Complete Thermodynamics

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Contents

1 Part I: General Principles of Classical Thermodynamics

1.1 Core ideas

Classical thermodynamics describes macroscopic equilibrium states without tracking microscopic motion. Its central variables are energy, entropy, volume, particle number, temperature, pressure, and chemical potential. The laws constrain possible processes and define useful state functions.

For review, be able to state the laws, distinguish state functions from path quantities, and identify equilibrium variables. Keep the physical question visible: identify the degrees of freedom, the conserved quantities, the approximation being made, and the observable that would be measured.

1.2 Mathematical spine

$$dU = T\,dS - P\,dV + \mu\,dN$$

Section summary Thermodynamics is a macroscopic theory of energy, entropy, and equilibrium.

2 Introduction: The Nature of Thermodynamics and the Basis of Thermostatistics

2.1 Core ideas

Thermodynamics is powerful because many microscopic details are irrelevant at equilibrium. Thermostatistics supplies the microscopic meaning: entropy measures multiplicity and temperature measures how entropy changes with energy.

For review, be able to connect thermodynamic and statistical entropy, explain why few variables describe equilibrium, and identify the thermodynamic limit. Keep the physical question visible: identify the degrees of freedom, the conserved quantities, the approximation being made, and the observable that would be measured.

2.2 Mathematical spine

$$S = k_B \ln \Omega, \qquad dS \geq 0 \quad \text{for isolated systems}$$

Section summary Thermodynamics summarizes microscopic complexity through state variables.

3 The Problem and the Postulates

3.1 Core ideas

The basic problem is to determine equilibrium states and allowed processes from a small set of postulates. A simple system has an entropy function $S(U, V, N, \ldots)$ that is extensive, concave, and maximized at equilibrium for isolated constraints.

For review, be able to use entropy maximization, extensivity, and concavity to infer equilibrium conditions. Keep the physical question visible: identify the degrees of freedom, the conserved quantities, the approximation being made, and the observable that would be measured.

3.2 Mathematical spine

$$S = S(U, V, N), \qquad S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N)$$

Section summary The entropy postulate defines equilibrium and thermodynamic stability.

4 The Conditions of Equilibrium

4.1 Core ideas

Two systems in contact exchange energy, volume, or particles until entropy is maximized. This produces equality of temperature, pressure, and chemical potential for the corresponding allowed exchanges.

For review, be able to derive thermal, mechanical, and diffusive equilibrium conditions from entropy maximization. Keep the physical question visible: identify the degrees of freedom, the conserved quantities, the approximation being made, and the observable that would be measured.

4.2 Mathematical spine

$$T_1 = T_2, \qquad P_1 = P_2, \qquad \mu_1 = \mu_2$$

Section summary Equilibrium means no entropy gain remains under allowed exchanges.

5 Some Formal Relationships, and Sample Systems

5.1 Core ideas

The fundamental thermodynamic relation generates equations of state and identities. Ideal gases, paramagnets, and elastic systems illustrate how different work terms enter and how measurable response follows from derivatives.

For review, be able to use Euler and Gibbs-Duhem relations, compute simple equations of state, and track conjugate pairs. Keep the physical question visible: identify the degrees of freedom, the conserved quantities, the approximation being made, and the observable that would be measured.

5.2 Mathematical spine

$$U = TS - PV + \mu N, \qquad S\,dT - V\,dP + N\,d\mu = 0$$

Section summary Formal identities reduce many derivatives to a consistent structure.

6 Reversible Processes and the Maximum Work Theorem

6.1 Core ideas

A reversible process proceeds through equilibrium states and produces no entropy internally. It gives the maximum useful work between specified states; irreversible processes lose availability through entropy production.

For review, be able to compute reversible work, distinguish heat and work, and connect free energy decreases to maximum work. Keep the physical question visible: identify the degrees of freedom, the conserved quantities, the approximation being made, and the observable that would be measured.

