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Johannes Diderik van der Waals: A Life of Achievements

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Abstract: Van der Waals is one of the most distinguished men in thermodynamics and author of an equation of state that has become the basis of all modern equations of state and theories of mixtures. Here we give a description of his life and his scientific and academic achievements. The van der Waals equation of state is discussed in detail with the goal of understanding the reasons for its inadequacy to give a quantitative prediction of the behavior of a real gas.

Johannes Diderik van der Waals (Figure 1) was born on November 23, 1837, in Leiden, the Netherlands, the son of Jacobus van der Waals and Elisabeth van den Burg. He was the eldest son in a family with eight children. After finishing his elementary education, he studied to become an elementary school teacher, and between 1856 and 1861 he was employed as such. Van der Waals finished his high school education without learning Greek and Latin and thus was not allowed to take science degree examinations at Leiden University. Nevertheless, he enrolled as a free student and continued studying mathematics, physics, and astronomy at the University during 1862–1865, ultimately obtaining teaching certificates in mathematics and physics. Between 1864 and 1866 he taught at a secondary school in Deventer and after that at La Hague, where eventually he became the principal of one the local schools. Finally, after the Dutch authorities removed the requirement that science students be proficient in classic languages, van der Waals was able to sit for university examinations and obtain, in 1873, his doctoral degree [1, 2]. In his thesis, entitled "Over de continuïteit van de gas- en vloeistoftoestand" ("On the continuity of the gas and liquid state"), he developed his famous equation of state and the theory that there is no basic difference between the liquid and gas states, so that below the critical temperature there is a continuous transition from one state to the other. His equation of state corrected the ideal gas law by considering that molecules have volume and that there are forces of attraction among them. Today, these forces are known as van der Waals forces.

In 1876, new higher-education legislation related to the Dutch University system promoted the Athenaeum Illustre of Amsterdam to university status, and in 1877 van der Waals was appointed its first Professor of Physics. Eventually other famous Dutch physicists such as W. H. Julius, Pieter Zeeman (Nobel Prize in Physics, 1902), and R. Sissingh joined the staff and expanded the research activity in physics. Together with other professors such as Jacobus van't Hoff (1852–1911; first Nobel Prize in Chemistry, 1901) and the geneticist Hugo de Vries (1848–1935), they contributed to the fame of the university. During his tenure at the University of Amsterdam (1877-1901), he collaborated actively with Kamerlingh-Onnes (1853–1926; Nobel Prize in Physics, 1913) at the University of Leiden on his research on cryogenic fluids, liquefaction of gases, and development of the virial equation of state. A memorial at the Laboratory of Physics of the University of Amsterdam lists Van der Waals' important scientific achievements [1].

The scientific achievements of van der Waals were acknowledged in the Netherlands and all over the world, and numerous institutions granted him honors and distinctions. He was a member of The Dutch Royal Academy of Science (1875–1895), he received an honorary doctorate from the University of Cambridge; he was made an honorary member of the Imperial Society of Naturalists of Moscow, the Royal Irish Academy, and the American Philosophical Society; a corresponding member of the Institut de France and the Royal Academy of Sciences of Berlin; an associate member of the Royal Academy of Sciences of Belgium; and foreign member of the Chemical Society of London, the National Academy of Sciences (USA), and of the Accademia dei Licei of Rome. A particularly significant honor was his being appointed one of only twelve foreign members of the Académie des Sciences in Paris.

In 1865, van der Waals married Anna Magdalena Smit, who died early; he never married again. They had three daughters and one son. The daughters were Anne Madeleine, who ran the house and looked after her father, Jacqueline Elisabeth, who was a teacher of history and a well-known poetess, and Johanna Diderica, who was a teacher of English. The son, Johannes Diderik Jr., was Professor of Physics at Groningen University between 1903 and 1908, and subsequently succeeded his father in the Physics Chair of the University of Amsterdam.

