

Summary according to H. B. Callen, *Thermodynamics*

Pure thermodynamics is about relations that are generally valid for all kinds of systems.

No ideal gas law. . .

Equilibrium states

Existence of certain simple states:

Postulate I: *There exist particular states—equilibrium states—which, macroscopically, are characterized completely by the specification of the internal energy U and a set of extensive parameters, V, N_1, \dots, N_k .*

The basic problem of Thermodynamics: Assume that we have two systems each with fixed parameters U , V , and N . We then remove some kind of constraint such that U , V , or N , may now be redistributed. The removal of this constraint will lead to a spontaneous process such that the system settles in a new equilibrium state. The basic problem of Thermodynamics is the calculation of the equilibrium values of these parameters.

The maximum entropy postulate

What is the *simplest conceivable formal solution* to our basic problem?

An extremum principle!

We also hope that this hypothetical function has several particular simple mathematical properties, designed to give a simple theory.

Postulate II: *There exists a function—the entropy S —of the extensive parameters, defined for all equilibrium states and having the following property: The values assumed by the extensive parameters are those that maximize the entropy.*

Example: For two systems (each with fixed V and N) in thermal contact the energy is distributed between them such that $S(U_1, V_1, N_1) + S(U_2, V_2, N_2)$ is maximum, under the constraint that $U_1 + U_2 = U_{\text{total}}$ is fixed.

Further properties of the entropy

Postulate III: *The entropy of a composite system is additive. The entropy is continuous and differentiable and is a monotonically increasing function of the energy.*

This implies that $S(U, V, N)$ may be inverted to give $U(S, V, N)$.

Postulate IV: *The entropy of any system vanishes in the state for which*

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = 0, \quad \text{i.e. at zero temperature.}$$

Note: Only extensive variables this far.

Also note: Postulate III excludes the possibility of a negative temperature, $\partial S/\partial U < 0$, which really is an oddity.

Energy representation, intensive parameters

The functions $S(U, V, N)$ and $U(S, V, N)$ each contain *all* thermodynamic information of the system.

- Introduce the *intensive* parameters T , V , and μ :

$$T = \left(\frac{\partial U}{\partial S} \right)_{VN}, \quad P = - \left(\frac{\partial U}{\partial V} \right)_{SN}, \quad \mu = \left(\frac{\partial U}{\partial N} \right)_{SV}.$$

- Equations of state—expressing the intensive parameters in terms of the independent extensive parameters:

$$\begin{aligned} T &= T(S, V, N), \\ P &= P(S, V, N), \\ \mu &= \mu(S, V, N). \end{aligned}$$

The Euler equation & The Gubbs-Duhem relation

A consequence of using only extensive variables:

$$U = \left(\frac{\partial U}{\partial S} \right)_{VN} S + \left(\frac{\partial U}{\partial V} \right)_{SN} V + \left(\frac{\partial U}{\partial N} \right)_{SV} N,$$

is the Euler equation:

$$U = TS - PV + \mu N.$$

Comparing

$$dU = TdS + SdT - PdV - VdP + \mu dN + Nd\mu,$$

$$dU = TdS - PdV + \mu dN,$$

gives the Gibbs-Duhem relation which shows how changes of the intensive variables are related

$$SdT - VdP + Nd\mu = 0.$$

Processes

- Thermodynamics is about *equilibrium* states
- It can nevertheless also be used for inferences concerning processes
- A *quasi-static process* is defined as a succession of *equilibrium states*

Real processes are irreversible!

- A process takes place because it gives an increase in entropy.
- Running the process in the opposite direction, would mean a decrease in entropy, which is against the second law.
- Real processes are therefore *irreversible*.

Reversible and/or quasi-static:

- Reversible processes are always quasi-static.
- Quasi-static processes need not be reversible.

Energy minimum principle

The functions $S(U, V, N)$ and $U(S, V, N)$ each contain *all* thermodynamic information of the system. Two equivalent formulations:

- $S(U, V, N)$ —the **maximum entropy** principle:

The equilibrium value of any unconstrained internal parameter is such as to maximize the entropy for the given value of the total internal energy.

In an insulated system with a movable wall, the wall will adjust itself to give maximum total entropy = equal pressure in the two parts.

- $U(S, V, N)$ —the **minimum energy** principle:

The equilibrium value of any unconstrained internal parameter is such as to minimize the energy for the given value of the total entropy.

Consider an thermally insulated system with a movable wall *connected to the outside world* such that the motion of this wall does work on the environment. The equilibrium state is the state with lowest internal energy.

Legendre transformations

It is often convenient to let intensive variables replace the extensive ones as the mathematically independent variables. This gives

$$F(T, V, N) = U - TS, \quad \text{Helmholtz free energy}$$

$$H(S, P, N) = U + PV, \quad \text{Enthalpy}$$

$$G(T, P, N) = U - TS + PV, \quad \text{Gibbs free energy.}$$

There are then new minimum principles:

For $F(T, V, N)$:

The equilibrium value of any unconstrained internal parameter is such as to minimize the Helmholtz free energy for a system in thermal contact with a heat reservoir (i.e. a system kept at a given temperature).

Maxwell relations

Mixed partial derivatives should be independent of the order of differentiation, e.g.

$$\frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V} \right)_{SN} = \frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S} \right)_{VN}.$$

And since

$$\left(\frac{\partial U}{\partial V} \right)_{SN} = -P, \quad \text{and} \quad \left(\frac{\partial U}{\partial S} \right)_{VN} = T,$$

the relation above implies the unexpected relation

$$-\left(\frac{\partial P}{\partial S} \right)_{VN} = \left(\frac{\partial T}{\partial V} \right)_{SN}.$$

There are three different Maxwell relations for each thermodynamic potential (U , F , ...).

Quantities and some relations

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P, \quad \text{thermal expansion coefficient,}$$

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T, \quad \text{isothermal compressibility.}$$

Many unexpected relations. One example:

$$C_P - C_V = \frac{TV\beta^2}{\kappa_T}, \quad (\text{from lengthy derivations}).$$