

Introduction to Advanced Thermodynamics

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Graduate-level overview – concise, organized, and ready for study or presentation.

1. Core Concepts Revisited

Concept	Classical Definition	Advanced Extension
System & Surroundings	Closed, open, isolated	Control volume with moving boundaries; non-equilibrium reservoirs
State Variables	(P, V, T, n) (intensive) and (U, H, S, G) (extensive)	Inclusion of internal variables (e.g., order parameters, defect densities) and non-equilibrium potentials
Equation of State	Ideal gas, Van der Waals, etc.	Multi-parameter equations (e.g., cubic-plus-association, SAFT) for complex fluids and mixtures
First Law	$\Delta U = Q - W$	Differential form with mass fluxes and chemical work : $dU = \delta Q - \delta W + \sum_i \mu_i dn_i$
Second Law	$\Delta S \geq 0$	Entropy production ($\sigma = \dot{S}_{\text{gen}} \geq 0$) expressed via flux-force pairs (Onsager relations)

2. Thermodynamic Potentials in Advanced Context

Potential	Natural Variables	Typical Use
Internal Energy $U(S, V, \{n_i\})$	(S, V, n_i)	Fundamental description; basis for Legendre transforms
Enthalpy $H(S, P, \{n_i\}) = U + PV$	(S, P, n_i)	Constant-pressure processes, flow work
Helmholtz Free Energy $A(T, V, \{n_i\}) = U - TS$	(T, V, n_i)	Canonical ensemble, phase stability at fixed (T, V)
Gibbs Free Energy $G(T, P, \{n_i\}) = H - TS$	(T, P, n_i)	Isothermal-isobaric systems, chemical equilibrium

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Potential	Natural Variables	Typical Use
Massieu–Planck Functions ($\Phi = -A/kT$)	($\beta = 1/kT$)	Statistical↯mechanical link; convenient for Monte↯Carlo sampling
Exergy (Available Work) ($B = U + P_0V - T_0S$)	(P_0, T_0) (environment)	Efficiency analysis, irreversibility quantification

Key point: Advanced thermodynamics often works with **Legendre↯transformed potentials** that match the constraints of the problem (e.g., open systems at constant temperature and pressure ↯ Gibbs free energy).

3. Non↯Equilibrium Thermodynamics

3.1. Local Equilibrium Hypothesis

- Assumes each infinitesimal element can be described by equilibrium variables ($(T, P, \mu_i, \dots)$) even though the whole system is out of equilibrium.
- Enables definition of **local entropy density** ($s(\mathbf{r}, t)$) and **fluxes**.

3.2. Entropy Balance Equation

$$\left[\frac{\partial s}{\partial t} + \nabla \cdot \mathbf{J}_s = \sigma \quad (\sigma \geq 0) \right]$$

- $\mathbf{J}_s$