1) $\boxed{S' = S - \frac{1}{T}U}$

$$dS' = dS - d\left(\frac{1}{T}\right)U - \frac{1}{T}dU$$

$$\boxed{dS' = -U\,d\left(\frac{1}{T}\right) + \frac{P}{T}dV - \frac{\mu}{T}dN}$$

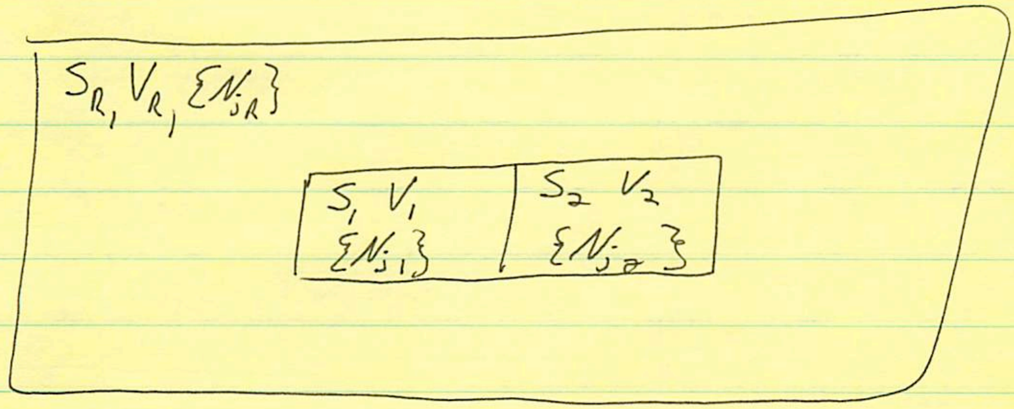
$$\boxed{S'' = S - \frac{1}{T}U - \frac{P}{T}V}$$

$$dS'' = dS - U\,d\left(\frac{1}{T}\right) - \frac{1}{T}dU - V\,d\left(\frac{P}{T}\right) - \frac{P}{T}dV$$

$$\boxed{dS'' = -U\,d\left(\frac{1}{T}\right) - V\,d\left(\frac{P}{T}\right) - \frac{\mu}{T}dN}$$

$$\boxed{\begin{gathered} S''' = S - \frac{1}{T}U + \frac{\mu}{T}N \\ dS''' = -U\,d\left(\frac{1}{T}\right) + \frac{P}{T}dV + N\,d\left(\frac{\mu}{T}\right) \end{gathered}}$$

2) Consider a composite system composed of a large reservoir and a subsystem with internal variables as in class. To invoke energy min principle, we must assume S_{TOT}, V_{TOT}, $N_{j_{TOT}}$ are all constant



We want the 1 & 2 subsystem to be maintained at constant $\{N_j\}$ V & T through interaction with the reservoir. This means S_1, S_2, S_R can all vary subject to $S_1 + S_2 + S_R = \text{constant}$

V_1, V_2 can vary subject to $V_1 + V_2 = \text{constant}$

N_{j_1}, N_{2_j} can vary subject to $N_{j_1} + N_{2_j} = \text{constant}$

$dU_{TOT} = 0$ at equilibrium

$dU_{TOT} = dU_R + dU_1 + dU_2$

$$dU_R = \left.\frac{\partial U_R}{\partial S_R}\right|_{V_R, \{N\}_R} dS_R = T_R\, dS_R$$

but, $dS_R = -dS_1 - dS_2$ since $S_R + S_1 + S_2 = \text{const.}$

so, $dU_R = dU_1 + dU_2 - T_R dS_1 - T_R dS_2$

$= d(U_1 - T_R S_1) + d(U_2 - T_R S_2)$

Reservoir is large, so T_R unaffected by changes in system.

$= dA_1 + dA_2$

$= dA_{sys}$

i.e. $\boxed{dA_{sys} = 0 \text{ at equilibrium for } V_{sys} \text{ constant, } \{N_j\}_{sys} \text{ constant, } T_{sys} = T_R \text{ constant}}$