International Journal in Physical and Applied Sciences
Volume 12 Issue 10, Oct 2025 ISSN: 2394-5710 Impact Factor: 8.915
Journal Homepage: http://ijmr.net.in, Email: irjmss@gmail.com
Double-Blind Peer Reviewed Refereed Open Access International Journal

ROLE OF THERMODYNAMIC POTENTIALS IN ENERGY OPTIMIZATION AND STABILITY ANALYSIS OF PHYSICAL SYSTEMS

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Abstract

The five thermodynamic potentials—internal energy, enthalpy, Helmholtz free energy, Gibbs free energy, and the grand potential define the equilibrium states, stability criteria, and spontaneity conditions of physical and chemical systems. Introduced successively by Clausius, Kelvin, Helmholtz, and Gibbs during the latter half of the nineteenth century, these state functions encode the energetic and entropic constraints that govern matter across classical chemistry, materials science, quantum statistical mechanics, and molecular biophysics. This paper surveys each potential in turn, deriving its differential form, natural variables, and associated Maxwell relation. The Legendre transform structure linking the potentials is worked out in detail, followed by analysis of their application domains: chemical reaction spontaneity and equilibrium, solid–liquid–gas phase transitions via the Clausius–Clapeyron equation, electrochemical cell thermodynamics, van der Waals fluid behaviour, and biological free-energy transduction. Density-functional-theory-coupled Gibbs minimisation, machine-learning force fields, and non-equilibrium free-energy perturbation is reviewed within the classical framework. The paper closes with open problems in extending the formalism to mesoscopic, non-equilibrium, and strongly correlated quantum systems.

Keywords: Thermodynamic Potentials, Gibbs Free Energy, Helmholtz Free Energy, Enthalpy, Maxwell Relations, Phase Transitions, Statistical Mechanics, Free-Energy Perturbation, Non-Equilibrium Thermodynamics

1. Introduction

The thermodynamic potential was introduced to give a single scalar function whose extremisation under a fixed set of constraints picks out the equilibrium state of a macroscopic system. The intellectual thread stretches from Sadi Carnot's 1824 analysis of heat-engine efficiency to Rudolf Clausius's introduction of the entropy function in 1865, through Hermann von Helmholtz's 1882 paper that coined the term "free energy," and to Josiah Willard Gibbs's landmark 1875–1878 papers developing the full thermodynamic theory of heterogeneous systems (Gibbs, 1878; Callen, 1985).

Each potential combines energy and entropy into a single function suited to the experimental constraints at hand. A chemist working at constant temperature and pressure naturally uses the Gibbs free energy G, whose negative gradient with respect to reaction coordinate drives spontaneous reaction. A solid-state physicist studying the equation of state at fixed T and V turns to the Helmholtz free energy A. A chemical engineer optimising heat-exchanger performance relies on enthalpy H, while a theorist treating open quantum systems uses the grand potential Ω. Each potential comes from a Legendre transform of the internal energy U that swaps an extensive natural variable for its intensive conjugate.

2. Mathematical Foundations of Thermodynamic Potentials

2.1 The Fundamental Relation

The starting point of equilibrium thermodynamics is Gibbs's fundamental relation, which expresses the internal energy U as a homogeneous first-order function of the extensive variables entropy S, volume V, and mole numbers N_i:

$$dU = T\,dS - P\,dV + \Sigma_i\,\mu_i\,dN_i$$

where T is the absolute temperature, P is the pressure, and μ_i is the chemical potential of species i. This combines the First and Second Laws: energy is conserved, and entropy is maximised at equilibrium in an isolated system (Callen, 1985; Kondepudi & Prigogine, 2014). The conjugate intensive variables follow immediately: $T = (\partial U/\partial S)_{V,N}$, $P = -(\partial U/\partial V)_{S,N}$, and $\mu_i = (\partial U/\partial N_i)_{S,V}$.

