

Citation:

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13. Finally we may combine our results with those of NEWCOMB and also with those derived by FRANZ.¹⁾

For the correction of the inclination we find :

NEWCOMB	1868	$\delta i = -0''15$	weight 3
FRANZ	1892	+ 0.37	1
BAKH.	1899	- 0.19	3
Mean result		$\delta i = -0''09$	

The correction of the inclination is thus found to be small.

For the correction of the longitude of the node we find :

NEWCOMB	1868	$\delta \theta = +4''5$	weight 3
FRANZ	1892	+ 7.4	1
BAKH.	1899	+ 11.5	3
Mean result	1885	$\delta \theta = +7''9$	

As NEWCOMB found for 1710 $\delta \theta = -16''$ (*Researches* p. 273), we obtain :

$$\text{Correction of the centennial motion} = +14''.$$

Physics. — “*On the critical mixing-point of two liquids*”. By J. P. KUENEN. (Communicated by Professor VAN DER WAALS in the meeting of October 31, 1903).

A critical mixing-point of two liquids is in general a point where two coexisting liquids become identical in every respect: it corresponds to a plaitpoint or critical point of the two-liquid plait on VAN DER WAALS'S ψ -surface or of its projection in the volume-composition diagram, the so-called saturationcurve for the two liquid phases; the term is used more especially to denote the condition, where the liquids are at the same time in equilibrium with their saturated vapour. In the $v-x$ diagram this condition corresponds to the point of contact between the two-liquid curve in its critical point with the vapour-liquid curve: in this condition a change of temperature will either make the critical point appear outside or disappear inside the vapour-liquid curve. The contact sometimes takes place on the inside of the latter-curve and the two-liquid curve then lies entirely in the metastable and unstable parts of the diagram, or it lies outside in the stable part of the figure. In other cases it is the vapour curve the critical point of which comes into contact with a two-liquid curve, but whatever the case may be, the geometrical conditions are the

¹⁾ The combined results of FRANZ from the observations at Königsberg and at Göttingen have been considered in my second paper. (*Added* Dec. 1903).

same and the conclusions to be derived from these must hold good in general.

For the sake of clearness we will consider a special case, viz. that in which the liquid curve falls outside the vapour curve and the contact takes place in the critical point of the former. As the saturation curves contract on heating, the two curves will in this case separate when the temperature is raised above the critical temperature; on the other hand the liquid curve begins to intersect the vapour curve when the temperature is lowered. The relative position of the curves here assumed is very common: it was discovered for the first time by VAN DER LEE for mixtures of phenol and water¹⁾.

When the liquid curve intersects the vapour-liquid curve an equilibrium between a vapour phase and two liquid phases is possible, but VAN DER WAALS²⁾ has shown how this equilibrium may be ignored and a continuous vapour-liquid curve traced out through the metastable and unstable parts of the diagram: along this curve the liquid phase passes twice through the spinodal curve of the two-liquid curve and at the same moments the vapour branch of the curve forms cusps; the vapour pressure considered as a function of the composition of the liquid passes at the same time through a maximum or minimum; the thermodynamical condition in these points is $\left(\frac{\partial^2 \zeta}{\partial x^2}\right)_p = 0$, where ζ is the thermodynamical potential.

In many cases the further complication arises that there is a condition, where the compositions of the liquid and the vapour, x_1 and x_2 , are the same and where therefore the pressure is again a maximum or minimum: if this point falls, as it often does, between the two points where $\frac{\partial^2 \zeta}{\partial x^2} = 0$, it can only be a minimum and both the other points are then maxima; the composition of the vapour in the three-phase equilibrium then lies between the compositions of the liquids and the three-phase pressure is higher than the pressure of neighbouring mixtures on both sides. This is the case which was assumed by VAN DER LEE in drawing his diagrams for phenol and water, but from subsequent measurements by SCHREINEMAKERS³⁾ it appears that for these mixtures the maximum where $x_1 = x_2$ lies outside the three-phase triangle in the $v-x$ diagram.

As the temperature approaches the critical point, where the two

1) VAN DER LEE, Dissertatie, Amsterdam 1898. Zeitschr. Physik. Chemie 33 p. 622.

2) VAN DER WAALS, Continuität II, p. 18, fig. 3.

