

To: Michael Barnes

Statistical Mechanics 8 Ziyang Li

1. (a) Equation of state: $P(V-b) = RT$

$$\rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b} = \frac{P}{T}$$

1st Law: $dU = TdS - PdV$

$$\rightarrow \left(\frac{\partial U}{\partial U}\right)_T = T\left(\frac{\partial S}{\partial U}\right)_T - P$$

$$= T\left(\frac{\partial P}{\partial T}\right)_V - P = T\left(\frac{P}{T}\right) - P$$

maxwell
relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$= P - P = 0$$

U can be expressed as $U(T, V)$

$$\text{With } dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$= \left(\frac{\partial U}{\partial T}\right)_V dT = C_V dT$$

$$\rightarrow dU = C_V dT$$

Only varying T can change U

$\rightarrow U$ is a function of T only

$$\text{cb)} \quad dU = C_v dT, \quad dU = dQ - PdV$$

$$dQ = dU + PdV = C_v dT + PdV$$

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p = C_v + P \left(\frac{\partial V}{\partial T}\right)_p$$

$$\therefore P(V-b) = RT \quad \therefore \cancel{V = \frac{RT}{P} + Pb}$$

$$\therefore V = \frac{RT}{P} + b \quad \rightarrow \left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{P}$$

$$\rightarrow C_p = C_v + P \left(\frac{R}{P}\right) = C_v + R$$

$$\gamma = \frac{C_p}{C_v} = \frac{C_v + R}{C_v} = 1 + \frac{R}{C_v}$$

R and 1 are constants

$\therefore dU = C_v dT \quad \therefore C_v$ cannot depend on P

~~The~~ C_v can only depend on T

However, the question requires that C_v is independent of T

$\rightarrow C_v$ is independent of P and T

$\rightarrow \gamma$ is independent of P and T

$$(c) \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial T}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T$$

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V$$

$$\rightarrow \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V}$$

$$\text{Maxwell's relation : } \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\rightarrow \left(\frac{\partial T}{\partial S}\right)_V \left(\frac{\partial T}{\partial V}\right)_S = -\frac{T}{C_V} \left(\frac{\partial P}{\partial T}\right)_V = -\frac{T}{C_V} \frac{R}{V-b}$$

Adiabatic change along constant S :

$$\frac{dT}{dV} = -\frac{T}{C_V} \frac{R}{V-b} \rightarrow \frac{dT}{T} = -\frac{R}{C_V} \frac{dV}{V-b}$$

$\therefore C_V$ can only depend on T but is independent of T

$\therefore C_V$ is a constant

$$\rightarrow \int_{T_1}^{T_2} \frac{dT}{T} = -\frac{R}{C_V} \int_{V_1}^{V_2} \frac{dV}{V-b}$$

$$\rightarrow \ln\left(\frac{T_2}{T_1}\right) = -\frac{C_P - C_V}{C_V} \ln \frac{V_2 - b}{V_1 - b}$$

$$\rightarrow \ln\left(\frac{T_2}{T_1}\right) = (1 - \gamma) \ln \frac{V_2 - b}{V_1 - b}$$

$$\rightarrow \ln\left(\frac{T_2}{T_1}\right) = \ln\left(\frac{V_2^{1-\gamma}}{V_1^{1-\gamma}}\right) = \ln\left(\frac{(V_2-b)^{1-\gamma}}{(V_1-b)^{1-\gamma}}\right)$$

$$\rightarrow T_1(V_1-b)^{\gamma-1} = T_2(V_2-b)^{\gamma-1}$$

$$\therefore P(V-b) = RT \rightarrow$$

$$\therefore P_1(V_1-b)(V_1-b)^{\gamma-1} = P_2(V_2-b)(V_2-b)^{\gamma-1}$$

$$\rightarrow P_1(V_1-b)^{\gamma} = P_2(V_2-b)^{\gamma}$$

$$\rightarrow P(V_1-b)^{\gamma} \text{ is constant}$$

$$2 \text{ (a)} \quad P(V-b) = RT e^{-a/RTV}$$

$$\rightarrow P = \frac{RT}{V-b} e^{-a/RTV}$$

Critical point is the inflection point

$$\text{set } 0 = \left(\frac{\partial P}{\partial V}\right)_T = RT \left[e^{-a/RTV} \left(-\frac{1}{(V-b)^2}\right) + \left(\frac{1}{V-b}\right) \left(e^{-a/RTV}\right) \left(\frac{a}{RTV^2}\right) \right]$$

$$= \frac{RT e^{-a/RTV}}{V-b} \left[-\frac{1}{V-b} + \frac{a}{RTV^2} \right] \quad \textcircled{1}$$

$$\text{and } 0 = \left(\frac{\partial^2 P}{\partial V^2}\right)_T = RT \frac{\partial}{\partial V} \left[e^{-a/RTV} \left(-\frac{1}{(V-b)^2} + \frac{a}{(V-b)RTV^2}\right) \right]$$

$$= RT \left(\underbrace{\left(-\frac{1}{(V-b)^2} + \frac{a}{(V-b)RTV^2}\right)}_{=0 \text{ already from } \textcircled{1}} \right) e^{-a/RTV} \left(\frac{a}{RTV^2}\right)$$

$$+ (e^{-a/RTV}) \left(+\frac{2}{(V-b)^3} - \frac{a}{RT} \frac{1}{(V-b)V^3} (3V^2 - 2bV) \right)$$

