General Physics II: Thermodynamics

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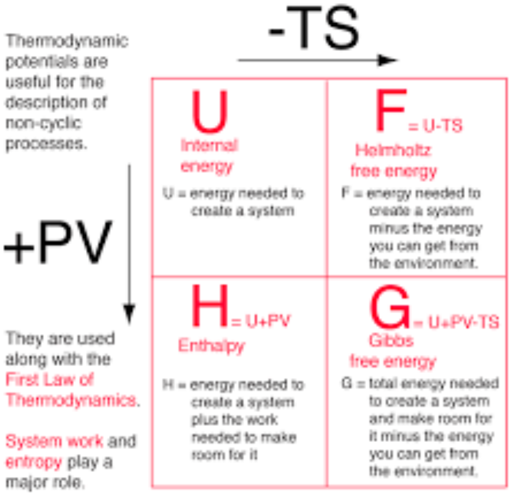


Thermodynamic potentials are useful for the description of non-cyclic processes.

U = energy needed to create a system

F = energy needed to create a system minus the energy you can get from the environment.

H = energy needed to create a system plus the work needed to make room for it

G = total energy needed to create a system and make room for it minus the energy you can get from the environment.

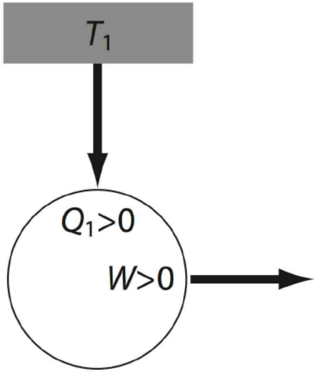
They are used along with the First Law of Thermodynamics.

System work and entropy play a major role.

Recap Chapter 9… — Thermal machines

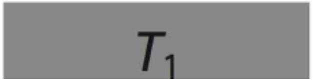
- What is a thermal machine?

- What is an equivalent formulation of 2nd law of TD?



Recap Chapter 9 — Thermal machines

- What is the set up and efficiency of a thermal machine?



Recap Chapter 9— Carnot cycle

- How does the Carnot cycle work? Plot the PV and TS diagrams of the Carnot cycle. What is the summed work/heat? What is the efficiency?

A B C

Recap — Refrigerators, heat pumps, perpetual motion machines

Recap Chapter 9— Which other thermal engines do you know?

Content of this course — today's lecture

Lecture 1: —Chapter 1. Introduction
—Chapter 2. Temperature and zeroth law of thermodynamics

Lecture 2: —Chapter 3. Gas laws

Lecture 3: —Chapter 4. Statistical thermodynamics I: Kinetic theory of gas (slides in previous file)
—Mathematical Excursion — Preparation for Chapter 5.

Lecture 4: —Chapter 5. Statistical thermodynamics II (Boltzmann factor, Maxwell-Boltzmann distribution)

Lecture 5: —Chapter 6. Energy, heat and heat capacity

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Lecture 7: — Mock exam I *with Dr. Tress*

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Lecture 9/10: —Chapter 9. Thermal machines

Lecture 11: —Chapter 10. Thermodynamic potentials and equilibria

Lecture 12: —Mock Exam II *with Dr. Tress*
Lecture 13: —Chapter 11. Heat transfer (Conduction, Convection, Radiation)

Lecture 14: —Final review and open questions

10. Thermodynamic potentials and equilibria

- 10.1 Basic relations of TD
    - Chemical potential
    - Gibbs (fundamental) relation
    - Euler equation
    - Gibbs-Duhem relation
- 10.2 Thermodynamic potentials and exact differentials
- 10.3 Enthalpy H
- 10.4 Free Energy F
- 10.5 Gibbs Free Enthalpy G
- 10.6 Equilibrium of subsystems coupled to a reservoir

10.1 Basic relations of TD

Summary 10.1 — Basic relations of TD

- Chemical potential:

$$dC = \sum_{i=1}^{N} \mu_i dn_i$$

- Gibbs fundamental relation:

$$dE_{int} = TdS - PdV + \sum_i \mu_i dn_i$$

- Euler relation:

$$E_{int} = TS - PV + \sum_i \mu_i n_i$$

- Gibbs-Duhem relation:

$$SdT - VdP + \sum n_i d\mu_i = 0$$

10.2 Thermodynamic Potentials and Exact Differentials

Mathematical concept of thermodynamic potentials

Introduce other TD potentials, in addition to E_{int}:

Disadvantage of $E_{int}(S, V, n)$: entropy hard to measure or fix, E_{int} in equilibrium is minimised when S & V are const. (internal equilibrium in an isolated system)

$$dE_{int} = TdS - PdV = 0 \text{ as } dS = 0 \ \& \ dV = 0$$

↳ new Energy fcts / TD potential to describe other experiments (e.g. at const. T or/and P)

↳ with other sets of natural variables which are easier to measure & control (e.g. T / P)

↳ Use these TD potentials to make estimates on related equilibrium states (when & how)

Summary 10.2 — Thermodynamic Potentials & Exact Differentials

- TD potentials play the analogue role as that in classical mechanics: Gradients of TD potentials result in state variables (V, P, T, S, …) whose change introduce a TD process (e.g., expansion)

    ➡TD process continues until TD system is in equilibrium, via reaching minima of TD potentials under given conditions.

- Thermodynamic potentials are mathematically exact differentials fulfilling the Schwartz theorem $\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$, describing a fct. f that can be integrated along any path between two points with the same result.
- Natural variables of a TD system allow for
    - a complete description of the potential
    - a direct derivation of remaining state variables from the derivatives of the potential with respect to the natural variables.

Summary 10.2 — Thermodynamic Potentials & Exact Differentials

- Applying the concept of exact differentials, the Schwartz theorem, to TD potentials results in the Maxwell equations.
- Example for TD potential: internal energy E_{int} with natural variables S, V, n:

$$dE_{int} = \left(\frac{\partial E_{int}}{\partial S}\right)_{V,n} dS + \left(\frac{\partial E_{int}}{\partial V}\right)_{S,n} dV + \left(\sum \frac{\partial E_{int}}{\partial n_i}\right)_{S,V} dn_i$$

with $T = \left(\frac{\partial E_{int}}{\partial S}\right)_{V,n}$; $P = -\left(\frac{\partial E_{int}}{\partial V}\right)_{S,n}$ and $\mu_i = \left(\frac{\partial E_{int}}{\partial n_i}\right)_{S,V}$

- Maxwell relations for E_{int}: $\left(\frac{\partial T}{\partial V}\right)_{S,n} = -\left(\frac{\partial P}{\partial S}\right)_{V,n}$

$$\left(\frac{\partial T}{\partial n_i}\right)_{V,S} = \left(\frac{\partial \mu_i}{\partial S}\right)_{V,n}$$

$$-\left(\frac{\partial P}{\partial n_i}\right)_{V,S} = \left(\frac{\partial \mu_i}{\partial V}\right)_{S,n}$$

10.3 Enthalpy H

10.4 Free Energy F

10.5 Gibbs Free Enthalpy G

Summary 10.3-5 — Enthalpy, Free Energy, Gibbs Free Enthalpy

- Enthalpy H = E_{int} + PV: natural variables are S, P, n

$$dH = \left(\frac{\partial H}{\partial S}\right)_{P,n_i} dS + \left(\frac{\partial H}{\partial P}\right)_{V,n_i} dP + \sum \left(\frac{\partial H}{\partial n_i}\right)_{S,P} d\mu_i$$

$$T = \left(\frac{\partial H}{\partial S}\right)_{P,n_i} ;\ V = \left(\frac{\partial H}{\partial P}\right)_{V,n_i} ;\ \mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,P}$$

- Free Energy F = E_{int} - TS: natural variables are T, V, n

$$dF = \left(\frac{\partial F}{\partial T}\right)_{V,n} dT + \left(\frac{\partial F}{\partial V}\right)_{T,n} dV + \sum \left(\frac{\partial F}{\partial n_i}\right)_{T,V} dn_i$$

$$-S = \left(\frac{\partial F}{\partial T}\right)_{V,n_i} ;\ V = \left(\frac{\partial F}{\partial V}\right)_{T,n_i} ;\ \mu_i = \left(\frac{\partial F}{\partial n_i}\right)_{T,V}$$

- Gibbs/Free Enthalpy G = E_{int} - TS + PV: T, P, n

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n} dP + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,P} dn_i$$

$$-S = \left(\frac{\partial G}{\partial T}\right)_{P,n} ;\ V = \left(\frac{\partial G}{\partial P}\right)_{T,n} ;\ \mu_i = \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,P}$$

