Physics. — Dr. J. E. VERSCHAFFELT: "*Contributions to the knowledge of* VAN DER WAALS' *ψ-surface* VII. *The equations of state and the ψ-surface in the immediate neighbourhood of the critical state for binary mixtures with a small proportion of one of the components.*" (*part* 3)[1]. (Supplement N°. 6 to the Communication from the Physical Laboratory at Leiden by Prof. KAMERLINGH ONNES).

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

15. *The ψ-surface in the immediate neighbourhood of the plaitpoint.*

By the application, after KEESOM[2], of KORTEWEG's projective transformation[3] to the equations of the ψ-surface, I have expressed the coefficients of my equation (20) in terms of those used by KORTEWEG to study the plait in the paper mentioned.

The following new coordinates must be introduced

$$\psi'' = (\psi-\psi_{Tpl}) - (v-v_{Tpl})\left(\frac{\partial\psi}{\partial v}\right)_{Tpl} - (x-x_{Tpl})\left(\frac{\partial\psi}{\partial x}\right)_{Tpl},$$
$$x'' = (x-x_{Tpl}) - m\,(v-v_{Tpl}),$$
$$v'' = v-v_{Tpl},$$

where m is determined by the equation

$$m\left(\frac{\partial^2\psi}{\partial x^2}\right)_{Tpl} + \left(\frac{\partial^2\psi}{\partial x\,\partial v}\right)_{Tpl} = 0\,;$$

to the first approximation and by the use of equation (20) this reduces to

$$m = \frac{m_{01}}{RT_k}\,x_{Tpl}\ {}^{4)}.$$

Since the equation of the ψ-surface contains a term with $log\ x$,

[1]) Proc. Amsterdam. 28 June and 27 Sept. 1902.

[2]) Proc. Amsterdam. 27 Sept. 1902, p. 341.

[3]) Wien. Ber., 98, 1159, 1889.

[4]) In agreement with KEESOM's expression (l.c. p. 342). The value of m must also fulfil the two other equations:

$$m\left(\frac{\partial^2\psi}{\partial x\,\partial v}\right)_{Tpl} + \left(\frac{\partial^2\psi}{\partial v^2}\right)_{Tpl} = 0$$

and

$$m^3\left(\frac{\partial^3\psi}{\partial x^3}\right)_{Tpl} + 3\,m^2\left(\frac{\partial^3\psi}{\partial x^2\,\partial v}\right)_{Tpl} + 3\,m\left(\frac{\partial^3\psi}{\partial x\,\partial v^2}\right)_{Tpl} + \left(\frac{\partial^3\psi}{\partial v^3}\right)_{Tpl} = 0\,;$$

this is really the case when the above values of x_{Tpl} and v_{Tpl} are substituted. Conversely we can use these equations to determine x_{Tpl} and v_{Tpl}, as KORTEWEG has done. (Proc. Amsterdam. 31 Jan. 1903, p. 526).

it can only be identified with KORTEWEG's equation (2), when *log x* can be expanded in a series. This can only happen when the difference between x and x_{Tpl} is so small that $x—x_{Tpl}$ is vanishingly small with regard to x_{Tpl}. We remain thus in the immediate neighbourhood of the plaitpoint [1]). In this case we find that the equation of the ψ-surface can be brought into the form

$$\psi'' = c_1\, x''^2 + d_1\, x''^3 + d_2\, x''^2\, v'' + d_3\, x'\, v''^2 + e_1\, x'^4 + \ldots$$

where, to the first approximation

$$c_1 = \frac{1}{2}\frac{RT_k}{x_{Tpl}} \quad , \quad d_1 = -\frac{1}{6}\frac{RT_k}{x^2{}_{Tpl}} \quad , \quad d_2 = -\frac{1}{2}\frac{m_{01}}{x_{Tpl}} \, ,$$

