

CHAPTER 7. CLASSICAL THERMODYNAMICS (Not examinable, except 7g)

7a Zeroth Law.

Two systems in thermal equilibrium have a common property, the temperature T . If 2 systems are in equilibrium with a 3rd system, they are in equilibrium with each other. (In Gibbs's generalization, chemical potential μ is added along with T .)

7b First Law (conservation of energy)

There exists a function of state, the internal energy U , such that

$$dU = dQ - dW \quad (7b.1)$$

where dQ is heat absorbed by the system and dW is the work done **by** the system. (E.g. for a reversible process we might have $dW = PdV + MdB$).

Note: there are no functions of state called Q or W : e.g. the amount of heat flowing depends on the manner in which the change is made and not just on the final and initial states of the system. For this reason, a d with a bar through the upright (like \hbar) is sometimes used to indicate that these small amounts of heat or work are not the differentials of well-defined functions of state. Something like $\delta U, \delta W$.

Connection of 1st law with statistical mechanics:

$U =$ (fixed) energy in microcanonical ensemble

$U = \langle E \rangle$ in canonical ensemble

$U = \langle E \rangle$ in grand ensemble

For sufficiently slow ("reversible") changes,

$$dQ = dQ^{rev} = \sum_i df_i E_i, \quad dW = dW^{rev} = -\sum_i f_i dE_i \quad dU = dQ - dW \quad (7b.2)$$

7c Second Law.

There exists a function of state, the thermodynamic entropy S , and an absolute temperature T such that heat absorbed from a reservoir at T is

$$dQ \leq TdS \begin{cases} \text{equality for reversible (slow) process} \\ \text{inequality for irreversible process} \end{cases}$$

Many other equivalent statements exist: e.g. "There exists no process whose sole effect is to transfer heat from lower temperature to higher temperature reservoir with no work done."

Discussion: How is this second statement an equivalent statement? (Or at least a consequence of the first statement?)

Connection of 2nd law with statistical mechanics:

Entropy is connected with logarithm of probability. Specifically, we can choose:

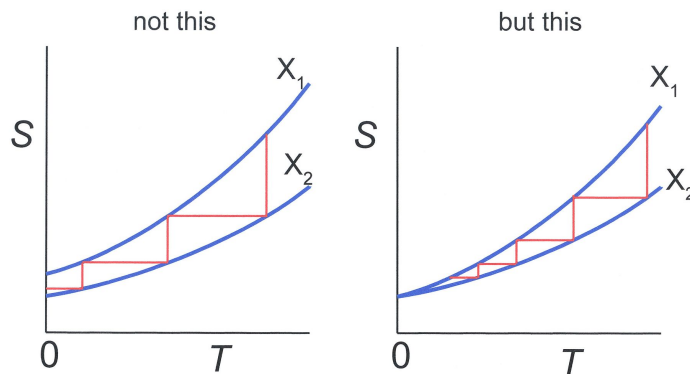
(i) General (nonequilibrium, Shannon) definition:

$$S = -k_B \sum_i f_i \ln f_i$$

(ii) Microcanonical (equil^m) definition: $f_i = 1/g$ for g states of equal energy, $S = k_B \ln(g)$.

(iii) Canonical, equilibrium definition. When $f_i = Z^{-1} \exp(-\beta E_i)$, Shannon entropy reduces to a definite function of T, V, B etc. This is the equilibrium entropy $S(T, V, [B, \dots]) = (U + k_B T \ln Z) / T$

7d Third Law. “As $T \rightarrow 0$, the entropy of a system in thermal equilibrium goes smoothly to a finite value S_0 , per particle, regardless of any control parameters” This law (also known as **Nernst’s law**) implies that the unattainability of absolute zero temperature in a finite number of steps:



[https://en.wikipedia.org/wiki/Third_law_of_thermodynamics]

Explanation of 3rd law from statistical mechanics. Typical Hamiltonians have a unique ground state, or at least a ground state degeneracy g_X that is not exponentially large in the size of the system. Here X denotes one or more control parameter such as pressure. That means that the entropy per particle $S/N \rightarrow N^{-1} \ln g_X \rightarrow O(N^{-1})$ as $T \rightarrow 0$. That is, the finite value of Nernst’s law is zero, by the SM definition of entropy (whereas in thermodynamics, an additive constant to entropy makes no difference).

