## Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

## Citation:

Johannes Diderik van der Waals, The exact numerical values for the properties of the plainpoint line on the side of the components, in:
KNAW, Proceedings, 8 I, 1905, Amsterdam, 1905, pp. 289-298

This PDF was made on 24 September 2010, from the 'Digital Library' of the Dutch History of Science Web Center (www.dwc.knaw.nl)
> 'Digital Library > Proceedings of the Royal Netherlands Academy of Arts and Sciences (KNAW), http://www.digitallibrary.nl'
the value of $\frac{d T_{x}}{d x}=0$, and for $T_{1}=T_{x}$ the value of $\frac{d T_{x}}{T_{x} d x}=-\frac{1}{6} \frac{d b}{b d x}$ so the well-known limits for mixtures for which $\frac{d p_{c}}{p_{c} d v}$ can be equal to 0 .

For the initial direction of the section normal to the $p$-axis, the following equation holds:

$$
-\frac{1}{T}\left(\frac{d T}{d x_{1}}\right)_{p}=\frac{R T}{r}\left\{\frac{x_{2}-v_{1}}{x_{1}}\right\}=\frac{R T}{r}\left\{e^{\frac{u}{R T} \frac{d p c}{d x}}-1\right\}
$$

and

$$
-\frac{1}{T}\left(\frac{d T}{d x_{2}}\right)_{p}=\frac{R T}{r}\left\{\frac{x_{2}-v_{1}}{x_{3}}\right\}=\frac{R T}{r}\left\{1-e^{-\frac{u}{R T} \frac{d p c}{d x}}\right\}
$$

Both yield at the critical temperature of the components:

$$
-\left(\frac{d T}{T d x}\right)_{p}=\frac{R T}{r} \frac{u}{R T} \frac{d p_{c}}{d x}=\frac{u}{r} \frac{d p_{c}}{d x}=\frac{\frac{1}{p_{c}} \frac{d p_{c}}{d x}}{\frac{T}{p} \frac{d p}{d T}}=\frac{1}{7} \frac{1}{p_{c}}\left(\frac{d p_{c}}{d x}\right)^{2}
$$

According to results obtained before, we may also write:

$$
-\frac{1}{T}\left(\frac{d T^{\prime}}{d x_{a}}\right)_{p}=-\frac{6}{7}\left\{\frac{d T_{k}}{T_{x}^{\prime} d x_{4}}+\frac{1}{6} \frac{1}{b} \frac{d b}{d x_{4}}\right\}
$$

Physics. - "I'he exact numerical values for the properties of the plaitpoint line on the side of the components." By Prof. van der Waals.

In my two previous communications, inserted in the proceedings of this meeting, viz. I on the properties of the plaitpoint line on the side of the components and II on the properties of the sections of the surface of saluration on the side of the components, it has again appeared, that the thermodynamic treatment of such problems enables us to find a complete general solution - but also that if we want to compute numerical values in special cases, the knowledge of the equation of state is indispensable. In some cases it will be sufficient, if we make use of an approximate equation of state; but as soon as the density of the substance is comparable to that in the critical state, the numerical values calculated by means of the approximate equation of state can deviate strongly from reality. This is specially the case with quantities which either refer to the volume, or are in close connection with it. Thus it is known, that already the critical volume of a simple substance is not

Proceedings Royal Acad. Amslerdam. Vol Vill.
equal to $3 b$, the value furnished by the equation of state, in which $b$ is put constant, but that this equation is found rather nearer to $2 b$. This may be accounted for by taking into account that $b$ is variable and decreases with the rolume. In a mixture $b$ also deperids on the composition. Accordingly the quautity $\frac{d b}{d x}$ is an intricate expression for mixtures, and must in general be distinguished from $\left(\frac{d b}{d x}\right)_{v}$. If the way in which $b$ depends on volume and composition, was accurately known, then there would not be left any difficulties but those of toilsome and intricate calculations. But it is sufficiently known, that the way in which $b$, even for a simple substance, depends on $v$, has not yet been fixed with perfect certainty, and that in any case the knowledge of the numerical values, which occur in given forms of $b$, is wanting. These considerations led me to believe that this would be an objection to deriving theoretically the properties of the beginning of the plaitpoint line with perfect certainty - and also to determining the numerical values exactly. It has however, appeared to me that the knowledge of how $b$ depends on $x$ and $v$ is not required for this exact determination; but that for this purpose it suffices to know two quantities which have been experimentally determined for the critical state of a simple substance.

