

Ideal and Real Gases

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1 The ideal gas law

The ideal gas law can be derived from the two empirical gas laws, namely, Boyle's law,

$$pV = k_1, \text{ at constant } T, \quad (1)$$

and Charles' law,

$$V = k_2T, \text{ at constant } p, \quad (2)$$

where k_1 and k_2 are constants. From Eq. (1) and (2), we may assume that V is a function of p and T . Therefore,

$$dV(p, T) = \frac{\partial V}{\partial p} \bigg|_T dp + \frac{\partial V}{\partial T} \bigg|_p dT. \quad (3)$$

Substituting from above, we get $(\partial V / \partial p)|_T = -k_1 / p^2 = -V / p$ and $(\partial V / \partial T)|_p = k_2 = V / T$. Thus,

$$\begin{aligned} dV &= -\frac{V}{p} dP + \frac{V}{T} dT, \text{ or} \\ \frac{dV}{V} + \frac{dp}{p} &= \frac{dT}{T}. \end{aligned}$$

Integrating this equation, we get

$$\ln V + \ln p = \ln T + c \quad (4)$$

where c is the constant of integration. Assigning (quite arbitrarily) $e^c = R$, we get

$$\begin{aligned} \ln V + \ln p &= \ln T + \ln R, \text{ or} \\ pV &= RT. \end{aligned} \quad (5)$$

The constant R is, of course, the gas constant, whose value has been determined experimentally.

2 Virial equations

The compressibility factor of a gas Z is defined as $Z = pV/(nRT) = pV_m/(RT)$, where the subscript on V indicates that this is a molar quantity. Obviously, for an ideal gas, $Z = 1$ always. For real gases, additional corrections have to be introduced. Virial equations are expressions in which such corrections can be systematically incorporated. For example,

$$Z = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \dots \quad (6)$$

We may substitute for V_m in terms of the ideal gas law and get an expression in terms of pressure, which is often more convenient to use:

$$\begin{aligned} Z &= 1 + \frac{B}{RT}p + \frac{C}{(RT)^2}p^2 + \dots \\ &\quad 1 + B'(T)p + C'(T)p^2 + \dots \end{aligned} \quad (7)$$

The constants B , C' etc., have to be found experimentally for each gas.

3 The van der Waals Equation

The equation of state proposed by van der Waals is the simplest two parameter equation that comes close to describing the behavior of real gases. The equation is written as (for one mole)

$$(p + \frac{a}{V_m^2})(V_m - b) = RT \quad (8)$$

where a and b are empirical parameters. The constant b is an attempt to account for the fact that real gas molecules occupy a definite volume and, therefore, the actual volume available for the gas is less than the volume of the container. The constant a is a way of accounting for the attractive and repulsive forces between the molecules. The van der Waals equation can be manipulated to give a Virial equation as follows. From Eq. (8), we get

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}. \quad (9)$$

Multiplying both sides by $V_m/(RT)$, we get

$$Z = \frac{pV_m}{RT} = \frac{V_m}{V_m - b} - \frac{a}{RT} \frac{1}{V_m}. \quad (10)$$

The first term in this expression is $1/(1 - b/V_m) = (1 - b/V_m)^{-1}$ which can be expanded as

$$(1 - b/V_m)^{-1} = 1 + (b/V_m) + (b/V_m)^2 + \dots$$

using the binomial theorem. Substituting this expression back into Eq. (10), and collecting terms that have the same powers of V_m , we get

$$Z = 1 + b - \frac{a}{RT} \frac{1}{V_m} + \frac{a}{V_m} \frac{b}{V_m} + \dots \quad (11)$$

which is of the same form as Eq. (6).

Under conditions where the quadratic and higher powers of $1/V_m$ can be ignored, we get

$$Z \simeq 1 + b - \frac{a}{RT} \frac{1}{V_m}.$$

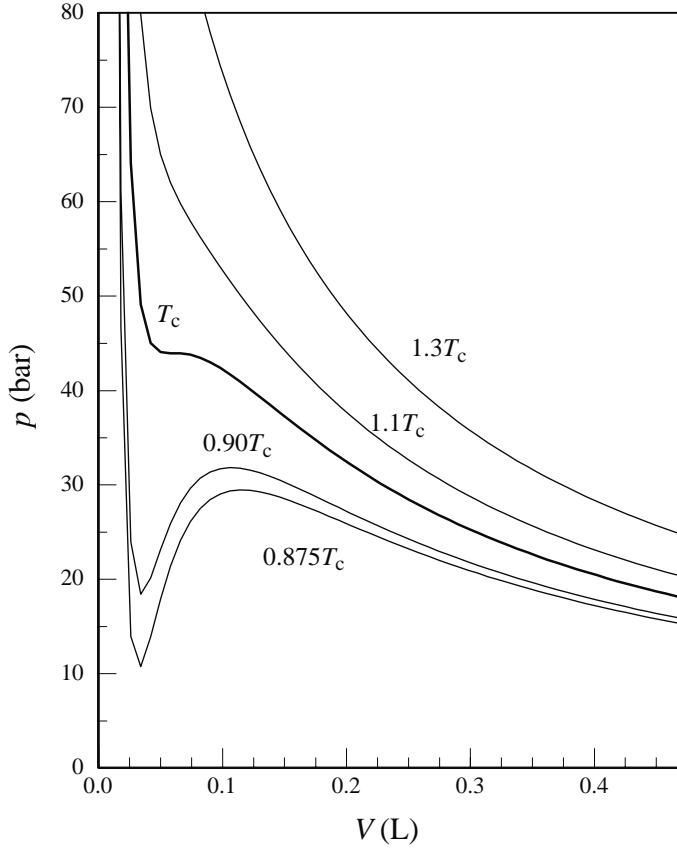
If the temperature is such that the second term vanishes, the compressibility factor will be unity, as in the case of an ideal gas. The temperature at which the second term vanishes is called the *Boyle temperature*, commonly denoted as T_B . For the van der Waals gas,