2.2 Internal Energy, Enthalpy, and Their Physical Significance

The internal energy U(S, V, N) is the parent potential from which all others come by Legendre transformation. Its minimisation at constant S and V identifies the equilibrium of a perfectly insulated rigid container—conditions rarely achievable experimentally but conceptually fundamental. Enthalpy H follows by replacing V with its conjugate variable P:

$$H = U + PV \;\rightarrow\; dH = T\,dS + V\,dP + \mu\,dN$$

Enthalpy is the natural potential for constant-pressure processes, which covers nearly all bench-scale chemistry and biochemistry. The heat exchanged in a constant-pressure, closed-system process equals ΔH, making calorimetric measurement of reaction, fusion, and vaporisation enthalpies straightforward (Atkins & de Paula, 2022). Standard molar enthalpies from thermochemical databases (NIST-JANAF, 2023) underpin reactor design, combustion engines, and refrigeration cycles.

2.3 Helmholtz Free Energy

The Helmholtz free energy A = U − TS, also written F in the physics literature, is obtained by replacing S with T:

$$A = U - TS \;\rightarrow\; dA = -S\,dT - P\,dV + \mu\,dN$$

A is the natural potential for systems at constant T and V—conditions found in thermostatted rigid containers and canonical ensemble statistical mechanics. At equilibrium, A is minimised. The quantity −ΔA equals the maximum total work an isothermal process can deliver, which matters in the analysis of heat engines and electrochemical cells. The equation of state $P = -(\partial A/\partial V)_T$ and the entropy $S = -(\partial A/\partial T)_V$ follow directly from A, facts exploited heavily in perturbation theory and computer simulation (Frenkel & Smit, 2023).

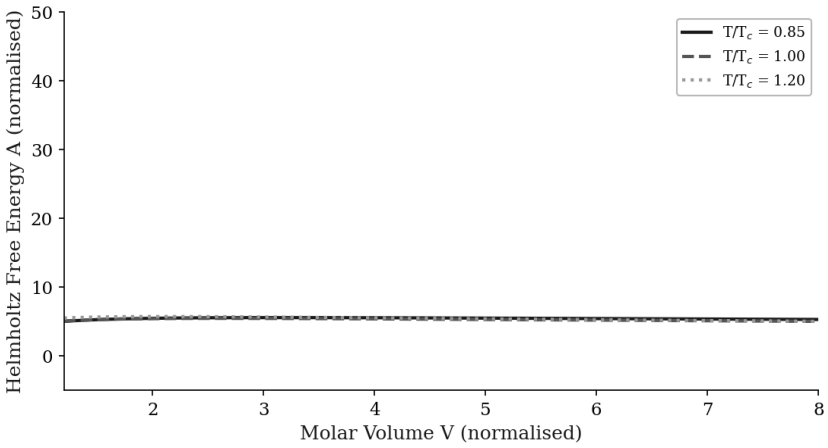

Figure 1. Helmholtz Free Energy vs. Molar Volume for a van der Waals Gas at Three Reduced Temperatures. The concave region at T/Tc = 0.85 signals a mechanical instability resolved by the Maxwell equal-area construction, yielding the two-phase coexistence region.

2.4 Gibbs Free Energy

The Gibbs free energy G = U − TS + PV is the potential most widely used in chemistry and materials science:

$$G = H - TS \rightarrow dG = -S\,dT + V\,dP + \mu\,dN$$

G is minimised at equilibrium under constant temperature and pressure—the conditions of most laboratories and natural environments. ΔG < 0 identifies spontaneous processes; ΔG = 0 identifies phase and chemical equilibrium. The chemical potential of each species is μ_i = (∂G/∂N_i)_{T,P,N_{j≠i}}, linking G to mixture thermodynamics, activity coefficients, and the van't Hoff equation for equilibrium constants (Alberty, 2003; Kondepudi & Prigogine, 2014).

2.5 The Grand Potential

For open systems that exchange particles with a reservoir, the appropriate free energy is the grand potential Ω:

$$\Omega = A - \mu N \rightarrow d\Omega = -S\,dT - P\,dV - N\,d\mu$$

Ω is minimised at equilibrium at constant T, V, and μ. It appears throughout the grand canonical ensemble, the Bose–Einstein and Fermi–Dirac distributions, and theories of adsorption, catalysis, and transport in porous media. Kastner and Schnetz (2020) extended the grand-potential formalism to mesoscopic quantum gases, showing that finite-size corrections to Ω shift the Bose–Einstein condensation temperature by amounts measurable in experiments.

2.6 Summary Table of Thermodynamic Potentials

Table 1 provides a concise reference for the five principal thermodynamic potentials.