Note however that statistical mechanics shows that this “law” is not, in fact, universal. A noninteracting system, of N spin-1/2 particles in zero B field has 2^N ground states, so the ground state entropy per particle is $N^{-1}(Nk_B \ln 2) = k_B \ln(2) \neq 0$. There are many subtleties here – we won’t dwell on it.

Ginsberg’s 1975 Statements of the Laws of Thermodynamics:

0. There is a game.
1. You can’t win.
2. In fact, you can’t break even.
3. Finally, you can’t even get out of the game.

7e. Energy quantities and their differentials

Start from 2nd law of thermodynamics for system with definite number of particles, combining with 1st law:

$$dU = dQ^{rev} - dW^{rev} = TdS - PdV \quad (7e.1)$$

Want to generalize to include changes in particle # N . In 2nd year Statistical Mechanics lectures we introduced changes in N via the Grand Ensemble. We then defined $A = F = U - TS$ (Helmholtz free energy). At fixed particle number, we have

$$\begin{aligned}
dF &= dU - d(TS) = (TdS - PdV) - (TdS + SdT) \\
&= -SdT - PdV \\
\left. \frac{\partial F}{\partial T} \right|_{V,N} &= -S, \quad \left. \frac{\partial F}{\partial V} \right|_{T,N} = -P
\end{aligned}$$

For a general change, including a change in N we have [This requires some work to show!]

$$\begin{aligned}
dF &= \left. \frac{\partial F}{\partial T} \right|_{V,N} dT + \left. \frac{\partial F}{\partial V} \right|_{T,N} dV + \left. \frac{\partial F}{\partial N} \right|_{V,T} dN \\
dF &= -SdT - PdV + \mu dN \quad \text{Helmholtz free energy } F(T,V,N) \quad (7e.2) \\
F &= U - TS
\end{aligned}$$

Using this we can find expressions for differentials of other commonly used energy quantities:

$$dU = dF + d(TS) = TdS - PdV + \mu dN \quad (\text{internal energy } U(S,V,N)) \quad (7e.3)$$

$$dH = d(U + PV) = TdS + VdP + \mu dN \quad (\text{enthalpy } H(S,P,N)) \quad (7e.4)$$

$$\begin{aligned}
dG &= d(F + PV) = d(U - TS + PV) \quad (\text{Gibbs free energy } G(T,P,N)) \quad (7e.5) \\
&= -SdT + Vdp + \mu dN
\end{aligned}$$

For each energy quantity, its "natural" arguments are those whose differentials appear on the RHS above: so we normally think of $F(T,V,N)$ etc. (They are only "natural" because the partial derivative. are simple physically meaningful quantities: e.g.

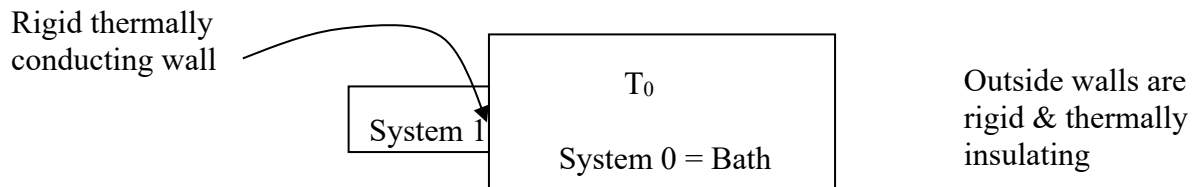
$$\left. \frac{\partial U}{\partial S} \right|_{V,N} = T, \quad \left. \frac{\partial G}{\partial N} \right|_{P,V} = \mu \quad \text{etc.}$$

7f: Equilibrium as an extremal condition with constraints

1. *Isolated system*: $dS > 0$ for irreversible changes therefore

$$S \rightarrow \text{maximum (given } U, N, V) \text{ at equilibrium for isolated system} \quad (7f.1)$$