②

$$\textcircled{1} \rightarrow \frac{a}{RTV^2} = \frac{1}{V-b} \rightarrow RTV^2 = aV + ab = 0$$

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

$$\textcircled{2} \rightarrow \frac{2}{(V-b)^3} = \frac{a}{RT} \frac{3V^2 - 2bV}{V^3} = \frac{a}{RT} \frac{3V - 2b}{V^2}$$

$$\textcircled{2} \rightarrow \frac{2}{(v-b)^3} = \frac{a}{RT} \frac{3v^2 - 2bv}{(v-b)^2 v^4}$$

$$\rightarrow \frac{2}{\cancel{v-b}} = \frac{\cancel{v^2}}{\cancel{v-b}} \frac{3v^2 - 2bv}{v^4 \cancel{2}}$$

$$\rightarrow 3v^2 - 2bv = 2v^2$$

$$\rightarrow \boxed{V_c = 2b}$$

$$\frac{a}{RT_c} = \frac{V_c^2}{V_c - b} = \frac{4b^2}{b}$$

$$\rightarrow \boxed{T_c = \frac{a}{4Rb}}$$

$$\begin{aligned} \boxed{P_c} &= \frac{RT_c}{V_c - b} e^{-a/RT_c V_c} \\ &= \frac{R(a/4Rb)}{b} e^{-\frac{a \times 4}{(R)(a/4Rb)(2b)}} \\ &= \frac{a}{4b} \frac{a}{4b^2} e^{-2} = \boxed{\frac{a}{4e^2 b^2}} \end{aligned}$$

(b) Starting from $P(V-b) = RT e^{-a/RTV}$

Divide by ~~(b)~~ $(\frac{a}{4e^2 b^2})$ on both sides
 $\frac{P}{P_c} (\frac{2V}{V_c} - \frac{b}{b}) = \frac{RT}{T_c R} e^2 \exp(-\frac{a}{RTV})$

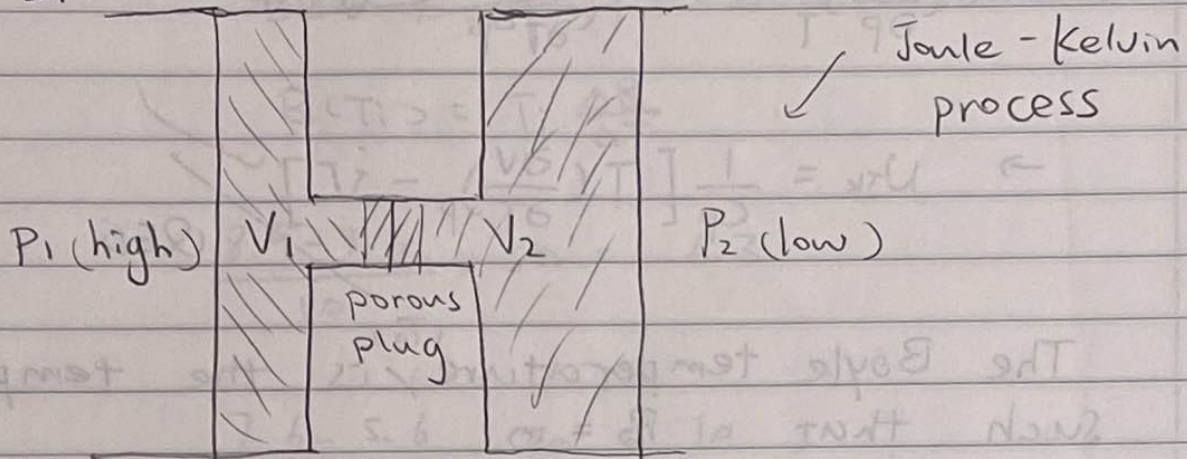
$$\frac{P}{P_c} \left(\frac{2V}{V_c} - \frac{b}{b} \right) = \frac{RT}{T_c R} e^2 \exp\left(-\frac{a}{RTV}\right)$$

$$\rightarrow \tilde{P} (2\tilde{V} - 1) = \tilde{T} \exp(2) \exp\left(-\frac{a}{RTV}\right)$$

$$\frac{a}{RTV} = \frac{a/(T_c V_c)}{R \tilde{T} \tilde{V}} = \frac{\alpha (4Rb/\alpha) (1/2b)}{R \tilde{T} \tilde{V}} = \frac{2}{\tilde{T} \tilde{V}}$$

$$\rightarrow \tilde{P} (2\tilde{V} - 1) = \tilde{T} \exp\left[2\left(1 - \frac{1}{\tilde{T} \tilde{V}}\right)\right] \quad \text{CED.}$$

3.



Consider a steady flow process in which gas at high pressure P_1 is forced through a porous plug to a lower pressure P_2 .

