Entropy and Helmholtz free energy

The entropy $S(E, V, N)$ of an isolated system can never decrease : $\Delta S(E, V, N) \geq 0$.

micro canonical ensemble: isolated system

$S(E, V, N)$ is a maximum at equilibrium.

$E = E(S, V, N)$ "bring in"

$$A = E - TS \quad \text{"get rid of"}$$

$A = A(T, V, N)$ — canonical ensemble: system at constant T, V, N

The Helmholtz free energy is a minimum at equilibrium.

Helmholtz free energy $\hat{=}$ thermodynamic potential

$\Delta A(T, V, N) \leq 0$.

$$dA = dE - S\,dT - T\,dS$$

$$= (T\,dS - P\,dV + \mu\,dN) - S\,dT - T\,dS$$

$dE = T\,dS - P\,dV + \mu\,dN$ fundamental thermodynamic relation

$$= -S\,dT - P\,dV + \mu\,dN$$

$$\left(\frac{\partial A}{\partial T}\right)_{V,N} \qquad \left(\frac{\partial A}{\partial V}\right)_{N,T} \qquad \left(\frac{\partial A}{\partial N}\right)_{T,V}$$