

Ensemble	Microcanonical	Canonical
Bath	Isolated	Heat
Fundamental Variables	E, N, V	T, N, V
Thermodynamic Potentials	$S(E, N, V), E(S, N, V)$	Helmholtz Free energy $A(T, N, V) = E - TS$
Thermodynamic Relation	$dE = TdS - PdV + \mu dN + \dots$	$dA = -SdT - PdV + \mu dN + \dots$
Stationarity Principle	S maximized	A minimized at fixed T, N, V
Extensivity ($\varepsilon = E/N$ etc.)	$\varepsilon = \varepsilon(s, v)$	$a = a(T, v)$
Euler Relation	$E = TS + \mu N - PV$	$A = -PV + \mu N$
Applications	Basic	Energy available in slow volume expansion

Ensemble	Constant Pressure	Gibbs
Bath	Volume	Heat, Volume
Fundamental Variables	S, N, P	T, P, N
Thermodynamic Potentials	Enthalpy $H(S, N, P) = E + PV$	Gibbs Free energy $G(T, N, P) = E - TS + PV$
Thermodynamic Relation	$dH = TdS + VdP + \mu dN + \dots$	$dG = -SdT + VdP + \mu dN + \dots$
Stationarity Principle	H minimized at constant S, N, P	G minimized at constant T, P, N
Extensivity ($\varepsilon = E/N$ etc.)	$h = h(s, P)$	$g = g(T, P)$
Euler Relation	$H = TS + \mu N$	$G = \mu N$
Applications	Heat produced in chemical reactions	Phase equilibria Chemical reactions

Ensemble	Grand Canonical
Bath	Heat, Particles
Fundamental Variables	T, μ, V
Thermodynamic Potentials	Grand Potential $\Omega(T, N, V) = E - TS - \mu N$
Thermodynamic Relation	$d\Omega = -SdT - PdV - Nd\mu + \dots$
Stationarity Principle	Ω minimized at constant T, μ, V
Extensivity ($\varepsilon = E/N$ etc.)	$\omega = \omega(T, v)$
Euler Relation	$\Omega = -PV$
Applications	Theoretical calculations