Gibbs-Duhem Relation

Extensive and Intensive Variables
extensive variables are proportional to size of the system
      i.e. if I start with a system A, and then duplicate it, these variables will double for the
combined pair
      examples: N, V, S, U, H, F, G, m, C

intensive variables are independent of the size of the system
      i.e. double system A, these variables remain the same for the pair
      examples: T, P, μ, c, density, any ratio of extensive variables

U, S, V, and N are all extensive variables
$$U(aS, aV, aN) = a\, U(S,V,N) \qquad \text{"homogeneous function of the 1st order"}$$

$$T(aS, aV, aN) = T(S,V,N) \qquad \text{"homogeneous function of the 0th order"}$$
      This is because T is intensive
      Note that $T(S,V,aN) \neq T(S,V,N)$

Consider
$$(1+\varepsilon)\, U(S,V,N) = U((1+\varepsilon)S,\ (1+\varepsilon)V,\ (1+\varepsilon)N) \qquad \text{Suppose that } \varepsilon \text{ is small}$$

$$f(x+dx, y+dy) \approx f(x,y) + \partial f/\partial x\ dx + \partial f/\partial y\ dy$$

$$U(S+\varepsilon S, V+\varepsilon V, N+\varepsilon N) \approx U(S,V,N) + (\partial U/\partial S)\,\varepsilon S + (\partial U/\partial V)\,\varepsilon V + (\partial U/\partial N)\,\varepsilon N$$

$$(1+\varepsilon)\, U \approx U + T\varepsilon S - P\varepsilon V + \mu\varepsilon N$$

$$\varepsilon U = \varepsilon(TS - PV + \mu N) \quad = \text{if } \varepsilon \text{ is infinitesimal}$$

$$U = TS - PV + \mu N$$

$$dU = d(TS) - d(PV) + d(\mu N)$$
$$dU = TdS + SdT - PdV - VdP + \mu dN + Nd\mu$$
$$T\,dS - P\,dV + \mu\,dN = TdS + SdT - PdV - VdP + \mu dN + Nd\mu$$
$$0 = S\,dT - V\,dP + N\,d\mu \qquad \textbf{Gibbs-Duhem Relation}$$

$$\left(\frac{\partial \mu}{\partial P}\right)_T = \frac{V}{N}$$

$$0 = -V\,dP + N\,d\mu$$

Equilibrium and Free Energy

Q=CΔT
Q=∞0

thermal reservoir (C=∞)

system

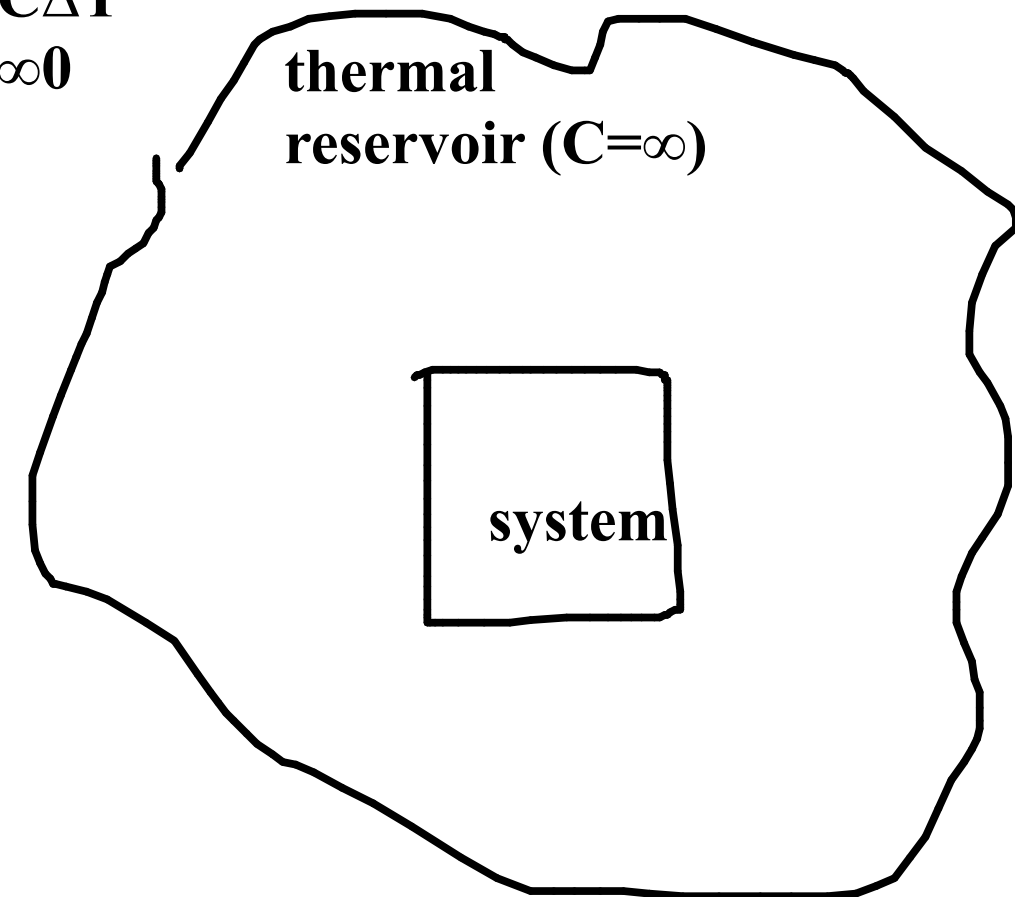**Suppose a system is in contact with a thermal reservoir**
Only energy can be exchanged with reservoir
T, N, V of system are constant (in thermal equilibrium with reservoir)
    T,V,N are natural variables of F (Helmholtz free energy)

$$dS_{tot} = dS_{sys} + dS_R$$

$$dS_{tot} = dS_{sys} + \left(\frac{1}{T}dU_R\right)$$

V,N are constant for the reservoir

$$dS_{tot} = dS_{sys} - \frac{1}{T}dU_{sys}$$

$$dS_{tot} = -\frac{1}{T}\left[-TdS_{sys} + dU_{sys}\right]$$

F=U–TS
dF = dU - TdS at constant T

$$dS_{tot} = -\frac{1}{T}dF$$

↑

dS>0 as approach equilibrium

dF<0 as approach equilibrium: F tends to decrease