

A NEW EQUATION OF STATE

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So many equations of state have been proposed that it seems, at first sight, almost useless to add still another. However, many of the equations of state so far proposed are nothing more than empirical modifications of van der Waals' famous equation of state without a thorough study of the theoretical side; in fact, almost all of the modifications which have been proposed to van der Waals' equation lead to conditions at the critical point which are not realized in nature; for example, many of the equations lead to the result that, at the critical temperature and the critical pressure, the critical volume has two or more different values whereas, as yet, only one value has been experimentally realized. There are, also, other objections which can be raised against many of these equations. I propose, therefore, to make a brief study of the original van der Waals' equation and modify it only where it is in error on the theoretical (mathematical) side.

In his classical dissertation,¹ J. D. van der Waals put forward the equation of state:

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

where P , V and T represent the pressure, volume and temperature, respectively, of the fluid; b is a volume proportional to the volume of the molecules, R is a constant and a/V^2 represents the cohesive pressure of the molecules. On expansion and rearrangement this equation becomes:

$$V^3 - \left(b + \frac{RT}{p}\right)V^2 + \frac{a}{p}V - \frac{ab}{p} = 0 \quad (2)$$

which is of third degree in V and, therefore, has three roots, two of which may be imaginary, at any given temperature and pressure. At the critical point, the reasonable assumption is made that the three roots of this equation are equal. This supposition imposes three conditions on the equation and, to satisfy these three conditions, the equation must contain three parameters, the values of which can be determined from the imposed conditions. Apparently, van der Waals' equation satisfies this requirement since it has the three parameters, a , b and R . But, as the volume V increases indefinitely, van der Waals' equation must reduce to the simple gas law:

$$PV = RT, \quad (3)$$

where R is a natural constant, independent of the nature of the gas. Hence, van der Waals' famous equation, in reality, contains only two parameters a , and b , and must, therefore, in general, be mathematically absurd. We can see this result more easily by writing equation (2) in the reduced state. To do this let us write:

$$\left. \begin{aligned} P &= P_r P_c; & T &= T_r T_c; & V &= V_r V_c; \\ a &= a_r P_c V_c^2; & b &= b_r V_c; & K &= \frac{RT_c}{P_c V_c} \end{aligned} \right\} \quad (4)$$

where P_c , T_c and V_c denote the values of the pressure, temperature and volume, respectively, at the critical point. Following the late Professor H. Kammerlingh Onnes, we shall call $RT_c/P_c V_c$ or K , the critical ratio or the critical constant. As we shall see below, this critical constant is one of the most important constants connected with equations of state of the van der Waals' type. If, now, we insert the above values and divide both sides by V_c^3 , equation (2) becomes:

$$V_r^3 - \left(b_r + \frac{KT_r}{P_r} \right) V_r^2 + \frac{a_r}{P_r} V_r - \frac{a_r b_r}{P_r} = 0. \quad (5)$$

Since, at the critical point, $P_r = T_r = 1$, equation (5) becomes:

$$V_r^3 - (b_r + K)V_r^2 + a_r V_r - a_r b_r = 0. \quad (6)$$

According to our hypothesis, at the critical point, all three values of V_r must have the same value, in this case, unity. Hence equation (6) must be identical with the equation:

$$(V_r - 1)^3 = 0 \quad (7)$$

i.e., with its expansion:

$$V_r^3 - 3V_r^2 + 3V_r - 1 = 0. \quad (8)$$

Hence, coefficients of like powers of V_r must be identical. If we carry through the calculations, we find:

$$a_r = 3; \quad b_r = \frac{1}{3}; \quad K = \frac{8}{3}. \quad (9)$$

Therefore, there is only one value of the critical constant K , namely, $8/3$, which satisfies the assumptions made in respect to van der Waals' equation at the critical point. As these assumptions, however, seem to be in accord with experimental evidence and as the values of K vary from 3.1 to about 5.0 but is never $8/3$, we are forced to the conclusion that van der Waals' equation is not true. Another point against this equation is that the experimental values of b_r vary from about 0.17 to about

0.28 but never reach the value of $1/3$ as demanded by his equation, although, in fact, as we shall find out below, the value of b_r , that is, the value of the ratio of the volume of the molecules to the critical volume, is a function of the critical constant K . Since, by van der Waals' equation, the values of K , a_r and b_r are the same for all substances and if the values of any two of the three variables, P_r , T_r and V_r , are the same for several substances, then, the value or values of the third variable must be the same for the several substances. This is known as the Law of Corresponding States. It is approximately true for many substances but, in general, it is far from true. The failure of this Law is due, as pointed out below, to the variability of the critical ratio K as well as to the variability of a fourth parameter which must be introduced to take care of the change of pressure due to a temperature change, when the volume is invariant.