$$T_B = \frac{a}{bR}. \quad (12)$$

4 Critical point behavior of gases

The figure below shows a few isotherms of a real gas as predicted by the van der Waals equation. The qualitative difference between the isotherms with $T > T_c$ and those with $T < T_c$ is immediately obvious. The temperature T_c which acts as a boundary for the two types of behavior is called the *critical temperature* of the gas.

Critical point behavior of a real gas



Below the critical temperature, as the gas is compressed at constant temperature, it turns into a liquid at a certain pressure. Since the van der Waals equation is not able to model this behavior, the predicted pressure appears to drop as the volume is decreased. Above the critical temperature, a gas cannot be turned into a liquid by applying pressure. The *critical point* is a point on the isotherm corresponding to $T = T_c$ at which the slope and the curvature of the isotherm are zero. The volume and pressure corresponding to this point are called the *critical volume* (V_c) and *critical pressure* (p_c). From Eq. (9), we get

$$\tilde{A} \frac{\frac{\mu}{\partial p} \frac{\partial p}{\partial V}}{\left. \frac{\partial V}{\partial p} \right|_{T_c}} = -\frac{RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = 0, \quad (13)$$

$$\tilde{A} \frac{\partial^2 p}{\partial V^2} \Big|_{T_c} = \frac{2RT_c}{(V_c - b)^3} - \frac{6a}{V_c^4} = 0. \quad (14)$$

From Eq. (13) and (13), we get

$$\frac{RT_c}{(V_c - b)^2} = \frac{2a}{V_c^3}, \quad (15)$$

$$\frac{2RT_c}{(V_c - b)^3} = \frac{6a}{V_c^4}. \quad (16)$$

Dividing Eq. (16) by Eq. (15), we get

$$\begin{aligned} \frac{V_c - b}{2} &= \frac{V_c}{3}, \text{ or} \\ b &= \frac{1}{3}V_c. \end{aligned} \quad (17)$$

Substituting for b in Eq. (15), we get

$$\begin{aligned} \frac{RT_c}{(2V_c/3)^2} &= \frac{2a}{V_c^3}, \text{ or} \\ a &= \frac{9}{8}RT_cV_c. \end{aligned} \quad (18)$$

At the critical point, the van der Waals equation is

$$p_c = \frac{RT_c}{V_c - b} - \frac{a}{V_c^2}.$$

Substituting for a and b in terms of critical variables, we get

$$p_c = \frac{3RT_c}{2V_c} - \frac{9}{8} \frac{RT_c}{V_c},$$

from which we immediately get

$$\begin{aligned} Z_c &= \frac{p_c V_c}{RT_c} = \frac{3}{8}, \text{ and} \\ R &= \frac{8}{3} \frac{p_c V_c}{T_c}. \end{aligned} \quad (19)$$

Therefore, at the critical point, the behavior predicted by the van der Waals equation is quite far from that given by the ideal gas law, which predicts $Z = 1$ always. Substituting for R in the expression for a , we also get

$$a = \frac{9}{8} \frac{8}{3} \frac{p_c V_c}{T_c} T_c V_c = 3p_c V_c^2. \quad (20)$$

Using this expression for a and that for b (see above), we can write the van der Waals equation in terms of the critical variables as

$$p + \frac{3p_c V_c^2}{V^2} \left(V - \frac{1}{3}V_c \right)^3 = \frac{8}{3} \frac{p_c V_c}{T_c} T. \quad (21)$$

We now introduce a set of *reduced* (i.e., dimensionless) variables, as $p_r = p/p_c$, $V_r = V/V_c$ and $T_r = T/T_c$. Substituting $p = p_r p_c$, etc., in Eq. (21), we get

$$p_r p_c + \frac{3p_c}{V_r^2} \left(V_r V_c - \frac{1}{3}V_c \right)^3 = \frac{8}{3} p_c V_c T_r.$$

The factor $p_c V_c$ can be factored out from both sides of this equation and cancelled, to yield

$$p_r + \frac{3}{V_r^2} \left(V_r - \frac{1}{3} \right)^3 = \frac{8}{3} T_r. \quad (22)$$

This is called a *reduced equation of state*, and is a completely parameter equation that describes the behavior of real gases.

We may also express the compressibility factor in terms of the reduced and critical variables as

$$Z = \frac{p_r V_r}{T_r} \left(\frac{p_c V_c}{R T_c} \right)^{\frac{1}{\gamma}}.$$

Since the quantity within parentheses is almost the same for all gases, we can conclude that *if two gases have the same reduced pressure and temperature, they will have the same reduced volume*. This is called the “Law of corresponding states.”