The process is thermally isolated so $\Delta Q = 0$

First Law : $\Delta U = \Delta Q + \Delta W = \Delta W$
 \hookrightarrow work done on the system

$$\rightarrow U_2 - U_1 = P_1 V_1 - P_2 V_2$$

$$\rightarrow U_1 + P_1 V_1 = U_2 + P_2 V_2$$

$\rightarrow H_1 = H_2 \rightarrow$ Enthalpy is conserved

$$N_{JK} = \left(\frac{\partial T}{\partial P} \right)_H = - \left(\frac{\partial H}{\partial P} \right)_T \left(\frac{\partial T}{\partial H} \right)_P = - \frac{1}{C_p} \left(\frac{\partial H}{\partial P} \right)_T$$

$$dH = TdS + Vdp \rightarrow \left(\frac{\partial H}{\partial P} \right)_T = T \left(\frac{\partial S}{\partial P} \right)_T + V$$

Maxwell's relation : $-\left(\frac{\partial S}{\partial P} \right)_T = \left(\frac{\partial V}{\partial T} \right)_P$

$$\rightarrow \left(\frac{\partial H}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P + V$$

$$\rightarrow N_{JK} = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T}\right)_P - V \right] \quad \text{QED}$$

The Boyle temperature (T_B) is the temperature such that $B = 0$

From data we see $T_B \approx 25K$

The inversion temperature (T_i) is given by

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{V}{T} \quad (1)$$

$$PV = RT \left(1 + \frac{B}{V}\right) \rightarrow PV^2 = RTV + RTB \quad (2)$$

$$\left(\frac{\partial}{\partial T}\right)_P \rightarrow 2PV \left(\frac{\partial V}{\partial T}\right)_P = \cancel{RT} + \cancel{RV} + RV + RT \left(\frac{\partial V}{\partial T}\right)_P + RB \quad (3)$$

(+ RT $\left(\frac{\partial B}{\partial T}\right)_P$)

Sub ① into ③ $\rightarrow 2PV \left(\frac{V}{T}\right) = RV + RT \left(\frac{V}{T}\right) + RB$

(+ RT $\left(\frac{\partial B}{\partial T}\right)_P$)

$$\rightarrow 2PV^2 = 2RVT + RB T + RT^2 \left(\frac{\partial B}{\partial T}\right)_P$$

$$\rightarrow 2V \left(RT + \frac{B}{V} RT \right) = 2RVT + RB T + RT^2 \left(\frac{\partial B}{\partial T}\right)_P$$

$$\rightarrow \cancel{2VRT} + 2BR\cancel{T} = \cancel{2VRT} + \cancel{BR\cancel{T}} + RT^2 \left(\frac{\partial B}{\partial T}\right)_P$$

$$\rightarrow B = T \left(\frac{\partial B}{\partial T}\right)_P \quad \text{for } T = T_i$$

→ For ~~$B \propto T_i \frac{\Delta B}{\Delta T}$~~ (B is a function of T only)

$$B(T_i) = T_i \frac{\Delta B}{\Delta T} = nRT$$

$$\therefore \frac{8.9 - 7.6}{10} \times 50 = 6.3$$

$$\frac{7.6 - 5.6}{10} \times 50 = 10$$

$$\text{and } 6.3 < 7.6 < 10$$

$\therefore \left(\frac{\partial B}{\partial T}\right)_P = \frac{B}{T}$ occurs roughly

at $T_i = 50\text{K}$

4. For Van der Waals gas :

$$\left(P + \frac{an^2}{V^2}\right)(V - bn) = nRT$$

$$\rightarrow P = \frac{nRT}{V - bn} - \frac{an^2}{V^2} \quad (1)$$

$$\left(\frac{\partial \mathcal{Q}}{\partial T}\right)_P \rightarrow 0 = \frac{\partial}{\partial T} \left[\frac{nRT}{V - bn} - \frac{an^2}{V^2} \right]_{n,P}$$

$$\rightarrow 0 = \frac{nR}{V - bn} - nRT \frac{1}{(V - bn)^2} \left(\frac{\partial V}{\partial T}\right)_P + \frac{2an^2}{V^3} \left(\frac{\partial V}{\partial T}\right)_P$$

$$\rightarrow \left(\frac{\partial V}{\partial T}\right)_P = \frac{-nR}{V - bn} \frac{1}{\left(\frac{2an^2}{V^3} - \frac{nRT}{(V - bn)^2}\right)}$$

$$N_{JK} = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T}\right)_P - V \right]$$

$$= \frac{1}{C_p} \left[\frac{TnRV^3(V - bn)}{nRTV^3 - 2an^2(V - bn)^2} - V \right]$$

$$= \frac{1}{C_p} \left[\frac{nRTV^4 - n^2RTV^3b - nRTV^4 + 2an^2(V - bn)^2V}{nRTV^3 - 2an^2(V - bn)^2} \right]$$