Let us call $f$ the value which $\frac{T}{p}\left(\frac{\partial p}{\partial T}\right)_{0}=\frac{T}{p} \frac{d p}{d T}$ has in the critical conditions of the component, and $x$, the critical coefficient, so that $M R T,=\varkappa(p v),$.

From $p=\frac{M R T}{v-b}-\frac{a}{v^{2}}$ follows $\frac{M R T}{p(v-b)}=f$ and $\frac{a}{p v^{2}}=f-1$.
The equality of $M R T=\kappa p v=f(v-b) p$, gives the value

$$
v=\frac{f}{f-x} b
$$

for the critical volume, in which we have to keep in view, that now that $b$ is put variable with the volume, $b$ represents the value which this quantity has in the critical state. With $f=7$ and $x=\frac{15}{4}$ we find $\frac{v}{b}=\frac{28}{13}$, whereas with $f=4$ and $x=\frac{8}{3}$ we should find the value $\frac{v}{b}=3$. For carbonic acid Keesom has found $f=6,7$ and $x=3,56$, from which would follow $\frac{v}{b}=\frac{6,7}{3,14}=2,134$,

If in $M R T=\kappa p v$ we put the value of $v$, we find:

$$
M R T \stackrel{\perp}{=} p z_{f f}^{f-x}
$$

With $f=4$ and $x=\frac{8}{3}$ the factor of $p b=8$, and with $f=7$ and $z=\frac{15}{4}$ this factor is found to be only slightly different viz. $8 \frac{1}{13}$. For the calculation of the value of $b$ in the critical condition we get therefore:

$$
b=\frac{M R T}{p} \frac{f-x}{x f} \quad \text { or } \quad \frac{T}{p_{r}} \frac{1}{273} \frac{f-x}{x f} .
$$

If we put the value of $v$ in the equation $\frac{a}{p v^{2}}=f-1$, we find:

$$
p=\frac{a}{b^{2} \frac{f^{2}(f-1)}{(f-x)^{2}}}
$$

The factor of $b^{2}$, which with $f=4$ and $x=\frac{8}{3}$ has the well known value of 27 , is found slightly above 27,8 with $f=7$ and $x=\frac{15}{4}$.

If in $M R T=x p v$ we substitute the values found for $p$ and $v$, we find:

$$
M R T=\frac{a}{b} \frac{x(f-x)}{f(f-1)}
$$

If we again put $f=4$ and $\mu=\frac{8}{3}$, we find $A R R T=\frac{8}{27} \frac{a}{b}$; with $f=7$ and $x=\frac{15}{4}$ the factor $\frac{a}{b}$ is equal to $\frac{1}{3.446} ;$ also this value differs but little from $\frac{8}{27}=\frac{1}{3.375}$.

For the calculation of $a$ with the critical values of $T$ and $p$, the formula:

$$
a=\frac{(M R T)^{3}}{p} \frac{f-1}{x^{2}}
$$

holds.
The factor $\frac{f-1}{x^{2}}$ is equal to $\frac{27}{64}=\frac{1}{2,37}$ with $f=4$ and $x=\frac{3}{3}$. With $f=7$ and $\%=\frac{15}{f}$ il is again only slightly different, viz. $\frac{96}{225}=\frac{1}{2,34}$.

For the critical condition $\left(\frac{\partial p}{\partial v}\right)_{T}$ must be 0 . From this follows:

$$
\frac{M R T}{(v-b)^{2}}\left(1-\frac{\partial b}{\partial v}\right)=2 \frac{a}{v^{3}},
$$

and after substitution of the values fom for $M R T$ and $v$

$$
1-\frac{\partial \dot{b}}{\partial v}=2 \frac{x(f-1)}{f^{2}} .
$$

With $f=4$ and $x=\frac{8}{3}$ it follows naturally that $\frac{\partial b}{\partial v}=0$, whereas with $f=7$ and $x=\frac{15}{4}$ it follows that:

