

A DISCUSSION OF THE VAN DER WAALS EQUATION AND ITS RELATED EQUATIONS OF STATE

by

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The failure of the ideal gas law recognized by the Joule-Thomson experiment led Van der Waals to derive his equation of state for gases and liquids. In this paper the limits of this equation are discussed in comparison with the ideal gas law, and a short remark is made for the related modifications of the Van der Waals Equation.

INTRODUCTION

1. The Ideal Gas Equation of State

An ideal gas may be regarded as one which obeys Boyle's Law and Joule's Law. The former states that at constant temperature

$$PV = a, \quad (\text{a constant}) \quad (1-1)$$

and the latter states that the internal energy U of an ideal gas depends on the absolute temperature T only, or

$$U = U(T). \quad (1-2)$$

From the kinetic theory viewpoint this amounts to neglecting the volume occupied by the molecules themselves, and to assuming that no intermolecular forces exist.

Based on these assumptions, we derive the ideal gas equation as follows: First, since the state of a gas could be defined by three variables P , V , and T , we may consider that P depends on V and T . Thus, $P = P(V, T)$, and we write

$$dP = \left(\frac{\partial P}{\partial V}\right)_T dV + \left(\frac{\partial P}{\partial T}\right)_V dT \quad (1-3)$$

From Eq. (1-1), $Vdp + pdV = 0$ at constant T , or

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{P}{V}. \quad (1-4)$$

From Maxwell's second relation of thermodynamics, we get

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T} \left(\frac{\partial Q}{\partial V}\right)_T$$

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and from the first law and Eq. (1-2)

$$\delta Q = dU + PdV = \left(\frac{dU}{dT}\right) dT + pdV$$

so that $\left(\frac{\delta Q}{\delta V}\right)_T = P$.

Hence $\left(\frac{\partial p}{\partial T}\right)_V = \frac{P}{T}$,

and by substituting for the partial derivatives in Eq. (1-3,)

we obtain $dp = -\frac{p}{V}dV + \frac{P}{T}dT$

$$\frac{dp}{p} + \frac{dV}{V} = \frac{dT}{T}.$$

If we integrate and call the constant of integration $\ln R$, we get finally

$$PV = RT, \tag{1-5}$$

which is the equation of state for an ideal gas.

2. The Joule-Thomson Experiment.

The deviations from the ideal gas law are hard to measure experimentally, since they represent small fractions of the total pressure at a given temperature and volume. For this reason, a method of detecting the departure from the ideal gas law, called the Joule-Thomson Effect, is of great experimental importance. In an earlier attempt, Joule allowed air to expand freely into an evacuated vessel, and measured the temperature at the beginning and end of the process. Because of the relatively large heat capacity of the surroundings, he was unable to detect any significant effects by using this method. Later, during they years 1852 to 1862, accompanied by Thomson in a series of experiments, they improved they free-expansion experiment by throttling the expansion so as to permit a continuous flow of gas from a region of higher pressure p_1 to one of slightly lower pressure p_2 . Both were kept constant through a porous plug separating the two regions in a thermally insulated device such as that shown in Fig. 1.

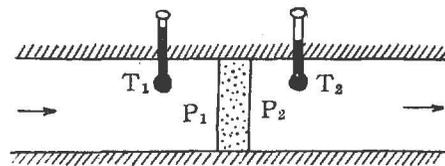


Fig. 1

After the experiment had run for some time, a steady state was reached in which no heat was exchanged between the wall and the gas. Any temperature difference between T_1 and T_2 is then due only to the expansion of the gas.