~~$$= \frac{1}{C_p}$$~~

$$\therefore P = \frac{nRT}{V - bn} - \frac{an^2}{V^2}, \text{ as } P \rightarrow 0, V \rightarrow \infty$$

$$\therefore \lim_{P \rightarrow 0} N_{JK} = \lim_{V \rightarrow \infty} N_{JK} \neq 0$$

as $V \rightarrow \infty$, $V - bn \approx V$, and we only need to keep the leading order

of V

$$\begin{aligned}\rightarrow \lim_{p \rightarrow 0} N_{JK} &= \frac{n}{C_p} \left[\frac{(2a - RTb)V^3}{RTV^3} \right] \\ &= \frac{n}{C_p} \left[\frac{2a}{RT} - b \right]\end{aligned}$$

For 1 mole of gas, $n=1$

$$\rightarrow \lim_{p \rightarrow 0} N_{JK} = \frac{1}{C_p} \left[\frac{2a}{RT} - b \right] \quad \text{QED}$$

~~Again for 1 mole of gas:~~

At inversion temperature: $\left(\frac{\partial V}{\partial T}\right)_p = \frac{V}{T}$

also
 $N_{JK}(T_i) = 0$
 $\Rightarrow \frac{2a}{RT} = b$
 $\Rightarrow T = \frac{2a}{Rb}$

$$\rightarrow \frac{V}{T} = \frac{\frac{nR}{V-bn}}{\frac{nRT}{(V-bn)^2} - \frac{2an^2}{V^3}} \rightarrow \frac{nRT}{V-bn} = \frac{nRTV}{(V-bn)^2} - \frac{2an^2}{V^2}$$

$$\rightarrow \frac{nRT}{V-bn} \left[\frac{V}{V-bn} - 1 \right] = \frac{2an^2}{V^2}$$

$$\rightarrow \frac{nRT}{V-bn} \left[\frac{bn}{V-bn} \right] = \frac{2an^2}{V^2}$$

$$\rightarrow T_i = \frac{2a}{Rb} \left[\frac{V-bn}{V} \right]^2$$

T_i increases monotonically with V , and as $V \rightarrow \infty$ ($p \rightarrow 0$), we have

$$\boxed{T_i^{\max} = \frac{2a}{Rb}} \quad \text{QED}$$

5. Dieterici Gas : $P(V-b) = RT \exp(-\frac{a}{RTV})$ ①

$$\left(\frac{\partial \ln P}{\partial T}\right)_P \Rightarrow P \left(\frac{\partial V}{\partial T}\right)_P = R \exp(-\frac{a}{RTV}) + RT \frac{\partial}{\partial T} \exp(-\frac{a}{RTV})$$

$$\Rightarrow P \left(\frac{\partial V}{\partial T}\right)_P = R \exp(-\frac{a}{RTV}) + RT \exp(-\frac{a}{RTV}) \left(-\frac{a}{R}\right) \frac{\partial}{\partial T} \left(\frac{1}{TV}\right)$$

$$\Rightarrow P \left(\frac{\partial V}{\partial T}\right)_P = R \exp(-\frac{a}{RTV}) + RT \exp(-\frac{a}{RTV}) \left(-\frac{a}{R}\right) \left[\frac{1}{T} \left(-\frac{1}{V^2}\right) \left(\frac{\partial V}{\partial T}\right)_P + \frac{1}{V} \left(-\frac{1}{T^2}\right)\right]$$

Along the inversion curve : $\left(\frac{\partial V}{\partial T}\right)_P = \frac{V}{T}$

$$\Rightarrow \frac{PV}{T} = R \exp(-\frac{a}{RTV}) + RT \left(\frac{a}{R}\right) \exp(-\frac{a}{RTV}) \left[\frac{1}{TV^2} \left(\frac{V}{T}\right) + \frac{1}{VT^2}\right]$$

$$= \exp(-\frac{a}{RTV}) \left[R + \frac{2aT}{V^2} \right]$$

$$\Rightarrow P = \left[R + \frac{2a}{V^2} \right] \exp(-\frac{a}{RTV}) \quad \text{②}$$

Compare ① and ② we have :

$$\exp(-\frac{a}{RTV}) = \frac{P(V-b)}{RT} \Rightarrow R = \left[\frac{RT}{V} + \frac{2a}{V^2} \right] \frac{P(V-b)}{RT}$$

along the inversion curve

$$\text{So, } \frac{RT}{V} + \frac{2a}{V^2} = \frac{RT}{V-b} \Rightarrow \frac{2a}{V^2} = \frac{RT}{V-b} - \frac{RT}{V}$$

$$\Rightarrow \frac{2a}{V^2} = \frac{RTb}{V(V-b)} \Rightarrow 2aV(V-b) = RTbV^2$$

$$\Rightarrow 2aV - 2ab = RTbV \Rightarrow (2a - RTb)V = 2ab$$

$$\Rightarrow V = \frac{2ab}{2a - RTb} \Rightarrow \frac{1}{V} = \frac{2a - RTb}{2ab} = \frac{1}{b} - \frac{RT}{2a}$$

$$\exp\left(-\frac{a}{RTV}\right) = \exp\left(-\frac{a}{R} \left(\frac{1}{bT} - \frac{RT}{2aT}\right)\right)$$