3) SCHREINEMAKERS, Zeitschr. Physik. Chemie, 35, p. 461.

saturation curves separate, the two liquid phases approach each other and finally coincide in the critical point: what becomes of the minimum ($x_1 = x_2$) during this change, if we suppose such a point to lie inside the three-phase triangle? The simplest supposition which we can make is that up to the last moment the minimum remains between the two maxima and thus a fortiori between the coexisting liquids; on that supposition the various points would all coincide in the critical point and unite into one maximum; in the critical point we should then have the condition $x_1 = x_2$, i. e. the liquid in the critical point would have the same composition as the vapour with which it is in equilibrium. This assumption was made as almost self-evident by myself¹⁾ as well as by VAN DER LEE²⁾, but on fuller consideration it now appears to me to be incorrect; VAN DER LEE³⁾ tried to prove its correctness by the aid of the thermodynamical relations for binary mixtures, but we shall show that the proof was not valid.

The equation to be used is the following :

$$\frac{dp}{dx_1} = \frac{x_2 - x_1}{v_{21}} \left(\frac{\partial^2 \zeta_1}{\partial x_1^2} \right)_p;$$

introducing into this the condition $\frac{\partial^2 \zeta_1}{\partial x_1^2} = 0$, which defines the spinodal curve and thus holds a fortiori in the critical point, we obtain the equation $\frac{dp}{dx_1} = 0$: but it does not follow from this that the vapour pressure has a maximum value ; for it may be proved that not only the first differential coefficient $\frac{dp}{dx_1}$, but also the second $\frac{d^2p}{dx_1^2}$ disappears.

Calculating the value of $\frac{d^2p}{dx_1^2}$ from $\frac{dp}{dx_1}$ we find :

$$\frac{d^2p}{dx_1^2} = \frac{x_2 - x_1}{v_{21}} \frac{d}{dx} \left(\frac{\partial^2 \zeta_1}{\partial x_1^2} \right)_p + \frac{1}{v_{21}} \left(\frac{dx_2}{dx_1} - 1 \right) \left(\frac{\partial^2 \zeta_1}{\partial x_1^2} \right)_p - \frac{1}{v_{21}^2} \frac{dv_{21}}{dx_1} (x_2 - x_1) \left(\frac{\partial^2 \zeta_1}{\partial x_1^2} \right)_p;$$

but in the point of contact of the two curves we have not only $\left(\frac{\partial^2 \zeta_1}{\partial x_1^2} \right)_p = 0$, but at the same time $\frac{d}{dx} \frac{\partial^2 \zeta_1}{\partial x_1^2} = 0$, because the spinodal curve of the two-liquid curve touches the connodal curve of the vapour-liquid curve in the critical point of contact ; thus as none of

1) KUENEN en ROBSON, Phil. Mag. (5) 48 p. 184, fig. 2.

2) VAN DER LEE, l. c. p. 69.

3) VAN DER LEE, l. c. p. 74.

the coefficients in the above expression become infinite, all the terms vanish and $\frac{\partial^2 p}{\partial x_1^2} = 0$. In the critical point the pressure is in general not a maximum, but the vapour branch of the saturation curve in the $p-x$ diagram ($t = \text{constant}$) has a point of inflexion with a tangent parallel to the x -axis.

In a special case VAN DER LEE'S conclusion drawn from the equation becomes valid, viz. when in the critical point the condition $x_1 = x_2$ is fulfilled; for in that case the next differential coefficient $\frac{d^3 p}{dx_1^3}$ becomes 0, as well as $\frac{dp}{dx_1}$ and $\frac{d^2 p}{dx_1^2}$. After substitution of the general conditions $\left(\frac{\partial^2 \xi_1}{\partial x_1^2}\right)_p = 0$ and $\frac{d}{dx} \left(\frac{\partial^2 \xi_1}{\partial x_1^2}\right)_p = 0$ the expression for $\frac{d^3 p}{dx_1^3}$ is reduced to :

$$\frac{d^3 p}{dx_1^3} = \frac{x_2 - x_1}{v_{21}} \frac{d^2}{dx^2} \left(\frac{\partial^2 \xi_1}{\partial x_1^2}\right)_p$$

and this expression is equal to 0, if $x_1 = x_2$, but not otherwise.

Without using the equations the same conclusions may be drawn geometrically from the properties of the saturation curve in the $p-x$ diagram; if there are only one minimum and one maximum in the $p-x_1$ curve, three points of intersection coincide in the critical point and consequently there is a point of inflexion, if on the other hand there is a minimum as well as two maxima, four points of intersection coincide in the critical point and there will be a maximum of the second order.