2. *System in contact with heat reservoir at temperature T .*



Define a Helmholtz free energy of system 1 (which could be out of equilibrium, and so not have a temperature T_1 of its own) as

$$\tilde{F}_1 = U_1 - T_0 S_1$$

(Note that this tilde doesn't mean the average, unlike with \tilde{N} in Chap. 6 which was a fudge for \bar{N} .) Considering the isolated system of bath (system 0) plus system 1, we have, for a spontaneous change toward equilibrium

$$\begin{aligned} 0 &\leq dS = dS_1 + dS_0 \\ &= dS_1 + \frac{dQ_0}{T_0} = dS_1 - \frac{dQ_1}{T_0} \\ &= \frac{1}{T_0} [T_0 dS_1 - dU_1 - dW_1] \\ 0 &\leq -d\tilde{F}_1 - dW_1 \\ dW_1 &\leq -d\tilde{F}_1 \end{aligned}$$

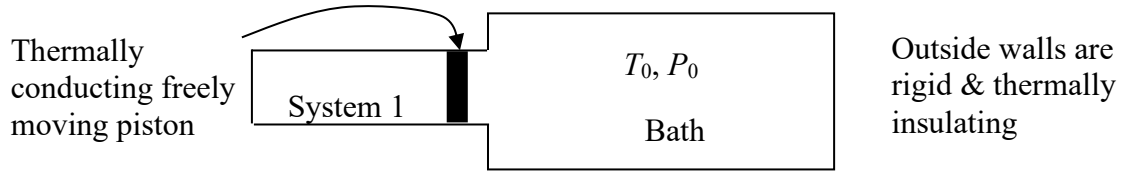
Conclusions:

(i) Loss of "free energy" = max work system 1 can do on outside world. Hence name "free" energy: energy available for useful work

(ii) At constant volume ($dW_1=0$) we have $d\tilde{F}_1 < 0$ for a spontaneous change.

$$\tilde{F}_1 \text{ is minimum at equilibrium (when in contact with bath at } T_0 \text{ at constant } V, N). \quad (7f.2)$$

3. System in thermal and pressure contact with bath at T_0, P_0



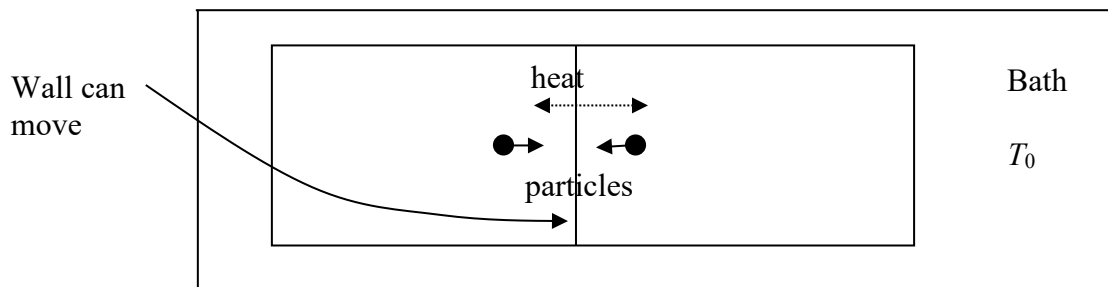
Consider isolated combined system as before

$$\begin{aligned}
 0 &\leq dS = dS_1 + dS_0 \\
 &= dS_1 + \frac{dQ_0}{T_0} \\
 &= dS_1 - \frac{dQ_1}{T_0} = dS_1 - \frac{dU_1 + dW_1}{T_0} \\
 &= dS_1 - \frac{dU_1 + P_0 dV_1}{T_0} \\
 &= -\frac{1}{T_0} d[U_1 - T_0 dS_1 + P_0 dV_1] \\
 &= -\frac{1}{T_0} dG_1
 \end{aligned}$$

Thus with T_0, P_0 imposed by the bath, we have

$$\boxed{\text{Gibbs free energy } G_1 = U_1 - T_0 S_1 + P_0 V_1 \text{ of system 1 minimised at equil}^m}, \quad (7f.3)$$

4. Conditions for equilibrium of 2 phases in diffusive and thermal contact at temperature T_0 : total volume Total V is fixed but wall can move, allowing V_1 and V_2 to change.



