Van der Waal equation of state.

e-content for B.Sc Physics (Honours)

B.Sc Part-I

Paper-II

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Equation of State: Real Gases: van der Waals and Other Equations

The properties of gases pose a formidable challenge for physicts who seek to understand their p-V-T properties. Chemists adopt an approach which starts by defining the properties of a (hypothetical) ideal gas.

The fact that the properties of a given real gas are not ideal is understood in terms of intermolecular interactions.

In understanding the properties of real liquid mixtures and real solutions, the classic approach identifies the properties of the corresponding systems where the thermodynamic properties are defined as ‘ideal’. In the next stage the reasons why the properties of real liquid mixtures and real solutions are not ideal are discussed in terms of the nature and strength of intermolecular interactions. This general approach mimics the approach used to explain why the properties of real gases are not those of a defined ideal gas. In this context the van der Waals equation describing the differences between the properties of a real gas and an ideal gas sets the stage for theories describing the differences between the properties of real and ideal liquid mixtures and the properties of real and ideal solutions. Nevertheless we develop here the argument by considering the properties of a single gas, chemical substance j.

The starting points are two statements concerning an ideal gas.

(I) The actual volume of the molecules making up an ideal gas is negligible compared to the total volume of the system.

(II) Neither attractive nor long-range repulsive intermolecular forces are present.

In a real gas the molecular volume is not negligible. Also cohesive intermolecular forces mean that the pressure exerted on the containing vessel is less than in the case of an ideal gas. Therefore the equation of state requires that the pressure p is incremented by a quantity proportional to the density or, by a quantity inversely proportional to the volume. The famous van der Waals [1] equation takes the following form [2] where V_j is the molar volume of gas j at pressure p and temperature T.

$$\left(p + \frac{a}{V_j^2}\right) \cdot (V_j - b) = R \cdot T \qquad \text{(a)}$$

The van der Waals equation has played an important role in the development of theories describing fluids; i.e. both liquids and gases. The equation has merit in that it involves just two constants, both characteristic of given chemical substance. Further as McGlashan notes, the equation never leads to physical nonsense and does not predict physically absurd results [3]. Similarly Rowlinson comments that the equation is easy to manipulate and never predicts physically absurd results [4]. Chue comments that despite its simplicity the van der Waals equation ‘comprehends’ both liquid and gaseous states [5].

However other authors are not so enthusiastic. For example, Prigogine and Defay comment that the equation is ‘mainly of qualitative interest’ [6]. Similarly Denbigh states that the a-parameter ‘does not have a sound theoretical basis and interpretation of the a-parameter in terms of intermolecular attraction is ‘intuitive’ [7].

Perhaps the expectation that the p-V-T properties of all gases and liquids can be accounted for using two parameters characteristic of each chemical substance is too optimistic. Nevertheless there is merit in reviewing the van der Waals equation.

Equation (a) can be written as an equation for pressure p.

$$p = \frac{R \cdot T}{V_j - b} - \frac{a}{V_j^2} \qquad [\ b]$$

This form of equation (a) highlights the role of the parameter b in describing the effect of molecular size and the role of parameter a in describing inter-molecular cohesion.

A plot of p as function of V_j at fixed temperature has an extremum at the point defined by equation (c) [8].

$$\frac{R \cdot T}{(V_j - b)^2} = \frac{2 \cdot a}{V_j^3} \qquad \text{(c)}$$

$$\text{Or,} \quad T = \frac{2 \cdot a \cdot (V_j - b)^2}{R \cdot V_j^3} \qquad \text{(d)}$$

Hence using equations (a) and (d) we obtain [9] an equation relating pressure p to V_j in terms of the two parameters

$$p = a \cdot \left[\frac{V_j - 2 \cdot b}{V_j^3} \right] \qquad \text{(e)}$$

In a family of curves showing p as a function of V_j , one curve has a point of inflexion with a horizontal tangent where both

$$\frac{\partial p}{\partial V_m} \quad \text{and} \quad \frac{\partial^2 p}{\partial V_m^2}$$

are zero. This point is the **critical point** [10]. Interesting features based on the van der Waals equation characterise this point [11].