Van der Waals died in Amsterdam on March 8, 1923, at the age of 85. Professor Went, chairman of the Koninklijke Academie van Wetenschappen (Dutch Royal Academy of Science) wrote in his memorial address: "With the decease of J. D. van der Waals the Netherlands has lost one of its great sons; natural science lost one of her most honorable practitioners."

The Scientific Work of van der Waals

Besides his famous equation of state, van der Waals made several fundamental contributions to the science of thermodynamics. He was keenly interested in the experiments done by Thomas Andrews, who, in 1869, had found that gases had a critical temperature and could be liquefied. In 1890 he

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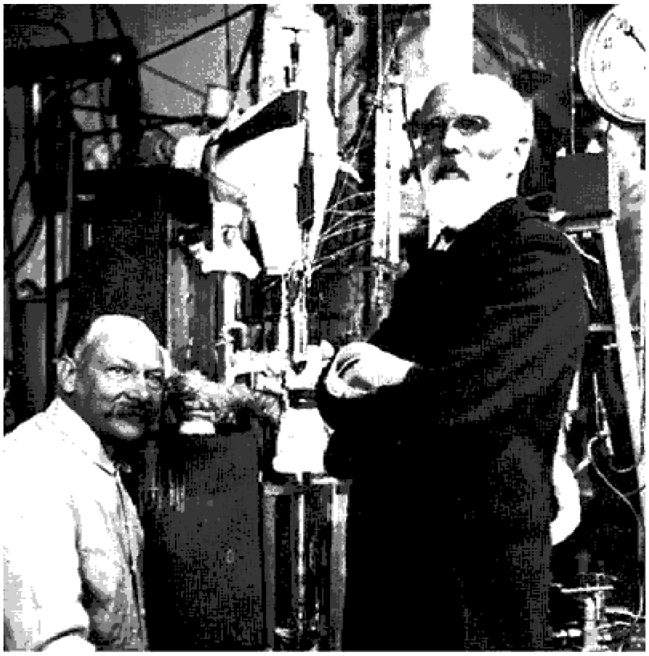

Figure 1. Picture of van der Waals (right) and K. Onnes (left). Onnes is sitting at the liquefier in which the first liquid helium was produced.

published his epoch-making paper "Theory of Binary Solutions," where he developed graphical representations of his mathematical development of the liquefaction phenomena in the form of a thermodynamic surface that he called "Psi-surface," in honor of J. W. Gibbs, who had chosen the Greek letter psi to designate the function that eventually would be called the Gibbs energy function (*G*). Van der Waals applied his Principle of Corresponding States to mixtures by assuming that a mixture behaves like a single fluid. This approach played an important role in the interpretation of phase diagrams and critical lines, and was adopted also by Kamerlingh-Onnes and van Laar. Numerous papers published on the subject gave origin eventually to his *Textbook of Thermodynamics* (Leipzig, 1912), co-authored with Ph. Kohnstamm. A thorough computer analysis of the capability of the van der Waals equation of state to describe the actual behavior of mixtures has been made by van Konynenburg and Scott [3]. They have concluded that one can distinguish among six main types of fluid phase behavior, which have been found experimentally. With the exception of Type 6, the equation of van der Waals, in spite of its oversimplifications, is capable of predicting the existence of all the other five types. Mention should also be made of van der Waals' thermodynamic theory of capillarity, which in its basic form first appeared in 1893 [4]. Van der Waals questioned the analysis of Laplace and Gauss, who assumed the phenomena to be strictly in the domain of statics. According to van der Waals, the theory of the nature of heat assumes that the molecules are in rapid movement everywhere, not only in the bulk of the fluid but also in the boundary layer. Thus the phenomenon must be analyzed on the basis of thermodynamics using the concepts of dynamic equilibrium. Gibbs had previously analyzed the phenomenon assuming a sudden transition of the density of the fluid into that of the vapor, while van der Waals claimed the existence of a gradual, though very rapid, change of density at the boundary layer between liquid and vapor. Eventually, experiments concerning the phenomena near the critical temperature favored van der Waals' ideas. Surface tension is intimately related to the metastable and unstable fluid phases, and to the *P–V–T* equation that describes these states. In 1893, van der Waals showed that the temperature dependence of surface tension, σ, could be predicted by the expression

