1) Consider a rubber band with eos:

$$l = \theta \frac{f}{T}$$

f ← tension

T ← temperature

θ ← const.

l ← length per unit mass

$l \sim V$

a) Compute $\left(\frac{\partial C_l}{\partial l}\right)_T$, where C_l is the constant length heat capacity per unit mass.

Heat capacity:

$$C_l = (C)_l = \frac{\cancel{d}Q}{dT} = T\frac{\cancel{d}Q/T}{dT} = T\left(\frac{dS}{dT}\right)_l$$

$$\left(\frac{\partial C_l}{\partial l}\right)_T = \frac{\partial}{\partial l}\left(T\left(\frac{dS}{dT}\right)_l\right)_T$$

$$\stackrel{!}{=} T\frac{\partial}{\partial l}\left(\left(\frac{\partial S}{\partial T}\right)_l\right)_T$$

$$\stackrel{!}{=} T\frac{\partial}{\partial T}\left(\left(\frac{\partial S}{\partial l}\right)_T\right)_l$$

swap differentiate order.

Use $A = E - TS$

$$dA = -SdT + fdl$$

then $-S = \left(\frac{\partial A}{\partial T}\right)_l \qquad f = \left(\frac{\partial A}{\partial l}\right)_T$

then maxwell: $\left(-\frac{\partial S}{\partial l}\right)_T = \left(\frac{\partial f}{\partial T}\right)_l = \frac{\partial^2 A}{\partial T \partial l}$

Since $\left(-\frac{\partial S}{\partial \ell}\right)_T = \left(\frac{\partial f}{\partial T}\right)_\ell$

$$\left(\frac{\partial C_\ell}{\partial \ell}\right)_T = -T\frac{\partial}{\partial T}\left(\left(\frac{\partial f}{\partial T}\right)_\ell\right)_\ell$$

$$\stackrel{!}{=} -T\left(\frac{\partial^2 f}{\partial T^2}\right)_\ell$$

$$f = \frac{\ell T}{\theta} \Rightarrow \frac{\partial f}{\partial T} = \frac{\ell}{\theta} \Rightarrow \frac{\partial^2 f}{\partial T^2} = 0.$$

so $\boxed{\left(\frac{\partial C_\ell}{\partial \ell}\right)_T = 0}$

b) For constant temperature T, $f_0 \Rightarrow f_0 + \Delta f$

Find the change in entropy per unit mass.

$$S_{init} = S(T, f, n)$$

$$S_{final} = S(T, f+\Delta f, n)$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_{f,n} dT + \left(\frac{\partial S}{\partial f}\right)_{T,n} df + \left(\frac{\partial S}{\partial n}\right)_{T,f} dn$$

Theres no change in T and n, so $dT = dn = 0$.

$$\int^{S_{final}} dS = S(T, f_0+\Delta f, n) - S(T, f_0, n) = \Delta S$$

Since

$\stackrel{!}{=} \left(\frac{\partial S}{\partial f}\right)_{T,n} df$

$$dG = -SdT - \ell df$$

$$S = \left(-\frac{\partial G}{\partial T}\right)_f \qquad \ell = \left(-\frac{\partial G}{\partial f}\right)_T$$

$$\rightarrow \quad \left(\frac{\partial S}{\partial f}\right)_T = \left(\frac{\partial \ell}{\partial T}\right)_f = -\frac{\partial^2 G}{\partial T \partial f}$$

Then $\quad \Delta S = \left(\frac{\partial \ell}{\partial T}\right)_f df \qquad \left(\frac{\partial \ell}{\partial T}\right)_f = \frac{-\theta f}{T^2}$

$$\stackrel{!}{=} \int_{f_0}^{f_0+\Delta f} \frac{-\theta f}{T^2} df$$

$$\stackrel{!}{=} \frac{-\theta}{2T^2}\left([f_0+\Delta f]^2 - f_0^2\right)$$

$$\boxed{\Delta S \stackrel{!}{=} \frac{-\theta}{2T^2}\left(2f_0\Delta f + \Delta f^2\right)}$$

2) For $dW = -pdV$, use Maxwell relation to show:

a) $TdS = C_V dT + T\left(\frac{\partial p}{\partial T}\right)_V dV$

let $S = S(T, V)$

we know $dA = -SdT - pdV$

so $S = \left(-\frac{\partial A}{\partial T}\right)_V$ $\quad p = \left(-\frac{\partial A}{\partial V}\right)_T$

then $\left(\frac{\partial S}{\partial V}\right)_T = -\frac{\partial^2 A}{\partial T \partial V} = \left(\frac{\partial P}{\partial T}\right)_V$

Maxwell Relation →

then:

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

Multiply by T on both sides.

$$TdS = \underbrace{T\left(\frac{\partial S}{\partial T}\right)_V}_{= C_V} dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$$

$$\therefore \boxed{TdS = C_V dT + T\left(\frac{\partial p}{\partial T}\right)_V dV}$$