$$
1-\frac{\partial b}{\partial v}=\frac{4 \check{5}}{49} .
$$

In the same way $\left(\frac{\partial^{2} p}{\partial v^{2}}\right)_{T}$ must be 0 in the critical state. From this follows:

$$
-b \frac{\partial^{2} b}{\partial v^{2}}=2 \frac{x(f-1)(f-x)(f-4)}{f^{4}}
$$

-With $f=4$ and $x=\frac{8}{3}$ this value is of course equal to 0 . With $f=7$ and $\%=\frac{15}{4}$ we find:

$$
\left.-b \frac{\partial^{2} b}{\partial v^{2}}=0,18 \cdot 27^{1}\right) .
$$

Let us now proceed to calculate the value of $\frac{d T}{T d x}$ at the beginning of the plaitpoint line. We have the formula:

$$
\frac{d T}{T d x_{0}}=\frac{\left(\frac{\partial^{2} p}{\partial v \partial x}\right)_{T}+\frac{1}{M R T}\left(\frac{\partial p}{\partial x}\right)_{v^{\prime} T}^{2}}{-\frac{\partial^{2} \varepsilon}{\partial v^{2}}}
$$

and have therefore to determine $\left(\frac{\partial p}{\partial x}\right)_{v T}$ and $\left(\frac{\partial^{2} p}{\partial x \partial v}\right)_{T^{\prime}}$ for the critical condition, but on the supposition that $b$ varies with the volume and that
${ }^{1}$ ) This high value of $-b \frac{\partial^{2} b}{\partial v^{2}}$ supports the liypothesis that $b$, in its dependence on the volune, las a more intricate form than is represented by a series of ascending powers of $\left(\frac{b_{\infty}}{v}\right)$.
$\frac{d b}{d x}$ has different values depending on the variations of the volume. Now
$\left(\frac{\partial p}{\partial x}\right)_{\cdot T}=\frac{M R T\left(\frac{\partial b}{\partial x}\right)_{v}}{(v-l)^{2}}-\frac{d a}{d x} \frac{1}{v^{2}}=-\frac{a}{v^{2}}\left\{\frac{1}{a} \frac{d a}{d x}-\frac{M R T}{a}\left(\frac{\partial b}{\partial x}\right)_{v} \frac{v^{2}}{(v-b)^{2}}\right\}$.
If we call $\frac{d b}{d x}$ the value denoting the change of $b$ with change of $x$, when we make also the volume vary in such a way that the mixture is again in the state which may be called the critical state of the unsplit mixture, then:

$$
\frac{d b}{d x}=\left(\frac{\partial b}{\partial x}\right)_{v}+\frac{\partial b}{\partial v}\left(\frac{d v}{d x}\right)_{L r}
$$

and $v$, being $=b \frac{f}{f-\varkappa},\left(\frac{d v}{d v}\right),=\frac{d b}{d x} \frac{f}{f-\varkappa}$, when $f$ and $\approx$ are constant, which is the case when the law of corresponding states is fulfilled. We find then:

$$
\left(\frac{\partial b}{\partial x}\right)_{v}=\left(1-\frac{\partial b}{\partial v} \frac{f}{f-x}\right) \frac{d b}{d x} .
$$

We have to know:

$$
\frac{M R T}{a}\left(\frac{\partial b}{\partial x}\right)_{v} \frac{v^{2}}{(v-b)^{2}}=\frac{M R T}{\frac{a}{\bar{b}}} \frac{v^{2}}{(v-b)^{2}}\left\{\frac{f\left(1-\frac{\partial b}{\partial v}\right)-x}{f-x}\right\} \frac{1}{b} \frac{d}{d v}
$$

When we substitute the values found above for $\operatorname{ART} T, v$ and $1-\frac{\partial b}{\partial v}$ we find $\frac{f-2}{f-1} \frac{1}{b} \frac{d b}{d x}$ - and so:

$$
\frac{1}{p}\left(\frac{\partial p}{\partial x}\right)_{v T}=-\frac{a}{p v^{2}}\left\{\frac{1}{a} \frac{d a}{d x}-\frac{f-2}{f-1} \frac{1}{b} \frac{d b}{d x}\right\}
$$

or

$$
\frac{1}{p}\left(\frac{\partial p}{d x}\right)_{v T}=-(f-1)\left\{\frac{d l \frac{a}{b}}{d x}+\frac{1}{f-1} \frac{d l b}{d x}\right\}
$$

This value is in a high degree dependent on $f$.
'With $f=4$ we find $\frac{1}{p}\left(\frac{\partial p}{\partial n}\right)_{v T}=-3\left\{\frac{d T_{x}}{T_{v} d x}+\frac{1}{3} \frac{d b}{b d x}\right\}$.
With $f=7$ on the other hand $\frac{1}{p}\left(\frac{\partial p}{\partial x}\right)_{v T}=-6\left\{\frac{d T_{v}}{T_{x} d x}+\frac{1}{6} \frac{d b}{b d x}\right\}$.

