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

$U(aS,aV,aN) = a\,U(S,V,N)$ **"homogeneous function of the 1st order"**

$T(aS,aV,aN) = T(S,V,N)$ **"homogeneous function of the 0th order"**

This is because T is intensive

Note that $T(S,V,aN) \neq T(S,V,N)$

Consider

$(1+\varepsilon)\,U(S,V,N) = U((1+\varepsilon)S, (1+\varepsilon)V, (1+\varepsilon)N)$ **Suppose that ε is small**

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

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

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

$\varepsilon U = \varepsilon(TS - PV + \mu N)$ **= if ε is infinitesimal**

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

$dU = d(TS) - d(PV) + d(\mu N)$

$dU = TdS + SdT - PdV - VdP + \mu dN + Nd\mu$

$T\cancel{dS} - P\,\cancel{dV} \cancel{+ \mu\, dN} = \cancel{TdS} + SdT - \cancel{PdV} - VdP \cancel{+ \mu dN} + Nd\mu$

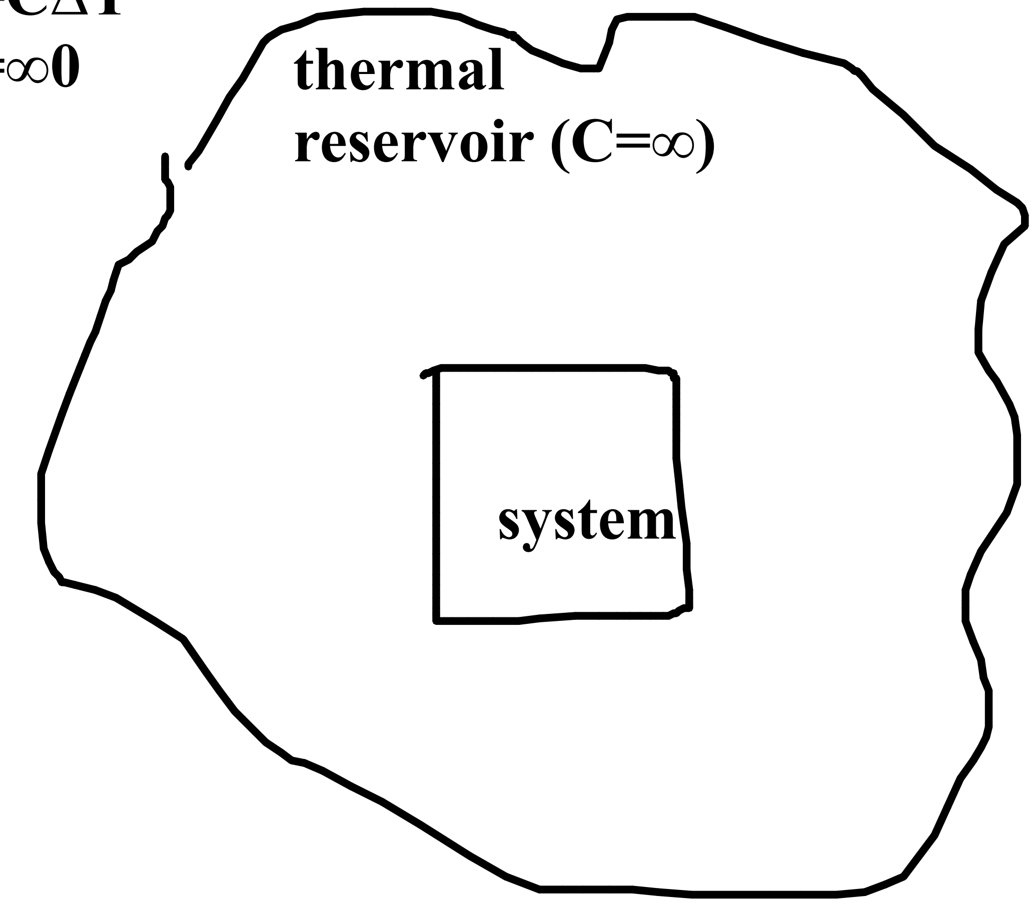
$$0 = S\,dT - V\,dP + N\,d\mu \qquad \textbf{Gibbs-Duhem Relation}$$

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

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

Equilibrium and Free Energy

Q=CΔT
Q=∞0



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

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

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

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