

# Interpretation of the Second Virial Coefficient

Jaime Wisniak

Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel; wisniak@bgumail.bgu.ac.il

The calculation of the thermodynamic properties of a gas requires some knowledge of its  $P$ - $V$ - $T$  behavior. The  $P$ - $V$ - $T$  surface for a real gas differs markedly from that of an ideal gas and cannot be described by the simple equation of state (EOS)  $Pv = RT$  for a molar sample. A three-dimensional surface of the  $P$ - $V$ - $T$  behavior is not a convenient observation tool for comparing the behavior of a real gas with that of an ideal gas; it is better to use a projection in the  $P$ - $V$  plane, as illustrated in Figure 1 for carbon dioxide (*1*). Inspection of this figure points to the following facts.

1. As the pressure of the gas is reduced at constant temperature, ideal behavior is observed and  $Pv \rightarrow RT$ . Nevertheless, if we define the residual volume  $\alpha$  as the difference between the volume of the ideal gas ( $RT/P$ ) and the molar volume of the real gas ( $v$ )

$$\alpha = \frac{RT}{P} - v \quad (1)$$

we see that  $\alpha$  does not necessarily go to zero when the pressure goes to zero. This unexpected result may be understood better by writing eq 1 in the form

$$\alpha P = RT - Pv \quad (2)$$

When  $P \rightarrow 0$  the left side of eq 2 will always go to zero, but the right side of eq 2 may become zero without the condition that  $\alpha = 0$ . We will return to this important point later.

2. As the temperature of the gas is increased at constant pressure, ideal gas behavior is approached at high temperatures.
3. A critical point, C, exists, identified by a nil value of the first and second derivatives of the pressure with respect to volume at the critical isotherm:

$$\left(\frac{\partial P}{\partial v}\right)_{T_c} = 0; \quad \left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c} = 0 \quad (3)$$

4. The isobars and isotherms are discontinuous in passing from the gas to the liquid state at values of  $P$  and  $T$  below the critical values. The isobars above the critical pressure ( $BB$ , for example) and the isotherms above the critical temperature pass continuously through a region of homogeneous fluid.

Additional important evidence about the behavior of a real gas may be gained by drawing its isothermal behavior in a different projection plane,  $Pv$  vs  $P$ . Experimental evidence indicates that for every real gas the isotherms have the shape illustrated in Figure 2 for carbon dioxide (*1*). The departure from ideal gas behavior is obvious, since for an ideal gas all the isotherms would be horizontal at a value  $RT$ . Figure 2 shows that if the temperature is low enough—say,  $T_1 = 460.15$  K in the figure—the value of  $Pv$  will first *decrease* with increasing pressure until it reaches a minimum value at A. A further increase of the pressure will cause an *increase* in the value of  $Pv$ . If the temperature is high enough (say,  $T_2 = 773.15$  K in the figure), the behavior of  $Pv$  with  $P$  will be substantially different: an increase in  $P$  will always result in an increase in the value of  $Pv$ . These results may be interpreted by looking

at the sign of the slope of the isotherm at  $P = 0$ : at temperature  $T_1$  the initial slope of the curve will be negative, whereas at temperature  $T_2$  the initial slope will be positive. Since the temperature can be changed continuously between  $T_1$  and  $T_2$ , an immediate consequence is that there must be a temperature

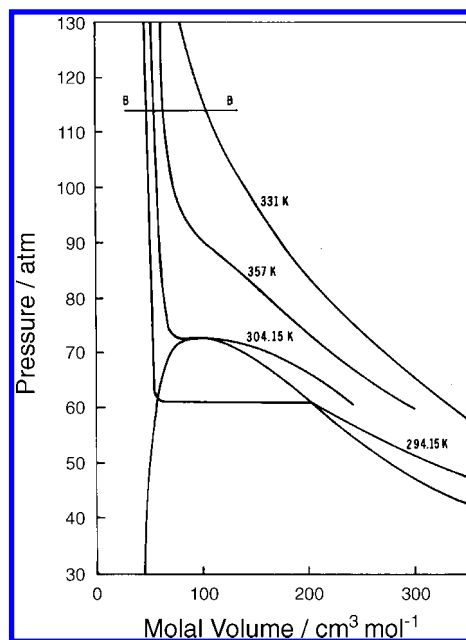


Figure 1. Behavior of a real gas in the plane  $P$ - $V$ .