In the prerodine communication I have concluded to the same

 memula linhon－
or
or

$$
\left(\begin{array}{l}
1 \\
11 \\
1 .
\end{array}\right), 1-(f-1)\left\{\frac{d T_{x}}{T_{2}^{\prime} d x}+\frac{1}{f-1} \frac{d b}{b d x}\right\} .
$$

Bia wa culla arive dr l！i－equation in a much simpler way still． トゥッバ

$$
\because \cdot-\left(\frac{\partial i}{i} \cdot, \quad \therefore \quad \therefore\left(\frac{\partial p}{\partial T}\right)_{v} d T \quad\left(\frac{\partial p}{\partial v_{x T}}=0\right)\right.
$$



：IIII ： 11





For this utantuy we dud：
or

In thi：exprowion onls the quantity $\frac{\partial^{2} b}{\partial x^{\partial v}}$ is unknown．We deter－ mille it trom：

$$
\left(\frac{\partial b}{\partial x}\right)_{v}=\left\{1-\frac{\partial b}{\partial v} \cdot \frac{f}{f-x}\right\} \frac{d \dot{b}}{d x}
$$

From this follows:

$$
\frac{\partial^{2} b}{\partial x \partial v}=-b \frac{\partial^{2} b}{\partial v^{2}} \frac{f}{f-x}\left(\frac{1}{b} \frac{d b}{d x}\right) .
$$

If we substitute the values given above for MRT, $v,\left(1-\frac{\partial b}{\partial v}\right)$ and $-b \frac{\partial^{2} b}{\partial v^{2}}$ in the expression for $\left(\frac{\partial^{2} p}{\partial x \partial v}\right)_{T}$, we find for the value of the second term $-\frac{1}{b} \frac{d b}{d x} 2 \frac{(f-2)}{f}$ and for the value of the third term $+\frac{1}{b} \frac{d b}{d x} \frac{f-4}{f}$.

The value of $\left(\frac{\partial^{2} p}{\partial r \partial \partial}\right)_{T}$ is then found equal to:

$$
\left(\frac{\partial^{2} p}{\partial x \partial v}\right)_{T}=\frac{2 a}{v^{3}}\left\{\frac{1}{a} \frac{d a}{d x}-\frac{1}{b} \frac{d b}{d x}\right\}
$$

or

$$
\left(\frac{\partial^{2} p}{\partial x \partial v}\right)_{T}=\frac{2 a}{v^{3}} \frac{d T_{x}^{\prime}}{T_{x} d x},
$$

and for $\frac{\left(\frac{\partial^{2} p}{\partial x \partial v}\right)_{T}}{-\frac{\partial^{2} \varepsilon}{\partial v^{2}}}$ we find the simple value $\frac{d T_{\kappa}^{\prime}}{T_{x}^{\prime} d v}$; so exactly the same value as follows from the equation of state, in which $b$ is pout constant. This gives rise to the conjecture that this relation might be found merely from thermo-dynamic relations independent of the knowledge of the equation of slate, and this is indeed the case.

Let us consider the quantity $\left(\frac{\partial p}{\partial v}\right)_{T}$. It is equal to 0 in the critical state of the component. Let us pass from this homogeneous critical phase to another in which the volume has changed with $d v$, the composition with $d x$, and the temperature with $d T$.

Let us put $d T$ again equal to $d T$ : so let us assume that the mixture with dx molecules of the second kind is again in an homogeneous critical phase, then $\left(\frac{\partial p}{\partial v}\right)_{T}$ is again equal to 0 .