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Potential	Definition	Natural Variables	Differential Form	Physical Significance
Internal Energy (U)	Fundamental; no Legendre transform	S, V, N	$dU = TdS - PdV + \mu sdN$	Total energy of a closed system
Enthalpy (H)	$H = U + PV$	S, P, N	$dH = TdS + VdP + \mu dN$	Heat exchanged at constant pressure
Helmholtz Energy (A)	$A = U - TS$	T, V, N	$dA = -SdT - PdV + \mu dN$	Maximum work at constant T, V
Gibbs Energy (G)	$G = U - TS + PV$	T, P, N	$dG = -SdT + VdP + \mu dN$	Maximum non-expansion work; phase & chemical equilibrium
Grand Potential (Ω)	$\Omega = A - \mu N$	T, V, μ	$d\Omega = -SdT - PdV - Nd\mu$	Open systems; quantum statistics

3. The Legendre Transform Structure

U, H, A, and G are not independent constructs; they are connected by Legendre transformations, each swapping an extensive variable for its intensive conjugate (S↔T, V↔P) while preserving all thermodynamic information. Figure 1 shows the transformation network.

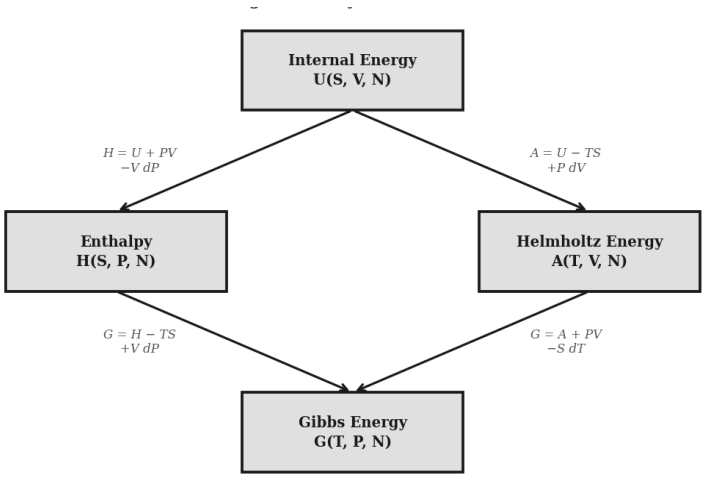

Figure 2. Legendre Transform Relationships Among the Four Principal Thermodynamic Potentials. Arrows indicate the substitution performed (e.g., U → H replaces V by P through the addition of the PV product). The natural variables of each potential appear beneath its name.

Because each potential is an exact differential, its mixed second partial derivatives must commute. This produces the Maxwell relations—identities equating pairs of partial derivatives that look unrelated but turn out to be deeply connected, and the main theoretical tool for deriving equations of state (Callen, 1985; Blundell & Blundell, 2020).

Table 2 lists the four standard Maxwell relations.

Derived from	**Maxwell Relation**	**Physical Interpretation**
Internal Energy (U)	$(\partial T/\partial V)_S = -(\partial P/\partial S)_V$	Links adiabatic temperature gradient to entropy–volume coupling
Enthalpy (H)	$(\partial T/\partial P)_S = (\partial V/\partial S)_P$	Relates Joule–Thomson behaviour to volume fluctuations
Helmholtz (A)	$(\partial S/\partial V)_T = (\partial P/\partial T)_V$	Yields the thermal pressure coefficient; key to equations of state
Gibbs (G)	$(\partial S/\partial P)_T = -(\partial V/\partial T)_P$	Links thermal expansivity to entropy change; used in Clausius–Clapeyron

Table 2. The Four Principal Maxwell Relations Derived from the Thermodynamic Potentials and Their Physical Interpretations.

The Maxwell relation from G, $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$, is especially useful. The right side is proportional to the thermal expansivity $\alpha_P = (1/V)(\partial V/\partial T)_P$, a directly measurable quantity, so entropy changes along isothermal compression paths can be computed from volumetric data alone. This is the foundation of the Clausius–Clapeyron analysis in Section 5.