$$= \exp\left(\frac{1}{2} - \frac{a}{RbT}\right) = \exp\left(\frac{1}{2} - \frac{4T_c}{T}\right)$$

$$T_c = \frac{a}{4Rb}$$

$$= \exp\left(\frac{1}{2} - \frac{4}{T}\right)$$

$$\frac{RT}{V} + \frac{2a}{V^2} = RT\left(\frac{1}{b} - \frac{RT}{2a}\right) + 2a\left(\frac{1}{b} - \frac{RT}{2a}\right)^2$$

$$= \frac{RT}{b} - \frac{R^2T^2}{2a} + 2a\left(\frac{1}{b^2} - \frac{RT}{ab} + \frac{R^2T^2}{4a^2}\right)$$

$$= \frac{RT}{b} - \frac{R^2T^2}{2a} + \frac{2a}{b^2} - \frac{2RT}{b} + \frac{R^2T^2}{2a}$$

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

$$= \frac{a}{4b^2} \left(8 - \frac{4Rb}{a} T\right) = P_c \left(8 - \frac{T}{T_c}\right) \exp(2)$$

$$\uparrow$$

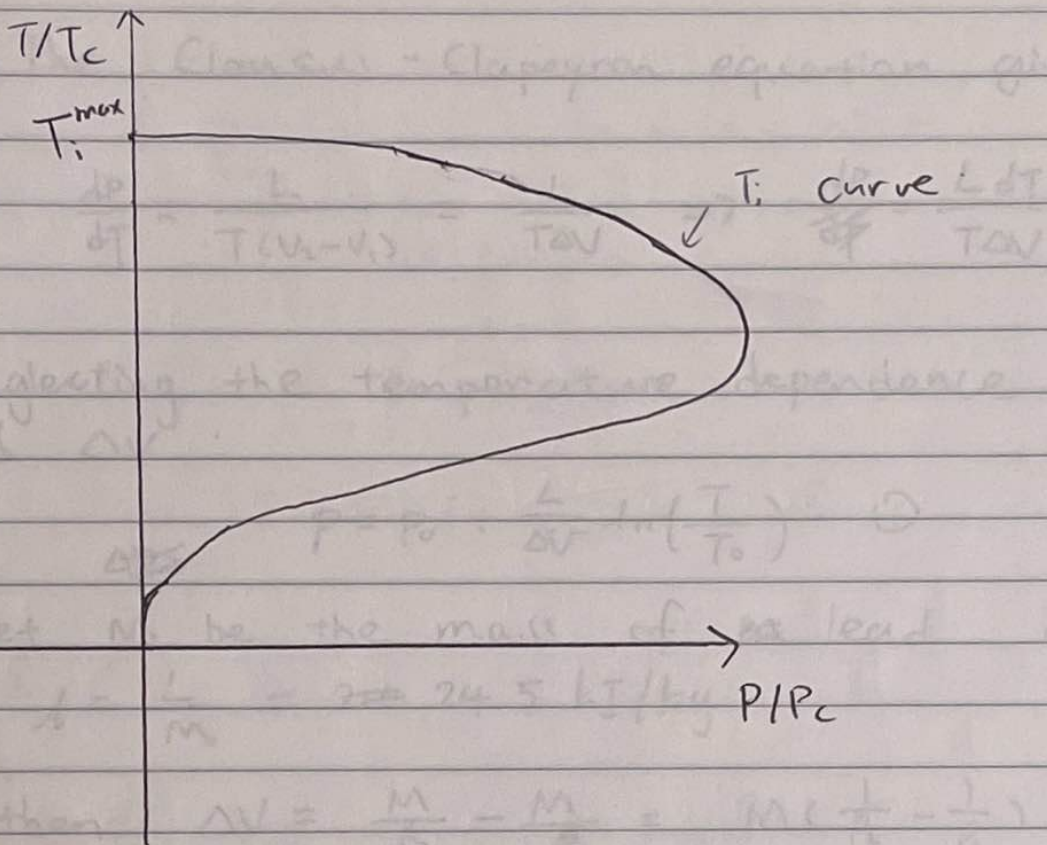
$$P_c e^2$$

$$\uparrow$$

$$\frac{1}{T_c}$$

$$\Rightarrow P = P_c \left(8 - \frac{T}{T_c}\right) \exp(2) \exp\left(\frac{1}{2} - \frac{4}{T}\right)$$

$$\Rightarrow \tilde{P} = (8 - \tilde{T}) \exp\left(\frac{5}{2} - \frac{4}{T}\right) \quad \text{QED} \quad \checkmark$$



Maximum inversion temperature is when $\tilde{p} = 0$ (but $\tilde{T} \neq 0$)

So we have $\delta - \tilde{T} = 0$

$$\Rightarrow T_i^{\max} = 8T_c = 8\left(\frac{a}{4Rb}\right) = \boxed{\frac{2a}{Rb}} \quad \text{QED}$$

6. The Clausius - Clapeyron equation gives

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)} = \frac{L}{T\Delta V} \Rightarrow \frac{dP}{P} = \frac{LdT}{T\Delta V}$$