The next advance was due, in my opinion, to Dieterici² who changed the term due to the cohesive pressure of the molecules from a/V^2 to a/V^n and determined what value of n would lead to b equal to one fourth of the critical volume, the mean of the experimental values for several substances. He found, on this assumption, that n must be equal to $5/3$. Nevertheless, Dieterici's equation, like its predecessor, contains only two parameters, a and b , and hence, in general, it must be mathematically absurd. Incidentally, Dieterici found that, as n was changed from 2 to $5/3$, the critical ratio K was changed from $8/3$ to $15/4$. As the experimental values of K vary over a wide range, it seems almost inconceivable to me that Dieterici did not regard n as variable from substance to substance in view of the fact that mathematics demands three parameters, although Dieterici seems to have overlooked this point completely.

Accordingly, the first modification that I propose to make in regard to van der Waals' equation is to change the term due to the cohesive pressure of the molecules from a/V^2 to a/V^n and to regard n as the missing third parameter which mathematical theory demands as pointed out above. Hence, our equation is:

$$\left(P + \frac{a}{V^n}\right)(V - b) = RT \quad (10)$$

which in the reduced state is:

$$\left(P_r + \frac{a_r}{V_r^n}\right)(V_r - b_r) = KT_r \quad (11)$$

where the variables and parameters have the same meaning as in equations (2) and (5) above, except that $a = a_r P_c V_c^n$.

As n will not be, in general, integral, we cannot solve our equation by

purely algebraic methods but are obliged to use the well-known methods of the calculus. If $f(x)$ be equal to zero, then the necessary and sufficient condition that this equation have two equal roots is that the first derivative of $f(x)$ with respect to x be equal to zero. If three roots of this equation be identical, then the necessary and sufficient conditions are that the first and the second derivatives of $f(x)$ with respect to x be equal to zero. If, in the equation: $f(x)$ equal to zero, there occurs another independent variable, y , then I shall assume, without proof, that the necessary and sufficient conditions that $f(x)$ have three equal roots in x are that the first and second derivatives of y with respect to x are equal to zero. If there occurs in this equation two or more independent variables, then we must use the partial derivatives of any one of the independent variables with respect to x .

In the case of our equation of state, in order that it may have three identical values for V_r , we must have the first and second partial derivatives of P_r or of T_r with respect to V_r equal to zero. It must be clearly understood that these are not two separate conditions but only one, for, as we shall see below, there exists a definite relationship among the three first partial derivatives. As I prefer the mathematical symbol, $\partial p/\partial V$, to the thermodynamical symbol, $(dp/dV)_T$, I shall use the former throughout this paper.

On rearrangement of our reduced equation, we obtain:

$$P_r = \frac{KT_r}{V_r - b_r} - \frac{a_r}{V_r^n} \quad (12)$$

On differentiating this equation twice, we have:

$$\frac{\partial P_r}{\partial V_r} = -\frac{KT_r}{(V_r - b_r)^2} + \frac{na_r}{V_r^{n+1}} \quad (13)$$

$$\frac{\partial^2 P_r}{\partial V_r^2} = \frac{2KT_r}{(V_r - b_r)^3} - \frac{n(n+1)a_r}{V_r^{n+2}} \quad (14)$$

Now at the critical point, the values of P_r , T_r and V_r are all unity and also the first and second partial derivatives are zero. On carrying through the calculations we find:

$$a_r = \frac{1}{b_r} = \frac{n+1}{n-1} = \frac{1}{2} \{ \pm (K^2 + 4)^{1/2} + K \}, \quad (15)$$

$$b_r = \frac{1}{a_r} = \frac{n-1}{n+1} = \frac{1}{2} \{ \pm (K^2 + 4)^{1/2} - K \}, \quad (16)$$

$$n = \frac{a_r + 1}{a_r - 1} = \frac{1 + b_r}{1 - b_r} = \frac{1}{K} \{ \pm (K^2 + 4)^{1/2} + 2 \}. \quad (17)$$