$$\frac{\sigma}{\sigma_0} = f\left(T_r\right) \int_{V_{L,r}}^{V_{G,r}} \frac{1}{V_r^{5/2}} \left[P_r^{sat}\left(V_r - V_{L,r}\right) - \int_{V_{L,r}}^{V_{G,r}} P_r dV_r \right]^{1/2} dV_r \quad (1)$$

where the index *r* indicates a reduced property (see below), and σ_0 is a reference value of the surface tension whose value van der Waals showed could be derived from molecular properties. Van der Waals used his equation of state in equation (1) and reduced it (without the use of a computer!) to the approximate expression, valid in the vicinity of the critical point

$$\lim \sigma\left(T_r \to 1\right) = \frac{16}{\sqrt{6}} \sigma_0 \left(1 - T_r\right)^{3/2} \quad (2)$$

The exponent 1.5 is quite close to the actual experimental values, which range from 1.28 to 1.29.

The van der Waals Equation of State

Many applications of thermodynamics are concerned with the behavior of fluids, mainly gases. Thermodynamic properties, such as the internal energy and enthalpy from which one calculates the heat and work requirements of industrial processes are not readily measurable. They can, however, be calculated from volumetric data using an appropriate equation of state (EOS), $\Phi(P,V,T)$. While the EOS primarily describes the properties of the gas phase, many modern equations are also useful for the prediction of the liquid phase of the substance.

Consider first an ideal gas. It is conceived as a collection of a very large number of individual molecules that do not exert forces upon each other (except by elastic collisions) and which are so small that they can be treated as if they were point-masses of no volume. This picture is adequate to describe the behavior of real gases only at very low pressures. To obtain a more realistic model, it is conventional to introduce corrections that account for the facts that molecules must have finite volumes and they must exert attractive forces (van der Waals forces) upon each other at sufficiently small distances. In each mole of gas there is a space of volume ($V–b$) available for free motion that is somewhat less than the total volume. The term *b* is the *excluded volume* of the particles per mole. The excluded volume is also representative of the forces of attraction present among molecules. These forces induce a volume larger than the actual volume of the molecules, because in their movement they do not truly touch one another. Van der Waals starts his analysis by considering that molecules in the bulk of a gas are attracted equally in all directions by the surrounding molecules, but this is not the case of molecules next to the wall of the container. These molecules experience a net inward force and thus they are decelerated when traveling in the direction of the wall. If we recall that the kinetic theory of gases postulates that pressure is the number of collisions per unit area and per unit time, this inward force results in fewer molecules hitting the wall, that is, the pressure observed in a real gas must be smaller than that present in an ideal gas. The reduction in pressure will be proportional to the number of molecules per unit volume (N_0/V) in the layer next to the wall, and to the number of molecules per unit volume in the next layer, which are attracting. Therefore, the reduction in pressure is

$$P - P' = a'\left(\frac{N_0}{V}\right)^2 \tag{3}$$

or

$$P' - P = a'\left(\frac{N_0}{V}\right)^2 = P + \frac{a}{V^2} \tag{4}$$

where P' is the pressure calculated from simple kinetic theory (called the *internal pressure* of the gas) and V is the molar volume. Taking both corrections into account leads to the well-known van der Waals equation of state.