Neglecting the temperature dependence of L and ΔV :

~~$$P = P_0 + \frac{L}{\Delta V} \ln\left(\frac{T}{T_0}\right) \quad \textcircled{1}$$~~

Let m be the mass of ~~the~~ lead and

$$l = \frac{L}{m} = 24.5 \text{ kJ/kg}$$

$$\text{then } \Delta V = \frac{m}{\rho_2} - \frac{m}{\rho_1} = m\left(\frac{1}{\rho_2} - \frac{1}{\rho_1}\right)$$

$$\frac{L}{\Delta V} = \frac{ml}{\frac{m}{\rho_2} - \frac{m}{\rho_1}} = \frac{l\rho_2\rho_1}{\rho_1 - \rho_2}$$

$$\textcircled{1} \text{ gives } \left(\frac{\Delta V}{L}\right)(P - P_0) = \ln\left(\frac{T}{T_0}\right)$$

$$\Rightarrow T = T_0 \exp\left(\frac{\Delta V}{L}(P - P_0)\right)$$

$$= T_0 \exp\left(\frac{[\rho_1 - \rho_2][P - P_0]}{\rho_1\rho_2 l}\right)$$

$$= (327.1 + 237.273) \exp\left(\frac{(11,01 - 10.65) \times 10^3 \times (100 - 1) \times 10^5}{11,01 \times 10^3 \times 10.65 \times 10^3 \times 24.5 \times 10^3}\right)$$

~~$$= 601 \text{ K}$$~~

$$= 600.8 \text{ K}$$

$$\approx \boxed{327.8^\circ\text{C}}$$

~~$$= 328^\circ\text{C}$$~~

7.

$$1 \text{ mbar} = 100 \text{ Pa}$$

$$\Rightarrow P_{\text{MKH}} = 615 \text{ mbar} = 6.15 \times 10^4 \text{ Pa}$$

$$P_{\text{ATM}} = 1.01 \times 10^5 \text{ Pa}$$

$$P_{\text{MKH}} = P_0 \exp\left(-\frac{L}{RT_{\text{MKH}}}\right) \quad (1)$$

$$P_{\text{ATM}} = P_0 \exp\left(-\frac{L}{RT_{\text{ATM}}}\right) \quad (2)$$

$$\frac{(1)}{(2)} \Rightarrow \frac{P_{\text{MKH}}}{P_{\text{ATM}}} = \exp\left(\frac{L}{R} \left(\frac{1}{T_{\text{ATM}}} - \frac{1}{T_{\text{MKH}}}\right)\right)$$

$$\Rightarrow \frac{L}{R} \left(\frac{1}{T_{\text{MKH}}} - \frac{1}{T_{\text{ATM}}}\right) = \ln\left(\frac{P_{\text{MKH}}}{P_{\text{ATM}}}\right)^{-1}$$

$$\Rightarrow \frac{1}{T_{\text{MKH}}} - \frac{1}{T_{\text{ATM}}} = \frac{R}{L} \ln\left(\frac{P_{\text{MKH}}}{P_{\text{ATM}}}\right)^{-1} = \frac{R}{L} \ln\left(\frac{P_{\text{ATM}}}{P_{\text{MKH}}}\right)$$

~~$$\Rightarrow \frac{1}{T_{\text{MKH}}} = \frac{R}{L} \ln\left(\frac{P_{\text{ATM}}}{P_{\text{MKH}}}\right) + \frac{1}{T_{\text{ATM}}}$$~~

$$\Rightarrow T_{\text{MKH}} = \left(\frac{R}{L} \ln\left(\frac{P_{\text{ATM}}}{P_{\text{MKH}}}\right) + \frac{1}{T_{\text{ATM}}}\right)^{-1}$$

$$= \left(\frac{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})}{(40.7 \times 10^3 \text{ J mol}^{-1})} \ln\left(\frac{1.01 \times 10^5 \text{ Pa}}{6.15 \times 10^4 \text{ Pa}}\right) + \frac{1}{(100 + 273)}\right)^{-1}$$

$$= 359.4 \text{ K}$$

$$= 86.4^\circ \text{C}$$

The boiling point at the Summit is 86.4°C which is less than 97°C , so we cannot make a good cup of tea there.

$$8. (a). \frac{d}{dT} = \left(\frac{\partial}{\partial T}\right)_P + \frac{dP}{dT} \left(\frac{\partial}{\partial P}\right)_T$$

Apply this to $\Delta S = S_V - S_L = \frac{L}{T}$
vapour liquid

We get: $\frac{d}{dT} \left(\frac{L}{T}\right) = \frac{d}{dT} (\Delta S) = \left(\frac{\partial (\Delta S)}{\partial T}\right)_P + \frac{dP}{dT} \left(\frac{\partial (\Delta S)}{\partial P}\right)_T$

$$= \frac{1}{T} \times \left[T \left(\frac{\partial S_V}{\partial T}\right)_P - T \left(\frac{\partial S_L}{\partial T}\right)_P \right] + \left[\left(\frac{\partial S_V}{\partial P}\right)_T - \left(\frac{\partial S_L}{\partial P}\right)_T \right] \frac{dP}{dT}$$