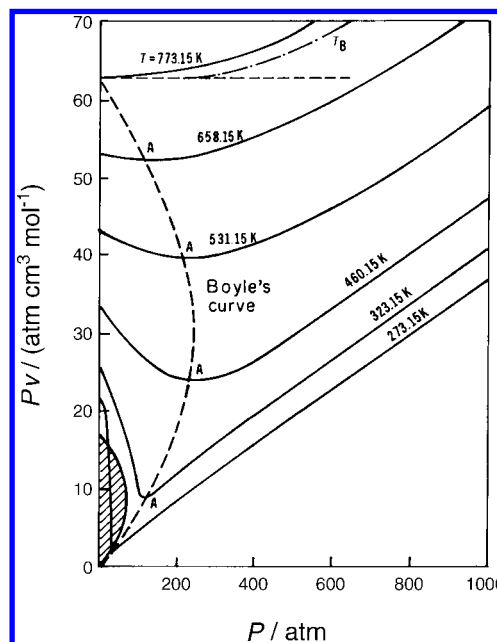


Figure 2. Behavior of a real gas in the plane  $Pv$ - $P$ .

( $T_B$ ) for which the initial slope is exactly zero. This particular temperature is called the *temperature of Boyle* of the gas and its mathematical definition is (2)

$$\lim_{P \rightarrow 0} \left( \frac{\partial P_V}{\partial P} \right)_{T_B} = 0 \quad (4)$$

It is important to notice that the limiting condition  $P \rightarrow 0$  is necessary to avoid having to calculate the minimum value present at  $P > 0$  for every isotherm under  $T_B$ . An additional observation is that the pronounced minima in all isotherms below the Boyle temperature fall in a smooth curve (AA) usually known as Boyle's curve. We can now distinguish between isotherms  $T_1$  and  $T_2$  by saying that below the temperature of Boyle an isotherm will always present a minimum value of its initial slope, and above the temperature of Boyle, the initial slope of the isotherm will always be positive.

Many equations of state have been proposed to describe the behavior of a real gas, some of them having as many as 30 constants. None of the EOS available today is capable of describing the behavior of the gas in the full range of variables. One important equation is the virial equation of state because it has a solid theoretical basis and a variable number of adjustable parameters that give it, in principle, a desirable flexibility for adjusting the experimental data. The virial equation of state can be derived from the principles of statistical mechanics to relate the  $P$ - $V$ - $T$  behavior of a gas to the forces between molecules. The standard form of this EOS expresses the compressibility factor  $z$  as an infinite series of the reciprocal of the specific volume (2, 3)

$$z = \frac{P_V}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots \quad (5)$$

where  $B$ ,  $C$ ,  $D$ , ... are the second, third, fourth, etc. virial coefficients. The virial coefficients have the important property that for a pure gas they are functions of the temperature alone, whereas for mixtures of gases they are functions of both temperature *and* composition. Figure 3 illustrates the typical behavior of the second virial coefficient with temperature, using the data for carbon dioxide (1). It is seen that at low temperatures  $B$  is very negative but above a certain temperature