$$d_3 = -\frac{1}{2RT_k}(m^2{}_{01} + RT_k m_{11}) \quad , \quad e_1 = \frac{1}{12}\frac{RT_k}{x^3{}_{Tpl}} \quad , \quad e_2 = \frac{1}{3}\frac{m_{01}}{x^2{}_{Tpl}} \, ,$$

$$e_3 = \frac{1}{2}\frac{m^2{}_{01}}{RT_k x_{Tpl}} \quad , \quad e_4 = \frac{1}{3R^2T^2{}_k}(m^3{}_{01} - R^2T^2{}_k m_{21}) \quad , \quad e_5 = -\frac{1}{4} m_{30} \ldots ,$$

$$f_6 = -\frac{1}{5} m_{40} \text{ etc. } ^2).$$

The expression $4\, c_1 e_5 — d_3{}^2 = -\frac{1}{2}\frac{RT_k m_{30}}{x_{Tpl}}$ is always positive hence m_{30} is always negative; it follows that the plaitpoint on the ψ-surface is always of the first kind [3]).

Since $d_3 = 0$ when $m^2{}_{01} + RT_k m_{11} = 0$, the second special case of border curve and connodal line treated by me [4]) agrees with the

[1]) The following expansion can thus be used to determine the coordinates of the critical point of contact, (cf. KEESOM l.c. p. 342).

[2]) The expressions for d_3 and e_5 agree with those found by KEESOM (l. c. p. 341).

[3]) See KORTEWEG, Wien. Ber., p. 1158.

[4]) Proc. Amsterdam 27 Sept. 1902 p. 329. The reference to this special case allows me to correct some mistakes in the formulae which are connected with this and the preceding special cases. In Proc. of 28 June 1902 p. 267 line 2, read:

$$p_1 - p_{Tk} = \left(m_{02} - \frac{1}{3}\frac{m_{11}m_{21}}{m_{30}} + \frac{1}{5}\frac{m^2{}_{11}m_{40}}{m^2{}_{30}}\right)\Xi^2 ,$$

and in Proc. 27 Sept. p. 328, line 12:

$$p - p_{Tk} = \frac{m^2{}_{30}}{m^2{}_{11}}\left(m_{02} - \frac{1}{3}\frac{m_{11}m_{21}}{m_{30}} + \frac{1}{5}\frac{m^2{}_{11}m_{40}}{m^2{}_{30}}\right)(v - v_{Tk})^4 .$$

Further in the last Proceeding p. 329 line 9 for the coefficient of $\frac{m_{01}\, m_{02}}{RT_k}$ read 4 instead of $\frac{5}{2}$

first double-plaitpoint case of KORTEWEG [1]). The second case for a double-plaitpoint, i. e. $4\,c_1e_5 - d_3{}^2 = 0$, does not occur on the ψ-surface.

16. *Application to a particular equation.*

In a communication published in the Proceedings of the Academy for 31 Jan. 1903, KORTEWEG has determined the plaitpoint and critical point of contact for mixtures with a small proportion of one component, but on the assumption that these mixtures satisfy VAN DER WAALS' equation of state

$$p = \frac{RT}{v - b_x} - \frac{a_x}{v^2},$$

where

$$a_x = a_1\,(1-x)^2 + 2\,a_{12}\,x\,(1-x) + a_2\,x^2$$

and

$$b_x = b_1\,(1-x)^2 + 2\,b_{12}\,x\,(1-x) + b_2\,x^2.$$

The formulae found by KORTEWEG can be immediately deduced from my formulae, when we introduce the special forms which my coefficients will then assume.