As a_r , b_r and n must obviously be positive, it is necessary to take the positive value of the radical. If, for purposes of calculation, we put:

$$\frac{K}{2} = \tan \theta \quad (18)$$

then:

$$a_r = \frac{1}{2} \{ (K^2 + 4)^{1/2} + K \} = \sec \theta + \tan \theta \quad (19)$$

$$b_r = \frac{1}{2} \{ (K^2 + 4)^{1/2} - K \} = \sec \theta - \tan \theta \quad (20)$$

$$n = \frac{1}{K} \{ (K^2 + 4)^{1/2} + 2 \} = \operatorname{cosec} \theta + \cot \theta \quad (21)$$

$$K = \frac{1 - b_r^2}{b_r} = \frac{a_r^2 - 1}{a_r} = \frac{4n}{n^2 - 1}. \quad (22)$$

Hence we have made the rather remarkable discovery that a_r , b_r and n are not only interconnected by very simple relationships but are definite, single-valued functions of the critical ratio, K , which now becomes of fundamental importance in the theory of equations of state. As the experimental values of K obtained by different observers differ widely, it is hardly necessary to point out that the values of K , or what amounts to the same thing, the values of the critical temperature, critical pressure and critical volume, of a large number of substances should be redetermined with as much precision as possible.

If K be put equal to $2/3$, then the calculated values of a_r , b_r and n are 3, $1/3$ and 2, respectively, which is van der Waals' equation. If K be put equal to $15/4$, then the calculated values of a_r , b_r and n are 4, $1/4$ and $5/3$, which is Dieterici's equation. Hence, both van der Waals' and Dieterici's equations are only particular cases of a very much more general equation, namely, equation (10) above.

Besides the mathematical requirement of a third parameter, is there any other support of the generalization of van der Waals' equation? In van der Waals' time, the cohesive forces acting between molecules were regarded as gravitational in origin, whereas it is now almost certain that these forces are electrical in origin. As the number of electrons and the radii of their orbits vary from an atom of one element to an atom of another element, the forces between atoms, and therefore, also, the forces between molecules, which are functions of the number of, and the radii of the orbits of, electrons in an atom as well as the distance apart of atoms, will be dependent on the nature of the atom and hence of the molecule. So

that we should expect n as well as a_r and b_r to vary from substance to substance.

Since a_r , b_r and n are all definite single-valued functions of K , we should expect, from equation (11), that two substances, having the same value of K , will obey the Law of Corresponding states in a very exact manner whereas if the two substances have different K values, this law should not be exactly obeyed. A study of the results obtained by S. Young³ seems to confirm these predictions. As, however, it is necessary to introduce a fourth parameter to take care of the temperature variability of the pressure at constant volume, it would be out of place to discuss this Law further here.

The values of b_r can be obtained by the extrapolation of the Cailletet-Mathias Law of Rectilinear Diameter to the absolute zero. The values so obtained are, within the limits of experimental error in the majority of cases, identical with those obtained by equation (20) from the experimental values of K . This seems to show that b_r is, in general, independent of the temperature, as the values calculated from K are true at the critical temperature, whereas those calculated by the other method are for the absolute zero. Accordingly, in this paper, I shall assume that b_r is not a temperature function.

Whether or not n is a temperature function, I am not ready to say. There are, however, strong reasons for supposing that, in equations of the van der Waals' type, a_r or a must decrease as the temperature rises. Accordingly, I shall assume that a_r is a function of the temperature but the choice of the temperature function must be more or less empirical at the present time. If, in equations of the type given by (10), which includes van der Waals' equation as a particular case, the absolute zero is approached, the term a/V^n remains finite if we regard a and n as constants, since the volume V approaches the limiting volume b ; whereas the term $RT/(V - b)$ takes the indeterminate value $0/0$; in this case, we can replace the indeterminate value, by the rules of calculus, by the expression, RdT/dV , as the experimental values of dT/dV increase as the temperature decreases and become very large, if not infinite, for the liquid state at the absolute zero. Accordingly, by equation (10), for the liquid state, we should expect that as the temperature decreases, the vapor pressure should first decrease due to the increase of the factor (a/V^n) , then should begin to increase due to the more rapid increase of the factor $RT/(V - b)$ and should reach very large, if not infinite, values at the absolute zero. Experiment does not, however, confirm this prediction. If the factor $RT/(V - b)$ becomes infinite at the absolute zero as we would expect by extrapolation to the absolute zero for the liquid state, since the extrapolated vapor pressure is zero, the factor (a/V^n) must become infinite and since V is finite and n has been chosen