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \tag{5}$$

The terms a and b, *characteristic* of each gas, are termed the *van der Waals constants*. Their values can be obtained by applying equation (5) to the critical point; at the critical point the first and second derivatives of pressure with respect to volume are zero. The result is

$$P_c = \frac{a}{27b^2} \tag{6}$$

$$V_c = 3b \tag{7}$$

$$T_c = \frac{8a}{27Rb} \tag{8}$$

$$z_c = 3/8 \tag{9}$$

where z_c is the compressibility (= PV/RT) at the critical point. Calculation of the values of a and b for different gases shows that a is of the order 10^6 atm(mL•mol)$^{-2}$ and b ranges between 20 and 60 mL/mol, that is, the values of b are very similar to that of the saturated liquid molar volumes at atmospheric pressure and about 10,000 times smaller that those of a. Although the van der Waals equation can only be justified theoretically for small deviations from ideal behavior, it nevertheless represents *qualitatively,* and in a remarkable way, the behavior of the real gas over the whole range of gas, vapor, and liquid. It does not give the numerical details correctly, yet it never leads to physical nonsense, it is a relatively simple equation, and it is widely used to illustrate the general behavior of nonideal gases.

Let us analyze some of the limitations of the van der Waals EOS:

According to equation (9), the critical compressibility should be a universal constant for all gases, a conclusion negated by experience (see Table 1). From this table we learn that although z_c is not constant, the majority of gases do have a critical compressibility around 0.27. In addition, van der Waals' z_c = 0.375 is well above the observed range. Nevertheless, and to the credit of van der Waals, it must said that very powerful EOS, such as those of Soave and Peng–Robinson, also present the same limitation of predicting a constant value for z_c, 0.333 for the Soave and 0.307 for the Peng–Robinson EOS.

In general, the equation is a poor quantitative predictor of the P–V–T behavior of the gas, particularly at high pressure. This results can be easily explained if we write the equation in a virial form. We have

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \tag{10}$$

Multiplying each side by V/RT we get

$$\frac{PV}{RT} = \frac{V}{V - b} - \frac{1}{1 - b/V} - \frac{a}{RTV} \tag{11}$$

In general, the term b/V will be very small compared to unity; we can use this fact to expand the first term in equation (11) as a convergent geometric series:

$$\frac{1}{1 - b/V} = 1 + \frac{b}{V} + \left(\frac{b}{V}\right)^2 + \left(\frac{b}{V}\right)^3 + \ldots \tag{12}$$

Replacing in equation (11) and rearranging in terms of powers of $1/V$

$$z = \frac{PV}{RT} = 1 + \frac{1}{V}\left[b - \frac{a}{RT}\right] + \left(\frac{b}{V}\right)^2 + \left(\frac{b}{V}\right)^3 + \ldots \tag{13}$$

Equation (13) is the virial form of the van der Waals equation. From it we get

$$B_{VW} = \left[b - \frac{a}{RT}\right] \tag{14}$$

$$C_{VW} = b^2 \tag{15}$$

$$D_{VW} = b^3 \tag{16}$$

where B_{VW}, C_{VW}, and D_{VW} are the second, third, and fourth virial coefficients. Equations (14) to (16) explain why the van der Waals equation is not very accurate. According to the virial theory, all virial coefficients are functions of temperature. In the case of van der Waals, only the second virial coefficient is so. In addition, equation (14) indicates that the second virial coefficient varies linearly with the reciprocal of T, which is contrary to theory and experience, as illustrated in Figure 2, for oxygen. This figure shows that although B_{VW} depends on temperature, the functionality is not appropriate, meaning that even at low pressures (B-truncated) the van der Waals equation cannot be expected to be accurate.

