

Review of Thermodynamics. 2: Potentials and First-Order Variables

Variational Statement of Second Law and Equilibrium Conditions

- *Internal constraint:* A partition of an equilibrium system at T (with values (N, V, \dots) , for the extensive variables \vec{X}) into two parts, followed by a variation in some of the parameter values for the subsystems away from what they were in the original system. (In each part, of course, the changes of the various extensive quantities must be related to each other by the first law of thermodynamics, as applied to the subsystem.)
- *Entropy maximization:* Consider an equilibrium system with given overall values of the extensive (E, \vec{X}) , divide it into two subsystems 1 and 2, and impose an internal constraint in which we transfer energy between the subsystems, $\delta E_2 = -\delta E_1$ without adding any overall δW or δQ . Then $\delta S \leq 0$, because if we now removed the constraint the system would (by assumption) approach equilibrium adiabatically and in such a transformation (by the second law) the entropy increases. Thus, $S(E, \vec{X}) \geq S(E, \vec{X}, \text{constraint})$.
- *Energy minimization:* If we impose an internal constraint on a system in which we vary the partial entropies, with $\delta S_2 = -\delta S_1$, then the variation must lead to $\delta E \geq 0$, because the total entropy S remained constant, but if we removed the constraint the system would approach an equilibrium state of the same energy $E' = E(S, \vec{X}, \text{constraint})$ and higher entropy $S' > S$, and since entropy is (usually) an increasing function of energy, we must have $E' > E$.

Legendre Transforms and Auxiliary Potentials

- *Motivation:* The energy E is naturally a function of all extensive variables (S, V, N, \dots) , as can be seen for example from the form of the thermodynamic identity for dE . We now introduce quantities with dimensions of energy that have useful physical interpretations and simplify calculations in situations where we control a different set of variables.
- *Idea:* Every pair of conjugate intensive-extensive variables can be used to replace one of the basic thermodynamical variables by its conjugate one. Specifically, for each pair (f_i, X_i) we can define a new thermodynamic potential by the Legendre transformation $A := E - f_i X_i$ (we can also use more than one pair of variables to define A). The most important effect is seen in the form of the fundamental identity of thermodynamics, where the role of E is taken over by A , using the fact that the definition of A implies

$$dA = dE - X_i df_i - f_i dX_i .$$

- *Helmholtz free energy:* It is defined as (many textbooks, including P&B, use the symbol A for it)

$$F := E - TS .$$

In terms of this potential, which for a neutral fluid is a function of (T, V, N, \dots) ,

$$dF = -S dT - p dV + \mu dN + \dots .$$

(Or $\mu dN \mapsto \sum_i \mu_i dN_i$ for a multicomponent fluid.) From the definition, $\Delta F = \Delta E - \Delta(TS)$ or $\Delta E - T \Delta S$ if T is constant, so F can be interpreted as the energy needed to put the system in place in an environment at fixed T , since then an amount of energy $Q = \int T dS = T \Delta S$ can be absorbed from the environment in the form of heat. This is the function that is minimized in thermal equilibrium at fixed T , rather than E .

- *Enthalpy:* The quantity defined as

$$H := E + pV ,$$

and seen as a function of (S, p, N, \dots) , in terms of which the fundamental identity for a neutral fluid becomes

$$dH = T dS + V dp + \mu dN + \dots .$$

From $\Delta H = \Delta E + \Delta(pV)$ or $\Delta E + p \Delta V$ if p is constant, H can be interpreted as the energy needed to put a system in place in an environment at pressure p , taking into account the fact that the environment needs to be pushed back to make space for the system, which requires an amount pV of work.

- *Gibbs free energy*: The quantity defined as

$$G := E - TS + pV ,$$

and seen as a function of (T, p, N, \dots) , in terms of which the fundamental identity for a neutral fluid becomes

$$dG = -S dT + V dp + \mu dN + \dots .$$

It can be interpreted as the energy needed to put a system in place in an environment at temperature T and pressure p , taking into account both the heat that can be absorbed from the environment and the work required to make space for the system. This is why G is important for phase transitions.

- *Grand potential*: The quantity defined as

$$\Omega := E - TS - \mu N ,$$

and seen as a function of (T, V, μ, \dots) , in terms of which the fundamental identity for a neutral fluid becomes

$$d\Omega = -S dT - p dV - N d\mu + \dots .$$

Euler and Gibbs-Duhem Relations

- *Extensive functions*: Using the fact that one variable in each conjugate pair is intensive, the first law can be integrated to give expressions for the thermodynamic potentials. For a multi-component system, from

$$dE = T dS - p dV + \mu_i dN_i ,$$

(where a sum over values of repeated indices is implied) since S , V and N_i are extensive and T , p and μ_i intensive, we can conclude that the energy can be written as

$$E = TS - pV + \mu_i N_i ,$$

a relationship known as Euler's equation. From this it follows that the variations of all intensive variables are related by the differential Gibbs-Duhem relation $S dT - V dp + N_i d\mu_i = 0$, and that we can write

$$G = E - TS + pV = \mu_i N_i .$$

[But, for example, from $dG = -S dT + V dp + \mu_i dN_i$ we cannot conclude that $G = -TS + pV + \mu_i N_i$].

- *Remarks*: (1) Euler's theorem can be invoked to make this argument more rigorous. (2) From $G = \sum_i \mu_i N_i$ we see that μ_i can be interpreted as the Gibbs free energy per particle of type i for the system in this state.

First-Order Quantities

- *First derivatives of potentials*: Given a complete set of thermodynamic variables and the corresponding potential, each of the remaining thermodynamic variables seen so far can be obtained as a derivative of the potential with respect to the conjugate one using the fundamental identity. For example, two expressions for the pressure are

$$p = -\left. \frac{\partial E}{\partial V} \right|_{S, N} = -\left. \frac{\partial F}{\partial V} \right|_{T, N} .$$

Reading

- *Kennett*: Appendix B, Section B.3.
- *Other books with summaries*: Chandler, Secs 1.5–1.8 (this would be my suggestion for a quick review); Halley, Second half of Ch 3; Kardar, Sec 1.7; Mattis & Swendsen, Sec 3.3; Plischke & Bergersen, Secs 1.3–1.4; Reichl, Secs 3.5, 3.7; Reif, Secs 5.5–5.6; Schwabl, Sec 3.1-3.3.
- *Good undergraduate-level textbooks with more complete treatments*: Schroeder 2000; Huang 2010.
- *Additional reference*: J.J. Prentis & M.J. Obsniuk, "Free energy in introductory physics," *Phys. Teach.* 54, 91 (2016); <http://dx.doi.org/10.1119/1.4940172>