It is easy to show that the enthalpy of unit mass of gas was unchanged as it flowed through the plug. When a volume V_1 of gas was pushed into the vessel at constant pressure p_1 , work $\int P_1 dV_1 = P_1 V_1$ was done on this sample of gas. After passing through the plug, the same mass had a volume V_2 , and did work $P_2 V_2$ in passing out of the vessel. Thus the external work done by the gas in the process was $P_2 V_2 - P_1 V_1$. It was assumed that no heat was absorbed, so that if U_1 was the internal energy when the gas entered, U_2 when it left, the first law of thermody-

namics gives

$$U_2 - U_1 = - (P_2 V_2 - P_1 V_1)$$

or
$$U_1 + P_1 V_1 = U_2 + P_2 V_2.$$

Hence
$$H_1 = H_2 \tag{2-1}$$

Thus the change was at constant enthalpy. We may write

$$dH = TdS + VdP = 0,$$

but
$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP;$$

then
$$dH = T \left(\frac{\partial S}{\partial T}\right)_P dT + [T \left(\frac{\partial S}{\partial P}\right)_T + V] dP = 0.$$

We have
$$T \left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_H + T \left(\frac{\partial S}{\partial P}\right)_T + V = 0, \tag{2-2}$$

but
$$\left(\frac{\partial S}{\partial P}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_P, \quad C_P = T \left(\frac{\partial S}{\partial T}\right)_P,$$

Hence Eq. (2-2) becomes

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P} [T \left(\frac{\partial V}{\partial T}\right)_P - V]. \tag{2-3}$$

The term $(\partial T / \partial P)_H$ is what we called the Joule-Thomson coefficient μ . It is measured from the change of temperature ΔT divided by the pressure difference ΔP . It is zero for an ideal gas and can be either positive or negative for a real gas. Under room temperature most real gases have positive values of μ , which means that when subject to expansion they will be cooled. As for hydrogen and helium, μ is negative and they will be heated when expanded, for an ideal gas neither heating nor cooling will be observed. Because molecules of a real gas have definite volume and there are intermolecular forces between them, in the process of free expansion, part of its energy must be used to increase its potential energy in order to offset these factors, and the temperature drops. Accordingly, a real gas will not follow the ideal gas law except under near ideal conditions, i. e. low pressure and high temperature. Pointing out the postulates described, J. D. Van der Waals in 1873 presented his dissertation "On the Continuity of the Gaseous and Liquid State" the famous equation of state for real gases and liquids, which bears his name.

3. The Van der Waals Equation of State

The original deduction of Van der Waals' equation lacks uniformity from a mathematical view point, in which two correction terms have been put together and substituted into the ideal gas equation. In this section we use concepts of statistical mechanics to derive it.

For monatomic gases the potential function U of two molecules is a function of distance r between them, we denote $U_{12}(r)$ to represent the potential energy between molecules (atoms) 1 and 2. This takes the form of the curve in Fig. 2; along the abscissa is plotted the distance r between the molecules. For small distances U_{12} increases for a decrease in distance, corresponding to repulsive forces

between the molecules. Starting approximately at the point where the curve crosses the axis, it rises steeply so that U_{12} soon becomes extremely large, corresponding to mutual "impenetrability" of the molecules. (For this reason the distance r_0 is sometimes called the "radius" of the atom.) For large distances U_{12} slowly increases asymptotically approaching zero. The increase of U_{12} with distance corresponds to mutual attraction of the molecules.

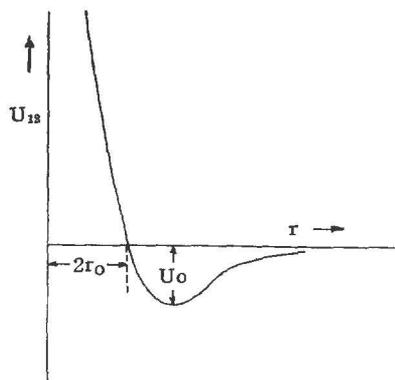


Fig. 2

Assume $B'(T)$ is the energy of interaction between two molecules in the gas of volume V ,

$$B'(T) = \frac{1}{2} \int (1 - e^{-U_{12}/kT}) dV. \quad (3-1)$$

Because U is a function of the distance between the molecules only, we write $dV = 4\pi r^2 dr$ in the above integrand. Splitting up the range of integration over dr into two parts we have

$$B'(T) = 2\pi \int_0^{2r_0} (1 - e^{-U_{12}/kT}) r^2 dr + 2\pi \int_{2r_0}^{\infty} (1 - e^{-U_{12}/kT}) r^2 dr \quad (3-2)$$

when r lies between 0 and $2r_0$, the potential energy U_{12} is generally very large. Thus in the first integrand the quantity $\text{EXP}(-U_{12}/kT)$ can be neglected compared with unity. This integrand is then equal to

$$b' = \frac{16}{3} \pi r_0^3.$$

This amounts to four times the "volume" of an atom (molecule) with radius r_0 . (For polyatomic gases the constant b' is not necessarily equal to four times the "volume" of the molecules.)