$C_{p,vap}$ $C_{p,liq}$

$$= \frac{C_{p,vap} - C_{p,liq}}{T} + \left[\left(-\frac{\partial V_V}{\partial T}\right)_P - \left(-\frac{\partial V_L}{\partial T}\right)_P \right] \frac{dP}{dT}$$

Maxwell's relation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

$$= \frac{C_{p,vap} - C_{p,liq}}{T} - \left[\left(\frac{\partial V_V}{\partial T}\right)_P - \left(\frac{\partial V_L}{\partial T}\right)_P \right] \frac{dP}{dT}$$

$\left(\frac{\partial V_{liq}}{\partial T}\right)_P \ll \left(\frac{\partial V_{vap}}{\partial T}\right)_P$ $\left(\frac{\partial S_{liq}}{\partial P}\right)_T \approx 0$ \because liquid is incompressible
neglecting this term as it is small compare to $\left(\frac{\partial V_V}{\partial T}\right)_P$

$$= \frac{\Delta C_p}{T} - \left(\frac{\partial V_{vap}}{\partial T}\right)_P \frac{dP}{dT}$$

Clausius-Clapeyron equation

$$\frac{dP}{dT} = \frac{L}{T\Delta V} \approx \frac{L}{TV_{vap}}$$

$$\because \Delta V = V_{vap} - V_{liq} \approx V_{vap}$$

$$(V_{liq} \ll V_{vap})$$

when heated volume of liquid ~~set~~ hardly change

$$= \frac{\Delta C_p}{T} - \frac{L}{TV_{vap}} \left(\frac{\partial V_{vap}}{\partial T}\right)_P$$

On the other hand:

$$\frac{d}{dT} \left(\frac{L}{T}\right) = \frac{1}{T} \frac{dL}{dT} - \frac{L}{T^2}$$

$$\Rightarrow \frac{1}{T} \frac{dL}{dT} - \frac{L}{T^2} = \frac{\Delta C_p}{T} - \frac{L}{TV_{vap}} \left(\frac{\partial V_{vap}}{\partial T}\right)_P$$

$$\Rightarrow \frac{dL}{dT} = \frac{L}{T} + \Delta C_p - \frac{L}{V_{vap}} \left(\frac{\partial V_{vap}}{\partial T}\right)_P$$

QED

(b) For ideal gas (as the vapour) :

$$PV_{\text{vap}} = RT \Rightarrow \left(\frac{\partial V_{\text{vap}}}{\partial T} \right)_P = \frac{R}{P}, \quad V_{\text{vap}} = \frac{RT}{P}$$

$$\Rightarrow \frac{dL}{dT} = \frac{L}{T} + \Delta C_p - L \left(\frac{P}{RT} \right) \left(\frac{R}{P} \right) = \Delta C_p$$

$\therefore \Delta C_p$ is assumed to be independent of temperature

$$\therefore \frac{dL}{dT} = \Delta C_p \Rightarrow \int_{L_0}^L dL = \int_0^T \Delta C_p dT \Rightarrow L = \Delta C_p T + L_0 \quad \text{QED}$$

(c) Starting from ~~$\frac{dL}{dT} = \frac{L}{T} + C_{p,\text{vap}} - C_{p,\text{liq}} = \frac{L}{T} + \left(\frac{\partial V_{\text{vap}}}{\partial T} \right)_P - \left(\frac{\partial V_{\text{liq}}}{\partial T} \right)_P$~~

$$\Rightarrow \frac{d}{dT} \left(\frac{L}{T} \right) = \frac{C_{p,\text{vap}} - C_{p,\text{liq}}}{T} + \left[\left(\frac{\partial S_V}{\partial P} \right)_T - \left(\frac{\partial S_L}{\partial P} \right)_T \right] \frac{dP}{dT}$$

$$\Rightarrow C_{p,\text{liq}} + T \frac{d}{dT} \left(\frac{L}{T} \right) = C_{p,\text{vap}} + T \left[\left(\frac{\partial S_V}{\partial P} \right)_T - \left(\frac{\partial S_L}{\partial P} \right)_T \right] \frac{dP}{dT}$$

$$\left(\frac{\partial S_V}{\partial P} \right)_T = - \left(\frac{\partial V_{\text{vap}}}{\partial T} \right)_P, \quad \left(\frac{\partial S_L}{\partial P} \right)_T = - \left(\frac{\partial V_{\text{liq}}}{\partial T} \right)_P$$

$\therefore \left(\frac{\partial V_{\text{liq}}}{\partial T} \right)_P$ is negligible ~~comp~~ compare to

$$\left(\frac{\partial V_{\text{vap}}}{\partial T} \right)_P \quad (V_{\text{vap}} \gg V_{\text{liq}}) \quad \text{a.}$$

\therefore We only keep the $\left(\frac{\partial S_V}{\partial P} \right)_T$ term

We then have

$$C_{p,liq} + T \frac{d}{dT} \left(\frac{L}{T} \right) = C_{p,vap} + T \left(\frac{\partial S_{vap}}{\partial P} \right)_T \frac{dP}{dT}$$

