Thermodynamics

Self-consistent axiomatic theory:

(0) equilibrium is transitive (equivalence relation):
$A \sim B$ and $B \sim C$ then $A \sim C$.

(1) energy conservation: total energy of isolated system is fixed.

$$\frac{1}{T} = \left.\frac{dS}{dE}\right|_{\text{no work}}$$

so

$$\begin{aligned} dE_1 &= T\,dS = dQ \\ dE_2 &= \begin{array}{l} -p\,dV \\ -F\,dx \qquad dW \\ \dots \end{array} \end{aligned}$$

$dE = dQ + dW$

(2) entropy decreases in an isolated system:
$dS \geq 0$. Internal transition: equal or more disorder.

(3) entropy of absolute zero temperature is zero
or: independent of other parameters ⇒ can be set zero
or: ground state of quantum system is finite (not exponential with N)

zero temperature heat capacity:

$$C_X = \left.\frac{\partial Q}{\partial T}\right|_X = T\left.\frac{\partial S}{\partial T}\right|_X \to 0 \quad \text{if } T \to 0$$

State variables: path independent quantities: $E, S, A, T, p, \dots$.
but: $\Delta W_{A\to B}$ or $\Delta W_{A\to B}$ depend on path.

Free energies. System kept at fixed T:
energy: $\Delta E = \Delta Q$
entropy: $\Delta S = \dfrac{\Delta Q}{T} + \Delta S_{\text{int}} \geq \dfrac{\Delta Q}{T}$
Helmholtz free energy: $A(T) = E - TS$:

$$\Delta A = \Delta E - T\Delta S \leq 0$$

Free energy of a system never increases: minimal at stable equilibrium.
Stat Mech: probability of macroscopic state: $\sim \exp -\frac{A(T)}{k_B T}$
for large system $A \gg k_B T$, only lowest A state observed.

Now system kept at fixed T, p:
energy: $\Delta E = \Delta Q - p\Delta V$
entropy: $\Delta S = \dfrac{\Delta Q}{T} + \Delta S_{\text{int}} \geq \dfrac{\Delta Q}{T}$
Gibbs free energy: $G(T,p) = E - TS + pV$:

$$\Delta G = \Delta E - T\Delta S + p\Delta V \leq 0$$