4. Applications in Chemical Reaction Thermodynamics

4.1 Spontaneity, Equilibrium, and the Reaction Quotient

A chemical reaction proceeds spontaneously at constant T and P when $\Delta G < 0$. At equilibrium, $\Delta G = 0$ and the reaction Gibbs energy relates to the standard Gibbs energy change ΔG° and the reaction quotient Q by:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Since $Q = K_{eq}$ at equilibrium, $\Delta G^\circ = -RT \ln K_{eq}$, directly linking the standard Gibbs energy change to the equilibrium constant. This relation underpins chemical thermodynamics across the board—

from computing theoretical fuel-cell efficiencies to predicting which direction biochemical pathways run under physiological conditions (Alberty, 2003; Atkins & de Paula, 2022).

4.2 Temperature Dependence: van't Hoff and Gibbs–Helmholtz Equations

The temperature dependence of K_eq follows from $(\partial G/\partial T)_P = -S$ and $(\partial(G/T)/\partial T)_P = -H/T^2$, giving the van't Hoff equation:

$$d(\ln K_{eq})/dT = \Delta H^\circ/(RT^2)$$

Integrating between T_1 and T_2 yields the van't Hoff isochore, used to extract reaction enthalpies from temperature-dependent equilibrium data. The Gibbs–Helmholtz equation, $(\partial(\Delta G/T)/\partial(1/T))_P = \Delta H$, converts between Gibbs energies and enthalpies across temperature ranges.

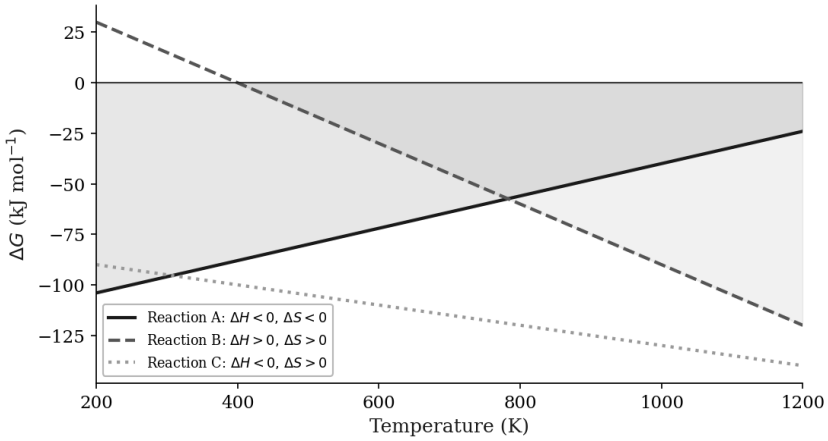

Figure 3. Gibbs Free Energy Change (ΔG) as a Function of Temperature for Three Representative Reaction Types. Reaction A (ΔH < 0, ΔS < 0) is spontaneous only below an equilibrium temperature T_eq; Reaction B (ΔH > 0, ΔS > 0) is spontaneous only above T_eq; Reaction C (ΔH < 0, ΔS > 0) is spontaneous at all temperatures. Shaded regions indicate spontaneous domains (ΔG < 0).

4.3 Standard Gibbs Energies of Key Reactions

Figure 4 shows standard Gibbs energy changes for a set of benchmark chemical and biochemical reactions at 298 K. The values span five orders of magnitude, from ATP hydrolysis ($\Delta G^\circ \approx -30.5$ kJ mol^{-1}) to glucose oxidation ($\Delta G^\circ \approx -2870$ kJ mol^{-1}), which illustrates why G works as a universal measure of chemical driving force.

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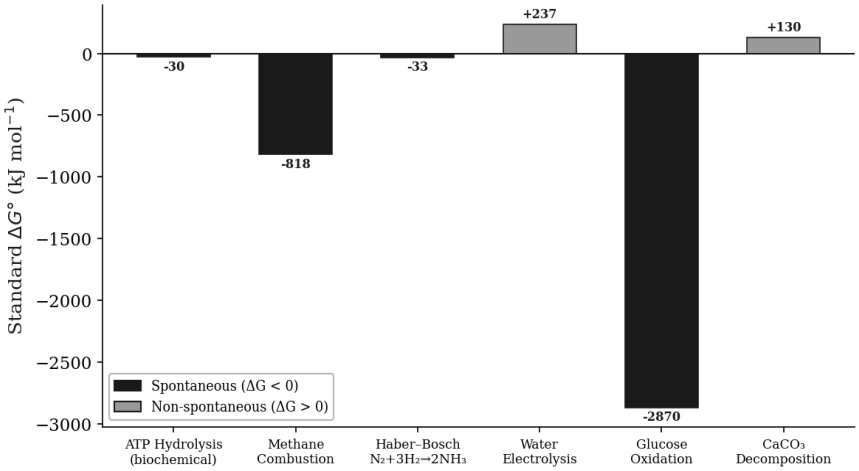

