

## M15T.2



Adiabatic process  $\rightarrow dS=0$  or  $dQ_L + dQ_R = 0$   
 $N$  is conserved

a.) As  $p$  and  $S$  is constant in this system, then we can guess that enthalpy is conserved where it is given by

$$H = U + pV$$

in the system we have

$$\begin{aligned} dH &= dU_L + dU_R + p_L dV_L + p_R dV_R \\ &= (dU_L + p_L dV_L) + (dU_R + p_R dV_R) \\ &= dQ_L + dQ_R \\ &= 0 \quad \square \end{aligned}$$

b.)  $H_f = H_o$

$$U_f + p_R V_R = U_i + p_L V_L$$

$$\Delta U = p_L V_L - p_R V_R$$

c.) As  $F = U - TS \Rightarrow dF = dU - TdS - dTS \Rightarrow S = -\left(\frac{\partial F}{\partial T}\right)_{N,V}$  we have  
 $= (-pdV + \mu dN) - SdT$

$$S = +Nk_B \left\{ \ln \left[ \left( \frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} \frac{V - Nb}{V} \right] + 1 \right\} + Nk_B T \frac{3}{2}$$

thus:

$$U = F + TS$$

$$= -Nk_B T \left\{ \ln \left[ \left( \frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} \frac{V - Nb}{V} \right] + 1 \right\} - \frac{N^2 a}{V} + Nk_B T \left\{ \ln \left[ \left( \frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} \frac{V - Nb}{V} \right] + 1 \right\} + \frac{3}{2} Nk_B T$$

$$= \frac{3}{2} Nk_B T - \frac{N^2 a}{V}$$

d.) Consider the change of temperature in this process as a function of change in pressure

$$dH = T dS + dpV = 0$$

then as  $dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$  we get :

$$= \frac{C_p}{T} dT - \left(\frac{\partial V}{\partial T}\right)_p dp$$

$$C_p dT - T \left(\frac{\partial V}{\partial T}\right)_p dp + V dp = 0$$

$$dT = \frac{dp}{C_p} \left[ T \left(\frac{\partial V}{\partial T}\right)_p - V \right]$$

in this process we have  $dp < 0$ , then for cooling where  $dT < 0$  we have

$$T \left(\frac{\partial V}{\partial T}\right)_p - V > 0 \quad \dots \text{ as } C_p > 0$$

for van der Waals we have

$$\left(p + \frac{N^2 a}{V^2}\right)(V - Nb) = Nk_B T$$

$$pV + \frac{N^2 a}{V} - pNb - \frac{N^2 ab}{V^2} = Nk_B T$$

$$V = \frac{Nk_B T}{p} - \frac{N^2 a}{pV} + Nb + \frac{N^2 ab}{p^2 V^2}$$

$$V \approx \frac{Nk_B T}{p} - \frac{Na}{k_B T} + Nb + \frac{Nabp}{k_B^2 T^2}$$

... substituting  $pV \approx Nk_B T$

then, we have

$$\left(\frac{\partial V}{\partial T}\right)_p \approx \frac{Nk_B}{p} + \frac{Na}{k_B T^2} - 2 \frac{Nabp}{k_B^2 T^3}$$

keeping only terms linear to  $a$  and  $b$  we get

$$T \left(\frac{\partial V}{\partial T}\right)_p - V \approx \frac{2Na}{k_B T} - Nb$$

thus the critical condition is given by

$$\frac{2a}{k_B T} - b > 0$$

$$\frac{2a}{k_B T} > b$$