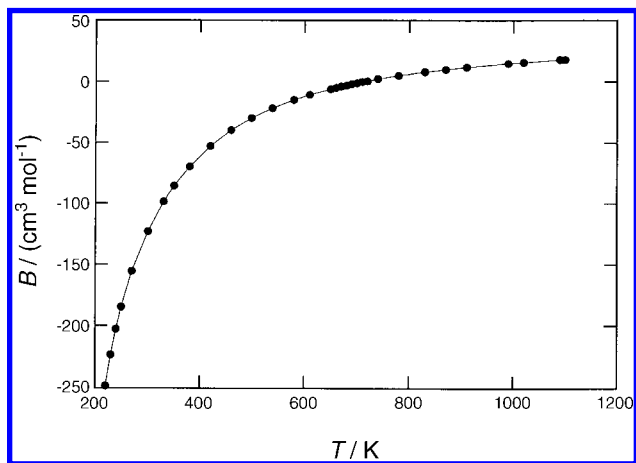


Figure 3. Typical variation of the second virial coefficient with temperature.

it becomes positive and less dependent on temperature. From the microscopic viewpoint, the virial coefficients account for a particular order of the collisions taking place between molecules. The second coefficient depends on an accounting of the collisions occurring in clusters of two molecules, the third coefficient depends on ternary collisions, and so on. If no interactions are present the virial equation reduces to the equation of state for the ideal gas. It can also be surmised that when the second virial coefficient is negative, the third and succeeding virial coefficients must be positive if the curve is to change its slope from negative to positive at sufficiently high pressures (curve  $T_1$  in Fig. 2). The consequence of this observation is that the number of terms that must be included in the virial EOS depends on the region under study. The virial EOS can also be represented by an infinite series of the pressure, as follows (2, 3):

$$z = \frac{P_V}{RT} = 1 + \tilde{B}P + \tilde{C}P^2 + \tilde{D}P^3 + \dots \quad (6)$$

where again the coefficients  $\tilde{B}$ ,  $\tilde{C}$ ,  $\tilde{D}$ , ... are functions of the temperature alone. Equations 5 and 6 are known as the volume and pressure expansion of the virial equation. Since they represent different mathematical forms of the same physical parameter,  $z$ , their coefficients must be related. For example, it can be shown that the second and third virial coefficients are connected as follows (2):

$$B = \tilde{B}RT \quad (7)$$

$$\tilde{C} = \frac{C - B^2}{RT} \quad (8)$$

The virial equation may be used to obtain a simple estimate of the temperature of Boyle, as follows. Differentiating eq 6 with respect to the pressure, at constant temperature (remember that the virial coefficients are functions of the temperature alone), yields

$$\frac{1}{RT} \left( \frac{\partial P_V}{\partial P} \right)_T = \tilde{B} + 2\tilde{C}P + 3\tilde{D}P^2 + \dots \quad (9)$$

Taking the limit  $P \rightarrow 0$  yields

$$\lim_{P \rightarrow 0} \left( \frac{\partial P_V}{\partial P} \right)_T = \tilde{B}RT \quad (10)$$

and substituting eq 7 in eq 10 we obtain

$$\lim_{P \rightarrow 0} \left( \frac{\partial P_V}{\partial P} \right)_{T_T} = B \quad (11)$$

In other words, the second virial coefficient represents the slope of the curves shown in Figure 2, for low values of the pressure. As mentioned before, this slope may be negative or positive depending on the temperature level, results which overlap exactly the experimental evidence on the variation of  $B$  with temperature shown in Figure 3. We can now apply eq 11 to the particular case of the temperature of Boyle (eq 4) and get

$$\lim_{P \rightarrow 0} \left( \frac{\partial P_V}{\partial P} \right)_{T_B} = B(T_B) = 0 \quad (12)$$

According to eq 12 the Boyle temperature may be identified as the temperature at which the second virial coefficient becomes equal to zero. At the temperature of Boyle the  $Pv$  product differs from  $RT$  only by the squared and higher terms in  $P$ , and hence the ideal gas behavior will be satisfied with greater accuracy over an increased interval of pressure starting with  $P = 0$  than is otherwise the case.

