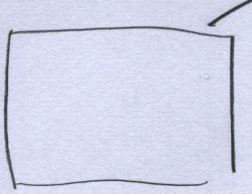
7.2 a. Show that the condition for equilibrium in a closed system at constant entropy and volume is that the internal energy U achieve a minimum value subject to the constraints.

7.2 b. Show that the condition for equilibrium in a closed system at constant entropy and pressure is that the enthalpy H achieve a minimum value subject to the constraints.

7.2

(a)



Mass Balance

$$\frac{dN}{dt} = 0$$

Energy Balance

closed system no shaft work

$$\frac{dU}{dt} = \sum_i \dot{N}_i \bar{H}_i + \dot{Q} + \dot{W}_s - P\frac{dV}{dt}$$

Vol. is fixed

$$\Rightarrow \frac{dU}{dt} = \dot{Q} \quad -①$$

Entropy Balance

constant S closed system

$$\frac{dS}{dt} = \sum_i \dot{N}_i \bar{S}_i + \frac{\dot{Q}}{T} + \dot{S}_{gen}$$

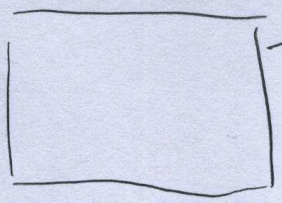
$$\Rightarrow 0 = \frac{\dot{Q}}{T} + \dot{S}_{gen} \quad -②$$

② into ① to replace $\dot{Q}$

$$\Rightarrow \frac{dU}{dt} = -T\dot{S}_{gen} \leq 0$$

$\dot{S}_{gen} \geq 0$

$\Rightarrow U$ is with a min. value at equilibrium at constant V & S.

(b)  → closed system

constant entropy & pressure

Mass Balance

$$\frac{dN}{dt} = 0$$

Energy Balance (closed system, no shaft work)

$$\frac{dU}{dt} = \sum_i \dot{N}_i \underline{H}_i + \dot{Q} + \dot{W}_s - P\frac{dV}{dt}$$

(constant P)

$$\Rightarrow \frac{dU}{dt} = \dot{Q} - P\frac{dV}{dt} \quad -①$$

Entropy Balance (closed system)

$$\frac{dS}{dt} = \sum_i \dot{N}_i \underline{S}_i + \frac{\dot{Q}}{T} + \dot{S}_{gen}$$

$$\Rightarrow 0 = \frac{\dot{Q}}{T} + \dot{S}_{gen} \quad -②$$

② into ① to replace $\dot{Q}$

$$\Rightarrow \frac{dU}{dt} + \frac{dPV}{dt} = -T\dot{S}_{gen}$$

$$\Rightarrow \frac{dH}{dt} = -T\dot{S}_{gen} \leq 0 \Rightarrow H \text{ is with a min value at equilibrium at constant } S \& P$$

($\dot{S}_{gen} \geq 0$)