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

let $S = S(T,p)$

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

know $dG = -S\,dT + V\,dp$

then $-S = \left(\frac{\partial G}{\partial T}\right)_p \qquad V = \left(\frac{\partial G}{\partial p}\right)_T$

so $-\left(\frac{\partial S}{\partial p}\right)_T = \frac{\partial^2 G}{\partial p\,\partial T} = \left(\frac{\partial V}{\partial T}\right)_p$

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

multiply by T and recognize $T\left(\frac{\partial S}{\partial T}\right)_p = C_p$

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

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

know $A = E(S,V) - TS$

then $E(S,V) = A + TS$.

$$\frac{\partial}{\partial V}\Big([A + TS]\Big)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

$$\left(\frac{\partial}{\partial V}A\right)_T + T\left(\frac{\partial S}{\partial V}\right)_T + S\underbrace{\cancel{\left(\frac{\partial T}{\partial V}\right)_T}}_{0} = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

since holding T constant.

know $dA = -SdT - PdV$

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

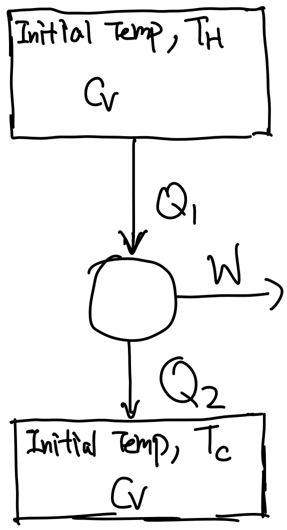
and $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T = -\frac{\partial^2 A}{\partial T \partial V}$ ← Maxwell relation.

using

we arrive:

$$\boxed{-P + T\left(\frac{\partial P}{\partial T}\right)_V = T\left(\frac{\partial P}{\partial T}\right)_V - P}$$ ← Same expression.

3)



→ constant volume.

→ constant C_V.

→ Different temperature, T_H, T_C.

Find max(W)?

$$dE = \underbrace{TdS}_{dQ_{rev.}} + dW = 0$$

$$0 = Q_1 - Q_2 - W$$

$$W = Q_1 - Q_2$$

know $\quad C_V = \frac{dQ}{dT} = T\left(\frac{\partial S}{\partial T}\right)_V = \text{const.}$

$$\int_{T_{init}}^{T_{final}} C_V \, dT = \int_{Q_{init}}^{Q_{fin}} dQ$$

$\hookrightarrow$
$$C_V(T_{final} - T_H) = -Q_1$$
$$C_V(T_{final} - T_C) = Q_2$$

Then $\quad W = Q_1 - Q_2$

$$= -C_V(T_{final} - T_H) - C_V(T_{final} - T_C)$$

$$W = C_V(-2T_{final} + T_H + T_C)$$

Need T_{final}?

$\rightarrow$ Max work when process is reversible.

$\rightarrow$ reversible implies:

$$\rightarrow \quad \Delta S_{tot} = \Delta S_1 + \Delta S_2 = 0$$

$$\rightarrow \quad dS = \frac{dQ)_{rev}}{T}$$

but $\quad C_V = \dfrac{dQ}{dT}$

$$\Delta S_1 = \int dS = \int_{T_H}^{T_{fin}} \frac{C_V \, dT}{T} = C_V \ln\left(\frac{T_{fin}}{T_H}\right)$$

$$\Delta S_2 = \int dS = \int_{T_C}^{T_{fin}} \frac{C_V \, dT}{T} = C_V \ln\left(\frac{T_{fin}}{T_C}\right)$$

we know for reversible

$$\Delta S_{tot} = \Delta S_1 + \Delta S_2 = 0$$

$$\hookrightarrow C_V\left(\ln\left(\frac{T_{fin}}{T_H}\right) + \ln\left(\frac{T_{fin}}{T_C}\right)\right) = 0$$

$$\hookrightarrow \quad C_V \ln\left(\frac{T_f^2}{T_H T_C}\right) = 0$$

$$\hookrightarrow e^{\ln\left(\frac{T_f^2}{T_H T_C}\right)} = e^0 = 1$$

$$\hookrightarrow \frac{T_f^2}{T_H T_C} = 1 \quad \text{or} \quad T_f = \sqrt{T_H T_C}$$

then
$$\boxed{\begin{aligned} W &= C_V\left(-2T_f + T_H + T_C\right) \\ &= C_V\left(-2\sqrt{T_H T_C} + T_H + T_C\right) \end{aligned}}$$