In the second integrand, the absolute value of U is never larger than U_0 (Fig. 2); thus U_{12}/kT in this integrand is always small compared with unity, even when $U_{12} = -U_0$. Hence we can expand $\text{EXP}(-U_{12}/kT)$ as a power series in U_{12}/kT keeping only the first two terms and we have the second part of Eq. (3-2) equal to

$$\frac{1}{kT} \int_{2r_0}^{\infty} 2\pi U_{12} r^2 dr.$$

Since, in the whole range of integration, U_{12} is negative, the whole integral is also negative; we shall write it in the form a'/kT , where a' is a positive constant. Then Eq. (3-2) becomes $B'(T) = b' - a'/kT$ (3-3)

The free energy of real gas is

$$F = F_b + \frac{NRT}{V} B'(T) \quad (3-4)$$

where F_b is the free energy of an ideal gas

$$F_b = -RT \log \frac{Ve}{N} + Nf(T)$$

and N is the Avogadro number, substituting this and Eq. (3-3) into Eq. (3-4), we then obtain

$$F = Nf(T) - RT \log \frac{e}{N} - RT \left(\log V - \frac{b}{V} \right) - \frac{a}{V} \quad (3-5)$$

where $b = Nb'$, $a = N^2a'$. For moderate density, we may say that the volume of the gas is certainly larger than b , hence $b/v \ll 1$, and making use of the fact that for $x \ll 1$, $\log(1+x) = x$, we find that the relation holds for

$$\log(V-b) = \log V + \log \left(1 - \frac{b}{V} \right) = \log V - \frac{b}{V}.$$

Therefore Eq. (3-5) may be written in the form

$$\begin{aligned} F &= Nf(T) - RT \log \frac{e}{N} (V-b) - \frac{a}{V} \\ &= F_b - RT \log \left(1 - \frac{b}{V} \right) - \frac{a}{V} \end{aligned} \quad (3-6)$$

In this form the formula satisfies the conditions stated for real gases, since for large V , it goes over to the formula for the free energy of an ideal gas; and, for small V , it ensures the impossibility of unlimited condensation of the gas (for $V < b$, the argument of the logarithm becomes meaningless, i. e. when the gas was liquefied further compression was impossible.) From thermodynamics we get

$$P = - \left(\frac{\partial F}{\partial V} \right)_T = \frac{RT}{V-b} - \frac{a}{V^2}$$

Hence $(P + \frac{a}{V^2})(V-b) = RT \quad (3-7)$

Here we have derived the Van der Waals equation of state.

DISCUSSION

4. Virial Equation and the Van der Waals Equation

At infinite volume, we know that real gases will approach an ideal gas with equation of state $PV = RT$, or $PV/RT = 1$. At smaller volumes, deviations occurred and we can expand the quantity PV/RT in series in $1/V$; the term independent of $1/V$ will be unity, but the other terms which are different from zero for real gases, will be functions of temperature. Thus we can write

$$\frac{PV}{RT} = 1 + B(T) \left(\frac{1}{V} \right) + C(T) \left(\frac{1}{V} \right)^2 + \dots \quad (4-1)$$

The quantity PV/RT is often called the virial, therefore Eq. (4-1) is called the virial equation of state; and the quantities 1 , $B(T)$, $C(T)$, etc., are called the virial coefficients. In the third section we derived the interaction between two molecules is $B'(T) = b' - a'/kT$, for one mole of them it will be equal to $NB'(T) = b'N - a'N/kT = b - a/RT$. This is the second virial coefficient $B(T)$, neglecting higher terms of $(1/V)$ we have from Eq. (4-1)

$$\frac{PV}{RT} = 1 + \left(b - \frac{a}{RT} \right) \left(\frac{1}{V} \right) \quad (4-2)$$

