

paper: Contribution to the knowledge of the  $p, x$ - and the  $p, T$ -lines<sup>1</sup>, at least when we take the maxima of pressure very much higher and the minima very much lower, so that on the left side the figure intersects itself twice. The detachment of the two binodal curves then takes place in a very intricate way by means of a series of modifications, which I shall, however, omit, with a view to the available space. So, for this I must refer to the lectures which I am arranging for publication as mentioned in the beginning of my preceding communication, though certainly some time will elapse before they see the light.

**Physics.** — “Contributions to the knowledge of the  $\psi$ -surface of VAN DER WAALS. XIII. On the conditions for the sinking and again rising of a gas phase in the liquid phase for binary mixtures. (continued). By Dr. W. H. KEESOM. Communication N<sup>o</sup>. 96<sup>c</sup> from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of January 26, 1907).

§ 6. *Conditions for the occurrence of barotropic plaitpoints for mixtures with  $M_2 = 2 M_1, v_{k_1} = 8 v_{k_2}$ .* Now that it had appeared in § 5 (These Proc. p. 510), that there exists a barotropic plaitpoint<sup>2</sup>) on the assumptions mentioned there, first of all the occurrence of barotropic plaitpoints with  $M_2/M_1 = 2, v_{k_2}/v_{k_1} = 1/8$  was subjected to a closer investigation, partly also on account of the importance of these considerations for mixtures of He and H<sub>2</sub><sup>3</sup>). The barotropic plaitpoints given in table I respectively for the ratio of the critical

<sup>1</sup>) These Proc. VIII, p. 200.

<sup>2</sup>) The proof that this barotropic plaitpoint really lies on the gas-liquid plait, is in connection with the discussion of the longitudinal plait. In a following Comm. by Prof. KAMERLINGH ONNES and me on this latter subject, the treatment of which was postponed for the present as stated in Comm. N<sup>o</sup>. 96<sup>b</sup>, the proof in question will be included.

<sup>3</sup>) To enable us to judge in how far this last assumption is in accordance with what is known about mixtures of He and H<sub>2</sub>, the following remark may follow here, in the name of Prof. KAMERLINGH ONNES too, (cf. Comm. N<sup>o</sup>. 96<sup>b</sup> § 4, Dec. '06 p. 506) on  $b$  (cf. VAN DER WAALS, These Proc. Jan. '07, p. 528) and  $a$  for helium: It proved in the preliminary experiment described in Comm. N<sup>o</sup>. 96<sup>a</sup> that on analysis the liquid phase contained at least (some He has evaporated from it during the drawing off of the liquid phase) about 3% He, the gas phase at least (a very small quantity of liquid has been drawn along with the gas phase being blown off) about 21% H<sub>2</sub> (estimations of the corrections which for the reasons mentioned ought to be applied to the results of the analysis make it probable that they will not considerably influence the results derived here [added in the English translation]). Let us put the density of liquid hydrogen boiling under

temperatures of the components given there are found in the way explained in § 5.

atmospheric pressure according to DEWAR (Roy. Institution Weekly Evening Meetings), 25 March '04) at 0.070, and let us derive the coefficient of compressibility according to the principle of the corresponding states, e.g. from that of pentane at 20° C., then the density at 40 atms. is 0.072. If we calculate the increase of density in consequence of the solution of helium from VAN DER WAALS' equation of state for a binary mixture by putting  $b_{MHe} = \frac{1}{2} b_{MH_2}$  for this correction term, we get for the density of the liquid phase at the  $p$  and  $T$  mentioned if it contained 3% He : 0.077.

The gas phase will have the same density at about the  $p$  and  $T$  mentioned (cf. Comm. N°. 96a, Nov. '06, p. 460). The theoretical density (AVOGADRO-BOYLE-GAY-LUSSAC) at  $T=20^\circ$  and  $p=40$  atms. = 0.0885. If we assume VAN DER WAALS' equation of state with  $a_x$  and  $b_x$  for constant  $x$  not dependent on  $v$  and  $T$ , to hold for this gas phase,

it follows with the above given value of the density that  $\frac{b_x}{v-b_x} - \frac{a_x}{RTv} = 0.15$ .

