

terms of the reduced quantities $v' \equiv v/v_c$, $T' \equiv T/T_c$ and $P' \equiv P/P_c$, the van der Waals equation becomes

$$\left(P' + \frac{3}{v'^2}\right)\left(v' - \frac{1}{3}\right) = \frac{8}{3}T'$$

2-6 Using the Berthelot equation of state,

$$P = \frac{RT}{v-b} - \frac{a}{Tv^2},$$

show that

$$v_c = 3b, \quad T_c = \sqrt{\frac{8a}{27bR}}, \quad P_c = \frac{1}{12b} \sqrt{\frac{2aR}{3b}}$$

(Hint: As noted in the text, $\partial P/\partial v = 0$ and $\partial^2 P/\partial v^2 = 0$ at the critical point.) Compare the numerical value of $RT_c/P_c v_c$ with the experimental values given in the following table:

Substance	$RT_c/P_c v_c$
He	3.06
H ₂	3.27
O ₂	3.42
CO ₂	3.61
H ₂ O	4.29

2-7 Using the Dieterici equation of state,

$$P = \frac{RT}{v-b} e^{-a/RTv},$$

show that

$$v_c = 2b, \quad T_c = \frac{a}{4Rb}, \quad P_c = \frac{a}{4e^2 b^2},$$

and find the numerical value of $RT_c/P_c v_c$. How does this compare with the tabulated experimental values?

2-8 (a) Making use of the cyclical relation (Equation (A.7) in Appendix A), find the expansivity β of a substance obeying the Dieterici equation of state in Problem 2-7.

(b) At higher temperatures and large specific volumes (low densities) all gases approximate an ideal gas. Show that for large values of T and v , the expression for β obtained in (a) goes over to the corresponding equation for an ideal gas.

2-9 Show that in general

$$\left(\frac{\partial \beta}{\partial P}\right)_T + \left(\frac{\partial \kappa}{\partial T}\right)_P = 0.$$

2-10 A hypothetical substance has an expansivity $\beta = 2bT/v$ and an isothermal compressibility $\kappa = a/v$, where a and b are constants. Show that the equation of state is

$$v - bT^2 + aP = \text{constant}.$$

2-11 Suppose that

$$\beta = \frac{v-a}{Tv}, \quad \kappa = \frac{3(v-a)}{4Pv}.$$

Show that the equation of state is

$$P^{3/4}(v-a) = AT,$$

where a and A are constants.

2-12 Show that β and κ are infinite at the critical point.

2-13 A glass bottle of nominal capacity 250 cm³ is filled brim full of water at 20°C. If the bottle and contents are heated to 50°C, how much water spills over? (For water, $\beta = 0.21 \times 10^{-3} \text{ K}^{-1}$. Assume that the expansion of the glass is negligible.)