Problema 1: $m = \frac{D\mathcal{H}}{T} \rightarrow \mathcal{H} = \frac{mT}{D}$; $c_m = c$: cte.

• Combinando el primer y segundo principio:

• $$T\,ds = du - \mathcal{H}\,dm = c\,dT - \frac{mT}{D}\,dm$$

$$\rightarrow ds = c\frac{dT}{T} - \frac{1}{D}m\,dm$$

$$\therefore \int_{s_0}^{s} ds' = c\int_{T_0}^{T}\frac{dT'}{T'} - \frac{1}{D}\int_{m_0}^{m} m'\,dm'$$

$$s - s_0 = c\ln\left(\frac{T}{T_0}\right) - \frac{1}{2D}(m^2 - m_0^2)$$

$$\therefore \boxed{S = S_0 + C\ln\left(\frac{T}{T_0}\right) - \frac{(M^2 - M_0^2)}{2mD}}$$

$S = ms$; $C = mc$; $M = mm$.

• Entalpía: $H = U + \mathcal{H}M = C(T - T_0) + \frac{TM^2}{mD}$

$$\boxed{h = c(T - T_0) + \frac{Tm^2}{D}} \boxed{= c(T - T_0) + \frac{D}{T}\mathcal{H}^2}$$

• Energía libre de Helmholtz: $A = U - TS$

$$A = C(T - T_0) - T\left\{S_0 + C\ln\left(\frac{T}{T_0}\right) - \frac{(M^2 - M_0^2)}{2mD}\right\}$$

$$A = CT - CT_0 - TS_0 - CT\ln\left(\frac{T}{T_0}\right) + \frac{T}{2mD}M^2 - \frac{T}{2mD}M_0^2$$

$$\boxed{A = CT\left[1 - \ln\left(\frac{T}{T_0}\right)\right] + \frac{T}{2mD}M^2 - T\left(S_0 + \frac{M_0^2}{2mD}\right) - CT_0}$$

• Energía libre de Gibbs $G = A - \mathcal{H}M$

$$\boxed{G = CT\left[1 - \ln\left(\frac{T}{T_0}\right)\right] - \frac{T}{2mD}M^2 - T\left(S_0 + \frac{M_0^2}{2mD}\right) - CT_0}$$

Problema 2: El estado crítico es un estado donde P, T y V satisfacen simultáneamente 3 ecuaciones: Ecuación de estado $(\partial P/\partial V)_T = 0$ y $(\partial^2 P/\partial V^2)_T = 0$. Así, para

$$P = \frac{mRT}{V-mb}\exp\left[-\frac{am}{RTV}\right],$$

tenemos

i) $$\left(\frac{\partial P}{\partial V}\right)_T = \frac{mRT}{V-mb}\times\left(\frac{am}{RTV^2}\right)\exp[\,] - \frac{mRT}{(V-mb)^2}\exp[\,]$$

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{mRT}{V-mb}\exp[\,]\left\{\frac{ma}{RTV^2} - \frac{1}{V-mb}\right\}$$

$$\rightarrow \boxed{\left(\frac{\partial P}{\partial V}\right)_T = P\left\{\frac{ma}{RTV^2} - \frac{1}{V-mb}\right\}} \quad (i)$$

ii) $$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = \left(\frac{\partial P}{\partial V}\right)_T\left\{\frac{ma}{RTV^2} - \frac{1}{V-mb}\right\} + P\left\{-\frac{2ma}{RTV^3} + \frac{1}{(V-mb)^2}\right\}$$

$$\boxed{\left(\frac{\partial^2 P}{\partial V^2}\right)_T = P\left\{\frac{ma}{RTV^2} - \frac{1}{V-mb}\right\}^2 + P\left\{-\frac{2ma}{RTV^3} + \frac{1}{(V-mb)^2}\right\}} \quad (ii)$$

De (i): $$\left(\frac{\partial P}{\partial V}\right)_T = 0 \Rightarrow \frac{V^2}{V-mb} = \frac{ma}{RT} \quad (iii)$$

De (ii) $$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 \Rightarrow \frac{V^3}{(V-mb)^2} = \frac{2ma}{RT} \quad (iv)$$

Dividiendo (iv) en (iii):
$$\frac{V_c}{V_c-mb} = 2 \Rightarrow \boxed{V_c = 2mb}$$