Consider small changes away from equil^m: $\delta N_1 (= -\delta N_2)$ and $\delta V_1 (= -\delta V_2)$. Since T, V are fixed the Helmholtz energy F is minimized at equilibrium, so

$$0 = dF = \left(\frac{\partial F_1}{\partial N_1} \bigg|_{V, T_0} - \frac{\partial F_2}{\partial N_2} \bigg|_{V_1, T_0} \right) dN_1 + \left(\frac{\partial F_1}{\partial V_1} \bigg|_{N_1, T_0} - \frac{\partial F_2}{\partial V_2} \bigg|_{N_2, T_0} \right) dV_1$$

This must vanish for arbitrary dN_1, dV_1 and so

$$\left. \frac{\partial F_1}{\partial N_1} \right|_{V_1} = \left. \frac{\partial F_2}{\partial N_2} \right|_V \quad \text{i.e. } \mu_1 = \mu_2$$

and also $\left. \frac{\partial F_1}{\partial V_1} \right|_{N_1} = \left. \frac{\partial F_2}{\partial V_2} \right|_{N_2} \quad \text{i.e. } P_1 = P_2$

Of course the temperatures are also equal $\beta_1 = \beta_2 = \beta_0$

7g: Stability conditions for equilibrium

For stability (i.e. *minimum* F rather than *maximum*) we need, at fixed V and *bath* temp. T_0 ,

$$\begin{aligned} 0 \leq \left. \frac{\partial^2 \tilde{F}}{\partial T_1^2} \right|_{T_0, V} &= \left. \frac{\partial^2}{\partial T_1^2} (U_1 - T_0 S_1) \right|_{T_0, V} \\ &= \frac{\partial}{\partial T_1} \left(\left. \frac{\partial U_1}{\partial T_1} \right|_{V_1} - T_0 \left. \frac{\partial S_1}{\partial T_1} \right|_{V_1} \right) \bigg|_{T_1 = T_0} \\ &= \frac{\partial}{\partial T_1} \left(\left. \frac{T_1 \partial S_1}{\partial T_1} \right|_{V_1} - T_0 \left. \frac{\partial S_1}{\partial T_1} \right|_{V_1} \right) \bigg|_{T_1 = T_0} \\ &= \frac{\partial}{\partial T_1} \left((T_1 - T_0) \left. \frac{\partial S_1}{\partial T_1} \right|_{V_1} \right) \bigg|_{T_1 = T_0} = \left((T_1 - T_0) \left. \frac{\partial^2 S_1}{\partial T_1^2} \right|_{V_1, T_1 = T_0} \right) + 1 \cdot \left. \frac{\partial S_1}{\partial T_1} \right|_{V_1, T_1 = T_0} \\ &= \left. \frac{\partial S_1}{\partial T_1} \right|_{V_1, T_1 = T_0} \end{aligned}$$

Multiply by T_1 to get

$$C_V = T_1 \left. \frac{\partial S_1}{\partial T_1} \right|_{V_1} \geq 0 \quad \text{for a system of +ve temp.} \quad (7g.1)$$

That is, the energy of the system increases as its temperature increases. If the opposite were true, the system could gain heat from a hotter environment but get still cooler, so would not come to thermal equilibrium. Alternatively, it could lose heat to a colder environment, but get ever hotter. Similarly by considering changes in G due to change in V_1 , get

$$\left. \frac{\partial P}{\partial V} \right|_T \geq 0 \quad (7g.2)$$

This says that the pressure will increase if the volume decreases. This is a reasonable result, since if the pressure were to decrease with decrease in volume the systems would collapse to zero volume.

7h: Maxwell relations.