From:

$$
\cdot d\left(\frac{\partial p}{\partial v}\right)_{T}=\left(\frac{\partial^{\mathrm{s}} p}{\partial v^{2}}\right)_{T x} d v+\left(\frac{\partial^{\mathrm{y}} p}{\partial x \partial^{\prime}}\right)_{T} d x+\left(\frac{\partial^{2} p}{\partial v \partial T^{\prime}}\right)_{x} d T_{n}^{\prime}
$$

follows, because $d\left(\frac{\partial p}{\partial v}\right)_{T}$ and $\left(\frac{\partial^{2} p}{\partial v^{3}}\right)_{T x}$ are equal to 0 :

$$
\left(\frac{\partial^{3} p}{\partial x \partial v}\right)_{T}=-\left(\frac{\partial^{2} p}{\partial v \partial T}\right)_{a} \frac{d T_{\gamma}}{d x}
$$

and from the relation:

$$
T\left(\frac{\partial p}{\partial T}\right)_{v}-p=\frac{\partial \varepsilon}{\partial v}
$$

follows:

$$
T\left(\frac{\partial^{2} p}{\partial v \partial T^{T}}\right)=\frac{\partial^{2} \varepsilon}{\partial v^{2}} .
$$

And from this we find again now only from thermodynamic relations what we have derived already above.

As we found, also by means of mere thermodynamics:

$$
\left(\frac{\partial p}{\partial a}\right)_{v T}=-f p\left\{\frac{d T_{x}^{\prime}}{T_{y} d w}-\frac{1}{f} \frac{d p}{p, d x}\right\}
$$

we may put without making use of the equation of state:

$$
\frac{d T}{T d x_{0}}=\frac{d T_{r}}{T_{r} d x}-\frac{f^{2} p^{2}}{M R T} \frac{\partial^{2} \varepsilon}{\partial v^{2}}\left\{\frac{d T_{r}}{T_{x} d x}-\frac{1}{f} \frac{d p_{r}}{p_{y} d x}\right\}^{2} .
$$

The factor - $\frac{f^{2} p^{2}}{M R T \frac{\partial^{2} \varepsilon}{\partial v^{2}}}$ may be reduced to a simple form, but for the determination of the value of this factor it is required to know the equation of state. If we write $f p=\frac{M R T}{v-b}$, and $\frac{\partial^{2} \varepsilon}{\partial v^{2}}=-2 \frac{a}{v^{3}}$, this factor becomes equal to $\frac{M R T}{(v-b)^{2}}: \frac{2 a}{v^{2}}$ and as $\frac{M R T}{(v-b)^{2}}\left(1-\frac{\partial b}{\partial v}\right)=\frac{2 a}{v^{3}}$ follows from $\left(\frac{\partial p}{\partial v}\right)=0$, we get:

$$
-\frac{f^{2} p^{2}}{M R T \frac{\partial^{2} \varepsilon}{\partial v^{2}}}=\frac{1}{1-\frac{\partial b}{\partial v}}=\frac{f^{2}}{2 \varkappa(f-1)}
$$

so with $f=7$ and $x=\frac{15}{4}$ the value of this factor becomes equal to $\frac{49}{45}$. Hence we have :

$$
\frac{d T}{T d x_{0}}=\frac{d T_{x}}{T_{y} d x}+\frac{49}{45}\left\{\frac{d T_{x}}{T_{y} d x}-\frac{1}{7} \frac{d p_{1}}{p_{x} d x}\right\}^{2} .
$$

If we introduce the quantity $b$ instead of $\frac{d p_{x}}{p_{y} d x}$, we find:

$$
\frac{d T}{T^{\prime} d x_{0}}=\frac{d T}{T^{\prime}, d x}+\frac{f-1}{2 x}\left\{\frac{d T}{T^{\prime}, d x}+\frac{1}{f-1} \frac{d b}{b d x}\right\}^{2} .
$$

With $f=4$ and $x=\frac{8}{3}$ we find again $\frac{f-1}{2 x}=\frac{9}{16}$, but with $f=7$ and $x=\frac{15}{4}, \frac{f-1}{2 x}$ rises to 0,8 . With $f=6,7$ and $x=3,56$ (Keesom's values for carbonic acid) the value is not appreciably different from 0,8 . If we calenlate with $\frac{d T}{T, d v}=-0,493$ and $\frac{1}{b} \frac{d b}{d x}=-0,271$, $f=6,7$ and $x=3,56$ the value of $\frac{d T}{T d x_{0}}$, we find for this value - 0,259 . Though 0,259 is smaller than the values calculated from Keesom's observations, 0,284 for $x=0,1047$ and 0,304 for $r=0,1994$, we must not forget that the calculated valne would hold for the limiting case, viz $x=0$, and the fact that for $\Delta x=0$ a sinaller value than 0,284 would have to be expected is at least in harmony with the circumstance that the amount is found higher for a higher value of $x$.