For  $a_{22} = a_{12} = 0$  with  $a_{11M} = 0.00042$  (KOHNSTAMM, LANDOLT-BÖRNSTEIN-MEYERHOFFER's Physik. Chem. Tabellen), and with  $v_M = 0.0021$ , putting  $x = 0.80$  for the gas phase, we should obtain:  $b_{xM} = 0.21 v_M = 0.00044$ . We should then, if we may put  $b_{12M} = \frac{1}{2} (b_{11M} + b_{22M})$ , get  $b_{22M} = 0.00033 = \frac{3}{8} b_{11M}$  ( $b_{11M} = 0.00088$ , KOHNSTAMM l. c.). If we wish to assume positive values for  $a_{12}$  and  $a_{22}$  (cf. Comm. N°. 96a, p. 460), we should have to put  $b_{22M} > \frac{3}{8} b_{11M}$  for  $T=20^\circ$ ; if we assumed that the gas phase contained 15% He we should derive from the above mentioned experiment for positive values of  $a_{11}$  and  $a_{12}$ :  $b_{22M} > 0.31 b_{11M}$ .

These results harmonize very well with what may be derived about  $b_{MHe}$  at 0° C.; the ratio of the refracting powers (RAYLEIGH) gives:  $b_{22M} = 0.31 b_{11M}$  while the ratio of the coefficients of viscosity and also that of the coefficients of the conduction of heat lead to a greater value for  $b_{MHe}$  (about  $\frac{1}{2} b_{MH_2}$ ).

If we take  $b_{22M}/b_{11M} = \frac{1}{2}$ , we should obtain from the above given considerations (putting  $a_{12M} = \sqrt{a_{11M} a_{22M}}$ ):  $a_{22M}/a_{11M} = \frac{1}{175}$ , so that  $T_{kHe} =$  about  $0.35^\circ$ . This renders a value for the critical temperature of He  $< 0.5^\circ$  probable.

This conclusion would not hold if  $b_{xM}$  for  $x=0.8$  were considerably greater than follows from the hypothesis that  $b_{xM}$  varies linearly with  $x$ . This however is according to the experiments of KUENEN, KEESOM and BRINKMAN on mixtures of  $CH_3Cl - CO_2$  and  $CO_2 - O_2$ , not to be expected. The experiments of VERSCHAFFELT on mixtures of  $CO_2 - H_2$  would admit the possibility, but give no indication for the probability of it. [Added in the English translation].

So though probably  $b_{22}/b_{11}$  for mixtures of He and  $H_2$  is larger, yet we shall here retain the supposition made in § 5 on  $b_{22}/b_{11}$ , with which the calculations were started, because the accurate amount is not yet known to us, and we only wish to give here an example for discussion; moreover the course of the  $\psi$ -surface will not be considerably modified by this difference in any essential respect.

TABLE I.				
Barotropic plaitpoints at $M_2/M_1 = 1/2, v_{k_2}/v_{k_1} = 1/8.$				
$T_{k_2}/T_{k_1}$	$x_{bpl}$	$v_{bpl}/v_{k_1}$	$T_{bpl}/T_{k_1}$	$p_{bpl}/p_{k_1}$
0.0002	0.6	0.3957	1.005	4.805
0.0210	0.65	0.3481	0.934	4.772
4/121	2/3	1/3	441/484	576/121
0.0604	0.7	0.3048	0.867	4.758
0.1044	0.75	0.2636	0.800	4.780
0.1472	0.8	0.2234	0.726	4.811
0.1842	0.85	0.1833	0.638	4.800
0.2106	0.9	0.1424	0.521	4.567
0.2176	0.925	0.1212	0.444	4.202
0.2190	0.94	0.1081	0.387	3.751
0.2182	0.95	0.0991	0.343	3.282
0.2148	0.965	0.0851	0.266	2.107
0.2106	0.975	0.0752	0.204	0.687
0.2040	0.985	0.0644	0.130	-1.927
0.1996	0.99	0.0585	0.078	-5.191
0.1980	0.995	0.0518	0.033	-9.723
0.1956	0.9965	0.0495	0.028	-10.326
0.1964	0.9975	0.0478	0.019	-12.086
1/4	1	1/24	0	-27