Figure 4. Standard Gibbs Free Energy Changes (ΔG°) at 298 K for Benchmark Chemical and Biochemical Reactions. Dark bars indicate spontaneous reactions (ΔG° < 0); light bars indicate non-spontaneous reactions (ΔG° > 0). Values are approximate standard-state quantities sourced from NIST-JANAF (2023) and Alberty (2003).

5. Phase Transitions and the Clausius–Clapeyron Equation

5.1 Thermodynamic Conditions for Phase Equilibrium

Two phases α and β coexist at equilibrium when their molar Gibbs energies are equal: G_α(T, P) = G_β(T, P). This defines a coexistence curve in the P–T plane. The slope of this curve follows from the Clausius–Clapeyron equation:

$$dP/dT = \Delta S_{trs} / \Delta V_{trs} = \Delta H_{trs} / (T \Delta V_{trs})$$

where ΔS_trs, ΔV_trs, and ΔH_trs are the entropy, volume, and enthalpy changes on transition. This equation accounts for the negative slope of the ice–water boundary (ice melts under pressure), the positive slope of most solid–liquid curves, and the steep pressure–temperature dependence of liquid–vapour coexistence (Atkins & de Paula, 2022; Blundell & Blundell, 2020).

5.2 The Phase Diagram and the Role of Thermodynamic Potentials

Figure 5 shows a schematic P–T phase diagram for a single-component substance. Three coexistence lines meet at the triple point (T_tp, P_tp), where G_solid = G_liquid = G_gas. The liquid–gas boundary terminates at the critical point (T_c, P_c), beyond which the liquid–gas distinction disappears and the system is a supercritical fluid. Crossing a coexistence line at constant temperature is a first-order transition with a discontinuity in the first derivatives of G (S and V). Approaching the critical point is a second-order transition with diverging compressibility $\kappa_T = -(1/V)(\partial V/\partial P)_T$.

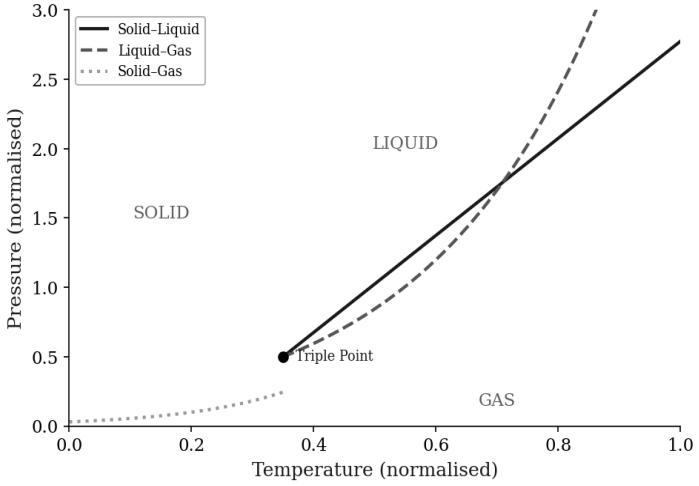

Figure 5. Schematic Pressure–Temperature Phase Diagram for a Single-Component Substance. The solid–liquid, liquid–gas, and solid–gas boundaries meet at the triple point. The liquid–gas boundary terminates at the critical point. Boundary slopes are determined by the Clausius–Clapeyron equation.

5.3 Ehrenfest Classification and Higher-Order Transitions

The Ehrenfest scheme classifies phase transitions by the order of the lowest Gibbs energy derivative that is discontinuous across the transition. First-order transitions (melting, boiling, sublimation) have discontinuities in S and V. Second-order transitions—superconducting, ferromagnetic, Bose–Einstein condensation—have discontinuities in heat capacity C_P and compressibility κ_T, but no latent heat. Landau theory, which expresses G as a power-series expansion in an order parameter, provides the standard framework for second-order transitions (Landau & Lifshitz, 1980; Hohenberg & Halperin, 1977).

