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The Volumetric and Thermodynamic Properties of Fluids. III. Empirical Equation for the Second Virial Coefficient[1]

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RECEIVED DECEMBER 22, 1956

An equation has been developed to represent the second virial coefficient of a normal fluid: $BP_c/RT_c = (0.1445 + 0.073\omega) - (0.330 - 0.46\omega)T_r^{-1} - (0.1385 + 0.50\omega)T_r^{-2} - (0.0121 + 0.097\omega)T_r^{-3} - 0.0073\omega T_r^{-8}$ where ω is the acentric factor (defined by $\omega = -\log (P/P_0)_{sat} - 1.000$ at $T_r = 0.7$) which was discussed in an earlier paper. This equation not only fits the volumetric data with considerable accuracy but its second derivative also yields agreement with measured values of the pressure derivative of the gas heat capacity.

In 1907 Berthelot[2] proposed a simple reduced equation for the second virial coefficient which has been of great value in correcting the properties of real gases at low pressures to the ideal gas state. We know, however, that real gases do not follow accurately the principle of corresponding states, hence any such equation is of limited accuracy. In the earlier papers of this series[3] we have shown that the introduction of the acentric factor as an additional parameter increases the accuracy of possible correlation by about one order of magnitude.

In this paper we present an empirical equation for the second virial coefficient in reduced form which includes the acentric factor dependence.

Basic Data.—In addition to the second virial coefficient values based on volumetric measurements,[4] we calculated the volume of the saturated vapor from vapor pressure, heat of vaporization and liquid volume data in several cases.[5]

We also used the information on the change with pressure of the gas heat capacity.[6] If the second virial coefficient is B, thermodynamics yields the equation

$$\lim_{P \to 0} \left(\frac{\partial C_p}{\partial P}\right)_T = -T\frac{\partial^2 B}{\partial T^2} \qquad (1)$$

Consequently, the pressure dependence of the heat capacity offers a very sensitive test of any equation for B.

(1) This research was part of the program of Research Project 50 of the American Petroleum Institute.

(2) D. Berthelot, *Trav. et Mém. Bur. Int. Poid et Mes.*, **13** (1907).

(3) K. S. Pitzer, D. Z. Lippmann, R. F. Curl, Jr., C. M. Huggins and D. E. Petersen, THIS JOURNAL, **77**, 3427, 3433 (1955).

(4) A, Kr, Xe: E. Whalley and W. G. Schneider, *J. Chem. Phys.*, **23**, 1644 (1955); N₂: values of Holborn and Otto given by T. Kihara, *Rev. Mod. Phys.*, **25**, 831 (1953); CO₂: K. E. MacCormack and W. G. Schneider, *J. Chem. Phys.*, **18**, 1269 (1950); n-heptane: J. O. Hirshfelder, *et al.*, *ibid.*, **10**, 201 (1942); benzene: P. G. Francis, M. L. McGlashan, S. D. Hamann and W. J. McManamey, *ibid.*, **20**, 1341 (1952).

(5) Kr: A. Michels, T. Wassenaar and Th. N. Zwietering, *Physica*, **18**, 63 (1952), K. Clusius, A. Kruis and F. Konneitz, *Ann. Physik*, **33**, 642 (1938); Xe: A. Michels and T. Wassenaar, *Physica*, **16**, 253 (1950); K. Clusius and L. Riccoboni, *Z. physik. Chem.*, **B38**, 81 (1937); hydrocarbons: F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, 1953; n-heptane: G. Thodos, *Ind. Eng. Chem.*, **42**, 1514 (1950); G. Waddington, S. Todd and H. Huffman, THIS JOURNAL, **69**, 22 (1947); benzene: D. W. Scott, G. Waddington, J. C. Smith and H. M. Huffman, *J. Chem. Phys.*, **15**, 565 (1947).

(6) n-Heptane: G. Waddington, S. Todd and H. Huffman, THIS JOURNAL, **69**, 22 (1947); C₆H₆: D. W. Scott, G. Waddington, J. C. Smith and H. M. Huffman, *J. Chem. Phys.*, **15**, 565 (1947); 2,2,3-trimethylbutane: G. Waddington, S. Todd and H. Huffman, THIS JOURNAL, **69**, 22 (1947); ethanethiol: J. P. McCullough *et al.*, *ibid.*, **74**, 2801 (1952).