Cyclic rule : $\left(\frac{\partial S_{vap}}{\partial P} \right)_T = - \left(\frac{\partial S_{vap}}{\partial T} \right)_P \left(\frac{\partial T}{\partial P} \right)_{S_{vap}}$

~~$$= - \frac{\left(\frac{\partial S}{\partial T} \right)_P}{\left(\frac{\partial T}{\partial P} \right)_{S_{vap}}}$$~~

$$\Rightarrow \left(\frac{\partial S_{vap}}{\partial P} \right)_T = - \frac{\left(\frac{\partial S_{vap}}{\partial T} \right)_P}{\left(\frac{\partial P}{\partial T} \right)_{S_{vap}}}$$

$\left(\frac{\partial P}{\partial T} \right)_{S_{vap}}$ is the ~~P~~ tangent of P-T curve for the adiabatic expansion of vapour

$$\left(\frac{\partial T}{\partial V} \right)_{S_{vap}} = - \left(\frac{\partial T}{\partial S_{vap}} \right)_V \left(\frac{\partial S_{vap}}{\partial V} \right)_T$$

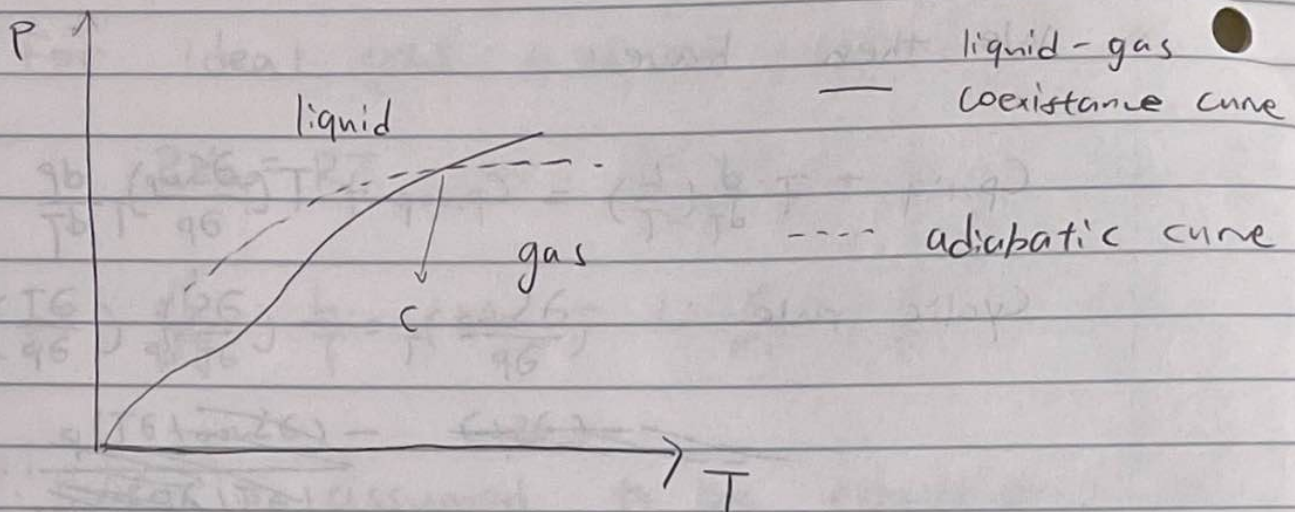
$$= \frac{T}{C_{p,vap}} > 0$$

> 0 for most gases
expand gas under constant T,
entropy increases. due to
more disorderness

$$\therefore \left(\frac{\partial T}{\partial V} \right)_{S_{vap}} < 0$$

\Rightarrow Adiabatic expansion results in decrease in temperature

So we need the adiabatic P-T curve to be such that as temperature decreases, the curve reaches the region representing liquid phase, if we want condensation under adiabatic expansion. ✓



From the ~~graph~~ diagram above we can see that if we want condensation we need

$\left(\frac{\partial P}{\partial T}\right)_{\text{svap}}$ to be smaller than $\frac{dP}{dT}$

because we are at point C ✓

So, for condensation:

$$C_{p, \text{liq}} + T \frac{d}{dT} \left(\frac{L}{T} \right) = C_{p, \text{vap}} + T \left(\frac{\partial S_{\text{vap}}}{\partial P} \right)_T \frac{dP}{dT}$$

$$= C_{p, \text{vap}} - T \frac{(\partial S_{\text{vap}} / \partial T)_P}{(\partial P / \partial T)_{\text{svap}}} \frac{dP}{dT}$$

$$= C_{p, \text{vap}} \left[1 - \frac{(\partial P / \partial T)}{(\partial P / \partial T)_{\text{svap}}} \right] < 0$$

$$\left(\frac{\partial P}{\partial T} \right)_{\text{svap}} < \frac{dP}{dT}$$

$$\Rightarrow C_{p, \text{liq}} + T \frac{d}{dT} \left(\frac{L}{T} \right) < 0 \quad \text{QED} \quad \checkmark$$