Reemplazando en (iii)
$$\frac{4\cancel{m^2}b^{\cancel{2}}}{\cancel{mb}} = \frac{\cancel{m}a}{RT_c} \rightarrow \boxed{T_c = \frac{a}{4Rb}}$$

Reemplazando en la ec. de estado:
$$P_c = \frac{mRT_c}{V_c-mb}\exp\left[-\frac{am}{RT_cV_c}\right] = \frac{\cancel{m}\,a/4\cancel{b}b}{\cancel{m}\,b}\exp\left[-\frac{\cancel{a}m}{\cancel{a}/4b\cdot 2mb}\right] = \frac{a}{4b^2}e^{-2}$$

$$\boxed{P_c = \frac{a}{4e^2b^2}}$$

Para obtener la expresión de los "estados correspondientes" usamos las variables reducidas, $\mathcal{V}=V/V_c$, $\tau=T/T_c$, $\mathcal{P}=P/P_c$

$$\rightarrow P = P_c\mathcal{P} = \frac{nRT_c\tau}{V_c\mathcal{V}-nb}\exp\left[-\frac{an}{RT_c\tau V_c\mathcal{V}}\right]$$

$$* \quad \frac{nRT_c\tau}{P_c(V_c\mathcal{V}-nb)} = \frac{nRT_c}{V_cP_c}\cdot\frac{\tau}{\mathcal{V}-\frac{nb}{V_c}} = \frac{\cancel{n}\,\cancel{a/4b}}{2\cancel{nb}\cdot\frac{\cancel{a}}{4e^2\cancel{b^2}}}\cdot\frac{\tau}{\mathcal{V}-\frac{nb}{2nb}} = \frac{e^2}{2}\,\frac{\tau}{\mathcal{V}-\frac{1}{2}}$$

$$* \quad \frac{an}{RT_cV_c}\times\frac{1}{\tau\mathcal{V}} = \frac{\cancel{an}}{\frac{\cancel{a}}{\cancel{4b}_{\,2}}\times 2\cancel{nb}}\times\frac{1}{\tau\mathcal{V}} = \frac{2}{\tau\mathcal{V}}$$

$$\therefore \quad \mathcal{P} = \frac{\tau e^2}{2\mathcal{V}-1}\cdot e^{-\frac{2}{\tau\mathcal{V}}} = \frac{\tau}{2\mathcal{V}-1}\,e^{-2\left(\frac{1}{\tau\mathcal{V}}-1\right)}$$

$$\Rightarrow \boxed{\mathcal{P} = \frac{\tau}{2\mathcal{V}-1}\,e^{+2\left(\frac{\tau\mathcal{V}-1}{\tau\mathcal{V}}\right)}}$$

Problema 3: Sólido: $\ln P = \ln P_1 - \frac{\ln(P_2/P_1) T_0^2}{T^2}$ (1)

(a) Líquido: $\ln P = \ln P_2 - \frac{2\ln(P_2/P_1) T_0}{T}$ (2)

En el punto triple se igualan las presiones de vapor:

$$\ln P_2 - \frac{2\ln(P_2/P_1) T_0}{T_{pt}} = \ln P_1 - \frac{\ln(P_2/P_1) T_0^2}{T_{pt}^2}$$

$$\Rightarrow \ln(P_2/P_1) - 2\ln(P_2/P_1)\frac{T_0}{T_{pt}} + \ln(P_2/P_1)\frac{T_0^2}{T_{pt}^2} = 0$$

$$\ln(P_2/P_1)\left[1 - \frac{2T_0}{T_{pt}} + \frac{T_0^2}{T_{pt}^2}\right] = 0$$

$$\Rightarrow T_{pt}^2 - 2T_0 T_{pt} + T_0^2 = 0$$

$$\boxed{T_{pt} = T_0 = 250\ K}$$

En la expresión para la presión de vapor del sólido:

$$\ln P_{pt} = \ln P_1 - \ln P_2 + \ln P_1 = 2\ln P_1 - \ln P_2$$

$$\ln P_{pt} = \ln(P_1^2/P_2) \Rightarrow \boxed{P_{pt} = \frac{P_1^2}{P_2} = 0{,}5\ atm}$$

(b) A partir de (2):

$$\frac{dP}{P} = 2\ln(P_2/P_1) \times \frac{dT}{T^2} \Rightarrow \boxed{\frac{dP}{dT} = 2\ln\left(\frac{P_2}{P_1}\right) \times \frac{P}{T^2}}$$

La ecuación de Clapeyron:

$$\frac{dP}{dT} = \frac{l_v}{T(v''' - v')} \simeq \frac{l_v}{T v'''}$$

← suponiendo que el volumen molar de vapor es mucho mayor que el volumen molar de líquido.