It indicates that for high temperatures ($b > a/RT$) the pressure should be greater than that calculated for an ideal gas, while at low temperatures ($b < a/RT$) the pressure should be less than for an ideal gas. The temperature

$$T_B = \frac{a}{Rb} \tag{4-3}$$

at which the second virial coefficient is zero so that Boyle's Law is satisfied exactly as far as terms $1/V$ are concerned is called the Boyle temperature.

We now take the Van der Waals equation (3-7), expand it in the form of Eq. (4-1), and see if the second virial coefficient agrees with the value given in Eq. (4-2.) We have

$$\begin{aligned} P &= \frac{RT}{V-b} - a \left(\frac{1}{V}\right)^2 \\ &= \frac{RT}{V} \left(1 - \frac{b}{V}\right)^{-1} - a \left(\frac{1}{V}\right)^2 \\ &= \frac{RT}{V} \left[1 + \frac{b}{V} + \left(\frac{b}{V}\right)^2 + \dots\right] - a \left(\frac{1}{V}\right)^2 \\ \frac{PV}{RT} &= 1 + \left(\frac{b}{V} - \frac{a}{RTV}\right) + b^2 \left(\frac{1}{V}\right)^2 + \dots \\ &= 1 + \left(b - \frac{a}{RT}\right) \left(\frac{1}{V}\right) + b^2 \left(\frac{1}{V}\right)^2 + \dots \end{aligned} \tag{4-4}$$

agreeing with Eq. (4-2) as far as the second virial coefficient is concerned, but the third virial coefficient found by another method is not consistent with b^2 . In other words, the Van der Waals equation is correct as far as the second virial term is concerned, but no further, and indicates that the equation is a new approach (not an exact one) to the description of the behavior of real gases.

5. Critical State and Van der Waals' Constants

In Fig. 3 we give isotherms as computed by the Van der Waals equation, for low temperatures the isotherms show a maximum and minimum - the minimum corresponding in some cases to a negative pressure. Also we note that there is one isotherm at which the two extrema coincide, so that there is a point of inflection on the curve. This is the point marked C on Fig. 3.

At every lower temperature, there are three separate volumes corresponding to pressures lying between the minimum and maximum of the isotherm. This is indicated by a horizontal line, corresponding to constant pressure, and which intersects one of the isotherms at V_1 , V_2 , and V_3 . We may say that there are three states possible. Thermodynamically the one which has the lowest Gibbs free energy will be the stable state; the other states, if they existed, would change

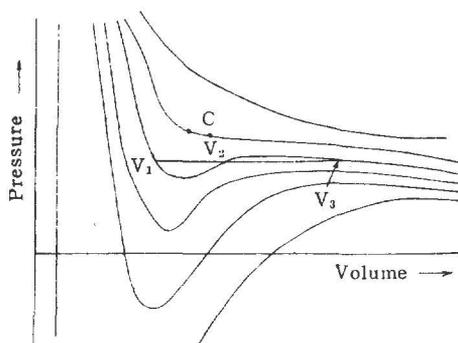


Fig. 3

irreversibly to this stable state.

Suppose we follow an isotherm, increasing the volume at constant temperature, and suppose the isotherm lies below the temperature corresponding to point C. Then at first, the smallest volume V_1 has the lowest Gibbs free energy. A pressure is reached, however, at which volumes V_1 and V_3 equal the lowest energy. The state V_2 has a higher free energy than either V_1 or V_3 under all conditions, so that it is never stable. Above a certain pressure (below a certain volume) the state of smallest volume is stable. At a definite pressure this state and that of larger volume can exist together in equilibrium, and below this pressure only the phase of largest volume exists.