For so far as the assumed suppositions hold, the barotropic plaitpoints given in the table have only physical significance if  $T_{bpl}$  does not become so low that solid phases make their influence felt (cf. Comm. N°. 96b, § 5 b), and if moreover the portion of the  $\psi$ -surface in the neighbourhood of the plait-point is not covered by a portion of the derived surface indicating more stable equilibria (as e. g. will be the case for negative pressures). In how far the indicated barotropic plaitpoints will belong to the gas-liquid-plait will be more fully treated in a following communication (cf. footnote 2, p. 660).

In the first place it follows from table I that with the assumed

ratios of the molecular weights and of the critical volumes, barotropic plaitpoints prove only possible (quite apart from the question whether they are physically realisable, and whether they belong to the gas-liquid plait) for  $T_{k_2}/T_{k_1} < \frac{1}{4}$ .

The barotropic plaitpoint for the ratio  $T_{k_2}/T_{k_1} = 0.0002$  is a plaitpoint for a mixture, one component of which is a gas almost without cohesion (Comm. No. 96*b* § 1). A further consideration of it would lead us again to the region of the longitudinal plait.

The conditions relating to barotropic plaitpoints for  $x_{bpl}$  near 1 furnish a contribution to the knowledge of VAN DER WAALS'  $\psi$ -surface for binary mixtures with a small proportion of one of the components<sup>1)</sup>. We find for  $T_{k_2}/T_{k_1}$  near  $\frac{1}{4}$ , putting  $x_{bpl} = 1 - \xi$ :

$$u = -\xi^{-2/3} \left\{ 1 - \frac{1}{2} \xi^{2/3} - \frac{1}{3} \xi \dots \right\}, \mu = -\frac{9}{7} \left\{ 1 - \frac{4}{9} \xi^{1/3} + \frac{20}{9} \xi^{2/3} - \frac{29}{9} \xi \dots \right\}, T_{k_2}/T_{k_1} = \frac{1}{4} \left\{ 1 - \frac{7}{2} \xi^{1/3} + \frac{315}{16} \xi^{2/3} - \frac{735}{16} \xi \dots \right\}.$$

It is seen from the series of the ratios  $T_{k_2}/T_{k_1}$  in table I, that in this a maximum and a minimum occur, respectively for about  $T_{k_2}/T_{k_1} = 0.219$  and 0.196. From the formulae derived for  $x_{bpl}$  near 1, a minimum and a maximum for  $\mu$  is found, and hence for  $T_{k_2}/T_{k_1}$ , respectively at  $x_{bpl} = 0.9968$  and 0.969. That the latter is in reality found at  $x_{bpl} = 0.94$  is due to following terms in the development.

For  $T_{k_2}/T_{k_1} < 0.196$  or  $0.219 < T_{k_2}/T_{k_1} < 0.25$  one barotropic plaitpoint is found, for  $0.196 < T_{k_2}/T_{k_1} < 0.219$  three. In connection with Comm. No. 96*b* § 2 (Dec. '06 p. 502, cf. also this Comm. § 1, Dec. '06, p. 508) it follows also from this that for the mixtures considered here at lower temperature the longitudinal plait makes its influence felt.

