Assignment 10

Reif Problem 5.19

The van der Waals equation of state is

$$\left(p + \frac{a}{v^2}\right)(v-b) = RT$$

where $v \equiv \frac{V}{\nu}$ is the molar volume and ν is the number of moles. Recall that the gas constant R is related to Boltzmann's constant k via $\nu R = Nk$ and therefore $R = N_A k$ where N_A = Avogadro's number. The critical point is defined by the conditions

$$\left(\frac{\partial p}{\partial v}\right)_T = 0 \quad , \quad \left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0$$

We have

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

$$\therefore \quad \frac{\partial p}{\partial v} = \frac{-RT}{(v-b)^2} + \frac{2a}{v^3}$$

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

Setting these derivatives equal to zero yields

$$\frac{RT}{(v-b)^2} = \frac{2a}{v^3} \quad , \quad \frac{RT}{(v-b)^3} = \frac{3a}{v^4}$$

Dividing ~~the~~ first by ~~the~~ second gives

$$v - b = \frac{2}{3} v \quad \Rightarrow \quad \boxed{v_c = 3b}$$

We also obtain

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

$$\therefore \quad RT_c = \frac{8b^2 a}{27 b^3} = \frac{8a}{27b}$$

$$\Rightarrow \quad \boxed{T_c = \frac{8a}{27bR}}$$

For ~~the~~ pressure we ~~obtain~~

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

$$\therefore \quad p_c = \frac{8a}{27b} \frac{1}{2b} - \frac{a}{9b^2}$$

or

$$p_c = \frac{4a - 3a}{27b^2} \quad \Rightarrow \quad \boxed{p_c = \frac{a}{27b^2}}$$

Combining these results we find that

(a)
$$\boxed{\begin{aligned} b &= \frac{v_c}{3} \\ a &= \frac{9 v_c T_c R}{8} \end{aligned}}$$

(b) From ~~the~~ equation of state we find that

$$p_c = \frac{a}{27b^2} = \frac{9 v_c T_c R}{8} \frac{9}{27 v_c^2}$$

$$\therefore \boxed{p_c = \frac{3 R T_c}{8 v_c}}$$

(c) We can write the equation of state as

$$\left[p' p_c + \frac{a}{(v' v_c)^2}\right](v' v_c - b) = R T' T_c$$

or

$$\left(p' \frac{3 \cancel{R} \cancel{T_c}}{8 \cancel{v_c}} + \frac{9 \cancel{v_c} \cancel{T_c} \cancel{R}}{8 v'^2 \cancel{v_c^2}}\right)\left(v' \cancel{v_c} - \frac{\cancel{v_c}}{3}\right) = \cancel{R} T' \cancel{T_c}$$

This reduces to

$$\left(\frac{3}{8} p' + \frac{9}{8 v'^2}\right)\left(v' - \frac{1}{3}\right) = T'$$

or

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

Assuming that C_V = constant, we can carry out the integration to obtain

$$T_2 - T_1 = \frac{a\nu^2}{C_V V}\Bigg|_{V_1}^{V_2}$$

or

$$\boxed{T_2 - T_1 = \frac{a\nu^2}{C_V}\left(\frac{1}{V_2} - \frac{1}{V_1}\right)}$$

Assignment 11

Reif Problem 6.1

Oscillator in contact with heat reservoir. This system is governed by ~~the~~ canonical distribution:

$$E_n = (n + \tfrac{1}{2})\hbar\omega$$

$$P_n = C e^{-E_n\beta} = C e^{-E_n/kT}$$

a) $$\frac{P_1}{P_0} = \frac{C e^{-E_1/kT}}{C e^{-E_0/kT}} = \frac{e^{-\frac{3}{2}\frac{\hbar\omega}{kT}}}{e^{-\frac{1}{2}\frac{\hbar\omega}{kT}}}$$

$$\Rightarrow \boxed{\frac{P_1}{P_0} = e^{-\hbar\omega/kT}}$$

b) If only the ground state and the first excited state are occupied, then the mean energy is given by

$$\bar{E} = P_1 E_1 + P_0 E_0$$

$$= \frac{E_1 e^{-E_1/kT} + E_0 e^{-E_0/kT}}{e^{-E_1/kT} + e^{-E_0/kT}}$$

$$= \frac{\frac{3}{2}\hbar\omega\, e^{-\frac{3}{2}\frac{\hbar\omega}{kT}} + \frac{1}{2}\hbar\omega\, e^{-\frac{1}{2}\frac{\hbar\omega}{kT}}}{e^{-\frac{3}{2}\frac{\hbar\omega}{kT}} + e^{-\frac{1}{2}\frac{\hbar\omega}{kT}}}$$

$\therefore$

$$\boxed{\bar{E} = \frac{\hbar\omega}{2} \; \frac{3 e^{-\frac{\hbar\omega}{kT}} + 1}{e^{-\frac{\hbar\omega}{kT}} + 1}}$$