6.2 Mathematical spine

$$dS = \frac{\delta Q_{\text{rev}}}{T}, \qquad W_{\max} = -\Delta F \quad (T, V, N \text{ fixed})$$

Section summary Reversibility sets ideal bounds on work and efficiency.

7 Alternative Formulations and Legendre Transformations

7.1 Core ideas

Different experiments control different variables, so different potentials are useful. Legendre transforms replace inconvenient extensive variables by their conjugate intensive variables, producing F, H, and G.

For review, be able to choose the correct thermodynamic potential and natural variables, and transform between potentials. Keep the physical question visible: identify the degrees of freedom, the conserved quantities, the approximation being made, and the observable that would be measured.

7.2 Mathematical spine

$$F = U - TS, \qquad H = U + PV, \qquad G = U - TS + PV$$

Section summary Thermodynamic potentials are adapted to controlled variables.

8 The Extremum Principle in the Legendre Transformed Representations

8.1 Core ideas

Equilibrium can be found by minimizing the appropriate potential: U at fixed entropy, F at fixed temperature and volume, G at fixed temperature and pressure. These criteria are equivalent forms of the entropy maximum principle.

For review, be able to apply minimum principles to common constraints and interpret metastability. Keep the physical question visible: identify the degrees of freedom, the conserved quantities, the approximation being made, and the observable that would be measured.

8.2 Mathematical spine

$$(T, V, N): \quad F \text{ minimum}, \qquad (T, P, N): \quad G \text{ minimum}$$

Section summary Equilibrium is an extremum principle in the right variables.

9 Stability of Thermodynamic Systems

9.1 Core ideas

Stable systems resist small fluctuations. Concavity of entropy and convexity of potentials imply positive heat capacities, compressibilities, and susceptibilities. Instability signals phase separation or a transition.

For review, be able to use second-derivative tests, identify stable response signs, and interpret spinodal regions. Keep the physical question visible: identify the degrees of freedom, the conserved quantities, the approximation being made, and the observable that would be measured.

9.2 Mathematical spine

$$C_V > 0, \qquad \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T > 0$$

Section summary Stability is encoded in the curvature of thermodynamic potentials.

10 First-Order Phase Transitions

10.1 Core ideas

First-order transitions occur when two phases have equal thermodynamic potential but different entropy or volume. Latent heat, coexistence curves, metastability, nucleation, and Maxwell constructions describe their behavior.

For review, be able to use equality of chemical potentials, apply Clapeyron equation, and interpret latent heat. Keep the physical question visible: identify the degrees of freedom, the conserved quantities, the approximation being made, and the observable that would be measured.

10.2 Mathematical spine

$$\mu_\alpha(T, P) = \mu_\beta(T, P), \qquad \frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{L}{T\Delta V}$$

Section summary First-order transitions are phase coexistence with discontinuous first derivatives.

11 Properties of Materials

11.1 Core ideas

Material properties are thermodynamic derivatives: heat capacities, compressibilities, expansion coefficients, susceptibilities, and elastic moduli. Maxwell relations connect derivatives that may be easier to measure.

For review, be able to derive response functions, use Maxwell relations, and relate microscopic behavior to macroscopic coefficients. Keep the physical question visible: identify the degrees of freedom, the conserved quantities, the approximation being made, and the observable that would be measured.

11.2 Mathematical spine

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V, \qquad C_P - C_V = TV\frac{\alpha^2}{\kappa_T}$$

Section summary Response functions summarize how materials react to changed conditions.

12 Part II: Statistical Mechanics

12.1 Core ideas

Statistical mechanics explains where entropy, temperature, equations of state, and fluctuations come from. It also extends thermodynamics to finite systems, fluctuations, and microscopic models.

For review, be able to connect partition functions to free energies and explain why thermodynamic laws emerge statistically. Keep the physical question visible: identify the degrees of freedom, the conserved quantities, the approximation being made, and the observable that would be measured.

12.2 Mathematical spine

$$Z = \sum_s e^{-\beta E_s}, \qquad F = -k_B T \ln Z$$

Section summary Statistical mechanics is the microscopic foundation of thermodynamics.