The isotherms of the Van der Waals equation then correspond over part of their length to states that are not thermodynamically stable, in the sense that their free energy is greater than that of other states, also described by the same equation, at same pressure and temperature. In Fig. 4 we give revised isotherms with only the stable phase shown. In the region where two phases are in equilibrium, horizontal lines are drawn, indicating that the pressure and temperature are constant over the whole range of volumes between the two phases in which the system is a mixture of them. The revised isotherms are plainly very similar to those of actual gases and liquids.

From Fig. 4 it is clear that the critical point is the point C of Fig. 3, at which the maximum and the minimum of the isotherm coincide. We can easily find the pressure, temperature, and volume of the critical point in terms of the constants a and b from this condition. The most convenient way to state the condition analytically is to demand that the first and second derivatives of P with respect to V for an isotherm vanish simultaneously at the critical point. Thus, denoting the critical pressure, volume and temperature by P_c , V_c , and T_c , we have

$$P_c = \frac{RT_c}{V_c - b} - \frac{a}{V_c^2}, \quad (5-1)$$

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 = -\frac{RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3}, \quad \frac{RT_c}{(V_c - b)^2} = \frac{2a}{V_c^3}, \quad (5-2)$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 = \frac{2RT_c}{(V_c - b)^3} - \frac{6a}{V_c^4}, \quad \frac{2RT_c}{(V_c - b)^3} = \frac{6a}{V_c^4}. \quad (5-3)$$

We can solve Eqs. (5-1), (5-2), and (5-3) simultaneously for P_c , V_c , and T_c , we get

$$P_c = \frac{1}{27} \left(\frac{a}{b^2}\right), \quad V_c = 3b, \quad RT_c = \frac{8}{27} \left(\frac{a}{b}\right). \quad (5-4)$$

These equations allow us to calculate the critical volume

$$V_c \text{ (Van der Waals)} = 3b = \frac{3}{8} \left(\frac{RT_c}{P_c}\right). \quad (5-5)$$

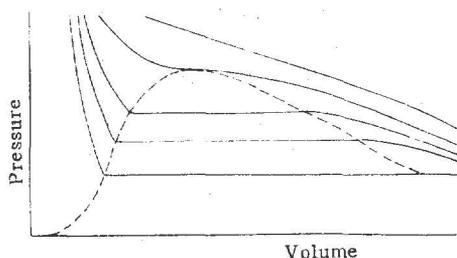


Fig. 4

If the Vander Waals equation were satisfied exactly by the gas, the critical volume determined in this way would agree with the experimentally determined critical volume. The real critical volume is not far different from $(3/8) (RT_c/P_c)$, but the latter is larger. This is one of the simplest ways of checking the equation and seeing that it really does not hold true, although it is qualitatively reasonable.

Using the values of P_c , V_c , and T_c from Eq. (5-4), we can easily write the Van der Waals equation with a little manipulation in the form

$$\left[\frac{P}{P_c} + 3 \left(\frac{V}{V_c} \right)^2 \right] \left[\frac{V}{V_c} - \frac{1}{3} \right] = \frac{8}{3} \left(\frac{T}{T_c} \right). \quad (5-6)$$

This form is expressed in terms of the ratios P/P_c , V/V_c , and T/T_c , showing that if the scales of pressure, temperature, and volume are adjusted to bring the critical points into coincidence, the Van der Waals equation for any two gases will agree. This is called the law of corresponding states. Real gases do not actually satisfy this condition, so this is another reason to doubt the accuracy of the Van der Waals equation.

6. Calculation of Van der waals' Constants

Using Eq. (5-4) we can calculate Van der Waals' constants a and b directly from the experimentally measured critical pressure and temperature;

$$a = \frac{27}{64} \frac{(RT_c)^2}{P_c}, \quad b = \frac{1}{8} \left(\frac{RT_c}{P_c} \right). \quad (6-1)$$

Also we can obtain these constants by means of measuring the Joule-Thomson coefficient and C_p for real gases assume they all obey the Van der Waals equation, we have from the next section

$$\left(\frac{\partial T}{\partial P} \right)_H = \frac{1}{C_p} \left(-b + \frac{2a}{RT} \right). \quad (6-2)$$

From this we can calculate the quantity $C_p (\partial T / \partial P)_H$, and plot the resulting function as a function of $1/T$. This should give a straight line, with intercept $-b$, and slope $2a/R$.