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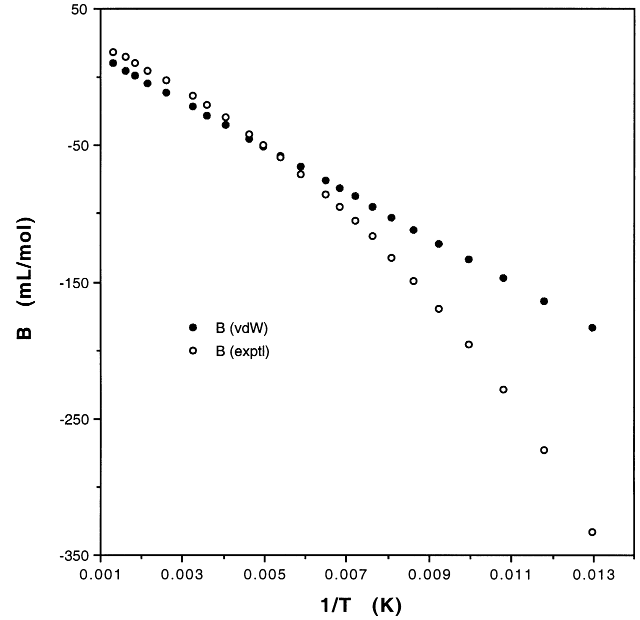

Figure 2. Comparison of the second virial coefficient, as predicted by the van der Waals equation of state and experimental data [6].

The second virial coefficient for every gas is zero at the Boyle temperature, T_B. For a van der Waals gas

$$T_B = \frac{a}{bR} \tag{17}$$

Writing equation (17) in the reduced form and using equations (6) to (8) yields

$$(T_B)_r = \frac{T_B}{T_c} = \frac{27}{8} = 3.38 \tag{18}$$

The experimental results indicate that for real gases $(T_B)_r$ is approximately 2.5 [5].

Consider one of the *TdS* equations [5]

$$TdS = C_V dT - \left(\frac{\partial P}{\partial T}\right) dV \tag{19}$$

Applying the condition that equation (19) is a perfect differential, we get

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V \tag{20}$$

Integrating between ideal gas behavior ($V = \infty$, marked *) and real gas behavior ($V = V$) yields

$$C_V(V,T) - c_V^*(V,T) = \int_\infty^V \left(\frac{\partial^2 P}{\partial T^2}\right)_V dV \tag{21}$$

Now, the van der Waals EOS predicts that the pressure varies linearly with the temperature [equation (10)], therefore

$$C_V(V,T) - C_V^*(V,T) \tag{22}$$

In other words, for a van der Waals gas, the heat capacity at constant volume is independent of the volume, a result that contradicts the experimental evidence.

Equation (22) can be used to develop a *macroscopic* interpretation of the term a/V^2. To do so we start from the Maxwell relations and the *TdS* equations for one mole of gas [5]

$$dU = Tds - PdV$$

$$Tds = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$$

so that

$$dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV$$

Applying equations (10) and (12) and integrating between the real gas state (*U, V*) and the ideal gas (U^*, $V = \infty$) we get

$$U^* - U = \frac{a}{V^2} \tag{22}$$

In other words, the term a/V^2 can be interpreted as the *residual internal energy* of the gas.

Comparing equation (5) with the EOS for an ideal gas points out that writing an EOS for a real gas has exacted a heavy price: The universality of the equation is lost and use of the new equation requires *identifying* the gas. Van der Waals realized that the reason for this drawback was that a real gas can be liquefied, and that the liquefaction phenomenon occurs at *P–T–V* conditions that are different for each gas. To recover the original advantage, van der Waals came out in 1880 with the idea of expressing the behavior of a gas on the basis of reduced properties, X_r, obtained by the *linear* scaling $X_r = X/X_c$. The reduced property is then the ratio between the value of the actual property and the value of the property at the critical state. He proceeded to replace X by X_rX_c obtaining

$$\left(P_rP_c + \frac{a}{V_r^2V_c^2}\right)(V_rV_c - b) = RT_rT_c \tag{23}$$

Finally, replacing the values of the critical properties given by equations (6) through (9) yields

$$\left(P_r + \frac{3}{V_r^2}\right)(3V_r - 1) = 8T_r \tag{24}$$

Equation 24, when represented in the (P_r, T_r, V_r) surface is a *universal relation* that carries *no identification* of the gas and expresses the *Principle of Corresponding States*: gases at the same reduced conditions display the same behavior. It should be recognized that the Principle of Corresponding States is only a translation of the EOS from the $P = (T, V)$ surface to the