The whole argument thus turns on the question, whether it is legitimate to assume as self-evident, that the point, where $x_1 = x_2$, remains between the two points, where $\left(\frac{\partial^2 \xi_1}{\partial x_1^2}\right)_p = 0$; that this is not the case follows from the fact that the condition $x_1 = x_2$ is totally independent of the condition of critical contact between the two saturation curves: in fact there are cases, such as those referred to above, where the point $x_1 = x_2$ lies at a far distance from the critical point, and others where there is no maximum or minimum at all, either outside or inside the three-phase triangle, such as for mixtures of ethane with the lower alcohol¹⁾. The question therefore arises and has to be answered: how does the point where $x_1 = x_2$, which is known in many cases to be inside the two other maximum

¹⁾ KUENEN en ROBSON, Phil. Mag. (5) 48, p. 192, foll.

points at some distance from the critical temperature, appear outside in the realisable part of the diagram before the critical point is reached? The answer to this question is the following: the minimum ($x_1 = x_2$) approaches one of the maxima ($\left(\frac{\partial^2 \xi_1}{\partial x_1^2}\right)_p = 0$) and at a given temperature coincides with it; from the expressions for $\frac{dp}{dx_1}$ and $\frac{d^2p}{dx_1^2}$, or by geometry, it follows that both coefficients vanish in this point and that the $p-x_1$ curve has a point of inflexion with a tangent parallel to the x -axis. Immediately afterwards the two points in question have passed each other and have exchanged their character, i. e. the point, where $\left(\frac{d^2 \xi_1}{dx_1^2}\right) = 0$, is now a minimum²⁾ and the other point, where $x_1 = x_2$, is a maximum: the latter point lies at first in the metastable part of the diagram between the minimum and one of the liquids of the three-phase equilibrium; a further change of temperature makes it coincide with this liquid and ultimately brings it outside into the stable part of the figure. The maximum and minimum in the non-stable part approach each other and finally coincide, as explained before.

For the sake of clearness we will once more go through the various changes as deduced above in the opposite order, i. e. while the temperature falls towards and passes through the critical point. Above the critical mixing-point there is a separate two-liquid curve turning its critical point towards the vapour-liquid curve: in the latter we assume a well defined maximum ($x_1 = x_2$). When the temperature falls the two curves approach and at a given moment come into contact; this contact takes place in the critical point of the liquid curve, but in general at a smaller or larger distance from the maximum on the vapour-liquid curve: doubtless the distance may in some cases be small, but that does not affect the general argument; on further lowering of the temperature the maximum is in many cases taken up inside the three-phase equilibrium and so disappears from the realisable portion of the diagram; it passes successively the connodal and the spinodal curves and lies then ultimately in the non-stable region, where it is found at low temperatures.

It was mentioned in the beginning that similar changes occur in other cases, e.g. when the two-liquid curve lies inside the vapour-

²⁾ Compare the figure for sulphurous acid and water, VAN DER WAALS, *Continuität II*, p. 18, fig. 3.

liquid curve at first and then appears outside, either on the temperature being raised, as is the case with mixtures of triethylamine and water ¹⁾, or on lowering the temperature, as with propane and methylalcohol ¹⁾, if in those cases a maximum vapour pressure exists, this maximum may disappear in a manner similar to the one sketched above.

The above conclusions may be summarised as follows:

The critical mixing-point of two liquids does not coincide with a point of maximum vapour pressure, if such a point exists; but the latter point may sooner or later at some distance from the critical point be enclosed inside the three-phase equilibrium; in the critical point the liquid branch of the saturation curve in the $p-x$ diagram has a point of inflexion with a tangent parallel to the x -axis.

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Physiology. — “*Something concerning the growth of the lateral areas of the trunkdermatomata on the caudal portion of the upper extremity.*” By Prof. C. WINKLER from researches made in connection with Dr. G. VAN RIJNBERK.

(Communicated in the meeting of November 28, 1903).

A methodical treatment of the dermatomata of the upper extremity offers very considerable difficulties, which have been confronted for the first time by the eminent labour of SHERRINGTON, though to our belief he has not wholly succeeded in conquering them.

The first difficulty we encounter, when essaying their physiological elaboration, is a technical one. The upper extremity transforms by its growth the dermatomata (of neck and trunk) situated above and beneath it. Owing to this transformation their extension-areas overlap one another mutually in a very peculiar manner, and only by means of cutting through numerous — sometimes from 7 to 9— adjacent posterior roots, it becomes possible to isolate them completely. The operation therefore presents greater difficulties, its duration is prolonged, its dangers are increased, partly because of the near vicinity of the medulla oblongata, partly because of the presence of the large perimedullar venous blood-reservoirs (air-embolus, hemorrhage).

The experimental definition of the extension of a root-area on the extremity, already more complicated than it is on the trunk, because

¹⁾ KUENEN, Phil. Mag. (6) 6, p. 637—653.