Así, comparando

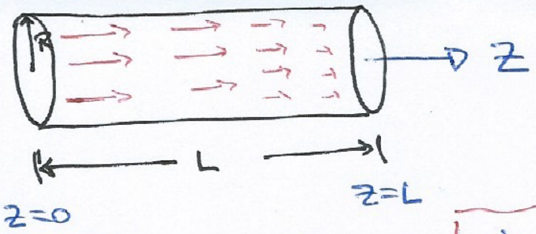
$$2\ln\left(\frac{P_2}{P_1}\right)\times\frac{P}{T^2}\simeq\frac{l_v}{\cancel{T}\,v'''}\Rightarrow\boxed{l_v\simeq 2\ln\left(\frac{P_2}{P_1}\right)\times\frac{Pv'''}{T}}$$

Podemos suponer que el vapor se comporta como un gas ideal, de manera que $Pv'''\simeq RT$, y así

$$\boxed{l_v\simeq 2R\ln\left(\frac{P_2}{P_1}\right)}\boxed{\simeq 2\times 0{,}69\times R}$$

$$\boxed{l_v\simeq 1{,}39R}\boxed{\simeq 2{,}75\left(\frac{cal}{mol\cdot K}\right)}$$

Problema 4:



$$\boxed{T(z)=T_0\left[1+\cos\left(\frac{\pi}{2}\frac{z}{L}\right)\right]}$$

(a)

Ley de Fourier: $\vec{q} = -K\vec{\nabla}T \rightarrow \boxed{\vec{q} = -K\frac{dT}{dz}\hat{k} \equiv q_z\hat{k}}$

$$q_z = -K\frac{dT}{dz} = -K \times T_0 \times \left(-\frac{\pi}{2L}\right) \times \sin\left(\frac{\pi}{2}\frac{z}{L}\right) \Rightarrow \boxed{q_z = \frac{K\pi T_0}{2L}\sin\left(\frac{\pi}{2}\frac{z}{L}\right)}$$

$$\rightarrow \boxed{\vec{q} = \frac{\pi K T_0}{2L}\sin\left(\frac{\pi}{2}\frac{z}{L}\right)\hat{k}}$$

- $\boxed{q_z(z=L) = \frac{K\pi T_0}{2L}}$
- $q_z(z=\frac{L}{2}) = \frac{K\pi T_0}{2L}\cdot\sin\left(\frac{\pi}{4}\right)$

$$\boxed{q_z(z=\tfrac{L}{2}) = \frac{K\pi T_0}{2L}\cdot\frac{\sqrt{2}}{2}}$$

$\Rightarrow$ La razón entre la densidad de flujo en $z=L \wedge z=L/2$ es

$$\eta = \frac{q_z(L/2)}{q_z(L)} = \frac{\cancel{(K\pi T_0/2L)}\cdot\sqrt{2}/2}{\cancel{(K\pi T_0/2L)}}$$

$$\rightarrow \boxed{\eta = \frac{\sqrt{2}}{2} \approx 0{,}7}$$

(b) $q_z(z=L/3) = \frac{K\pi T_0}{2L}\cdot\sin\left(\frac{\pi}{6}\right) = \frac{K\pi T_0}{2L}\times\frac{1}{2}$

$$A = \pi r^2 = \pi\left(\frac{R}{2}\right)^2 = \frac{\pi}{4}R^2$$

$$\Rightarrow \dot{Q}(z=\tfrac{L}{3}) = q_z(\tfrac{L}{3})\cdot A = \frac{K\pi T_0}{2L}\times\frac{1}{2}\times\frac{\pi}{4}R^2 = \frac{\pi^2 R^2 K T_0}{16L}$$

$$\Rightarrow \boxed{\dot{Q}(z=\tfrac{L}{3}) = \frac{\pi^2}{16}\times\frac{R^2 K T_0}{L}}$$