A study between constant a and the ionization potential (V) of inert gases by Y. P. Varshni* showed that a plot of constant a against $1/V^4$ will give a straight line, with the relation

$$a = -0.0004478 + \frac{188.33}{V^4} \quad (6-3)$$

where a is in atmosphere x cm^4 and V in volts.

Other methods to determine the Van der Waals second constant b are:

(I) Measurement of the mean free path of gases, from which molecular radius is calculated and using the approximate relation

$$b = \frac{16}{3} N \pi r^3 \quad (6-4)$$

where N is the Avogadro number.

* Y. P. Varshni, J. Chem. Phys., 21, 1119 (1953).

(II) Measurement of the coefficient of viscosity of the gas (η), if molecular diameter d is known, we may have b from the relation

$$b = \frac{2d}{3} \frac{1}{(\pi/RTM)^{1/2} \eta} \quad (6-5)$$

M is the molecular weight of the gas measured.

7. The Joule-Thomson Effect

We take Van der Waals' equation in the form

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad (7-1)$$

We have

$$\begin{aligned} \left(\frac{\partial V}{\partial T}\right)_P &= - \frac{(\partial P / \partial T)_V}{(\partial P / \partial V)_T} = - \frac{R / (V-b)}{-RT / (V-b)^2 + 2a / V^3} \\ &= \frac{1}{T} \frac{V-b}{1 - \frac{2a(V-b)^2}{RTV^3}} = \frac{V-b}{T} \left[1 + \frac{2a(V-b)^2}{RTV^3} + \dots \right] \\ &= \frac{1}{T} (V-b + \frac{2a}{RT} + \dots) \end{aligned}$$

Neglecting the higher terms of $1/T$, then we have

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{T} (V-b + \frac{2a}{RT}) \quad (7-2)$$

Substitute in Eq. (2-3) and the result is

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p} (-b + \frac{2a}{RT}) \quad (7-3)$$

From Eq. (7-3) we see that at high temperatures $b > (2a/RT)$, the coefficient is negative; at low temperatures $b < (2a/RT)$, the coefficient is positive. That is, since ΔP is negative in the experiment, corresponding to a decrease in pressure, the change of temperature is positive at high temperatures, leading to a heating of the gas, while it is negative at low temperatures, cooling the gas. The temperature $2a/Rb$, where the effect is zero, is called the inversion temperature; by comparison with Eq. (4-3), and is twice the Boyle temperature.

If $a=b=0$, Van der Waals' equation of state reduces to the ideal gas law, and

$$\left(\frac{\partial T}{\partial P}\right)_H = 0 \quad (7-4)$$

Hence an ideal gas would show no heating or cooling for the Joule-Thomson Effect.

8. Difference between C_p and C_v

The difference in heat capacities may be expressed as

$$C_p - C_v = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \quad (8-1)$$

For a gas which obeys Van der Waals' equation

$$\begin{aligned} \left(\frac{\partial P}{\partial T}\right)_V &= \frac{R}{V-b} \\ \left(\frac{\partial V}{\partial T}\right)_P &= \frac{R / (V-b)}{RT / (V-b)^2 - 2a / V^3} \end{aligned}$$

Thus

$$C_p - C_v = \frac{R}{1 - \frac{2a(V-b)^2}{RTV^3}}$$

$$=R\left[1+\frac{2a(V-b)^2}{RTV^3}+\dots\dots\dots\right] \quad (8-2)$$

and by neglecting the higher terms we obtain

$$C_p - C_v = R \left[1 + \frac{2a}{RTV}\right]. \quad (8-3)$$

This shows that only when the gas is at high temperature the difference in heat capacities is always greater than that for an ideal gas (R). If temperature is slowly raised, the value decreases more rapidly when approaching R .

