and have brought some harmony into the multiplicity of the phenomena, the question arises, whether there is a still farther synthesis, a still higher unity. More than once the occasion presented itself in the treatment of the different general types to remark striking agreements and continuous transitions, often accompanied with great differences. Equally the fact, that with a higher alcohol or a higher hydrocarbon, suddenly a quite different type often appears, must certainly draw attention in a high degree. All this induces us to look for the *one* fundamental type, of which the three types, treated above, are special cases.

Also the *analytical* consideration of the question suggests that idea to us. Indeed, the coexistence of two liquid phases and one gaseous phase, or of two liquid phases, or finally of one liquid phase and one gaseous phase, is determined by one and the same equation of state, and it must consequently always be possible to reduce all the different cases, which may occur to *two* fundamental proportions: that of the *critical temperatures* and that of the *critical pressures* of the two components — entirely in the same way as I have formerly deduced *all* the different types in the case of mixed crystals, where appear two solid phases by the side of one liquid phase, from *two* fundamental proportions: that of the *melting temperatures* and that of the *latent heats of melting* of the two components.

In a following communication it will be shown theoretically, that the three types may be deduced from the ordinary equation of state of Prof. VAN DER WAALS, even in the case of *normal* components. In connexion with this we must not forget, that in the neighbourhood of the critical points of each of the components the influence of anomaly vanishes nearly always. In the case of $C_2H_6 + H_2O$ for instance the water will be in the neighbourhood of $365^\circ C.$ already normal long before, and in the neighbourhood of $32^\circ C.$ the liquid phase, which consists nearly entirely of ethane, will contain the water in such a dilute state, that this will be passed for the greater part into the state of simple molecules.

Chemistry. — “*An exact expression for the course of the spinodal curves and of their plaitpoints for all temperatures, in the case of mixtures of normal substances.*” By J. J. VAN LAAR. (Communicated by Prof H. A. LORENTZ).

(Communicated in the meeting of March 25, 1905.)

1. It is well-known, that the points of the ζ -surface, corresponding to points of the spinodal curve on the ψ -surface, are given by the simple relation

