Physics. — *"Contributions to the knowledge of the ψ-surface of* VAN DER WAALS. XIII. *On the conditions for the sinking and again rising of the gas phase in the liquid phase for binary mixtures,"* by Dr. **W. H. KEESOM**. Communication N°. 96c from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

§ 1. *Introduction.* As has been observed in Communication N°. 96b (See the preceding paper) (cf. Comm. N°. 96a, Nov. '06, p. 459, note 1) it lies to hand, to take as point of issue the ψ-surface for the unity of mass of the mixture considered, in the investigation according to VAN DER WAALS' theory of binary mixtures, of the sinking and subsequent rising of the gas phase in the liquid phase, i.e. the barotropic phenomenon. Two coexisting phases of equal density are joined on this ψ-surface by a tangent-chord whose projection on the x, v-plane [1]) is parallel to the x-axis. It has already been observed in Comm. N°. 96b, that with decrease of temperature starting from the critical temperature of the first (least volatile) component such a barotropic tangent-chord may make its appearance in two ways:

a. by the angle of inclination of the tangent to the plait in the 'plaitpoint, θ_{pl}, reaching the value of $\frac{\pi}{2}$ at a certain temperature $T_{b,pl}$ and by its exceeding this value at lower temperature.

b. by θ showing a maximum and a minimum on the plait at a certain temperature, and by this maximum reaching or exceeding the value of $\frac{\pi}{2}$. Also in this latter case one of the two barotropic tangents-chords which then appear, might reach the plaitpoint at lower temperature, and thus become $\theta_{pl} = \frac{\pi}{2}$.

In both cases in which $\theta_{pl} = \frac{\pi}{2}$ at a certain temperature it should be expected apart from complications as e. g. a longitudinal plait etc. (cf. Comm. N°. 96b, p. 502), the description of which will be given later on, that θ_{pl} becomes again $= \frac{\pi}{2}$ for mixtures of the same substances at a lower temperature.

In the first part of this paper the conditions are discussed on which a plaitpoint with $\theta_{pl} = \frac{\pi}{2}$, barotropic plaitpoint, occurs on the ψ-sur-

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[1]) Cf. for the meaning of x and v Comm. N°. 96b.

_face, whereas in the second part the conditions are treated for the appearance of a barotropic tangent-chord on the plait.

A. On the conditions for the occurrence of a barotropic-plaitpoint.

§ 2. In a barotropic plaitpoint the isobar, which in a plaitpoint always touches the plait, must run parallel to the x-axis. This gives the condition:

$$\left(\frac{\partial^2\psi}{\partial x \partial v}\right) = 0 \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (1a)$$

Moreover a section $v = v_{pl}$ of the ψ-surface with the limiting position of the tangent-chord must then have a contact of the 3^{id} order. This furnishes:

$$\left(\frac{\partial^2\psi}{\partial x^2}\right) = 0 \; \cdot \; , \quad \left(\frac{\partial^3\psi}{\partial x^3}\right) = 0 \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (1 \; b \text{ and } c)$$

The two conditions (1 b) and (1 c) follow also by applying (1 a) to the general relations for the plaitpoint of Comm. N°. 75 (Dec. 1901) p. 294.

The same may be obtained from the property of the barotropic points on the connodal curve that there $\left(\frac{\partial\psi}{\partial x}\right)$ along the connodal shows a maximum or minimum [1], so that the substitution-curve $\left(\frac{\partial\psi}{\partial v}\right) = $ const. (see for the substitution curves on the ψ-surface for the molecular quantity Comm. N°. 59^n), touches the connodal line in these points.

§ 3. For a first investigation we shall use VAN DER WAALS' equation of state:

$$p = \frac{R_x T}{v - b_x} - \frac{a_x}{v^2} . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (2)$$

with an a_x and b_x not depending on v and T for a definite x. In this:

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[1] This property for coexistence with $v_2 = v_1$ is analogous to the property that $\left(\frac{\partial\psi}{\partial v}\right) = -p$ along the connodal line is a minimum or a maximum for coexisting phases with $x_2 = x_1$. In the same way the mean value of $\left(\frac{\partial\psi}{\partial x}\right)$ along an isometric line $v = v_b$, which joins two barotropic phases on the ψ-surface, is equal to the value of $\left(\frac{\partial\psi}{\partial x}\right)$ for these phases.