9. Some Remarks On Other Equations of State

The fundamental concepts which are expressed by the Van der Waals equation are undoubtedly true, but it could hardly be expected that it would be possible to develop a complete theory of the gaseous and liquid state from such simple assumptions - those upon which the theory was based. The equation does not enable us to connect in a quantitative manner the properties of gases at low pressures.

Various attempts have been made to modify the Van der Waals equation, and a very large number of equations nearly all of them empirical have been put forward. Thus Clausius proposed his second equation*

$$\left[P + \frac{a}{T(V+c)^2}\right](V-b) = RT \quad (9-1)$$

in which a , b , and c are constants. This and other equations were examined by Kammerlingh-Onnes and all were found to be unsatisfactory. In 1901 they proposed a virial equation similar to Eq. (4-1)

$$PV = RT + BP + CP^2 + DP^3 + \dots\dots\dots \quad (9-2)$$

It can be extended to as many terms as are needed to represent the experimental data (PVT) to any desired accuracy.

D. Berthelot gave the equation of state as:

$$\left(P + \frac{a}{TV^2}\right)(V-b) = RT \quad (9-3)$$

This equation is somewhat better than Van der Waals' at pressures not much above one atmosphere, and is preferred for application in this range.

One of the best empirical equations is that proposed by Beattie and Bridgeman.**

$$P = [RT(1-e)/V^2](V+B) - A/V^2 \quad (9-4)$$

$$A = A_0 \left(1 - \frac{a}{V}\right), \quad B = B_0 \left(1 - \frac{b}{V}\right), \quad e = \frac{c}{VT^3} \quad (9-5)$$

It contains five constants in addition to R , and fits the PVT data over a very wide range of pressures and temperatures, even near the critical point to within 0.5%.

Other equations of state analogous to Van der Waals' can be expressed in a

* Clausius' first equation is $P(V-b) = RT$

** J. A. Beattie and O. C. Bridgeman, Proc. Am. Acad. Arts Sci., '63, 229-308 (1928)

general form*

$$(P+aV^nT^m) (V-bV^s) =RT \quad (9-6)$$

- (a) Van der Waals $n=-2, m=0, s=0;$
 (b) Benson & Golding $n=-5/3, m=-2/3, s=-1/2;$
 (c) Eyring $n=-2, m=0, s=2/3;$
 (d) Dranen
 1. $n=1.69, m=0, s=0;$
 2. $n=2, m=1/3, s=1/3;$
 (e) Ishikawa & Ikeda**

$$n = -(2-e), m=0, s=0.$$

Benson & Golding's equation is better than Van der Waals' and that of Berthelot's, under the critical conditions. Preliminary calculations based on Dranen's equations give satisfactory qualitative agreement for the experimental isotherms of argon and nitrogen. The equation proposed by Ishikawa & Ikeda includes the concept of molecular association, and is valid for 66 kinds of normal and slightly polar substances extended to the liquid-vapor coexistence region.

10. Conclusion

The Van der Waals equation of state has inspired much theoretical and experimental work and it is believed that a general qualitative equation of state is possible for gases and liquids. But two features are still vague to us: (1) a complete picture of molecular interaction and (2) the related molecular forces which govern these interactions. Recent attempts to apply modern concepts of atomic structure and quantum mechanics to the derivation of an equation of state have not led to any noteworthy success.

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van der Waals 氣體方程式與其 相關狀態方程式之討論

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摘 要

焦耳—湯姆森之實驗，確理想氣體定律不適用於普通氣體，導致 Van der Waals 對普通氣體分子附加二項假定：

- (1) 分子本身佔有體積，故氣體分子活動之空間較理想氣體者為小。
- (2) 分子間有引力存在，此力使外界對於普通氣體所施之壓力較施諸於理想氣體者為大。

由以上之假定 Van der Waals 導出其著名之狀態方程式 $(P + \frac{a}{V^2})(V - b) = RT$

本文除對此方程式用統計方法導證外，並將之與理想氣體定律相比較，且討論其缺點並附此狀態方程式之各種修正式。

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