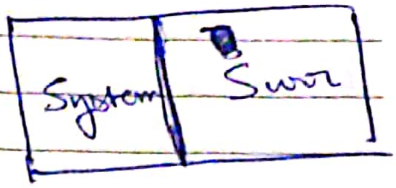
$$dS_T = dS_0 + dS$$
$$= -\left[\frac{dU + p_{ext}dV}{T_{surr}}\right] + dS \geq 0.$$

Thermodynamic Potential: $-dU = T_{surr}dS - p_{ext}(-dV)$



$$dU = \text{đ}Q + \text{đ}W$$

$$TdS \geq \text{đ}Q$$

Spontaneous process: Energy fixed
Entropy maximized

$$dU \leq TdS - pdV$$

$$dU \leq T_{surr}dS - p_{ext}dV$$

At equilibrium thermodynamic parameters do not change.

1.) Consider an ~~...~~ isolated system;

$\text{đ}Q = 0$, $\text{đ}W = 0$, $dV = 0$, $dU = 0$.

$$(dS)_{U,V} \geq 0$$

⇒ Equilibrium of an isolated system achieved when entropy is maximized.

At equilibrium/maximum entropy no spontaneous changes can occur.

2.) Consider S, V const

$$\left(dU\right)_{S,V} \leq 0$$

At constant S & V, equilibrium is achieved when energy is minimized.

3. Consider S & p_{ext} is const.

$$dU + p_{ext} dV \leq 0$$

$$\Rightarrow d(U + p_{ext} V) < 0.$$

$$\Rightarrow dH \leq 0.$$

Enthalpy is minimized at constant entropy and pressure spontaneous process.

4. Constant H & p_{ext} = const

$$dU + p_{ext} dV \leq T_{surr} dS$$

$$dH \leq T_{surr} dS$$

$$\Rightarrow dS \geq 0.$$

5.) $T = T_{surr} = \text{const}$, constant V

$\Rightarrow dU - T_{surr} dS \leq 0$

$\Rightarrow d(U - TS) < 0.$

$F = U - TS$ define

At const V and $T = T_{surr}$ equilibrium is achieved when Helmholtz free energy is minimized.

6.) $T = T_{surr} = \text{const}$,

$p = p_{ext} = \text{Const.}$

$\Rightarrow (dU - p\,dV - T\,dS) \leq 0$

$\Rightarrow d(U - pV - TS) \leq 0.$

Define $G = U - pV - TS$ = Gibb's free energy

$\Rightarrow dG \leq 0.$

At constant pressure and Temp Gibb's free energy is minimized