We have shown that at sufficiently low temperatures the second virial coefficient is negative. Qualitatively, this may be attributed to the preponderance of long-range attractive forces. As temperature increases, molecular collisions become more energetic, increasing the contribution of short-range repulsive forces and causing  $B$  to become less negative. At the Boyle temperature attractive and repulsive forces between pairs of molecules are approximately balanced and  $B$  becomes zero. For higher temperatures, repulsive forces dominate and  $B$  is positive, increasing slowly with temperature. Experimental evidence shows that when two molecules are sufficiently close to each other, there is a net repulsive force between them, which increases very rapidly as the distance between the molecular centers decreases further. If the distance between the molecular centers is increased gradually, the repulsive force rapidly decreases to zero, then changes sign and becomes an attractive force. The attractive force reaches a maximum and then falls asymptotically to zero as the distance between the molecular centers is increased further. From Figure 3 we see that at temperatures below the Boyle temperature ( $B < 0$ ) the second virial coefficient shows a very strong dependence on temperature; above the Boyle temperature ( $B > 0$ ), this dependence weakens substantially.

Vetere has proposed two simple empirical correlations for the Boyle temperature as a function of either the normal boiling point,  $T_b$ , or the critical temperature,  $T_c$  (4):

$$T_B = 110.0 + 2 T_b \quad (13)$$

for compounds having a boiling temperature below 120 K (such as hydrogen and helium) and

$$T_B = 110.0 + 2 T_c \quad (14)$$

for the other compounds. In eqs 13 and 14,  $T$  is always in kelvins. An important consequence of eq 14 is that for a given gas the temperature of Boyle is much larger than the critical temperature. This result can also be obtained by applying eq 4 to other analytical EOS to determine the value of  $T_B$ . For example, the van der Waals EOS yields

$$T_B = \frac{a}{RT}$$

and the Redlich-Kwong EOS

$$T_B = \left[ \frac{a}{RT} \right]^{1/1.5}$$

where  $a$  is the parameter of the particular EOS (5). Table 1 gives the experimental values of  $T_B$  and the critical temperature  $T_c$  for some common gases. It is interesting to note how little the reduced temperature of Boyle varies from one gas to another.

We can use the virial equation of state to find an interesting explanation for the residual volume. From eq 6 we have

$$v = \frac{RT}{P} + \tilde{B}RT + \tilde{C}RT^2 + \tilde{D}RT^3 + \dots \quad (15)$$

Replacing eq 7 in eq 15 and rearranging we get

$$\alpha = -B - \tilde{C}RT - \tilde{D}RT^2 - \dots \quad (16)$$

and at sufficiently low pressures

$$\lim_{P \rightarrow 0} \alpha = -B \quad (17)$$

Combination of eq 17 with Figure 2 shows that at low pressures the residual volume  $\alpha$  will, in general, have a value different from zero. The results of eqs 12 and 17 can be used to obtain an alternative explanation to the second virial coefficient. Consider, for example, the case where  $T < T_B$ . When  $P \rightarrow 0$  both the slope  $(\partial Pv / \partial P)_T$  and  $B$  will be negative, while  $\alpha$  will be positive. If  $\alpha > 0$ , then

$$\alpha = \frac{RT}{P} - v > 0$$

$$\frac{RT}{P} > v$$

That is, the real gas occupies less volume than the ideal one at the same conditions. At a microscopic level we say that the attractive forces are larger than the repulsive ones. An important additional observation is that at the temperature of Boyle and pressures sufficiently low to neglect the influence of higher virial coefficients, the real gas will show ideal behavior according to the EOS but not for other thermodynamic properties such as internal energy and enthalpy (see eq 21). Table 2 expresses the different possibilities for the above relations.

The temperature of Boyle is not the only single temperature at which a real gas may show ideal behavior for certain properties. For example, let us inquire how does pressure influence the enthalpy of a real gas, at constant temperature. In other words, we are interested in finding the value of  $(\partial h / \partial P)_T$

**Table 1. Critical Temperature and Boyle Temperature for Some Common Gases**

Substance	$T_c / K$	$T_B / K$	$T_B / T_c$
Ne	44.8	121.0	2.70
Ar	150.7	411.5	2.73
Kr	209.4	575.0	2.75
Xe	289.8	768.3	2.65
N <sub>2</sub>	126.0	327.0	2.59
O <sub>2</sub>	154.3	405.9	2.63
CO	133.0	345.0	2.59
CH <sub>4</sub>	190.3	491.0	2.58

NOTE: Data from refs 6 and 7.