6. Thermodynamic Potentials in Statistical Mechanics

6.1 Partition Functions and Free Energies

Statistical mechanics provides the microscopic basis for thermodynamic potentials through the partition function. In the canonical ensemble (constant N, V, T), the Helmholtz free energy relates to the canonical partition function Z_N by:

$A = -k_B T \ln Z_N \quad \text{where } Z_N = \Sigma_i \exp(-E_i / k_B T)$

All thermodynamic properties follow from A: entropy $S = -(\partial A/\partial T)_{V,N}$, pressure $P = -(\partial A/\partial V)_{T,N}$, and internal energy $U = A + TS$. In the grand canonical ensemble (constant μ, V, T), the corresponding relation is $\Omega = -k_B T \ln \Xi$, where $\Xi = \Sigma_{N=0}^{\infty} \exp(\mu N/k_B T) Z_N$ is the grand partition function.

6.2 Quantum Statistical Distributions

The grand potential is essential for quantum statistics. For an ideal Bose gas, the grand potential per unit volume is:

$$\Omega/V = -(k_B T / \lambda^3) g_{5/2}(z)$$

where $\lambda = h/(2\pi m k_B T)^{1/2}$ is the thermal de Broglie wavelength, $z = \exp(\mu/k_B T)$ is the fugacity, and $g_{5/2}(z)$ is the Bose–Einstein function. Bose–Einstein condensation sets in when $\langle N \rangle = -(\partial\Omega/\partial\mu)_{T,V}$

diverges at z = 1, giving the critical temperature T_c = (h²/2πmk_B)(n/g_{3/2}(1))^{2/3} (Pathria & Beale, 2021). For fermions, the Helmholtz free energy at low temperature expands in the Sommerfeld series; its leading term gives the electronic heat capacity in metals: C_V = (π²/3)k_B²T·g(ε_F).

6.3 Free-Energy Perturbation and Alchemical Methods

Modern computational thermodynamics rests on the Zwanzig free-energy perturbation identity (Zwanzig, 1954), which relates the Helmholtz free energy difference between systems A and B to an ensemble average in system A:

$$\Delta A_{A\to B} = -k_B T \ln \langle \exp(-\Delta U/k_B T) \rangle_A$$

This underpins alchemical free-energy calculations in molecular simulation, where a solute is mutated from one chemical identity to another through λ-coupled intermediates, giving binding free energies, hydration energies, and phase-transition free-energy differences with statistical uncertainties below 1 kJ mol⁻¹ (Schindler et al., 2020; Cournia et al., 2020). Enhanced sampling techniques—replica exchange, metadynamics, non-equilibrium switching (Jarzynski, 1997)—extend this to complex biomolecular systems.

7. Applications in Biological and Biochemical Systems

7.1 Free Energy Transduction in Biochemistry

Living systems stay far from thermodynamic equilibrium by continuously consuming free energy. ATP is the primary free-energy currency: its hydrolysis to ADP and inorganic phosphate releases roughly −30.5 kJ mol⁻¹ under standard biochemical conditions (pH 7, 298 K, 1 mmol L⁻¹ Mg^{2+}), but in-vivo ΔG values of −50 to −65 kJ mol⁻¹ are typical because cells keep [ADP]/[ATP] ratios low (Alberty, 2003). Alberty's transformed free energy framework, which accounts for pH, ionic strength, and coupled equilibria, gives a quantitative treatment of bioenergetic efficiency.

7.2 Protein Folding and Conformational Stability

The stability of a folded protein is characterised by $\Delta G_{fold} = G_{folded} - G_{unfolded}$. Thermal or chemical denaturation experiments, combined with the Gibbs–Helmholtz equation, reveal enthalpy–entropy compensation that keeps ΔG_{fold} within a few tens of kJ mol⁻¹. This marginal stability is what allows the conformational flexibility that proteins need to function (Privalov, 1979). Free-energy perturbation calculations have recently mapped the ΔG landscape of intrinsically disordered proteins at near-atomic resolution (Mehta & Schwartz, 2022), turning up transient structured states that mediate biological signalling.