4) Consider column of atmospheric gas to have constant T, with constant $\vec{g} = -g\hat{e}_z$

with eos:

$$p = \frac{\rho}{M} RT$$

a) use $-\nabla p + \rho\vec{g} = 0$, to find $\rho(z)$

$$-\rho g \hat{z} = \nabla p$$

$$-\rho g = \frac{\partial}{\partial z}\left(\frac{\rho}{M} RT\right)$$

$$-\rho g = \frac{\partial \rho}{\partial z} \frac{RT}{M}$$

$$\int_{z=0}^{z} -\frac{Mg}{RT}\, dz = \int_{\rho_0}^{\rho} \frac{\partial \rho}{\rho}$$

$$-\frac{Mg}{RT} z = \ln \frac{\rho}{\rho_0}$$

$$\boxed{\rho(z) = \rho_0 e^{-\frac{Mg}{RT} z}}$$

b) The energy difference $\mu_{gravity} = Mgz$.

but μ must be constant in equilibrium,
so the change in $\mu_{gravity}$ is counter acted by the density dependence. of the chemical potential.

$\Rightarrow$ Find $\mu(\rho)$

$\rightarrow$ previously we know density, $\rho(z)$ and pressure $P(\rho)$
$\rightarrow$ We know it is in equilibrium.

Since μ_{gas} is constant at equilibrium:

$$\mu(\rho) + \mu_{gravity} = \text{const}$$

then $$d\mu + d\mu_{gravity} = 0$$

or $$d\mu = -Mg\,dz$$

from part a)

$$\rho(z) = \rho_0 e^{\frac{-Mg}{RT}z}$$

$$\frac{d\rho}{dz} = \rho_0\left(\frac{-Mg}{RT}\right) e^{\frac{-Mg}{RT}z}$$
$$\overset{!}{=} \frac{-Mg}{RT}\rho$$

then $$dz = \frac{-RT}{Mg}\frac{1}{\rho}\,d\rho$$

For $$d\mu = -Mg\,dz$$

$$\int_{\mu(\rho_0)}^{\mu} d\mu \overset{!}{=} -Mg\left(\frac{-RT}{Mg}\right)\int_{\rho_0}^{\rho} \frac{1}{\rho}\,d\rho$$

$$\mu - \mu(\rho_0) = RT\ln\frac{\rho}{\rho_0}$$

$$\hookrightarrow \boxed{\mu(\rho) = \mu(\rho_0) + RT\ln\left(\frac{\rho}{\rho_0}\right)}$$

Just to confirm, let $\rho = \rho_0 e^{\frac{-Mg}{RT}z}$

$$\mu(\rho) + Mgz = \text{const}$$
$$\mu(\rho_0) + RT\ln\left(e^{\frac{-Mg}{RT}z}\right) + Mgz = \text{const}$$
$$\mu(\rho_0) \cancel{- Mgz + Mgz} = \text{const.}$$
$$\mu(\rho_0) = \text{const.} \checkmark$$

5) For a reversible heat transfer $dQ)_{rev}$, for a closed system:

$$đQ)_{rev} = dE + pdV$$

\# of moles

Consider ideal gas: $dE = \frac{3}{2}nRdT$ $\quad pdV = \left(\frac{nRT}{V}\right)dV$

So $\quad đQ)_{rev} = \frac{3}{2}nRdT + \frac{nRT}{V}dV$

a) Show $đQ)_{rev}$ for ideal gas is an inexact differential.

- inexact differential: path dependent integral, which means $đQ$ will not be a total differential of $Q(T,V)$

$$đQ)_{rev} = \left(\frac{\partial Q}{\partial T}\right)_V dT + \left(\frac{\partial Q}{\partial V}\right)_T dV$$

If exact differential:

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

$$\frac{\partial}{\partial V}\left(\frac{3}{2}nR\right)_T = \frac{\partial}{\partial T}\left(\frac{nRT}{V}\right)_V$$

$\hookrightarrow$ $\boxed{0 \neq \frac{nR}{V}}$ ← Since it doesn't match $đQ)_{rev}$ is an inexact differential

b) $dS = \frac{đQ_{rev}}{T}$

$$dS = \frac{3}{2}\frac{nR}{T}dT + \frac{nR}{V}dV$$

$$\stackrel{!}{=} \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

Similarly, exact differential if:

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

$$\frac{\partial}{\partial V}\left(\frac{3}{2}\frac{nR}{T}\right)_T = \frac{\partial}{\partial T}\left(\frac{nR}{V}\right)_V$$

$\boxed{0 = 0}$ ← since they match, dS is an exact differential

c) Integrate $dS = đQ/T$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$= \frac{3}{2}\frac{nR}{T}dT + \frac{nR}{V}dV$$

$$\int_{S_0}^{S} dS' = \int_{T_0}^{T} \frac{3}{2} nR \frac{1}{T'}dT' + \int_{V_0}^{V} nR\frac{1}{V'}dV'$$

$$S - S_0 = \frac{3}{2}nR\ln\frac{T}{T_0} + nR\ln\frac{V}{V_0}$$

$$\boxed{S(T,V) = \frac{3}{2}nR\ln\frac{T}{T_0} + nR\ln\frac{V}{V_0} + S_0}$$