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The Relation Between the Volume Virial Coefficients and the Pressure Virial Coefficients

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The virial equation of state is generally written in the form:

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \frac{E}{V^4} + \frac{F}{V^5} + \cdots$$

or if $c = \frac{1}{V}$

$$Z = \frac{PV}{RT} = f\left(\frac{1}{V}, T\right) = f(c, T) = 1 + Bc + Cc^2 + Dc^3 + Ec^4 + Fc^5 + \cdots$$

A similar expansion of Z as a power series in P is:

$$Z = \frac{PV}{RT} = \bar{f}(P, T) = 1 + B'P + C'P^2 + D'P^3 + E'P^4 + F'P^5 + \cdots$$

Several procedures[1–4] have been proposed to derive the relations between the coefficients of (2) and those of (1). It is the purpose of note to give by a rather simple procedure the expression for the relations between the coefficients.

By successive differentiation of Eq. (1) and (2) with respect c and P respectively at constant temperature and taking the limit the derivatives as c and P approaches zero one obtains:

$$\lim_{c\to 0} \frac{\partial f}{\partial c} = B, \quad \lim_{c\to 0} \frac{\partial^2 f}{\partial c^2} = 2C, \quad \lim_{c\to 0} \frac{\partial^3 f}{\partial c^3} = 6D, \quad \lim_{c\to 0} \frac{\partial^4 f}{\partial c^4} = 24E, \ldots$$

[1] The Properties of Gases and Liquids, R. Reid and T. Sherwood ed. McGraw Hill Book Co.

[2] L. F. Epstein, J. chem. Physics 20 (1952) 1981.

[3] L. F. Epstein, J. chem. Physics 21 (1953) 762.

[4] W. E. Putnam and J. E. Kilpatrick, J. chem. Physics 21 (1953) 951.

$$\lim_{P\to 0}\frac{\partial \bar f}{\partial P} = B', \lim_{P\to 0}\frac{\partial^2 \bar f}{\partial P^2} = 2C', \lim_{P\to 0}\frac{\partial^3 \bar f}{\partial P^3} = 6D', \lim_{P\to 0}\frac{\partial^4 \bar f}{\partial P^4} = 24E', \ldots \tag{3}$$

ne also has the relations:

$$\frac{\partial \bar f}{\partial P} = \frac{\partial f}{\partial c}\,\frac{\partial c}{\partial P} \tag{4}$$

$$\frac{\partial^2 \bar f}{\partial P^2} = \frac{\partial^2 f}{\partial c^2}\left(\frac{\partial c}{\partial P}\right)^2 + \frac{\partial f}{\partial c}\,\frac{\partial^2 c}{\partial P^2} \tag{5}$$

$$\frac{\partial^3 \bar f}{\partial P^3} = \frac{\partial^3 f}{\partial c^3}\left(\frac{\partial c}{\partial P}\right)^3 + 3\,\frac{\partial^2 f}{\partial c^2}\,\frac{\partial^2 c}{\partial P^2}\,\frac{\partial c}{\partial P} + \frac{\partial f}{\partial c}\,\frac{\partial^3 c}{\partial P^3} \tag{6}$$

$$\frac{\partial^4 \bar f}{\partial P^4} = \frac{\partial^4 f}{\partial c^4}\left(\frac{\partial c}{\partial P}\right)^4 + 6\,\frac{\partial^3 f}{\partial c^3}\,\frac{\partial^2 c}{\partial P^2}\left(\frac{\partial c}{\partial P}\right)^2 + 4\,\frac{\partial^2 f}{\partial c^2}\,\frac{\partial^3 c}{\partial P^3}\,\frac{\partial c}{\partial P} + 3\,\frac{\partial^2 f}{\partial c^2}\left(\frac{\partial^2 c}{\partial P^2}\right)^2 + \frac{\partial f}{\partial c}\,\frac{\partial^4 c}{\partial P^4}\,. \tag{7}$$

hus the relations between the coefficients $B, C, \ldots$ and $B', C', \ldots$ can obtained from equations (4—7), if the derivatives $\frac{\partial c}{\partial P}$, $\frac{\partial^2 c}{\partial P^2}$, $\frac{\partial^3 c}{\partial P^3}, \ldots$, for $P = 0$, are known.

Eq. (1) can be written:

$$\frac{P}{RT} = c + Bc^2 + Cc^3 + Dc^4 + Ec^5 + \cdots \tag{8}$$

$$\frac{1}{RT}\,\frac{\partial P}{\partial c} = 1 + 2Bc + 3Cc^2 + 4Dc^3 + 5Ec^4 + \cdots \tag{9}$$

nd

$$\frac{\partial c}{\partial P} = [RT(1 + 2Bc + 3Cc^2 + 4Dc^3 + 5Ec^4 + \cdots)]^{-1}. \tag{10}$$

y successive differentiation of Eq. (10) with respect to P and taking e limits of the derivatives as c approaches zero one obtains:

$$\lim_{c\to 0}\frac{\partial c}{\partial P} = \frac{1}{RT}, \quad \lim_{c\to 0}\frac{\partial^2 c}{\partial P^2} = -\frac{2B}{(RT)^2}$$

$$\lim_{c\to 0}\frac{\partial^3 c}{\partial P^3} = \frac{12B^2 - 6C}{(RT)^3}, \quad \lim_{c\to 0}\frac{\partial^4 c}{\partial P^4} = \frac{120BC - 120B^3 - 24D}{(RT)^4}\,. \tag{11}$$

Substitution of the last equations into Eqs. (4—7) yields:

$$B' = \frac{B}{RT}, \quad C' = \frac{C - B^2}{(RT)^2}, \quad D' = \frac{D - 3BC + 2B^3}{(RT)^3}$$

$$E' = \frac{10B^2C - 5B^4 - 4BD - 2C^2 + E}{(RT)^4} .$$

These relations also may be inverted to give

$$B = RTB', \; C = (RT)^2(C' + B'^2), \; D = (RT)^3(D' + 3B'C' + B'^3)$$

$$E = (RT)^4(E' + 4B'D' + 6C'B'^2 + 2C'^2 + B'^4) .$$

The first four terms given in Eqs. (12) are in exact agreement with results given by L. Epstein[2,3] and W. Putnam-E. Kilpatrick[4].

The virial equation truncated to three terms represents data curately to moderate pressures, and is therefore entirely adequate the vast majority of applications.

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