Citation:

§ 5. Further approximations. By second approximation we get by taking also \( B^2 \) into consideration:

\[
\frac{p_1 v_1}{p_2 v_2} - 1 = \frac{B}{A_1} (p_1 - p_2) - \frac{B^2}{A_1} (p_1 - p_2) (p_1 + 2p_2). \tag{2}
\]

If, however, we take \( B^2 \) into consideration, it is more rational to do the same with \( C \), and we have:

\[
\frac{p_1 v_1}{p_2 v_2} - 1 = \frac{B}{A_1} (p_1 - p_2) - \frac{B^2}{A_1} (p_1 - p_2) \left( p_2 + \left( 1 - \frac{CA}{B^2} \right) (p_1 + p_2) \right). \tag{3}
\]

According to the reduced equation of state \( \frac{CA}{B^2} \) is about \( \frac{1}{5} \) for methyl chloride at 20°.

The repetition of the calculations of § 2 yields:

\[
\begin{array}{|c|c|c|c|c|c|}
\hline
\text{approxim.} & \text{composit. } x & \frac{B}{A_1} \text{ from I a. II} & \frac{B}{A_2} \text{ from I a. III} & \frac{B}{A_3} \text{ mean} & \frac{B}{A_3} \text{ mean} \\
\hline
2nd & 1 & -0.01698 & -0.01710 & -0.01704 & -0.01704 \\
3rd & -0.01741 & -0.01723 & -0.01717 & -0.01717 & -0.01738 \\
2nd & 0.0045 & -0.01240 & -0.01269 & -0.01258 & -0.01258 \\
3rd & -0.01260 & -0.01282 & -0.01271 & -0.01271 & -0.01464 \\
2nd & 0.5030 & -0.01001 & -0.00976 & -0.00988 & -0.00988 \\
3rd & -0.01000 & -0.00983 & -0.00996 & -0.00996 & -0.01147 \\
2nd & 0 & -0.00575 & -0.00547 & -0.00558 & -0.00558 \\
3rd & 0.00575 & -0.00547 & -0.00551 & -0.00546 & -0.00546 \\
\hline
\end{array}
\]

The repetition of the calculations of § 3 and § 4 with these corrected values gives:

1) Here are two determinations of Keesom agreeing with I and II and I and III, calculated according to (2) and (3) (data see Comm. No. 88).
The comparison of the values found with those of the quadratic formula and the law of corresponding states (using Brinkman's \(^1\)) critical data gives:

\[
\begin{align*}
\left(\text{Cl Me}\right) &\quad B_{200} = -0.01983 \\
\left(\text{Cl Me, CO}\right) &\quad B_{200} = -0.01005 \\
\left(\text{CO}_2\right) &\quad B_{200} = -0.00644
\end{align*}
\]

In the conclusions of § 3 and § 4 no further modification is brought about by these further approximations. It is noteworthy that the deviation now only applies to the methyl chloride.

§ 6. Comparison of the results with those of Leduc and Chappuis.

The compressibility of methyl chloride with small densities has been examined by Leduc \(^2\) in collaboration with Sacerdote. He does not give the observed results but the quantity calculated from it at 160, viz.:

\[
\pi \mathcal{A}_4 = - \pi \frac{1}{\rho^2} \frac{\partial (\rho v)}{\partial \rho} \text{ at } \pi = 73 \text{ cm.}
\]

According to Kamke's empirical equation of state:

\[
-\left(\frac{1}{\rho^2} \frac{\partial (\rho v)}{\partial \rho}\right) = -\frac{B}{A^2} \left(1 - \frac{2CA}{3B^2}\right) p.
\]

In order to pass from our \(B_{200}\) to \(B_{160}\) we have calculated \(\frac{\partial B}{\partial t}\) according to the formula given in § 4 for the reduced value of

\(^1\) Brinkman, Thesis for the doctorate, Amsterdam 1904.
\(^2\) Recherches sur les gaz, p. 82.
(379)

\[ B, \mathcal{B}, \text{and found} \quad \frac{\partial B}{\partial t} = 0.0001194, \text{so that} \quad B_{16^\circ} = -0.02026, \]
while \( A_{16^\circ} = 1 + 16 \alpha_\infty \). Thus we find

\[ \pi A_\tau = 0.01814 \quad (\text{K. O. and Z.}) \]

while

\[ \pi A_\tau = 0.01935 \quad (\text{L.}) \]
was found by Leduc (l.c.). The uncertainty of \( \frac{\partial B}{\partial t} \) contributes probably but little to the difference. It is noteworthy that in contradiction with our result the value of \( B \) derived from Leduc's observations \( B_{20^\circ} = -0.0215 \) perfectly agrees with that according to the law of corresponding states: \(-0.0216\).