Selection of the Equation.—Our earlier studies[3] indicated that an equation linear in the acentric factor was usually adequate and we find this to be the case for the second virial coefficient. We have then, in reduced dimensionless form

$$\frac{BP_c}{RT_c} = \frac{B^{(0)}P_c}{RT_c} + \omega\frac{B^{(1)}P_c}{RT_c}$$

where $B^{(0)}$ and $B^{(1)}$ are functions of the reduced temperature, and ω is the acentric factor. Although ω was defined as

$$\omega = -\log P_r - 1.000 \qquad (2)$$

where P_r is the reduced vapor pressure (P/P_c) at $T_r = 0.7$, it may be evaluated readily from any vapor pressure value well removed from the critical point by the use of Table VI of Paper II of this series.[3]

The simple fluids of zero acentric factor are the heavier inert gases A, Kr, Xe. We know their properties are quite well represented by a Lennard-Jones intermolecular potential. Consequently, we took the equation of Stockmayer and Beattie[7] as a point of departure. This was converted from the molecular potential constants to the macroscopic critical constants and then modified slightly to improve the fit at the lowest temperatures by the addition of a small T^{-3} term and other small adjustments. The resulting equation is

$$\frac{B^{(0)}P_c}{RT_c} = 0.1445 - \frac{0.330}{T_r} - \frac{0.1385}{T_r^2} - \frac{0.0121}{T_r^3} \qquad (3)$$

Figure 1 shows the reduced virial coefficient data for a number of substances together with calculated curves. The agreement of the curve for $\omega = 0$ with the points for A, Kr and Xe demonstrates the adequacy of equation 3.

It is impractical to show all of the data considered in the development of the equation for $B^{(1)}$. The resulting fit with the data for benzene and for n-heptane is shown on Fig. 1 for B and on Fig. 2 for the pressure derivative of the heat capacity. Similar agreement is obtained for other substances. The resulting equations are

$$B = B^{(0)} + \omega B^{(1)} \qquad (4)$$

$$\frac{B^{(1)}P_c}{RT_c} = 0.073 + \frac{0.46}{T_r} - \frac{0.50}{T_r^2} - \frac{0.097}{T_r^3} - \frac{0.0073}{T_r^8} \qquad (5)$$

The selection of a term in T_r^{-8} is, of course, somewhat arbitrary, but a very high power is required to fit the data at low temperatures.

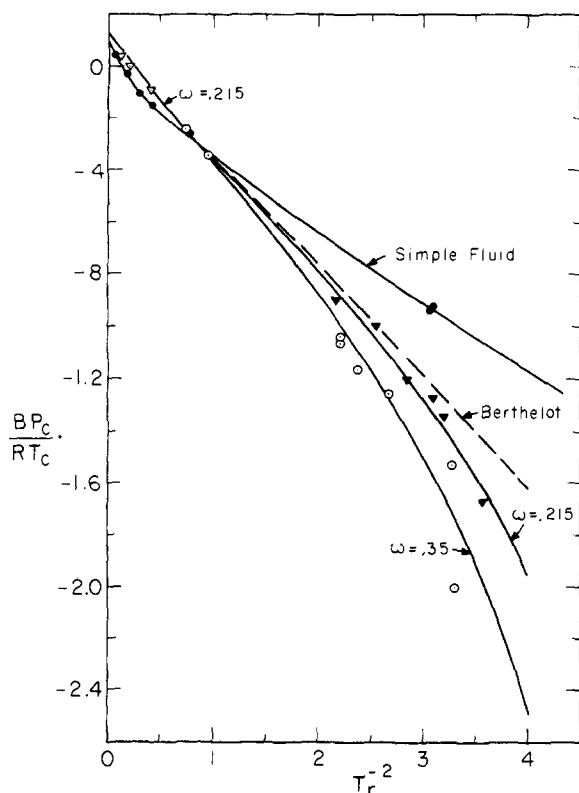(7) W. H. Stockmayer and J. A. Beattie, *J. Chem. Phys.*, **10**, 476 (1942).

Fig. 1.—A comparison of calculated and experimental values of the second virial coefficient. Solid circles are A, Kr or Xe points and the line through these points is that of equation 3. The open triangles are CO_2 and solid triangles are benzene points. These are to be compared with the line for $\omega = 0.215$. The open circles are points for n-heptane ($\omega = 0.35$). It is to be noted that the Berthelot equation yields excellent agreement for ω in the range 0.15 to 0.20.

The work leading to the selection of equation 5 indicated certain small changes in the previously published values of $z^{(1)}$, the term in the compressibility factor expression which is multiplied by ω. The revised values are given in Table I (the upper right-hand portion of each section is unchanged but included for convenience).

