

In-class problem linked to lecture pages 303-320:

Find the volume v_c at which a Van der Waals liquid attains its critical point, in terms of the Van der Waals parameters a and b .

Find the critical temperature T_c .

Find the critical pressure p_c .

In-class 303-320

$$P = \frac{RT}{v-b} - \frac{a}{v^2} = RT(v-b)^{-1} - av^{-2}$$

$$\text{@ } T_c, \quad \frac{dp}{dv} = 0 \quad \text{and} \quad \frac{d^2p}{dv^2} = 0$$

$$\frac{dp}{dv} = \frac{RT(-1)}{(v-b)^2} - \frac{(-2)a}{v^3} = 0 \Rightarrow \frac{2a}{v^3} - \frac{RT}{(v-b)^2} = 0$$

$$\frac{d^2p}{dv^2} = \frac{-RT(-2)}{(v-b)^3} + \frac{2a(-3)}{v^4} = 0 \Rightarrow \frac{2RT}{(v-b)^3} - \frac{6a}{v^4} = 0$$

To find v_c , eliminate RT

$$\frac{2a}{v^3} (v-b)^2 = \frac{3 \cdot 6a}{v^4} (v-b)^3$$

$$2 = \frac{3(v-b)}{v}$$

$$2v = 3v - 3b$$

$$0 = v - 3b$$

$$3b = v$$

To find T_c , substitute $v = 3b$

$$\frac{2a}{3^3 b^3} - \frac{RT_c}{(3b-b)^2} = 0$$

$$T_c = \frac{2a}{27b^3} \cdot \frac{1}{R} \cdot 4b^2$$

$$= \frac{8a}{27bR}$$

To find p_c , substitute into $p = \frac{RT}{v-b} - \frac{a}{v^2}$

$$p_c = \frac{R \left(\frac{8a}{27bR} \right)}{3b-b} - \frac{a}{3^2 b^2}$$

$$= \frac{8a}{27b} - \frac{a}{9b^2}$$

$$\frac{2b}{2b}$$

$$= \frac{4a}{27b^2} - \frac{3a}{27b^2} = \frac{a}{27b^2}$$