

On the Influence of the Finite Volume of Molecules on the Equation of State.[†] By
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It is wellknown that the departure of the actual behaviour of gases from the ideal state defined by the equation $p = \frac{NK\theta}{v}$ is due to two causes : (1) the finiteness of the volume of the molecules, (2) the influence of the forces of cohesion, i.e. the attractive forces amongst the molecules. van der Waals was the first to deduce an equation of state in which all these factors are taken into account; according to van der Waals, we have

$$p = \frac{NK\theta}{v-b} - \frac{a}{v^2} \quad \dots \quad \dots \quad \dots \quad (1)$$

where $b = 4 \times$ volume of the molecules, a defines the forces of cohesion.

In all subsequent modifications of this equation (Clausius, Dieterici, or D. Berthelot) the changes which have been proposed all relate to the influence of the cohesive forces; the part of the argument dealing with the finiteness of molecular volumes is generally left untouched.

But it has been found that the results of experiments do not agree with the predictions of theory if we regard a and b as absolute constants. Accordingly it has been proposed to regard both a and b as functions of volume and temperature.*

But before proceeding to these considerations, it is necessary to scrutinize whether the influence of finite molecular volumes is properly represented by the term b . From theoretical considerations, the conclusion has been reached that this is not the case. The argument is as follows :

According to Boltzmann's theory,

$$\text{the entropy } S = K \log W + C,$$

where $K =$ Boltzmann's gas-constant, $W =$ probability of the state. Let us now calculate the probability that a number N of molecules originally confined within the volume V_0 and possessing finite volumes, shall be contained in a volume V . Neglecting the influence of internal forces, the probability for the first molecule is $\frac{V}{V_0}$, for the second molecule the probability is $\frac{V-\beta}{V_0-\beta}$, where $\beta = 8 \times$ volume of a single molecule, for when

[†] Communicated by the Authors.

*Compare van der Waals, *Proc. Amst.* 1916 ; Van Laar, *Proc. Amst.* Vol: xvi, p. 44.

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the first molecule is in position, the space enclosed by a concentric sphere of double the radius of the molecule will not be available for the second molecule. The available space is therefore $V-\beta$, whence the probability is $\frac{V-\beta}{V_0-\beta}$. Introducing similar considerations for the rest of the molecules, we have

$$W = \frac{V}{V_0} \cdot \frac{V-\beta}{V_0-\beta} \cdot \frac{V-2\beta}{V_0-2\beta} \cdots \frac{V-\overline{N-1}\beta}{V_0-\overline{N-1}\beta} \quad \dots \quad (2)$$

We are, of course, neglecting those cases in which partial overlapping of the regions occupied by two or more molecules occurs; for the number of such cases can at best be a small fraction of the total number. Even cases of actual association do not include these, for in that case, two discrete molecules become merged into one, without their outer surfaces being actually in contact.

From the relations $S = K \log W + C$

and
$$\left(\frac{\partial S}{\partial V} \right)_\mu = \frac{p}{\theta}$$

we can easily verify that

$$\begin{aligned} p &= -\frac{K\theta}{\beta} \log \frac{V-n\beta}{V} \\ &= -\frac{R\theta}{2b} \log \frac{V-2b}{V} \quad (R = NK) \quad \dots \quad (3) \end{aligned}$$

As a first approximation, when b is small compared to v , we obtain $p = \frac{NK\theta}{v}$ (Boyle-Charles-Avogadro Law), and as a second approximation we obtain

$$p = \frac{NK\theta}{v-b} \quad (\text{van der Waals correction}).$$

We also note that

$$pV = NK\theta \cdot \frac{x}{1-e^{-x}} \quad \text{where } x = \frac{\beta p}{K\theta} \quad \dots \quad (4)$$

To account for the influence of internal forces, we multiply, following the lead of Dieterici, the above expression (3) by $e^{-\frac{a}{NK\theta v}}$ having the same significance as before.

From this equation of state, we can easily verify the following results for the critical point :

$$\begin{aligned} \text{Critical volume,} \quad V_c &= \frac{2c}{e-1} \quad b = 3.166b, \\ K &= \frac{NK\theta}{p_c V_c} = 3.513. \end{aligned}$$

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The corresponding values of V_c from the van der Waals and the Dieterici equations are (3b, 2b) respectively, and of K are $\left(\frac{8}{3} = 2.66, \frac{e^2}{2} 3.695\right)$ respectively.

As a matter of fact, for the simpler gases, the value of ' K ' obtained in this paper agrees better with the experimental results that the Dieterici value $\frac{e^2}{2}$ we have for oxygen* $K = 3.346$, for nitrogen† $K = 3.53$, for argon‡ $K = 3.424$, for xenon** $K = 3.605$. We need not consider the van-der-Waals value $\frac{8}{3}$, for it fails entirely.

The most serious drawback to Dieterici's equation is, according to Prof. Lewis (vide Lewis's Physical Chemistry, vol. ii. p. 117) that it makes b or the limiting volume $\frac{V_c}{2}$, while the limiting volume, obtained by the extrapolation of Cailletet-Mathias mean density line to the temperature $\theta = 0^\circ\text{K}$ is about $\frac{V_c}{4}$. The value of b obtained in this paper, viz., $\frac{V_c}{3.16}$ therefore agrees better with this value.

It is yet premature to predict what influence this investigation will have on the speculations concerning the variability of the volume of molecules with temperature. A more detailed investigation dwelling upon this point, and the application of the formula (4) to Amagat's (pv, p) curves, will be communicated shortly. Meanwhile we point out that the factor $e^{-\frac{a}{Nk\theta v}}$ has been introduced into the expression for ' p ' only as a provisional measure, though it is considered that this step, though not quite exact, is one in the right direction. In the next paper an attempt will be made to introduce energy into probability calculations.

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Note added in proof—On consulting the literature on the subject, we noticed that in several papers in the Amsterdam Proceedings (*vide* vol xv, p. 240et seq.), Dr. Keesom of Leyden had also made attempts to deduce the equation of state from Boltzmann's entropy principle. But, in the expression (2) for W , he introduces, before differentiation, an approximation in which terms up to second order in $\frac{b}{v}$ are retained only.

In this way, he arrives at the van der Waals' form $v-b$ for the influence of finite molecular volumes. In obtaining our present equation of state (4), no such approximation has been made.

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*Mathias and K. Onnes, *Proc. Amst.* Feb. 1911.

†Berthelot, *Bull. de la Soc. France de Phys.* 167 (1901)

‡Mathias, Onnes, and Crommelin, *Proc. Amst.* 1913, p. 960, Vol. xv.

**Paterson, Cripps, Whvltlaw-Gray, *Proc. Roy. Soc. Lond. A.* lxxvi, p. 579 (1912).

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