TABLE I

REVISED VALUES OF Z^1 FOR COMPRESSIBILITY FACTOR CALCULATION (SEE TABLE IV, PAPER II)

T_r	0.2	0.4	0.6	0.8	1.0
1.20	0.009	0.018	0.028	0.044	0.069
1.25	.011	.023	.036	.050	.069
1.3	.013	.027	.041	.055	.072
1.4	.016	.032	.049	.065	.082
1.5	.017	.035	.052	.070	.088
1.6	.018	.036	.054	.072	.090

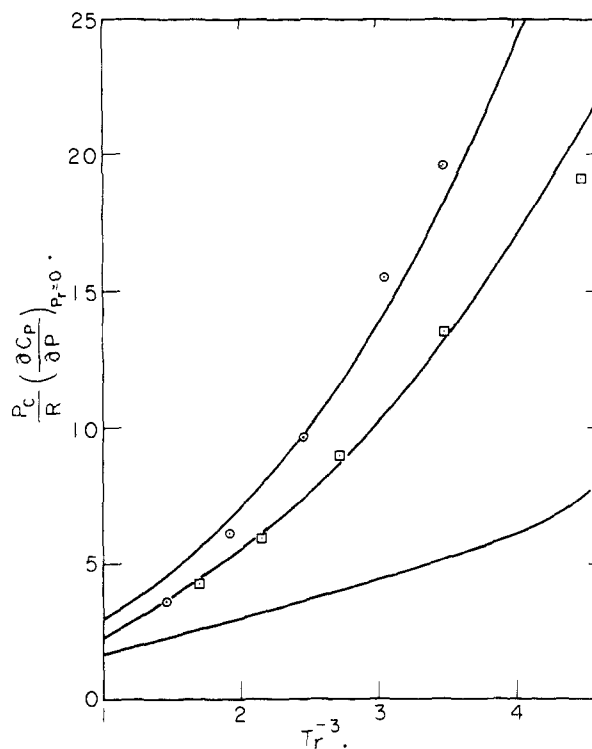| T_r	1	2	3	4	5	6	7	8	9
1.7	0.09	0.16	0.21	0.24	0.25	0.26	0.25	0.24	0.22
1.8	.09	.16	.21	.26	.29	.31	.32	.32	.30
1.9	.09	.16	.21	.26	.30	.35	.38	.40	.40
2.0	.08	.15	.21	.26	.30	.35	.40	.43	.45
2.5	.07	.13	.20	.25	.30	.35	.40	.45	.50
3.0	.06	.11	.17	.23	.28	.34	.38	.45	.50
3.5	.05	.09	.14	.19	.24	.28	.33	.38	.42
4.0	.04	.08	.12	.16	.20	.23	.27	.31	.35

Fig. 2.—A comparison of calculated and experimental values of the pressure derivative of the heat capacity. The circles and upper curve are for n-heptane ($\omega = 0.35$); the squares and intermediate curve are for benzene ($\omega = 0.215$). The bottom curve is for $\omega = 0$, but no experimental data are available for comparison.

Discussion.—This equation should be valuable for the estimation of gas imperfection corrections to various data on gases at low pressures. The substances which can be expected to conform are those forming normal liquids. Metals and hydrogen bonding substances must be excluded. The limitations are discussed in greater detail in Papers I and II.[3] The final equations for various properties are readily derived from thermodynamics. In these equations H^*, S^*, C_p^* refer to the properties of the hypothetical ideal gas at the same pressure as the real gas; f is the fugacity.

$$\frac{BP_c}{RT_c} = (0.1445 + 0.073\omega) - (0.330 - 0.46\omega)T_r^{-1} - (0.1385 + 0.50\omega)T_r^{-2} - (0.0121 + 0.097\omega)T_r^{-3} - 0.0073\omega T_r^{-8} \quad (6)$$

$$\log\left(\frac{f}{P}\right) = \left(\frac{P_r}{2.303}\right)[(0.1445 + 0.073\omega)T_r^{-1} - (0.330 - 0.46\omega)T_r^{-2} - (0.1385 + 0.50\omega)T_r^{-3} - (0.0121 + 0.097\omega)T_r^{-4} - 0.0073\omega T_r^{-9}] \quad (7)$$

$$\frac{H - H^*}{RT} = P_r[(0.1445 + 0.073\omega)T_r^{-1} - (0.660 - 0.92\omega)T_r^{-2} - (0.4155 + 1.50\omega)T_r^{-3} - (0.0484 + 0.388\omega)T_r^{-4} - 0.0657\omega T_r^{-9}] \quad (8)$$

$$\frac{S - S^*}{R} = P_r[-(0.330 - 0.46\omega)T_r^{-2} - (0.2770 + 1.00\omega)T_r^{-3} - (0.0363 + 0.29\omega)T_r^{-4} - 0.0584\omega T_r^{-9}] \quad (9)$$

$$\frac{C_p - C_p^*}{R} = P_r[(0.660 - 0.92\omega)T_r^{-2} + (0.831 + 3.0\omega)T_r^{-3} + (0.145 + 1.16\omega)T_r^{-4} + 0.526\omega T_r^{-9}] \quad (10)$$

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