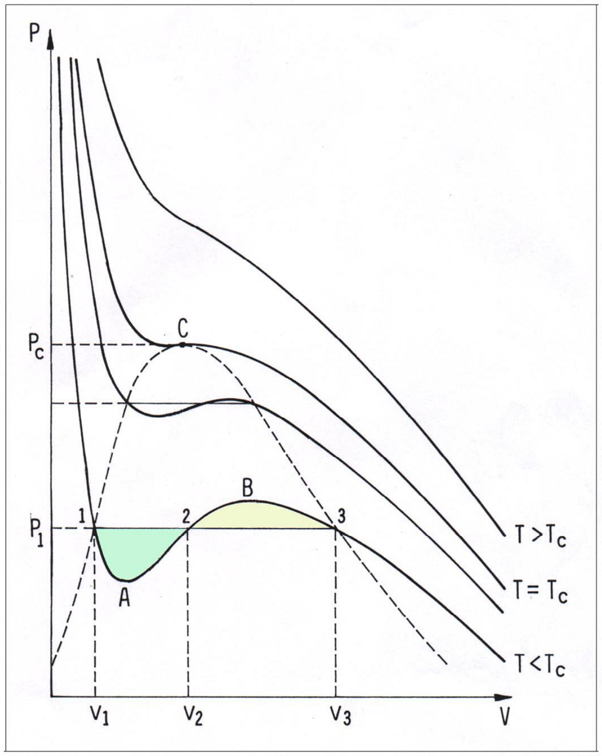

Figure 3. Maxwell theorem.

Table 1. Range of values of the critical compressibility factor

Z_c	representative compounds
0.147	sulfuric acid
0.211	acetic acid
0.224	methanol
0.229	water, acetone
0.24 to 0.26	ammonia, esters, alcohols, phenol
0.26 to 0.28	60% of compounds, mostly hydrocarbons, CCl_4
0.28 to 0.30	O_2, N_2, CO, H_2S, CH_4, C_2H_6, Ar, Ne, $CHCl_3$
0.321	methylamine

$P_r = (T_r, V_r)$ one. It does not improve the fitting quality of the EOS, but does makes it *universal*. The reduced EOS is subject to the condition that at low pressures the gas behaves ideally, so that the number of adjustable parameters is *two*. From the microscopic viewpoint it can be shown that the Principle of Corresponding States applies to substances in which the molecules are spherically symmetrical and for which the potential energy curve for interaction between molecules is of universal shape. Since no sharp distinction can be made between substances that do and those that do not conform to the Principle of Corresponding States, such a differentiation must be made about the properties to which it applies. It applies to properties that depend only on the intermolecular energy. The principle therefore applies to the second virial coefficient and does *not* apply to the heat capacity.

Consider now the EOS written in the form $Z = PV/RT$. Changing the variables to the reduced ones yields

$$Z = \frac{P_r P_c V_r V_c}{RT_r T_c} = \frac{P_c V_c}{RT_c}\frac{P_r T_r}{V_r} = Z_c \frac{P_r T_r}{V_r} \qquad (25)$$

According to equation (25), the Principle would be correct if all gases had the *same* critical compressibility, as predicted by the van der Waals EOS. We have seen already that this prediction is not justified by experiment (Table 1). In other words, *two* parameters are not enough to generalize the behavior of real gases. Modern EOS are based on a modified expression of the Principle: gases that have the same values of the reduced properties and the same value of a *third* parameter (such as the acentric factor, the critical compressibility, the radius of gyration, etc.) behave in the same manner. It is of interest to note that the Principle of Corresponding States served as a guide during the experiments that ultimately led to the liquefaction of hydrogen by J. Dewar in 1898 and of helium by H. Kamerlingh-Onnes in 1908 (1913 Nobel Prize for his low-temperature studies and his production of liquid helium).