It is evident from all $t \mathrm{l}$ is that though we cannot do quite without the equation of state for the calculation of $\frac{d T}{T d x}$ for the plaitpoint line, yet it is not necessary to know the form of the quantity $b$.

For the calculation of the quantity $\frac{T}{p} \frac{d p}{d T}$ for the beginning of the plaitpoint line we have from the formula:

$$
d p=\left(\frac{\partial p}{\partial x}\right)_{v T} d x+\left(\frac{\partial p}{\partial T}\right)_{v v} d T
$$

the relation:

$$
\left(\frac{T}{p} \frac{d p}{d T}\right)_{\mu l}=\frac{T}{p}\left(\frac{\partial p}{\partial T}\right)_{v}+\frac{1}{p}\left(\frac{\partial p}{\partial v}\right)_{T_{0}} \frac{T d v_{0}}{d T^{\prime}}
$$

or

$$
\left(\frac{T}{p} \frac{d p}{d T^{\prime}}\right)_{\mu l}=f+\frac{-(f-1)\left\{\frac{d T_{a}}{T, d x}+\frac{1}{(f-1)} \frac{1}{b} \frac{d b}{d x}\right\}}{\frac{d T_{l}}{T_{,}, d_{2}}+\frac{f-1}{2 x}\left\{\frac{d T_{v}}{T_{y} d x}+\frac{1}{(f-1)} \frac{1}{b} \frac{d b}{d x}\right\}^{2}}
$$

or in numerical value for the mixture of oxygen and carbonic acid:

$$
\left(\frac{T}{p} \frac{d p}{d T}\right)_{\mu l}=6,7+\frac{-5,7\{-0,493-0,047\}}{-0,259}=6,7-11,28=-4,58
$$

With the mixture $x=0,1047$ Kerson has found $-6,3$ and with $x=0,1995$ the amount found was $-6,08$.

If we take the product of $\frac{T}{p} \frac{d p}{d T}$ and $\frac{d T}{T d x}$ we tind the value of $\frac{1}{p} \frac{d p}{d x}$ for the begiming of the plaitpoint line．As both $\frac{T}{p} \frac{d p}{d T}$ and $\frac{d T}{T^{\prime} d x}$ are negative for the mixture of carbonic acid and oxygen，the value of


Anatomy．．＂Bown＇s centra in the cerebellum of the mannmatia＂． li：1）．J．Hulshory Pol（from the laboratory for Psychiatry and Saritogy at Amsterdam）．（Communicated by Prof． （ $\therefore$ W以には！）

In h：－wei－known researches about the cerebella of mammalia ${ }^{1}$ ）；
 renime wi cundia：：on for the muscle－groups of the head，the Lobus ：mun，wher worm of coordination for those of the neck；the non－
 $\therefore$－i．ullut in the Lobus medianus posterior，whilst each of the I．abl！ari：umbs is the seat of one of the symmetrical centra， r－p．otively lin woth right，and for both left extremities．＂${ }^{3}$ ）

Wilinin lim arme line of research，Van Rujnberk ${ }^{9}$ ）at Lucian＇s Ialumatu：y i，limbia，experimenting on two dogs，extirpated a portion
 1．ain．simpla．

The＇oundi：！symptoms，which were observed during the first Al．．－：iller the I！eration，having passed away，the animal experi－

liti－－rm：Nom resembled very much a trouble in the coordination， ant and ： Ina－ㅅ：Mon．Therefore it was important to determine with as muth exirlio．－is possible，which portion of the cerebellum had Deer remiarem．

Th）：ix privne the preparation，fixed in formol，was offered


$\because$ P．．i．J．：．I．Lי，z．Over de physiologische beteekenis van het cerebellum．De




