Exercise 71

(a) The *van der Waals equation* for n moles of a gas is

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

where P is the pressure, V is the volume, and T is the temperature of the gas. The constant R is the universal gas constant and a and b are positive constants that are characteristic of a particular gas. If T remains constant, use implicit differentiation to find dV/dP.

(b) Find the rate of change of volume with respect to pressure of 1 mole of carbon dioxide at a volume of $V = 10$ L and a pressure of $P = 2.5$ atm. Use $a = 3.592$ L^2-atm/mole^2 and $b = 0.04267$ L/mole.

Solution

Part (a)

Expand the left side.

$$PV - nbP + \frac{n^2 a}{V} - \frac{n^3 ab}{V^2} = nRT$$

Differentiate both sides with respect to P, noting that T is a constant.

$$\frac{d}{dP}\left(PV - nbP + \frac{n^2 a}{V} - \frac{n^3 ab}{V^2}\right) = \frac{d}{dP}(nRT)$$

Use the chain rule to differentiate $V = V(P)$.

$$\frac{d}{dP}(PV) - \frac{d}{dP}(nbP) + \frac{d}{dP}\left(\frac{n^2 a}{V}\right) - \frac{d}{dP}\left(\frac{n^3 ab}{V^2}\right) = 0$$

$$\left[\frac{d}{dP}(P)\right]V + P\left[\frac{d}{dP}(V)\right] - nb + \left(-\frac{n^2 a}{V^2}\right)\frac{dV}{dP} - \left(-2\frac{n^3 ab}{V^3}\right)\frac{dV}{dP} = 0$$

$$(1)V + P\left(\frac{dV}{dP}\right) - nb - \frac{n^2 a}{V^2}\left(\frac{dV}{dP}\right) + \frac{2n^3 ab}{V^3}\left(\frac{dV}{dP}\right) = 0$$

Solve for dV/dP.

$$V - nb + \left(P - \frac{n^2 a}{V^2} + \frac{2n^3 ab}{V^3}\right)\frac{dV}{dP} = 0$$

$$\left(P - \frac{n^2 a}{V^2} + \frac{2n^3 ab}{V^3}\right)\frac{dV}{dP} = nb - V$$

Multiply both sides by V^3.

$$(PV^3 - n^2 aV + 2n^3 ab)\frac{dV}{dP} = V^3(nb - V)$$

Therefore, dividing both sides by $PV^3 - n^2aV + 2n^3ab$,

$$\frac{dV}{dP} = \frac{V^3(nb - V)}{PV^3 - n^2aV + 2n^3ab}.$$

Part (b)

If $n = 1$ mol, $V = 10$ L, $P = 2.5$ atm, $a = 3.592$ L^2-atm/mol^2 and $b = 0.04267$ L/mol, then

$$\frac{dV}{dP} = \frac{(10\text{ L})^3\left[(1\text{ mol})\left(0.04267\ \frac{\text{L}}{\text{mol}}\right) - 10\text{ L}\right]}{(2.5\text{ atm})(10\text{ L})^3 - (1\text{ mole})^2\left(3.592\ \frac{\text{L}^2\cdot\text{atm}}{\text{mol}^2}\right)(10\text{ L}) + 2(1\text{ mol})^3\left(3.592\ \frac{\text{L}^2\cdot\text{atm}}{\text{mol}^2}\right)\left(0.04267\ \frac{\text{L}}{\text{mol}}\right)}$$

$$= \frac{10^3(0.04267 - 10)\text{ L}^4}{[2.5(10)^3 - 3.592(10) + 2(3.592)(0.04267)]\text{ L}^3\cdot\text{atm}}$$

$$\approx -4.04\ \frac{\text{L}}{\text{atm}}.$$