**Table 2. Significance of Boyle's Temperature and the Second Virial Coefficient**

$\frac{T}{T_B}$	$\left( \frac{\partial Pv}{\partial P} \right)_T$	$B$	$\lim_{P \rightarrow 0} \alpha$	$\frac{(RT/P)}{v}$	Control Force
$< 1$	$< 0$	$< 0$	$> 0$	$> 1$	Attraction
$> 1$	$> 0$	$> 0$	$< 0$	$< 1$	Repulsion
1	0	0	0	1	None

where  $h$  is the molar enthalpy. From Maxwell's relations (2) we have

$$\left(\frac{\partial h}{\partial P}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_P \quad (18)$$

From eqs 7 and 15 we get

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P} + \frac{dB}{dT} + \frac{d\tilde{C}RT}{dT}P + \dots \quad (19)$$

and, finally, replacing eqs 7, 15, and 19 in eq 18 we get

$$\left(\frac{\partial h}{\partial P}\right)_T = \left(B - T\frac{dB}{dT}\right) + \left(\tilde{C}RT - T\frac{d\tilde{C}RT}{dT}\right)P + \dots \quad (20)$$

At low pressures we can neglect the second and succeeding terms on the right side of eq 20 to get

$$\left(\frac{\partial h}{\partial P}\right)_T = \left(B - T\frac{dB}{dT}\right) \quad (21)$$

The right side of eq 21 will become zero when

$$\frac{B}{T} = \frac{dB}{dT} \quad (22)$$

that is to say, at the temperature  $T_H$  at which the tangent to the curve  $B(T)$ , goes through the origin. The pertinent construction is shown in Figure 4 for carbon dioxide, using the upper part of the curve that appears in Figure 3.

The reader familiar with the Joule–Thomson effect (flow of a gas through a restriction) will recognize that eqs 20 and 21 represent the thermodynamic conditions for the inversion curve. The Joule–Thomson effect  $\mu$  is defined as (2)

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h = -\frac{1}{c_P} \left(\frac{\partial h}{\partial T}\right)_P \quad (23)$$

where  $c_P$  is the specific heat at constant pressure. The inversion curve is the geometric locus that separates the positive values of  $\mu$  from the negative ones; that is, it corresponds to the case  $\mu = 0$ . This locus is determined by setting eq 20 equal to zero. For low values of the pressure eq 21 indicates that the lower temperature limit of the inversion curve occurs exactly at  $T_H$ . The calculation of the Joule–Thomson effect at very low pressures has been discussed by Rasiel and Freeman (8), who have shown that the coefficient of a real gas is generally finite and nonzero in the limit of zero pressure. We can use the Joule–Thomson effect to understand the significance of temperature  $T_H$  as follows. Replacing the molar enthalpy in terms of the internal energy  $u$ ,  $h = u + Pv$ , we can write eq 23 as

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h = -\frac{1}{c_P} \left(\frac{\partial h}{\partial T}\right)_P = -\frac{\left(\frac{\partial u}{\partial P}\right)_T - \left(\frac{\partial Pv}{\partial P}\right)_T}{c_P} \quad (24)$$

The first term in eq 24 represents the change in internal energy per unit pressure drop and the second term is the excess work done on the gas on the upstream side of the restriction over the work lost by the gas on the downstream side. The pressure drop across the restriction increases the separation