The experiment described in Comm. N<sup>o</sup>. 96*a* proved that for mixtures of He and H<sub>2</sub> at  $-253^\circ$ , i.e. about  $T = 0.65 T_{kH_2}$ , a barotropic tangent chord is found on the  $\psi$ -surface. If at that temperature only *one* barotropic tangent chord occurs, this will point to this (Comm. N<sup>o</sup>. 96*b* p. 504) that for the mixtures of these substances  $T_{bpls} > 0.65 T_{kH_2}$ , and therefore according to this table  $T_{kHe} < 0.18 T_{kH_2}$ , while the found considerable difference in concentration between the gas and the liquid phase (see Footnote 3,

<sup>1)</sup> Cf. Comm. N<sup>o</sup>. 75 (Dec. '01), N<sup>o</sup>. 79 (April '02), N<sup>o</sup>. 81 (Oct. '02), Suppl. N<sup>o</sup>. 6 (May, June '03).

p. 660) indicates, that  $T_{b,pls}$  would have to lie still pretty much higher, and therefore  $T_{k,H}$  pretty much lower (probably  $<$  about  $4^\circ$ )<sup>1)</sup>. Of this result we availed ourselves in the treatment of the estimation of the critical temperature of He in Comm. N<sup>o</sup>. 96b.

(To be continued).

**Physics.** — “Contributions to the knowledge of the  $\psi$ -surface of VAN DER WAALS. XIV. Graphical deduction of the results of KUENEN'S experiments on mixtures of ethane and nitrous oxide.” Supplement 14 to the Communications from the Physical Laboratory of Leiden. By Prof. H. KAMERLINGH ONNES and Miss T. C. JOLLES.

(Communicated in the meeting of Januari 26, 1907).

§ 1. *Introduction.* In what follows we have endeavoured to derive quantitatively by first approximation the behaviour of the mixtures of  $N_2O$  and  $C_2H_6$  (mixtures of the II type<sup>2)</sup>), which has become known through KUENEN'S experiments<sup>3)</sup>, by the aid of VAN DER WAALS' free-energy surface. The  $\psi$ -surfaces construed for this purpose (see plate I) are the counterparts of those construed in Comm. N<sup>o</sup>. 59 (These Proc. Sept. 1900) and Comm. N<sup>o</sup>. 64<sup>4)</sup> for the derivation of the results of KUENEN'S and HARTMAN'S experiments on mixtures of  $CO_2$  and  $CH_3Cl$  (mixtures of the I type). In the graphical treatment<sup>5)</sup> of our problem we have chiefly followed the method given in Comm. N<sup>o</sup>. 59, where the critical temperature and pressure of some mixtures were borrowed from KUENEN'S determinations, and then the results of another group of experiments — those referring to the conditions of coexistence of two phases at a certain temperature — were deduced by the aid of VAN DER WAALS' theory.

KUENEN'S results for  $N_2O$  and  $C_2H_6$  are principally laid down in

1) If  $b_{22}/b_{11}$  is taken larger than  $1/3$  (Cf. Footnote 3 p. 660) this supposition too makes the upmost limit for  $T_{k,H}$  on the said supposition smaller. This is seen when we compare with table I that we obtain  $T_{b,pl}/T_{k_1} = 0.679$  for  $b_{22}/b_{11} = 1/4$  with  $T_{k_2}/T_{k_1} = 0.15$ .

2) HARTMAN, Leiden Comm. Suppl. no. 3, p. 11.

3) KUENEN, Leiden Comm. no. 16, Phil. Mag 40, p. 173, 1895, cf. also KAMERLINGH ONNES and ZAKRZEWSKI, Leiden Comm. Suppl. no. 8. (These Proc. Sept. 1904).

It is remarkable that the possibility of this case was foreseen by VAN DER WAALS, Contin. II, p. 49 [added in the English translation].

4) Arch. Néerl. Serie II, Tome V, p. 636.

5) Only graphical solutions for definite cases are here possible. (Cf. Suppl. 8, These Proc. Sept. 1904. § 1).