$$B' = \frac{B}{RT} = \frac{-(110 \text{ cm}^3 \text{ mol}^{-1})(10^{-3} \text{ L cm}^{-3})}{(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(400 \text{ K})}$$

$$= -3.31 \times 10^{-3} \text{ bar}^{-1}$$

$$Z = 1 + B'P = 1 - (3.31 \times 10^{-3} \text{ bar}^{-1})(50 \text{ bar})$$

$$= 0.835$$

7. 1.5 Show that the virial equation written in terms of pressure has the following form for a van der Waals gas Z = 1 + [b - (a/RT)](P/RT) if terms in P<sup>2</sup>, P<sup>3</sup>, etc., are neglected.

#### SOLUTION

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \qquad \frac{PV}{RT} = \frac{V}{V-b} - \frac{a}{VRT}$$

Adding and subtracting  $\frac{V-b}{V-b}$  on the right side of the equation

$$\frac{PV}{RT} = 1 + \frac{b}{V-b} - \frac{a}{VRT}$$

Since the second and third terms are small correction terms, b can be ignored in comparison with V; and V in the second and third term can be replaced by RT/P.

$$Z = 1 + \frac{bP}{RT} - \frac{aP}{(RT)^2} = 1 + \left(b - \frac{a}{RT}\right) \left(\frac{P}{RT}\right)$$

1.6 Show that for a gas of spherical molecules b in the van der Waals equation is four times the molecular volume times Avogadro's constant.

#### SOLUTION

The molecular volume for a spherical molecule is  $\frac{4}{3}\pi \left(\frac{d}{2}\right)^3 = \frac{\pi}{6}d^3$ 

# **Alberty Physical Chemistry Manual Solution**

Robert A. Alberty, Robert J. Silbey

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