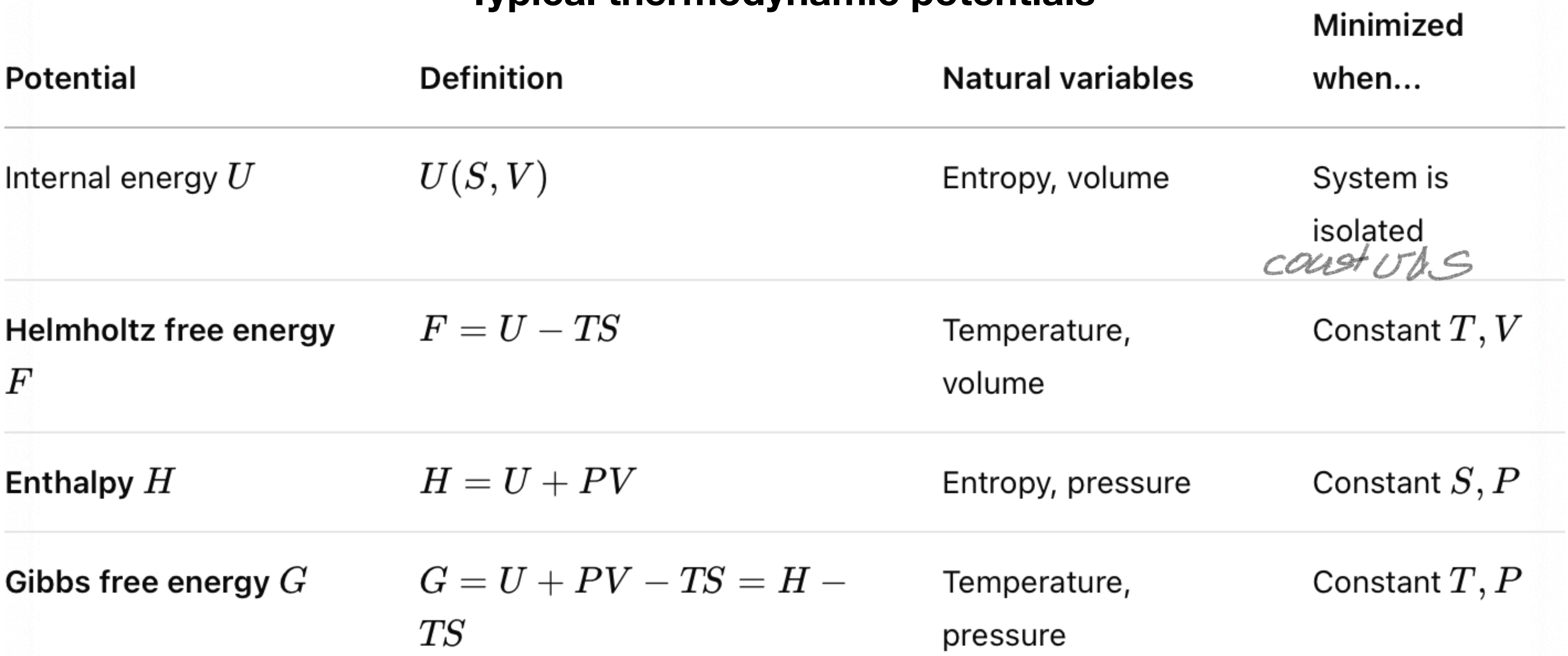
10.6 Equilibria of subsystems coupled to a reservoir

1. Minimum of free energy

2. Minimum of enthalpy

1. Minimum of Gibbs enthalpy

Typical thermodynamic potentials



Potential	Definition	Natural variables	Minimized when...
Internal energy U	$U(S, V)$	Entropy, volume	System is isolated const U & S
Helmholtz free energy F	$F = U - TS$	Temperature, volume	Constant T, V
Enthalpy H	$H = U + PV$	Entropy, pressure	Constant S, P
Gibbs free energy G	$G = U + PV - TS = H - TS$	Temperature, pressure	Constant T, P

- Think of thermodynamic potentials as the **"right form" of energy** to track when certain variables are held fixed.
- Systems **spontaneously evolve to minimize the relevant potential** under the given constraints.
- **Analogy**: Just like a ball rolls down a hill to minimize gravitational potential energy, a system 'rolls down' its thermodynamic potential to equilibrium.

Summary 10.6 — Equilibria of (sub)systems coupled to a reservoir

Minimization principles are a fundamental concept in thermodynamics and underlies the behavior of thermodynamic systems approaching equilibria states.

- At constant S and P, the thermal equilibrium state of a system corresponds to a minimum in the enthalpy H, i.e. the system naturally evolves towards a state where H is as low as possible.
- At constant T and V, the mechanical equilibrium state of a system corresponds to a minimum in the free energy F, i.e. the system naturally evolves towards a state where F is as low as possible.
- At constant T and P, the chemical equilibrium state of a system corresponds to a minimum in the Gibbs/free enthalpy G, i.e. the system naturally evolves towards a state where G is as low as possible.

(For the internal energy, this is true at constant S and V)

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