as finite, then a must be infinite. The choice of the function must be arbitrary at the present time but an exponential function seems to have the surest foundation. Accordingly, I shall put

$$a = ce^{A/T} = a_r P_c V_c^n e^{A_r(1/T_r-1)} \quad (23)$$

Hence, our equation becomes:

$$\left(P + \frac{ce^{A/T}}{V^n} \right) (V - b) = RT \quad (24)$$

which is equivalent to the following reduced form:

$$\left\{ P_r + \frac{a_r e^{A_r(1/T_r-1)}}{V_r^n} \right\} (V_r - b_r) = KT_r \quad (25)$$

where a_r has the same value as calculated above from the critical constant, because, at the critical point, T_r is unity and e^0 is unity.

Since a mathematical relationship exists among the three variables, P_r , T_r , and V_r , then the following relationship connects the three first partial derivatives:

$$\frac{\partial P_r}{\partial T_r} \cdot \frac{\partial T_r}{\partial V_r} \cdot \frac{\partial V_r}{\partial P_r} = -1. \quad (26)$$

On rearrangement we have:

$$\frac{\partial P_r}{\partial T_r} = - \left(\frac{\partial P_r}{\partial V_r} \right) / \left(\frac{\partial T_r}{\partial V_r} \right). \quad (27)$$

At the critical point, both $\partial P_r / \partial V_r$ and $\partial T_r / \partial V_r$ are zero, so that $\partial P_r / \partial T_r$ is indeterminate. So that the only way that $\partial P_r / \partial T_r$ can be obtained is by actual measurement. Let us denote by J_c the experimental value of this quantity at the critical point. As the fluid is unstable at the critical volume below the critical temperature, the only way of obtaining J_c is at temperatures slightly above the critical point. The data on this new magnitude is, so far, very scanty and for the most part unreliable. If, however, we assume that it is known, it is possible to calculate A_r as follows:

$$J_c = \frac{\partial P_r}{\partial T_r} = \frac{K}{1 - b_r} + \frac{a_r A_r}{1} = \frac{1}{b_r} (1 + b_r + A_r) \quad (28)$$

where the values of K and a_r , in terms of b_r , are inserted in order to avoid radicals. Whence:

$$A_r = (J_c - 1)b_r - 1. \quad (29)$$

It is clearly seen that two substances will exactly obey the Law of Corresponding States when, and only when, they have the same values for both K and J_c .

More extended details of this new equation of state, which is nothing more than a generalization of van der Waals' equation, will be published elsewhere. Furthermore, I hope to treat other equations of state in a manner similar to that outlined above.

¹ Dissertation, Leyden, 1873.

² *Ann. Phys.*, 69, 685, 1899; 5, 51, 1901.

³ *Stoichiometry*, 2nd edition, London.

*THE EFFECT OF DIFFUSION AT A MOVING BOUNDARY
BETWEEN TWO SOLUTIONS OF ELECTROLYTES*

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In the determination of the transference number of an electrolyte by the method of moving boundaries, a sharp boundary is formed between the solution to be studied (an aqueous solution of silver nitrate, for instance) and another "indicator" solution containing an electrolyte with a common ion and an ion of lower mobility. Lithium nitrate fulfils these conditions as an indicator for silver nitrate. Such a boundary will move when a current is passed through it. From measurements on this motion the transference number T of one ion constituent of the leading solution may be computed from the formula

$$T = \frac{v}{V} \cdot \frac{F}{it} \quad (1)$$

in which v is the volume swept through by the boundary, V the volume containing 1 gram equivalent of the electrolyte, F the faraday equivalent, i the current, and t the time. It has, however, been found necessary to have the concentration of the indicator solution adjusted so as not to be very far from the concentration given by the relation

$$C' = C \frac{T'}{T}$$

in which C and C' are the concentrations of the leading and indicator solutions and T and T' the corresponding transference numbers. In