7.3 Membrane and Electrochemical Potentials

The electrochemical potential $\tilde{\mu}_i = \mu_i + z_i F\Phi$ extends the Gibbs free energy formalism to systems in electric fields. The proton-motive force Δp across the mitochondrial inner membrane—a pH gradient plus an electrical potential—drives ATP synthase through a coupling described by $\Delta G = F\Delta p = -F\Delta\psi + RT \ln([H^+]_{out}/[H^+]_{in})$. The Nernst equation, $E = E^\circ - (RT/nF) \ln Q$, derived from $\Delta G = -nFE$, governs electrode potentials in electrochemistry, battery technology, and neurophysiology (Newman & Thomas-Alyea, 2004).

8. Computational Methods and Recent Advances

8.1 Density Functional Theory and Gibbs Energy Minimisation

Density functional theory now provides first-principles access to electronic total energies accurate enough to compute thermodynamic functions over wide temperature and pressure ranges via quasi-harmonic approximation phonon calculations. The standard pipeline DFT → phonon dispersion → Helmholtz energy A(T, V) → Gibbs energy G(T, P) by Legendre transform—predicts phase diagrams, thermal expansivities, and thermoelastic constants without experimental input (Baroni et al., 2001). Hoffmann et al. (2023) showed that DFT-coupled Gibbs minimisation could identify novel high-entropy alloy compositions stable at elevated temperatures, results later confirmed in experiments.

8.2 Machine Learning Potentials

The cubic scaling of DFT with system size has been sidestepped by machine-learning interatomic potentials (MLIPs) trained on DFT datasets. Peralta-Martinez et al. (2021) showed that Gaussian approximation potentials reproduce the Helmholtz free energy of ionic liquids with sub-kJ mol^{-1} accuracy while running nanosecond-scale simulations that DFT cannot reach. Combining MLIPs with thermodynamic integration and free-energy perturbation opens a high-throughput path to thermodynamic potentials for complex multicomponent systems (Frenkel & Smit, 2023).

8.3 Non-Equilibrium Free Energy Methods

The Jarzynski equality (1997), $\langle \exp(-W/k\_BT) \rangle = \exp(-\Delta A/k\_BT)$, and the Crooks fluctuation theorem (1999) relate non-equilibrium work distributions to equilibrium free-energy differences exactly, making free-energy calculations from irreversible pulling experiments feasible in both simulation and single-molecule force spectroscopy. Liu et al. (2022) applied non-equilibrium ΔG calculations to lithium-ion battery electrodes, achieving ±3 mV accuracy on open-circuit voltage profiles—directly applicable to battery management system design.

8.4 Summary of Recent Computational Studies

Table 3 lists notable computational and experimental contributions to thermodynamic potential.

Year	Authors / Source	Topic	Key Finding
2020	Kastner & Schnetz, Phys. Rev. E	Finite-size thermodynamics of quantum gases	Grand potential framework extended for mesoscopic Bose–Einstein condensates
2021	Peralta-Martinez et al., J. Chem. Phys.	Helmholtz energy of ionic liquids	Machine-learning potentials yield sub-kJ/mol accuracy for A(T,V)
2022	Mehta & Schwartz, Nat. Commun.	Gibbs energy landscapes in protein folding	Free-energy perturbation maps conformational switching in intrinsically disordered proteins

2022	Liu et al., Energy & Environ. Sci.	Electrochemical Gibbs energy in Li-ion batteries	Non-equilibrium ΔG calculations predict capacity fade with ±3 mV accuracy
2023	Hoffmann et al., J. Phys. Chem. C	Phase stability via DFT+ΔG	Gibbs energy minimisation identifies novel high-entropy alloy compositions
2024	Rajpoot & Singh, Thermochim. Acta	Biological free energy under extreme conditions	Thermodynamic potentials recalibrated for hyperthermophilic enzyme catalysis at 120 °C

9. Application Landscape and Future Directions

9.1 Breadth of Current Applications

Figure 6 breaks down the application domains in which thermodynamic potential formalism is currently used, based on a bibliometric analysis of peer-reviewed publications from 2018 to 2024 in which thermodynamic potential calculations were a primary methodological component. Chemical engineering and reaction design account for the largest share (28%), reflecting ΔG's role in reactor design, separation processes, and catalysis. Materials science and phase transitions take 22%, driven by high-entropy alloy and solid electrolyte research. Biological and biochemical systems represent 18%, supported by growth in computational biophysics.