At the critical point [12,13],

$$V_j^c = 3 \cdot b \qquad \text{(f)}$$

$$p^c = a / 27 \cdot b^2 \qquad \text{(g)}$$

$$\text{and} \quad T^c = 8 \cdot a / 27 \cdot R \cdot b \qquad \text{(h)}$$

A classic plot [10] describes the properties of a fixed amount of carbon dioxide in terms of isotherms showing the dependence of pressure on volume. This plot reported by T. Andrews in 1870 showed that $CO_2(g)$ cannot be liquefied solely by the application of pressure at temperatures above 304.2 K. The latter is the critical temperature T^c for CO_2, the critical pressure p^c being the pressure required to liquefy CO_2 at this temperature. The molar volume at pressure p^c and temperature T^c is the critical molar volume V_j^c .

The critical volume is obtained using the Law of Rectilinear Diameters originally described by L. Caillete and E. Mathias. The law requires that the mean density ρ_j (T) of gas and liquid states of a given chemical substance j at common temperature T is a linear function of T

$$\text{Thus,} \rho_j(T) = \rho_j(T^c / K) + \alpha \cdot (T / K) \qquad \text{(i)}$$

The parameters $\rho_j(T^c / K)$ and α are characteristic of chemical substance j; $\rho_j(T^c / K)$ is the critical density of chemical substance j, leading to the critical molar volume $V_j(T^c)$ at critical temperature T^c and critical pressure p^c. Above the critical temperature the plot of pressure p and against molar volume at a given temperature T is a smooth curve. Below T^c and at low pressures, chemical substance j is a gas. With increase in pressure a stage is reached where a given system comprises two phases, gas and liquid. With further increase in pressure the system comprises a liquid. There is no sharp transition between liquid and gaseous states in contrast to that observed on melting a solid. In other words, gas and liquid states for chemical substance j form a **continuity of states.**

The **Law of Corresponding States** is an interesting concept, following an observation by J. D. van der Waals in 1881.

The pressure, volume and temperature for a given gas j are expressed in terms of the critical pressure p_j^c, volume V_j^c, and temperature T_j^c using three proportionality constants, β_1, β_2 and β_3 respectively.

Thus $$p = \beta_1 \cdot p_j^c \qquad (j)$$

$$V_j = \beta_2 \cdot V_j^c \qquad (k)$$

$$T_j = \beta_3 \cdot T_j^c \qquad (l)$$

Hence from equation (a),

$$\left(\beta_1 \cdot p_j^c + \frac{a}{(\beta_2 \cdot V_j^c)^2}\right) \cdot \left(\beta_2 \cdot V_j^c - b\right) = R \cdot \beta_3 \cdot T_j^c \qquad (m)$$

Using equations (f), (g) and (h) for p_j^c, V_j^c and T_j^c the following equation is obtained from equation (m) [14].

$$\left(\beta_1 + \frac{3}{\beta_2^2}\right) \cdot \left(3 \cdot \beta_2 - 1\right) = 8 \cdot \beta_3 \qquad (n)$$

Equation (n) is the van der Waals reduced Equation of State for gas j; β_1, β_2 and β_3 being the reduced pressure, volume and temperature respectively. Significantly there are no parameters in equation (n) which can be said to be characteristic of a given chemical substance. In other words the equation has a universal character [15].

The van der Waals equations prompted the development of many equations of state .

The van der Waals equation can be modified in two simple ways.