Measurements on the compressibility of \( \text{CO}_2 \) have been made by Chappuis \(^1\) at \( 20^\circ \) C. He found (mean from some determinations with about the same pressure each time):

\begin{align*}
\text{I} & \quad \rho = 1260.670 \text{ mm. } \quad \mu v = 1312485 \\
\text{II} & \quad 1117.228 \text{ " } \quad 131326 \\
\text{III} & \quad 992.911 \text{ " } \quad 1314981
\end{align*}

By third approximation yield

\[(\text{CO}_2) B_{20^\circ}^0 = \begin{bmatrix} 1 \text{ and II} : \\ -0.005309 \\ \frac{1}{2} A_{20^\circ}^0 \end{bmatrix} \quad \text{assumed mean } -0.005296, \]

\[ \text{II and III } \quad -0.005282 \]

\[ \text{I and III } \quad -0.005297 \]

from which follows \( B_{20^\circ} = -0.006100 \), whereas according to Keesom \( B_{20^\circ} = -0.00646 \).

From the observations of Leduc on carbon dioxide Keesom derived \( B_{20^\circ} = -0.0059 \).

II. Conditions of coexistence at low temperatures.

\( \text{§ 7. Determination of the begin condensation pressure at } -25^\circ. \)

In the introduction we mentioned a determination of the begin condensation pressure at \(-25^\circ\) for testing the results obtained with the \( \psi \)-surface. This determination was made with a mixture with the composition \( x = 0.5042 \) of methylchloride.

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\(^1\) Trav. et Mém. du Bureau Intern. des Poids et Mesures, t. 13, 1903.
A condensation was seen on the mirror of the dew-point apparatus (see § 1 and Comm. N°. 92 p. 233) at a pressure of 157.4 cm. mercury and disappeared at 154.6 cm. As mean we may take 156.0 cm., and the accuracy may be put at 1/10.

§ 8. Determination of the end condensation pressure. In the first place the condensation pressure (vapour tension) of pure methyl chloride was determined with the aid of the small piezometer (§ 5 Comm. N°. 92). At — 25° we found 72.9 cm. when the piezometer was filled to the capillary tube, 72.8 cm. when the liquid had nearly all evaporated. In both cases the liquid in the piezometer was stirred. The agreement of these values speaks for the purity of the methyl chloride. At — 37°.4 the vapour tension was found to be 42.7 cm.

In order to determine the end condensation pressure of the mixture with \( x = 0.5042 \) of methyl chloride the temperature of the piezometer had to be lowered down to — 38°.5; at higher temperatures condensation took place at other places in the apparatus. (Cf. § 5 of the Comm. N°. 92 "On the determination of the conditions of coexistence etc." It may further be observed, that no arrangement was applied to heat the press tube and the capillary tube above the ordinary temperature). For the determination of the conditions of coexistence (according to § 5 just mentioned), are wanted: in the first place the observed end pressure \( p_{nT} \), for which 6.13 atms. was found. Then the volume \( V_p \) of the vapour with the composition \( x = 0.0375 \). From these data follows (see l.c. § 5)

\[
x_{vT} = 0.5084, \quad p_{nT} = 6.13, \quad t = -38.5°.
\]

The circumstances were not favourable for an accurate determination of the correction. It appears, however, to be so slight, that we may safely assume the composition to be accurate down to 1/10.

§ 9. Comparison of the conditions of coexistence with theory. For this purpose it is required in the first place to know the vapour tension of methyl chloride and carbon dioxide at — 25° C. and — 38°.5 C.

We have calculated the coefficients for methyl chloride in the formula of Dupré and Rankine \( \ln p = A - \frac{B}{T} - C \ln T \) with Hartman's value.
(3.48 atm. at 9°.5 C.)\(^1\), and the two values found by us (§ 8). Extrapolation to \(-38°.5\) C. gives 0.53 atm. For carbon dioxide follows from Kuenen's observations\(^2\) at \(-25°\) C., \(p_{\text{max}} = 16.5\) atm., at \(-38°.5\) C., \(p_{\text{max}} = 10.4\) atm.