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$$R_c = R_1 (1-x) + R_2 x \quad . \quad . \quad . \quad . \quad . \quad . \quad (3a)$$

if $R_1 = R/M_1$, $R_2 = R/M_2$, R representing the molecular gas-constant, M_1 and M_2 representing the molecular weights; we put for this first investigation $a_{12} = \sqrt{a_{11}\, a_{22}}$, so that

$$a_x = \{\sqrt{a_{11}} \cdot (1-x) + \sqrt{a_{22}} \cdot x\}^2 \quad . \quad . \quad . \quad . \quad (3b)$$

and when we put for the molecular volumes $2b_{12M} = b_{11M} + b_{22M}$, the relation for b_x given by VAN DER WAALS Contin. II p. 27, reduces to:

$$b_x = b_{11} (1-x) + b_{22}\, x \quad . \quad . \quad . \quad . \quad . \quad . \quad (3c$$

We get then (VAN DER WAALS Contin. II p. 28):

$$\psi = - R_1 T \, ln \, (v-b_1) - \frac{a_x}{v} + T \{R_1 (1-x) \, ln \, (1-x) + R_2\, x \, ln \, x\} \quad . \quad (4)$$

§ 4. Taking equations (3) into consideration, and putting

$$\frac{b_{22} - b_{11}}{v - b} = u, \quad x = \frac{1+z}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

we get by the conditions (1):

$$R_2 \cdot \frac{1+z}{2} \left\{u + \frac{2}{1+z}\right\} + R_1 \frac{1-z}{2} \left\{u - \frac{2}{1-z}\right\} = \frac{v-b}{Tv^2} \frac{da}{dx} \quad . \quad . \quad . \quad (6a)$$

$$R_2 \cdot \frac{1+z}{2} \left\{u + \frac{2}{1+z}\right\}^2 + R_1 \frac{1-z}{2} \left\{u - \frac{2}{1-z}\right\}^2 = \frac{1}{Tv} \frac{d^2 a}{dx^2} \quad . \quad . \quad . \quad (6b)$$

$$R_2 \cdot \frac{1+z}{2} \left\{u + \frac{2}{1+z}\right\}^2 \left\{u - \frac{1}{1+z}\right\} + R_1 \frac{1-z}{2} \left\{u - \frac{2}{1-z}\right\}^2 \left\{u + \frac{1}{1-z}\right\} = 0 \quad (6c)$$

These equations are sufficient to calculate the data for a barotropic plaitpoint x_{bpl}, v_{bpl}, T_{bpl} for a definite pair of substances. Eliminating T from (6a) and (6b), we get, taking (6c) into consideration and putting:

$$(\sqrt{a_{22}} + \sqrt{a_{11}}) / (\sqrt{a_{22}} - \sqrt{a_{11}}) = \mu . \quad . \quad . \quad . \quad (7a)$$

$$\tfrac{1}{2} (v-b) \left\{u + \frac{2}{1+z}\right\} \left\{u - \frac{2}{1-z}\right\} (\mu+z) + v \left\{u + \frac{4z}{1-z^2}\right\} = 0, \quad (8)$$

while elimination of v from this equation and (5), putting:

$$(b_{22} + b_{11}) / (b_{22} - b_{11}) = v \quad . \quad . \quad . \quad . \quad . \quad . \quad (7b)$$

yields:

$$\tfrac{1}{2} \left\{u + \frac{2}{1+z}\right\} \left\{u - \frac{2}{1-z}\right\} (\mu+z) + \left\{u + \frac{4z}{1-z^2}\right\} \{\tfrac{1}{2} (v+z) u + 1\} = 0 . \quad (9)$$

From this equation with (6c): z_{bpl} may be found for given R_2/R_1, μ and v, after which x_{bpl}, v_{bpl} and T_{bpl}, as well as p_{bpl} follow easily.

§ 5. That a barotropic plaitpoint exists on the liquid-gas-plait with the assumed suppositions (2), (3b), (3c) and with suitable

values of the constants, appears as follows: for $z = 0.5$, $R_2/R_1 = {}^1/_2$, $b_{22}/b_{11} = {}^1/_8$, (6c) yields: $u = -1.957$, after which (9) yields: $\mu = -1.176$, so that $a_{22}/a_{11} = 0.00653$. Thus we find for a mixture of two substances with $M_2 = 2 M_1$, $v_{k_2} = {}^1/_8 v_{k_1}$ (so that the ratio of the molecular critical volumes is ${}^1/_4$), $T_{k_2} = 0.052 T_{k_1}$, a barotropic plaitpoint for $v_{bpl} = 0.26 v_{k_1}$, $T_{opl} = 0.80 T_{k_1}$, $p_{hpl} = 4.8 p_{k_1}$.

(To be continued).

ERRATUM.

In the Proceedings of the meeting of September 29, 1906.

p. 209, line 15 from the bottom: for § 10 read § 9.

p. 210, Table I, line 5 and 4 from the bottom, for: 5 July read 6 July.

„ 3   from the bottom, for 3 March '05 read 3 March '06.

(January 24, 1907).