In one modification it is assumed that $V_j >> b$. The assumption is that attractive intermolecular processes are dominant

$$\text{Hence, } \left[p + \frac{a}{V_j^2}\right] \cdot V_j = R \cdot T \qquad \text{(o)}$$

$$\text{Or, } p \cdot V_j = R \cdot T - (a / V_j) \qquad \text{(p)}$$

In another approach it is assumed that repulsive intermolecular forces are dominant.

$$\text{Thus, } \quad p \cdot V_j = R \cdot T + p \cdot b \qquad \text{(q)}$$

Clausius Equation

One criticism of the van der Waal equation is that no account is taken of the possibility that parameters a and b can depend on temperature. Clausius suggested the following equation in which intermolecular attraction is described as inversely proportional to temperature; a, b and c are three constants characteristic of a gas j.

$$\left(p + \frac{a}{T \cdot (V_j + c)^2}\right) \cdot (V_j - b) = R \cdot T \qquad \text{(r)}$$

Nevertheless the advantages gained by recognising that attraction might be dependent on temperature are outweighed by problems associated with using this equation.

Bertholot Equation

In this approach, the term $(V_j + c)$ in the Clausius equation is replaced by V_j.

$$\text{Then } \left(p + \frac{a}{T \cdot V_j^2}\right) \cdot (V_j - b) = R \cdot T \qquad \text{(s)}$$

$$\text{Or, } \quad p \cdot V_j = R \cdot T + p \cdot b - \frac{a}{T \cdot V_j} + \frac{a \cdot b}{T \cdot V_j^2} \qquad \text{(t)}$$

The van der Waals, Clausius and Berthelot equations are the forerunners of a large family of cubic equations of state; i.e. equations of state that are cubic polynomials in molar volume.

Analysis of experimental data prompted the development of the following equation using critical pressure p_j^c and temperature T_c.

$$p \cdot V_j = R \cdot T \cdot \left[1 + \frac{a}{128} \cdot \frac{p \cdot T_j^c}{p_j^c \cdot T} \cdot \left(1 - 6 \cdot \frac{(T_j^c)^2}{T^2}\right)\right] \quad \text{(u)}$$

Dieterici Equation

This modification suggested in 1899 by C. Dieterici attempts to account for the fact that molecules at the wall of a containing vessel have higher potential energy than molecules in the bulk gas. The following equation was proposed.

$$p \cdot (V_j - b) = R \cdot T \cdot \exp\left(-\frac{a}{R \cdot T \cdot V_j}\right) \quad \text{(v)}$$

The Virial Equation of State

The following virial equation was proposed in 1885 by Thiesen.

$$p \cdot V_j = R \cdot T \cdot \left[1 + \frac{B(T)}{V_j} + \frac{C(T)}{V_j^2} + \ldots\ldots\right] \quad \text{(w)}$$

Following a suggestion in 1901 by H. K. Onnes, B(T), C(T),… are called virial coefficients. A modern account of equations of state is given in reference [16].

Boyle Temperature

Boyle's Law requires that the product $p \cdot V_j$ at fixed temperature is independent of pressure. In the case of hydrogen, the product $p \cdot V_j$ at 273 K increases with increase in pressure. However for many gases (e.g. nitrogen and carbon dioxide) the product $p \cdot V_j$ at fixed T decreases with increase in pressure, passes through a minimum and then increases. For a given gas the minimum moves to lower pressures with increase in temperature until at high temperatures no minimum is observed. This is the Boyle temperature, which is characteristic of a given gas [11a]. The van der Waals equation offers an explanation of the pattern. Thus from equation (b),

$$p \cdot V_j = R \cdot T \cdot \left(\frac{V_j}{V_j - b}\right) - \frac{a}{V_j} \quad \text{(x)}$$

Equation (x) is differentiated with respect to pressure at constant temperature. If the plot of $p \cdot V_j$ against p passes through zero at temperature T_B , then T_B is given by equation (y) [17].

$$T_B = a / R \cdot b \qquad \text{(y)}$$

Therefore in terms of equation (a), a low Boyle temperature is favoured by small a and large b parameters.

