

1939

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### Recommended Citation

Price, E. O. (1939) "The Second Virial Coefficient as a Measure of Gas Imperfection," *Proceedings of the Iowa Academy of Science*: Vol. 46: No. 1, Article 25.

Available at: <https://scholarworks.uni.edu/pias/vol46/iss1/25>

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## THE SECOND VIRIAL COEFFICIENT AS A MEASURE OF GAS IMPERFECTION

E. O. PRICE

The combined laws of Boyle and of Gay-Lussac give the familiar formula  $pV = nRT$  for the equation of state of any gas. No single gas, however, obeys this law exactly under all conditions. The classical experiment of Joule, moreover, seemed to show that the internal energy of a gas is independent of the volume, or  $\left(\frac{\delta U}{\delta V}\right)_\tau = 0$ . More exact measurements subsequently performed

by Joule and Thomsen established the fact that this conclusion is also inexact for all real gases, but that it is approached more closely the more a gas approaches the 'ideal state'. Deviations from these two laws are caused by the same phenomena, namely, the complexities of the force fields surrounding the molecules and other properties of the individual molecules composing the gas. It may be said that no real gas is ideal and that every gas approaches ideality as the pressure approaches zero or the volume approaches infinity.

The literature contains many equations attempting to define the state of any gas under any condition, the most famous of which is van der Waals' equation. Another equation of state often used at low temperature and at low pressure is that of Berthelot, which is

$$pV = RT \left[ 1 + \frac{9pT_c}{128p_c T} \left( 1 - \frac{6T_c^2}{T^2} \right) \right]$$

For representing observed data of state most workers have used a purely empirical equation in the form of power series of the type first used by Kamerlingh Onnes in 1910:

$pV = A + B/V + C/V^2 + D/V^4 + E/V^6 + F/V^8 + \dots$   
 or  $pV = A_p + B_p p + C_p p^2 + D_p p^4 + \dots$ ,  
 where the coefficients  $A, B, C, \dots$  are called the first, second, third,  $\dots$  virial coefficients.

A common way to examine experimental  $p$ - $v$ - $T$  data is to graph the value of  $pV$  against  $p$ , keeping the temperature constant. The first slide will show two of these isotherms for methane, one at  $0^\circ \text{C}$ . and the other at  $200^\circ$ . These data were taken from the

work of Kvalnes and Gaddy, published in the *Journal of the American Chemical Society*, Vol. 53, page 394.

It will be seen that all of the isotherms for temperatures below 200° drop in an approximately straight line below the line for the perfect gas until a minimum is reached, and then the isothermal steadily rises to points above the line for the ideal gas.

The author under the direction of Prof. H. L. Johnston of the Ohio State University determined the data of state for nitrogen at the temperature of liquid air to above room temperature and at pressures of one atmosphere or less using a constant-volume gas thermometer. In this region it is possible to use the modified relation  $pv = RT + Bp$  as an empirical equation of state. Here B is called 'the second virial coefficient' and is valuable because it is a measure of gas imperfection. On the graph it is the slope of the isothermal at low pressures. It is interesting to compare the values of B with the calculated values of B from Berthelot's Equation. Here

$$B = \frac{9RT_c}{128p_c} \left( 1 - \frac{6T_c^2}{T^2} \right)$$

The second slide shows the values of the second virial coefficient of nitrogen plotted against absolute temperature. Each circle containing a cross is a value obtained by Cath and Onnes at the lower temperatures or by Holborn and Otto at the higher temperatures. All other circles give the values obtained in this experimental work. A smoothed curve was drawn through these points and an empirical equation fitted to the curve. This curve is best defined by the equation

$$B = 35.5 - 6000/T - \frac{1.651 \times 10^6}{T^2} + \frac{6.5 \times 10^9}{T^4} - \frac{2.5 \times 10^{13}}{T^6}$$

The dotted-line curve gives B calculated from Berthelot's Equation.

Examination of Berthelot's Equation shows that B against  $1/T^2$  should give a straight line. This was tried for the experimental data, and it was found that there was a slight deviation from a straight line, thereby explaining the disagreement with Berthelot's Equation on the B vs. T graph. The term in  $1/T^2$  is therefore the most important term in the empirical equation. This was computed first by a graphical method, and the other terms were adjusted to care for the deviation of B from the Berthelot values.

The third slide gives a summary of the determinations of the second virial coefficient of nitrogen made by Cath and Onnes and by Holborn and Otto. It also gives the result of the calculation of B from the empirical equation and from Berthelot's Equation. It

can be seen that  $B$  is negative up to a temperature of about  $320^\circ$ , the Boyle temperature for nitrogen. Above the Boyle temperature  $B$  is positive.

The nature of the curve for  $B$  can be explained by the fact that the intermolecular forces are such that there is attraction which increases as the molecules approach each other, reaches a maximum, and then quickly changes into a repulsion.

The van der Waals energy yielding attractions at greater distances may be given by the empirical  $-\mu r^{-t}$ . This was first used by Keesom. Fowler has shown that the nature of the van der Waals forces may be adequately represented by letting  $t = 5$ . The 'overlap' energy can be given by the simple empirical  $\lambda r^{-8}$ . For purposes of calculation, then, we may use the function

$$E(r) = -\mu r^{-5} + \lambda r^{-8}$$

to represent the intermolecular energy. This calculation has not yet been completed on the basis of the known values of the second virial coefficient of nitrogen.

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