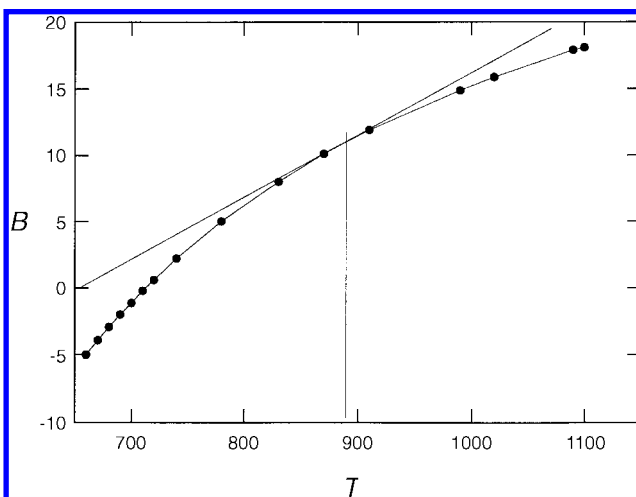


Figure 4. Solution of eq 22.

between the molecules, and the derivative  $-(\partial u/\partial P)_T$  is positive. The first term contributes a cooling effect, since the molecules moving in an attractive field increase their potential energy at the expense of their kinetic energy. The second term is the slope of the isotherms represented in Figure 2. For temperatures above the temperature of Boyle the slope will always be positive. For temperatures below  $T_B$  where  $Pv$  vs  $P$  goes through a minimum value, the sign of the slope will depend on whether the pressure is lower or higher than the pressure at the minimum. At low values of  $P$ ,  $-(\partial Pv/\partial P)_T$  will be positive and contribute an additional cooling effect. When the pressure rises beyond the minimum point,  $-(\partial Pv/\partial P)_T$  will become negative and eventually will be large enough to cancel the value of  $-(\partial u/\partial P)_T$ , causing  $\mu$  to become zero.

Simultaneous inspection of eqs 17 and 21 will help to bring home more clearly the meaning and physical significance of the two singular values of the temperature,  $T_B$  and  $T_H$ .

1. At the temperature of Boyle and sufficiently low pressures, the behavior of the gas is described by the equation  $Pv = RT$ . From Figure 3 we see that although at this temperature the second virial coefficient is nil, it is strongly dependent on temperature ( $dB/dT \neq 0$ ). Thus, according to eq 20, the enthalpy of the gas is dependent on both temperature and pressure, as expected from a real gas. The internal energy  $u$  will also be a function of the pressure and the temperature. From this we learn that behavior according to  $Pv = RT$  is a necessary but not sufficient condition for a gas to be ideal.
2. At temperature  $T_H$  and low pressures, eq 21 shows that the enthalpy of the gas is independent of pressure, as for an ideal gas, but the gas exhibits real behavior since  $B \neq 0$  (Fig. 3). Although the enthalpy is not a function of pressure, the internal energy  $u$  is. Again, the fact that under certain conditions the enthalpy of gas is a function of the temperature alone does not imply that under those conditions the behavior of the gas is ideal.

## Literature Cited

1. IUPAC. *International Thermodynamic Tables of the Fluid State Carbon Dioxide*, Angus, S.; Armstrong, B.; de Reuck, K. M., Eds.; Pergamon: Oxford, 1976.

2. Kestin, J. *A Course in Thermodynamics*, Vol. II; Blaisdell: Waltham, MA, 1968.
3. Kamerlingh Onnes, H. *Commun. Phys. Labs. Leiden* **1901**, Nos. 71, 74.
4. Vetere, A. *Chem. Eng. Sci.* **1988**, 43, 3119.
5. Walas, S. M. *Phase Equilibria in Chemical Engineering*, Butterworth: Boston, 1985.
6. Guggenheim, E. A. *Thermodynamics. An Advanced Treatment for Chemists and Physicists*, North-Holland: Amsterdam, 1967.
7. IUPAC. *Experimental Thermodynamics, Vol. II: Experimental Thermodynamics of Non-Reacting Fluids*, Le Neindre, B.; Vodar, B., Eds.; Butterworths: London, 1975.
8. Rasiel, Y.; Freeman, W. A. *J. Chem. Educ.* **1969**, 46, 310.