14) A system$^{(1)}$ can exchange energy & volume with a large reservoir$_{(R)}$

a) show that $S_{tot} = S_{max}$ when $T_1 = T_R$

AND when $P_1 = P_R$.

SPRING 2003

In general

$\Delta S_{tot} = \Delta S_1 + \Delta S_R$

$$\Delta E_1 = T_1 \Delta S_1 - P_1 \Delta V_1 \quad \& \quad \Delta E_R = T_R \Delta S_R - P_R \Delta V_R$$

Here $\Delta E_1 = -\Delta E_R$ & $\Delta V_1 = -\Delta V_R$

$$T_1 \Delta S_1 - P_1 \Delta V_1 = -T_R \Delta S_R + P_R \Delta V_R$$

$$T_1 \Delta S_1 + T_R \Delta S_R = P_1 \Delta V_1 + P_R \Delta V_R$$

$$T_1 \Delta S_1 + T_R \Delta S_R = (P_1 - P_2) \Delta V_1$$

IF $P_1 = P_2$ then $\Delta S_1 = -\frac{T_R}{T_1} \Delta S_R$

and $\boxed{\Delta S_{tot} = \left(1 - \frac{T_R}{T_1}\right) \Delta S_2}$

and IF $T_1 = T_R$ then $\Delta S_{tot} = 0$ so $\boxed{S_{tot} = S_{max}}$

b) Expanding the entropy of the subsystem (1) to second order . . .

$$dS_1 = \underbrace{\frac{1}{T_1} dE_1 - \frac{P_1}{T_1} dV_1}_{\text{first order}} + \underbrace{\left(\frac{\partial \, 1/T_1}{\partial E}\right)_V \frac{(\delta E)^2}{2} + \left(\frac{\partial \, P_1/T_1}{\partial V}\right)_E \frac{(\delta V)^2}{2}}_{\text{second order}} \cdots$$

we find

$$dS_{tot} = \frac{1}{T_1} dE_1 - \frac{P_1}{T_1} dV_1 + \frac{1}{T_R} dE_R - \frac{P_R}{T_R} dV_R$$

$$+ \left(\frac{\partial \frac{1}{T_1}}{\partial E}\right)_V \frac{(\delta E)^2}{2} + \left(\frac{\partial \, P_1/T_1}{\partial V}\right)_E \frac{(\delta V)^2}{2} \cdots$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_R}\right) dE_1 - \left(\frac{P_1}{T_1} - \frac{P_R}{T_R}\right) dV_1$$

$$+ \left(\frac{\partial \, 1/T_1}{\partial E}\right)_V \frac{(\delta E)^2}{2} + \left(\frac{\partial \, P_1/T_1}{\partial V}\right)_E \frac{(\delta V)^2}{2}$$

where the second order expations for the reservoir are neglected because it is large. At equilibrium

$T_1 = T_R$, $P_1 = P_R$ (from part a)

So the first two terms vanish

$$\boxed{dS_{tot} = \left(\frac{\partial \, 1/T_1}{\partial E}\right)_V \frac{(\delta E)^2}{2} + \left(\frac{\partial \, P_1/T_1}{\partial V}\right)_E \frac{(\delta V)^2}{2}} \quad (\mathrm{I})$$

from $\delta E = \underbrace{\left(\frac{\partial E}{\partial T}\right)_V}_{C_V} \delta T + \underbrace{\left(\frac{\partial E}{\partial V}\right)_T}_{P} \delta V$

$$(\delta E)^2 = C_V^2 (\delta T)^2 + P^2 (\delta V)^2 + 2 P C_V (\delta T)(\delta V)$$

Now the first term in dS_{tot}:

$$\left(\frac{\partial\, {}^1/_{T_1}}{\partial E}\right)_V (\delta E)^2 = -\frac{1}{T_1^2}\left(\frac{\partial T_1}{\partial E}\right)_V \frac{(\delta E)^2}{2}$$

$$= -\frac{1}{T_1^2 C_V}\frac{(\delta E)^2}{2}$$

$$\doteq -\frac{1}{2T_1^2 C_V}\left[C_V^2(\delta T)^2 + p^2(\delta V)^2\right] \quad (\mathrm{II})$$

the $(\delta V)(\delta T)$ term vanishes due to the equilibrium condition $\Rightarrow \langle \delta V\rangle = 0$, $\langle \delta T\rangle = 0$. These are independent variables and so $(\delta V)(\delta T) \approx 0$

Now the second term in ΔS_{tot}.

$$\left(\frac{\partial\, {}^{P_1}/_{T_1}}{\partial V}\right)_E = \frac{1}{T_1}\left(\frac{\partial P_1}{\partial V}\right)_{T_1} - \frac{P_1}{T_1^2}\left(\frac{\partial T_1}{\partial V}\right)_{P_1}$$

$$= \frac{1}{T_1}\left(\frac{\partial P_1}{\partial V}\right)_{T_1} - \frac{P_1}{T_1^2}\left[\underbrace{\left(\frac{\partial T_1}{\partial E}\right)_V}_{1/C_V}\underbrace{\left(\frac{\partial E}{\partial V}\right)_{T_1}}_{-P_1}\right]$$

$$= \frac{1}{T_1}\left(\frac{\partial P_1}{\partial V}\right)_{T_1} + \frac{P_1^2}{T_1^2 C_V} \quad (\mathrm{III})$$

Combining (II) & (III) into (I) ...

$$dS_{tot} = -\underbrace{\frac{C_v}{T_1^2}\frac{(\delta T)^2}{2} - \frac{P_1^2}{T_1^2 C_v}\frac{(\delta v)^2}{2}}_{(\mathrm{II})} + \underbrace{\left[\frac{1}{T_1}\left(\frac{\partial P_1}{\partial V}\right)_{T_1} + \frac{P_1^2}{T_1^2 C_v}\right]}_{\mathrm{III}}\frac{(\delta v)^2}{2}$$

$$dS_{tot} = -\frac{C_v}{2T_1^2}(\delta T)^2 + \frac{1}{2T_1}\left(\frac{\partial P_1}{\partial V}\right)_{T_1} \quad (\mathrm{IV})$$

from the second law $\rightarrow$ $\Delta S_{tot} \geq 0$

so $$\boxed{\left(\frac{\partial P}{\partial V}\right)_T (\delta v)^2 \geq \frac{C_v}{T}(\delta T)^2}$$