First we may note that, in this case, the critical constants for the homogeneous mixture are

$$T_{xk} = \frac{8}{27}\frac{a_x}{b_xR} \quad , \quad p_{xk} = \frac{1}{27}\frac{a_x}{b^2{}_x} \quad \text{and} \quad v_{xk} = 3\,b_x,$$

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1) l. c. p. 1166. In using the same method with KORTEWEG's equation (2), as I have used to determine the critical constants, I have found the following expression:

$$y_2 + y_1 = \frac{4c_1e_4e_5 + d^2{}_3e_4 - 4d_2d_3e_5 - 4c_1d_3f_6}{4e_5(d^2{}_3 - 4c_1e_5)}\,(x_2 + x_1),$$

$$(y_2 - y_1)^2 = -\frac{d_3}{e_5}\,(x_2 + x_1),$$

and

$$x_2 - x_1 = \frac{4d_2e^2{}_5 - 2d_3e_4e_5 + d^2{}_3f_6}{2e_5(d^2{}_3 - 4c_1e_5)}\,(x_2 + x_1)\,(y_2 - y_1),$$

where x_1, x_2, y_1 and y_2 are the coordinates of the ends of the tangent-chord.
In the special case when $d_3 = 0$ we get

$$y_2 + y_1 = -\frac{1}{4}\frac{e_4}{e_5}\,(x_2 + x_1) \quad , \quad x_2 - x_1 = -\frac{1}{2}\frac{d_2}{c_1}\,(x_2 + x_1)\,(y_2 - y_1)$$

and

$$(y_2 - y_1)^2 = \frac{1}{2e_5}\left(\frac{d^2{}_2}{c_1} - e_3 + \frac{3}{8}\frac{e^2{}_4}{e_5}\right)(x_2 + x_1)^2.$$

By the introduction of the above values for the coefficients, my expressions for Φ, φ and ξ are again found. The *first* approximation for d_2, c_1 and e_3 will then be certainly *in*sufficient in the last expression.

so that KAMERLINGH ONNES' coefficients α, β and γ become

$$\alpha = 2\left(\frac{a_{12}}{a_1} - \frac{b_{12}}{b_1}\right) \quad , \quad \beta = 2\left(1 + \frac{a_{12}}{a_1} - 2\frac{b_{12}}{b_1}\right) \quad , \quad \gamma = 2\left(\frac{b_{12}}{b_1} - 1\right).$$

Further we find, by comparing my equation (18) with the above equation of state:

$$m_{01} = \left(\frac{\partial p}{\partial x}\right)_{Tk} = \frac{2\,a_1}{27\,b_1^2}\left(1 - 3\frac{a_{12}}{a_1} + 2\frac{b_{12}}{b_1}\right)$$

$$m_{11} = \left(\frac{\partial^2 p}{\partial v\,\partial x}\right)_{Tk} = \frac{4\,a_1}{27\,b_1^3}\left(\frac{a_{12}}{a_1} - \frac{b_{12}}{b_1}\right)$$

$$m_{21} = \frac{1}{2}\left(\frac{\partial^3 p}{\partial v^2\,\partial x}\right)_{Tk} = -\frac{1}{27}\frac{a_1}{b_1^4}\left(1 + 2\frac{a_{12}}{a_1} - 3\frac{b_{12}}{b_1}\right)$$

$$m_{30} = \frac{1}{6}\left(\frac{\partial^3 p}{\partial v^3}\right)_{Tk} = -\frac{1}{486}\frac{a_1}{b_1^5}.$$

If these special values are substituted in my general formulae, KORTEWEG's special formulae are obtained, and in addition some which he has not given. These are not given here as they are not sufficiently simple and they can also be easily reproduced.

KORTEWEG has already given the results obtained from these formulae. I will here only remark that the special cases 1, 2, 3 and 4 of KORTEWEG's fig. 1 agree with my fig. 15 and the cases 5, 6, 7 and 8 with 14. As fig. 15 is obtained for the case that $m^2_{01} + RT_k\,m_{11} > 0$ and fig. 14 when $m^2_{01} + RT_k\,m_{11} < 0$, the boundary between the two cases is determined by $m^2_{01} + RT_k\,m_{11} = 0$, which in connection with the special equation of state can be written

$$\left(1 - \frac{3\,a_{12}}{a_1} + 2\frac{b_{12}}{b_1}\right)^2 + 8\left(\frac{a_{12}}{a_1} - \frac{b_{12}}{b_1}\right) = 0.$$

This is the equation of the parabolic border curve given by KORTEWEG.

(June 24, 1903).