Criteria for Irreversible Processes

$dU = đq + đw$

Closed system

$dU_{system} = đq_{system} + đw_{system}$

$dU_{sys} = đq_{sys} - P_{ext}\, dV_{sys}$

$đq_{sys} = T\, dS_{system}$

↑ system temperature

how to get $T_{surroundings}$?

$dS_{system} + dS_{surr} \geq 0$

$dS_{sys} \geq -dS_{surr}$

$dS_{sys} \geq -\frac{đq^{rev}_{surr}}{T_{surr}}$

$đq_{surr} = -đq_{sys}$

$dS_{sys} \geq \frac{đq_{sys}}{T_{surr}}$

$$đq_{sys} \leq T_{surr}\, dS_{sys}$$

$$dU_{sys} = đq_{sys} + đW_{sys}$$

$$đq_{sys} = dU_{sys} - đW_{sys} \leq T_{surr}\, dS_{sys}$$

$$\boxed{dU_{sys} + P_{ext}\, dV_{sys} - T_{surr}\, dS_{sys} \leq 0}$$

Few Cases :

Isolated System: $dV_{sys} = 0$

$dU_{sys} = 0$

$$-T_{surr}\, dS_{sys} \leq 0$$

$$-dS_{sys} \leq 0$$

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

Isolated System $(dS)_{U,V} = 0$ at Equil.

$(dS)_{U,V} > 0$ Irreversible Process

$dV_{sys} = 0$; $dS_{sys} = 0$

$$(dU_{sys})_{S,V} \leq 0$$

$(dU_{sys})_{S,V} = 0$ at Equil.

$(dU_{sys})_{S,V} < 0$ for Irreversible Process!

Control T_{surr} & V_{sys}

$$T_{sys} = T_{surr} \qquad dT = 0$$

$$dV_{sys} = 0$$

$$dU_{sys} + P_{ext}\, dV_{sys} - T_{surr}\, dS_{sys} \leq 0$$

$$\underline{dU_{sys} - T\, dS_{sys}} \leq 0$$

Define: $A \equiv U - TS$

$$A_{sys} \equiv U_{sys} - T S_{sys}$$

$$dA = dU - d(TS)$$

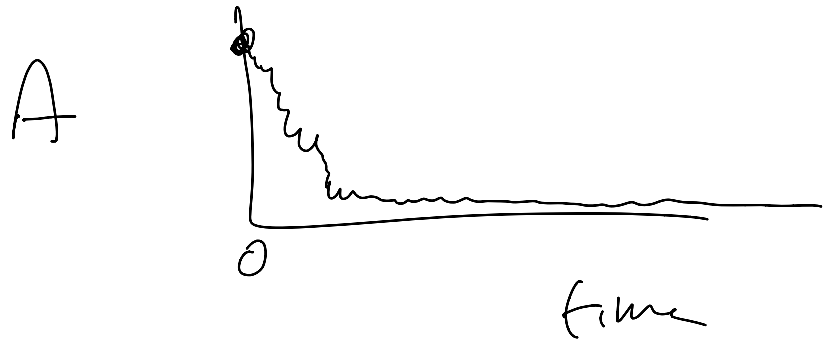
$$= dU - T dS - S dT$$

($dT = 0$)

$$\underline{dA = dU - T dS}$$

$$(dA)_{T,V} \leq 0$$

A = Helmholtz Free Energy



$$A = U - TS$$

Energy vs Entropy Function

T & p constant

$$dp,\ dT = 0$$

$$dU_{sys} + p_{ext}\, dV_{sys} - T_{surr}\, dS_{sys} \le 0$$

Define $G \equiv U - TS + pV$

$$dG = dU - TdS - SdT + pdV + Vdp$$

$$dG = dU - TdS + pdV$$

$$(dG)_{T,P} \leq 0$$

Gibbs Free Energy

G minimized at Equil
under T, P constant

$$(dG)_{T,P} < 0$$ Irreversible Process under T & P constant!

$$dU = TdS - pdV$$

$$dS = \frac{1}{T}dU + \frac{P}{T}dV$$

$$dH = dU + pdV + Vdp \qquad H = U + PV$$

$$= TdS - pdV + pdV + Vdp$$

$$dH = TdS + Vdp$$ enthalpy

A = Helmholtz Free Energy

$$A = U - TS$$

$$dA = dU - TdS - SdT$$

$$= \cancel{TdS} - pdV - \cancel{TdS} - SdT$$

$$\boxed{dA = -pdV - SdT}$$

G = Gibbs Free Energy

$$G = U - TS + pV$$

$$\boxed{dG = Vdp - SdT}$$

↗ natural variables of G

$$G(T, P)$$

$$A(T, V)$$