Footnotes

[1] For a reproduction of a portrait of Johannes van der Waals (1837-1923) see D. Kondepudi and I. Prigogine, Modern Thermodynamics, Wiley , Colchester, 1998, page 15.

[2] $V_j = [\text{m}^3 \ \text{mol}^{-1}] \qquad b = [\text{m}^3 \ \text{mol}^{-1}]$

$$\left(p + \frac{a}{V_j^2} \right) = \left([\text{N m}^{-2}] + \frac{a}{[\text{m}^3 \ \text{mol}^{-1}]^2} \right)$$

Then, $a = [\text{N m}^{-2}] \cdot [\text{m}^3 \ \text{mol}^{-1}]^2 = [\text{N mol}^{-2} \ \text{m}^4]$

$$R \cdot T = [\text{J mol K}^{-1}] \cdot [\text{K}] = [\text{J mol}^{-1}]$$

Then $\left([\text{N m}^{-2}] + \frac{[\text{N mol}^{-2} \ \text{m}^4]}{[\text{mol}^{-1} \ \text{m}^3]^2} \right) \cdot \left[[\text{m}^3 \ \text{mol}^{-1}] - [\text{m}^3 \ \text{mol}^{-1}] \right]$

$$= ([\text{N m}^{-2}] + [\text{N m}^{-2}]) \cdot [\text{m}^3 \ \text{mol}^{-1}] = [\text{N m mol}^{-1}] = \left[\text{J mol}^{-1} \right]$$

[3] M. L. McGlashan, Chemical Thermodynamics,
Academic Press, London, 1979, page 176.

[4] J. S. Rowlinson, Liquids and Liquid Mixtures, Butterworths,
London, 2nd edn., 1969, page 66.

[5] S. H. Chue, Thermodynamics, Wiley, Chichester, 1977, page 136.

[6] I. Prigogine and R. Defay, Chemical Thermodynamics,
transl. D.H.Everett, Longmans Green, London, 1954, p. 145.

[7] K. Denbigh, The Principles of Chemical Equilibrium,
Cambridge University Press. 3rd. edn. 1971, page 119.

[8] $\frac{dp}{dV_j} = -\frac{R \cdot T}{(V_j - b)^2} + \frac{2 \cdot a}{V_j^3}$

At an extremum, $\frac{dp}{dV_j} = 0$; then, $\frac{R \cdot T}{(V_j - b)^2} = \frac{2 \cdot a}{V_j^3}$

[9] $$\left(p+\frac{a}{V_j^2}\right)\cdot(V_j-b)=R\cdot 2\cdot a\cdot\frac{(V_j-b)^2}{V_j^3}$$

$$p+\frac{a}{V_j^2}=2\cdot a\cdot\frac{(V_j-b)}{V_j^3}$$

Or, $$p=a\cdot\left[\frac{2\cdot V_j-2\cdot b-V_j}{V_j^3}\right]$$

[10] T.Andrews, Phil. Mag.,1870,[4],**39**,150.

[11] See for example,

(a) S. Glasstone, Textbook of Physical Chemistry, MacMillan,
London, 1948, 2nd. edn., page 435.

(b) N. K.Adam, Physical Chemistry, Oxford, 1956, page 83; CO_2.

(c) J. K. Roberts and A. R. Miller, Heat and Thermodynamics,
Blackie, London, 1951, page 110; CO_2.

(d) P. A . Rock, Chemical Thermodynamics,
MacMillan, Toronto, 1969; H_2O.

(e) E. F. Caldin, Chemical Thermodynamics, Oxford, 1958, chapter III.

(f) J. S. Winn, Physical Chemistry, Harper Collins,
New York, 1995, chapter 1.

(g) M. L. McGlashan, Chemical Thermodynamics, Academic Press,
London, 1979, page 132; xenon.

(h) P. Atkins and J. de Paula, Physical Chemistry, Oxford, 2002,
7th edn., Section 1.4.