We assume that U, F, G, H are well behaved functions of their "natural" arguments, so that mixed 2nd partial derivatives are equal:

e.g.

$$\left. \frac{\partial V}{\partial S} \right|_{N,P} = \left. \frac{\partial}{\partial S} \frac{\partial H}{\partial P} \right|_N = \left. \frac{\partial}{\partial P} \frac{\partial H}{\partial S} \right|_N = \left. \frac{\partial T}{\partial P} \right|_{N,S}$$

How to decide which energy function to pick: "bottom" variables must be "natural" variables, top variable must be conjugate to one of fixed natural variables. So in this case S, N and P are the bottom variables $\Rightarrow H$ is the energy function to use.

Exercise: (i) show that

$$\left. \frac{\partial T}{\partial V} \right|_{S,N} = - \left. \frac{\partial P}{\partial S} \right|_{V,N}, \quad \left. \frac{\partial T}{\partial P} \right|_{S,N} = \left. \frac{\partial V}{\partial S} \right|_{F,N} \quad \text{subscript } P \text{ not } F$$

$$\left. \frac{\partial S}{\partial V} \right|_{T,N} = \left. \frac{\partial P}{\partial T} \right|_{V,N}, \quad \left. \frac{\partial S}{\partial P} \right|_{T,N} = - \left. \frac{\partial V}{\partial T} \right|_{F,N} \quad \text{subscript } P \text{ not } F$$

These 1st 4 are the standard "Maxwell relations" relevant to Canonical Ensembles. That is, N and μ aren't significantly involved. But we can find others for the GCE. e.g. (ii) show

$$\left. \frac{\partial \mu}{\partial P} \right|_{N,T} = \left. \frac{\partial V}{\partial N} \right|_{P,T}.$$

Thus (iii) answer: "if P is increased at constant N and T , does μ increase or decrease?"

7i: Extensive and intensive parameters : conjugate variables

Extensive parameters are additive for two pieces of a system - eg U, V, N, S are additive for most systems. (Caution: U, S may not be additive for systems with uncompensated long-ranged forces e.g. non neutral plasma). *Intensive parameters* are equal for two pieces of a system e.g. β, P, μ as proved just previously.

Combinations: From above definitions its clear that

(extensive) + (extensive) = extensive
 (extensive) × (intensive) = extensive (intensive) × (intensive) = intensive

Conjugate pairs of intensive and extensive variables:

T, S
 $-P, V$
 μ, N
 \mathbf{B}, \mathbf{M} (magnetic induction, magnetization)
 $\mathbf{E}, \mathbf{\mu}$ (electric field, electric dipole moment)

These always occur together in pairs, in energy quantities e.g. TS , and they are related by differential relations e.g. $S = \left. \frac{\partial U}{\partial T} \right|_{N,V}$.

Legendre transformation: takes one between two extensive quantities: eg $F = U - TS$ is a Legendre transformation. Converts from U , with natural variable S (dU contains dS) to F with natural variable T (dF contains dT)

Note also that F, G, H are all extensive (for well-behaved systems) since U is: this follows because the Legendre terms (PV, TS) are extensive.

7j: Alternative expression for G

The particle number N is a "natural" variable of all of U, F, G, H , therefore in all cases, these quantities are proportional to N , for fixed values of intensive variables (say P, T). In particular, $G = g(P, T)N$ (g = Gibbs energy/particle). Now G , defined as $G = U + PV - TS$, is special in that its other natural variables (apart from N) are intensive, being P and T .

Noting $\mu = \left. \frac{\partial G}{\partial N} \right|_{P,T}$ from previously, we see $g = \mu$. That is,

$$\boxed{G = \mu N.}$$

Thus μ has the interpretation of the Gibbs free energy/particle, for extensive systems. It also has an interpretation in terms of rabbits (Schroeder, *An Introduction to Thermal Physics*):



Figure 5.1. To create a rabbit out of nothing and place it on the table, the magician need not summon up the entire enthalpy, $H = U + PV$. Some energy, equal to TS , can flow in spontaneously as heat; the magician must provide only the difference, $G = H - TS$, as work. (Illustration by Karen Thurber.)