# Thermodynamics: Summary and Reflections

Winter 2025

## 1. Conservation of Energy

- (a) Ideal gas law: PV = NkT = nRT.
- (b) Equipartition theorem: At temperature T the average energy of any quadratic degree of freedom is (1/2)kT.
- (c) Heat and Work.
- (d) First law of thermodynamics  $\Delta U = Q + W$ .
- (e) Compression work. PV diagrams.
- (f) Adiabatic and isothermal expansion/compression.
- (g) Heat capacities and latent heat.
- (h) Enthalpy.

## 2. Entropy and the Second Law

- (a) Probability and counting. Binomial distribution.
- (b) Multiplicity. Micro- and macro-states.
- (c) Einstein model of solid.
- (d) Normal vs. large vs. very large numbers. Stirling approximation.
- (e) Sharpness of the multiplicity function.
- (f) The second law: any large system in equilibrium will be found in the macrostate with the greatest multiplicity, aside from fluctuations that are normally too small to measure.
- (g) Multiplicity function for the ideal gas.
- (h) Entropy  $S = k \ln \Omega$ .
- (i) The second law: any large system in equilibrium will be found in the macrostate with the greatest entropy, aside from fluctuations that are normally too small to measure. Or, entropy tends to increase.
- (j) Entropy of the ideal gas (Sakur-Tetrode equation).
- (k) Entropy of mixing.
- (l) Temperature:  $T = (\frac{\partial S}{\partial U})^{-1}$ .
- (m) When two objects are in thermal equilibrium, their temperatures are equal.
- (n) Pressure:  $P = T(\frac{\partial S}{\partial V})$ .

- (o) When two objects are in mechanical equilibrium, their pressures are equal.
- (p) Chemical potential:  $\mu = -T(\frac{\partial S}{\partial N})$ .
- (q) When two objects are in diffusive equilibrium, their chemical potentials are equal.
- (r) Thermodynamic identity: dU = TdS PdV. True for any infinitesimal change in any system.
- (s) Using Q = TdS (quasi-static) to calculate entropies.
- (t) Macroscopic views of entropy.

# 3. Applications: Heat Engines

- (a) Upper bound on efficiency:  $e \le 1 \frac{T_c}{T_h}$ .
- (b) Carnot cycle.
- (c) Refrigerators and heat pumps.
- (d) Otto cycles and diesel engines.
- (e) Steam engines and steam tables.

# 4. Applications: Chemistry

- (a) Helmhotz free energy: F = U TS.
- (b) Gibbs free energy: G = U TS + PV.
- (c) Free energies as available work.
- (d) Free energies for "energy and entropy accounting".
- (e) Thermodynamic identity:  $dG = -SdT + VdP + \mu dN$ .
- (f) System in contact with thermal reservoir at constant P will, at equilibrium, minimize G.
- (g) Phase transitions and phase diagrams.
- (h) Clausius-Clapeyron relationship.
- (i) Vapor pressure equation.
- (j) Chemical potential is Gibbs free energy per particle:  $G = \mu N$ .
- (k) Relative humidity, partial pressure, and dew point.

# Some math topics:

- 1. Combinatorics and probability.
- 2. Taylor expansions.
- 3. Normal vs. large vs. very large numbers.
- 4. Lots of Calc I, II and III material.

#### Some themes and ideas:

- 1. Structure and style of physics
- 2. Physics vs. chemistry
- 3. Physics vs. math
- 4. Thermodynamics is a broadly applicable theory built from a small number of general principles: the first law (conservation of energy); the second law (entropy increases, which is really a mathematical result concerning very large systems); and a number of useful definitions and constructions (temperature, Gibbs free energy, etc.).
- 5. Some features of large systems are independent of the system's constituents.

## Thoughts on the course:

- 1. This is the fourth time I've taught this course at COA. I think I'm happy with how it went.
- 2. I think this is a good course for COA because it is a broadly applicable area of physics, touching on physics, chemistry, geology, and some aspects of biology.
- 3. I find myself lecturing in this course more than I have in almost any other class. I think that's ok, even though I think there are limits to the effectiveness of lecturing.

#### Goals for the course:

- 1. Stay physically and mentally healthy and maintain intellectual and personal connection in a time of dispersal and isolation.
- 2. Experience the challenge, joy, and beauty of physics. I want you to gain an understanding and appreciation of the structure and style of physics as an intellectual approach and discipline.
- 3. I want to learn the basic principles and techniques of thermodynamics, and be able to apply thermodynamics to problems across the sciences.
- 4. Improve your problem solving skills and mathematical confidence. Leave this course with an increased ability to do mathematics and physics.
- 5. Have fun while learning a lot.