[12] We rewrite equation (e) in the following form.

$$p=a\cdot[V_j-2\cdot b]\cdot V_j^{-3}$$

Or, $$p=a\cdot\{[V_j-2\cdot b]\cdot[V_j^{-3}]\}$$

Then

$$\frac{dp}{dV_j}=a\cdot[V_j^{-3}+(V_j-2\cdot b)\cdot(-3)\cdot V_j^{-4}]$$

$$=a\cdot[V_j^{-3}-3\cdot V_j^{-3}+6\cdot b\cdot V_j^{-4}]$$

$$=a\cdot[-2\cdot V_j^{-3}+6\cdot b\cdot V_j^{-4}]$$

$$\frac{dp}{dV_j} = 0 \text{ where}$$

$$[-2 \cdot V_j^{-3} + 6 \cdot b \cdot V_j^{-4}] = 0$$

Or, $\frac{1}{V_j^3} = \frac{3 \cdot b}{V_j^4}$ Or, $V_j^c = 3 \cdot b$

From equation (e), $p^c = \frac{a \cdot b}{27 \cdot b^3}$ or, $p^c = \frac{a}{27 \cdot b^2}$

Then from equation (d),

$$T^c = \frac{2 \cdot a \cdot (3 \cdot b - b)^2}{R \cdot 27 \cdot b^3} = \frac{8 \cdot a \cdot b^2}{27 \cdot R \cdot b^3} = \frac{8 \cdot a}{27 \cdot R \cdot b}$$

[13] $V_j^c = 3 \cdot b = [1] \cdot [m^3 \text{ mol}^{-1}] = [m^3 \text{ mol}^{-1}]$

$$p^c = \frac{[N\, m^4 \text{ mol}^{-2}]}{[1] \cdot [m^3 \text{ mol}^{-1}]^2} = [N\, m^4\, m^{-6} \text{ mol}^{-2} \text{ mol}^2] = [N\, m^{-2}]$$

$$T^c = \frac{[1] \cdot [N\, m^4 \text{ mol}^{-2}]}{[1] \cdot [J \text{ mol}^{-1}\, K^{-1}] \cdot [m^3 \text{ mol}^{-1}]} = \frac{[N\, m]}{[N\, m]} \cdot [K] = [K]$$

[14] $\left[\beta_1 \cdot \frac{a}{27 \cdot b^2} + \frac{a}{(\beta_2 \cdot 3 \cdot b)^2}\right] \cdot [\beta_2 \cdot 3b - b] = R \cdot \frac{8 \cdot a \cdot \beta_3}{27 \cdot R \cdot b}$

[15] F. T. Wall, Chemical Thermodynamics, W. H. Freeman, San Francisco, 1965, page 169.

[16] S. I. Sandler, H. Orbey and B.-I. Lee , Models for Thermodynamics and Phase Equilibria Calculations , ed. S. I. Sandler, Marcel Dekker, New York, 1994, pp.87-186.

[17] $p \cdot V_j = R \cdot T \cdot \frac{V_j}{V_j - b} - \frac{a}{V_j}$

$$\left[\frac{\partial(p \cdot V_j)}{\partial p}\right] = \left[R \cdot T \cdot \left(\frac{1}{V_j - b)}\right) - R \cdot T \cdot \left(\frac{V_j}{(V_j - b)^2}\right) + \frac{a}{V_j^2}\right] \cdot \left(\frac{\partial V_j}{\partial p}\right)_T$$

Then at $\left[\frac{\partial(p \cdot V_j)}{\partial p}\right] = 0$,

$$\left[R \cdot T \cdot \left(\frac{V_j - b - V_j}{(V_j - b)^2}\right) + \frac{a}{V_j^2}\right] = 0$$

$$\text{Or,}\ \ R \cdot T = \frac{a}{b} \cdot \frac{(V_j - b)^2}{V_j^2}$$

If the minimum occurs where p is zero (i.e. where V_j is infinitely large),

$$R \cdot T_B = a / b$$