The van der Waals equation is a cubic equation in the volume. If we plot it in the *P–V* plane we get the graph shown in Figure 3 and learn the following:

(a) For a given pressure and for all isotherms $T > T_c$, only one root is real while for $T < T_c$ the three roots V_1, V_2, and V_3, are real.

(b) The van der Waals equation is analytical in nature, and at temperatures below the critical it predicts a continuous passage from one phase to the other, contrary to experience. (Recall the provocative title of van der Waals' Ph.D. thesis!) Root V_1 represents the saturated liquid, and root V_3 the saturated dry vapor; for section A-2-B where the intermediate root V_2 lies, we have $\left(\frac{\partial P}{\partial V}\right)_T > 0$, which contradicts the experimental evidence with stable systems. The two-phase isotherm can be used to illustrate the so-called *Maxwell Principle* (true for every EOS that shows the behavior illustrated in Figure 1). Let us assume a cyclic machine that operates according to the path 1-A-2-B-3-1. In the forward stage it goes 1-A-2-B-3 and in the return stage it goes 3-2-1. Applying the First Law to a closed system, neglecting kinetic and potential effects, we have

$$\sum Q - \sum W = \Delta U = 0$$

$$\sum Q = \sum W$$

consonant for cyclic processes of similar nature. But in our particular situation ΣQ, the *total* thermal effect, is zero because in the forward stage we add heat as heat of vaporization and in the return stage we withdraw it as heat of condensation. Hence

$$\sum W = 0$$

Since

$$\left| W_{1AB3} \int_1^3 PdV \right| \qquad (26)$$

and

$$\left| W_{123} = P\left(V_3 - V_1\right) \right| \qquad (27)$$

to have $\Sigma W = 0$ requires that areas 1-A-2 and 2-B-3 be equal (Maxwell's Principle).

What is the practical implication of Maxwell's principle? *Any* EOS that presents the van der Waals loop can be used to predict the saturation dome (where both the liquid and vapor phases are present) as follows:

1) Assume $T < T_c$,
2) Draw the pertinent isotherm on the *P*-*V* plane,
3) Find the value of the pressure (graphically or otherwise) that splits the 1-A-2-B-3 curve into equal parts,
4) Repeat for a new value of $T < T_c$.

Each step (b) determines the values of the specific volume of the saturated liquid and saturated vapor at the pertinent pressure.

The Maxwell principle illustrates another brilliant contribution of van der Waals: the same EOS can be used to represent *both* the gas and liquid state.

A very interesting feature of the equation is that a Carnot cycle operating with a van der Waals gas has exactly the *same thermal efficiency* (expression) as the cycle operating with the ideal gas, as will be shown now. Let us assume a Carnot cycle that operates between the temperature levels T_H and T_C, where the expansion stage occurs between states 1 and 2, and the compression stage between states 3 and 4. Stages 2–3 and 4–1 are reversible and adiabatic (isentropic). Integration of equation (19) for any reversible process between states *i* and *f* yields

$$\Delta S = \int_{T_i}^{T_f} C_V dT + R\ln\frac{V_f - b}{V_i - b} \tag{28}$$

Assuming that the heat capacity C_V^* of the ideal gas varies with the temperature, as follows

$$C_V^* = a + bT + cT^2 + \ldots \tag{29}$$

yields, after some algebra

$$\Delta S = a\ln\left[\left(\frac{T_f}{T_i}\right)\left(\frac{V_f - b}{V_i - b}\right)^{R/a}\right] + \ln\left(T_f - T_i\right) + \frac{c}{2}\left(T_f^2 - T_i^2\right) + \ldots \tag{30}$$