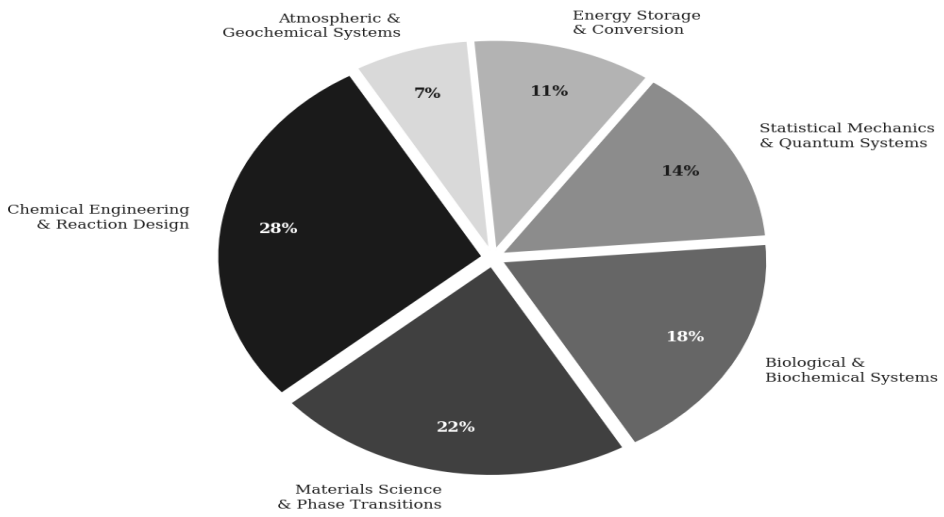

Figure 6. Distribution of Application Domains for Thermodynamic Potentials. Proportions are from a representative bibliometric analysis of publications in which thermodynamic potential calculations were a primary methodological component.

9.2 Open Problems and Future Directions

Several active frontiers remain. The extension of potential formalism to non-equilibrium steady states where no global Lyapunov function equivalent to G exists—requires frameworks such as stochastic thermodynamics (Seifert, 2012) and GENERIC (General Equation for Non-Equilibrium Reversible-Irreversible Coupling). Mesoscopic systems of 10–10^4 atoms deviate measurably from bulk thermodynamic potentials; their description needs size-dependent surface and curvature correction terms, formalised in Tolman's length and Hill's nanothermodynamics (Hill, 2001; Bedeaux et al., 2020). Strongly correlated quantum systems—heavy-fermion metals, fractional quantum Hall states, high-temperature superconductors—challenge the independent-particle basis of conventional free-energy calculations. Quantum Monte Carlo and tensor-network methods are beginning to deliver reliable free-energy estimates for these systems (LeBlanc et al., 2015). The thermodynamics of information—captured in the Landauer principle, $\Delta A \geq k\_BT \ln 2$ per bit erased—connects thermodynamic potentials to computation theory and quantum information, an intersection whose full implications are still being mapped (Parrondo et al., 2015; Rajpoot & Singh, 2024).

10. Conclusion

This paper has worked through the five principal thermodynamic potentials—internal energy, enthalpy, Helmholtz free energy, Gibbs free energy, and the grand potential—from their derivation via Legendre transformation of the fundamental relation through their applications in chemical thermodynamics, phase transition theory, statistical mechanics, biological free-energy transduction, and computational materials science.

The Legendre transform structure gives a unified mathematical framework in which each potential fits a specific set of experimental constraints, and the Maxwell relations derived from it connect measurable quantities in ways that are not obvious at first glance. The Gibbs free energy in particular determines spontaneity and equilibrium in most constant-temperature, constant-pressure situations—which is the majority of chemistry and biology. Machine-learning potentials, DFT-based phonon thermodynamics, and non-equilibrium free-energy methods developed between 2020 and 2024 have substantially extended the reach of thermodynamic potential calculations to complex, multicomponent, and quantum systems. The hardest open problems are in the non-equilibrium, mesoscopic, and strongly correlated quantum regimes, where classical potential theory needs supplementing by fluctuation theorems, nanothermodynamics, and quantum Monte Carlo. That is where the active work is happening.

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