From our model for \(-25°\) C. (Comm. Suppl. N°. 8) follows for methyl chloride at \(-25°\) C. \(p_{\text{max}} = 0.59\) atm. and for carbon dioxide \(p_{\text{max}} = 16\) atm. (instead of 0.96 and 16.5). The begin condensation pressure of the mixture \(x = 0.5084\) is according to the model 1.30 atm. instead of 2.05 atm., as was found by us.

The insufficient concordance on the side of methyl chloride shows once more clearly that for methyl chloride and ether the agreement required for the validity of the law of corresponding states leaves much to be desired.

In order to judge about the degree of deviation of the mixtures from this law, we must first free ourselves as much as possible from the deviations of the separate components. We have tried to do so by raising the \(px\)-curve 0.4 atm. Then we get for \(p_{\text{max}} = 0.99\) atm. for methyl chloride, 16.4 atm. for carbon dioxide, and \(p_{\text{vx}} = 1.7\) atm. for the examined mixture. The remaining difference with the observed \(p_{\text{vx}} = 2.05\) atm. is, no doubt, partly due to the fact that the surface had not yet been constructed with sufficient care, to determine with sufficient certainty the place of the points of contact when the plate of glass is rolled over the ridge and over the convex part. More points should have been calculated if we wished to render the model sufficiently precise for an accurate determination.

This uncertainty when rolling, makes it also doubtful whether on account of the law of corresponding states, with an accurately executed theoretical model, a straight line would really be found for the liquid branch of the border curve in the \(px\)-diagram, as was derived from our model. We got the impression, that a curve of the same character as that derived by Hartman in his experiments and from his model, ought to be found also by us, on our model (Comm. Suppl. N°. 8), but we had not enough data for ascertaining the deviations from the straight line, and had therefore to adopt the straight line as the simplest approximation.

That the experimental liquid branch of the border curve in the

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\(^1\) Comm. N°. 64.

$p_x$-diagram at $-25^\circ$C. is not straight, could not be proved with our mixtures and our apparatus, as has been said. The measurements at $-38.5^\circ$C. raised it however beyond doubt, that the line under consideration is not straight at $-38.5^\circ$C., but is for the greater part convex to the x-axis. According to the straight line $p_x$ would have to be 5.38 atms. for $x = 0.5084$, instead of the value 6.13 atms. found. This difference is much too large to be accounted for by errors of observation or of the value ascribed to the composition. There is therefore no doubt that the liquid branch is curved in the same way at $-25^\circ$C. In concordance with this deviation is also the fact that the begin pressure at the same temperature does not agree with the hyperbolic function for the composition (Van der Waals, Continuitat II, p. 154). For according to this formula the begin pressure would have to be 1.78 atms. instead of 2.05 atms., as was found ($\S$ 6).

It appears from all this, that from the conditions of coexistence deviations from the law of corresponding states follow for isothermals of mixtures of methyl chloride and carbon dioxide, which become very distinct for liquid densities and low temperatures.

The comparison of the conditions of coexistence, derived from the law of corresponding states by means of the $\psi$-surface, with the really observed data, is an indirect method for judging about the deviations from the law of corresponding states for the isothermals of mixtures. It was our purpose to give an instance of the application of this method and to do this at low temperatures.

In order to ascertain the accurate amount of the deviations new measurements at low temperatures will be required, and for the temperature of observation a $\psi$-surface will have to be constructed with more precision than that devised in Comm. Suppl. No. 8 for the sake of preliminary elucidation and for the sake of corrections.


Page 214, line 14 from top and line 10 from bottom, for "mass" read "massif".
" 215, " 4 from bottom, after "Belfeld" add "and".
" 215, " 10 " " for "14" read "13.5".
" 215, " 14 and 16 from bottom, for "her" read "its".
" 216, " 2 from top, dele "and probably also to the east".
Page 216, line 4 from top after "removed" add "by denudation".

216, 6, for "under layer" read "underlying".

216, 8, delete "even".

218, 3, for "uninjured" read "uninjured".

218, 14, after "strong" add "undoubtedly artificial".

218, 16, for "straighter" read "rather straight".

218, 4 from bottom, read "process of the development of".

218, bottom-line, after "level", add "it".

219, line 19 from bottom, after "possession" add "of Rhinoceros etruscus,"

219, 18, for "an" read "two".

219, 14, after "species" add "of".

219, 5, after "of" add "Cervus Sedgwickii".

220, 18, top, for "indignous" read "indigenous".

(December 21, 1904).