For an isentropic process we get, after some algebra

$$\begin{gathered} T_f\left(V_f - b\right)^{R/a}\exp\left(\frac{b}{a}T_f\right)\exp\left(\frac{c}{2a}T_f\right) = \\ T_i\left(V_i - b\right)^{R/a}\exp\left(\frac{b}{a}T_i\right)\exp\left(\frac{c}{2a}T_i\right) \end{gathered} \tag{31}$$

$$T\left(V - b\right)^{R/a} F\left(T\right) = \text{constant} \tag{32}$$

where *F(T)* is a known function of the temperature. Consider now the isentropic processes 2–3 and 4–1 that take place between the two heat sources of Carnot's cycle, T_H, and T_C. Applying equation (32) to each of them we get

$$T_H\left(V_2 - b\right)^{R/a} F\left(T_H\right) = T_C\left(V_3 - b\right)^{R/a} F\left(T_C\right) \tag{33}$$

$$T_H\left(V_1 - b\right)^{R/a} F\left(T_H\right) = T_C\left(V_4 - b\right)^{R/a} F\left(T_C\right) \tag{34}$$

Dividing equations (33) and (34) yields

$$\frac{V_1 - b}{V_2 - b} = \frac{V_4 - b}{V_3 - b} \tag{35}$$

Now, let us apply the First Law to stage 1–2, neglecting kinetic and potential energy effects and assuming that the only work interactions are compression and expansion. We have

$$Q_H = \int_{V_1}^{V_2} PdV + \Delta U \tag{36}$$

where Q_H is the heat absorbed. Using equations (10) and (22). and integrating and rearranging, yields

$$Q_H = RT_H\ln\left(\frac{V_2 - b}{V_1 - b}\right) + \left(\frac{a}{V_2} - \frac{a}{V_1}\right) - \left(\frac{a}{V_2} - \frac{a}{V_1}\right) \tag{37}$$

$$Q_H = RT_H\ln\left(\frac{V_2 - b}{V_1 - b}\right) \tag{38}$$

A similar relation can be written for Q_C, the heat rejected in stage 3–4,

$$\left|Q_C\right| = RT_C\ln\left(\frac{V_3 - b}{V_4 - b}\right) \tag{39}$$

The thermal efficiency of the cycle (van der Waals) is

$$h = 1 - \frac{\left|Q_C\right|}{Q_H} = 1 - \frac{T_C}{T_H} \tag{40}$$

exactly the same as that for an ideal gas operating between the same temperatures. The observant reader will say (and be correct) that this is not a surprising result because the efficiency of a reversible Carnot cycle is independent of the structure of the engine and the material (gas) used for operating it.

Before closing the description of the van der Waals equation, we recall that for a gas mixture, the constants *a* and *b* must be calculated using the following *mixing rules*

$$a = \left(\sum y_i\sqrt{a_i}\right)^2 = \sum\sum y_i y_j\sqrt{a_i a_j} = \sum\sum y_i y_j a_{ij} \tag{41}$$

$$b = \sum y_i b_i \tag{42}$$

An adequate epilogue to the scientific work of van der Waals is the closing remarks of the Presentation Speech by the Rector General of National Antiquities, Professor 0. Montelius, President of the Royal Swedish Academy of

Sciences, on the occasion of presenting to van der Waals the 1910 Nobel Prize in Physics:

> "Professor van der Waals. The Royal Academy of Sciences has awarded you this year's Nobel Prize for Physics in recognition of your pioneering studies on the physical state of liquids and gases. Hamurabi's and Moses' laws are old and of great importance. The laws of Nature are older still and even more important. They apply not just to certain regions on this Earth, but to the whole world. However, they are difficult to interpret. You, Professor, have succeeded in deciphering a few paragraphs of these laws. You will now receive the Nobel Prize, the highest reward that our Academy can give you."

Conclusion

After Carnot, Clapeyron, and Clausius, van der Waals is probably the scientist who has had the most profound influence in the development of thermodynamics. His contributions to the study of phase behavior of pure compounds and their mixtures, in particular of gases, have set the basis for all modern theories on the subject.

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