

which it depends are experimentally controlled parameters. This is perhaps easiest to see when one considers the thermodynamic identities they satisfy:

$$\begin{aligned}
 dU &= T dS - P dV + \mu dN \\
 &= \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN \\
 dH &= dU + P dV + V dP \\
 &= T dS + V dP + \mu dN \\
 &= \left(\frac{\partial H}{\partial S}\right)_{P,N} dS + \left(\frac{\partial H}{\partial P}\right)_{S,N} dP + \left(\frac{\partial H}{\partial N}\right)_{S,P} dN \\
 dF &= dU - T dS - S dT \tag{29} \\
 &= -S dT - P dV + \mu dN \\
 &= \left(\frac{\partial F}{\partial T}\right)_{V,N} dT + \left(\frac{\partial F}{\partial V}\right)_{T,N} dV + \left(\frac{\partial F}{\partial N}\right)_{T,V} dN \\
 dG &= dU - T dS - S dT + P dV + V dP \\
 &= -S dT + V dP + \mu dN \\
 &= \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dP + \left(\frac{\partial G}{\partial N}\right)_{T,P} dN.
 \end{aligned}$$

[EOC, Mon. 2/27/2006, #21; HW07 remains open]

[EOC, Wed. 3/1/2006, #22; Review for exam 1]

[EOC, Fri. 3/3/2006, #23; Exam 1]

So, for example, the Helmholtz free energy F is convenient when the temperature is constant, so that $dT = 0$ and changes in F depend only on changes in volume and particle number. The Gibbs free energy G is convenient when both pressure and temperature are fixed, as is commonly the case in chemical reactions performed in a vessel that is open to the air.

One other important result follows from the information in (29): each of the derivative quantities, T , P , and μ , as well as the variables S , V , and N , can be expressed in terms of derivatives of some of the potentials. The correspondence between the terms in the thermodynamic identity satisfied by any one of the potentials and the total differential of that potential when viewed as a function of its natural variables gives the definitions of the three derivative quantities of that potential. The meanings of the derivatives of the energy are familiar, but we can also easily extract from (29) things like

$$T = \left(\frac{\partial H}{\partial S}\right)_{P,N} \quad \text{and} \quad V = \left(\frac{\partial G}{\partial P}\right)_{T,N}. \tag{30}$$

These can be very handy bits of information to have available when one is manipulating thermodynamic expressions.

One can, of course, construct several additional thermodynamic potentials through other combinations of Legendre transformations of the energy. In addition, each of the potentials can be expressed in terms of Legendre transformations of other potentials. For example,

$$G = F + PV = H - TS \quad \text{and} \quad F = G - PV = H - TS - PV. \quad (31)$$

You can see that there are many possibilities.

There is also an analogous family of Legendre transformations of the entropy, those functions often being called *Massieu functions*.

One important thing to keep in mind is that you need not memorize this entire blizzard of formulas. Nor need you spend time looking through several books for just the right one when you need one. If you only remember the thermodynamic identity for the energy, $dU = T dS - P dV + \mu dN$, and either the natural variables upon which each potential depends or the definition of each potential in terms of a Legendre transformation of the energy, together with the list of variables upon which U depends, it is extremely easy to construct all the other formulas in a matter of seconds. Even the definitions of the derivative quantities T , P , and μ in terms of U need not be memorized.

HW Problem. Schroeder problem 5.12, pp. 158–159.

HW Problem. Schroeder problem 5.14, p. 159.

HW Problem. Schroeder problem 5.17, p. 160.

Reading assignment. Schroeder, section 5.3.

0.1.3 Variational principles

The second law of thermodynamics asserts that whenever any constrained internal parameter of an isolated system is permitted to vary, the ultimate equilibrium state of the system will be the one that maximizes the entropy over all possible values of that parameter. This is an example of a variational principle, and it states the condition for equilibrium in terms of the entropy.

For systems in contact with reservoirs, which are large systems with fixed values of parameters like temperature or pressure, it is often more convenient to express the relations among the thermodynamic variables in the form of a thermodynamic potential function. In such circumstances it is also convenient to express the condition for equilibrium in terms of the thermodynamic potential, rather than the total entropy of the system plus reservoir. The advantage gained in casting the problem in terms of the appropriate thermodynamic potential is that the variables that enter are then the ones characterizing the system of interest, allowing the attached

reservoir, or the environment generally, to be treated as a fixed external influence, rather than having to be treated as part of the system we analyze.

Our goal then is to find the appropriate variational principles that can be used to find the equilibrium state in such cases. But first, we'll review the variational principle satisfied by the entropy and then take a look at an alternative characterization of the condition for equilibrium in terms of the energy, rather than the entropy.

Variational principle for the entropy

We'll begin by supposing that the system is in some way internally constrained away from its equilibrium state—a convenient way to picture this is to suppose it consists of two subsystems initially prevented from exchanging something, possibly energy, volume, or particles. Denoting the constrained parameter generically by λ , we'll write the entropy of the combined system as

$$S = S(U, \lambda), \quad (32)$$

where the explicit dependence of S on V and N has been suppressed, since they won't play a significant role in the analysis, and we'll take them to be fixed. You might find it helpful to think of λ as the energy of the first subsystem, with the energy of the second subsystem being $U - \lambda$, and to think of the type of contact to be established between the subsystems as thermal contact, in which λ is allowed to vary to establish thermal equilibrium between the subsystems.

When the systems are placed into the appropriate type of contact, so that λ can change, the equilibrium value of λ will be the one that maximizes the function $S(U, \lambda)$ over all possible values of λ , with U held fixed. That is, the equilibrium value of λ is the one that satisfies the conditions

$$\left(\frac{\partial S}{\partial \lambda}\right)_U = 0 \quad \text{and} \quad \left(\frac{\partial^2 S}{\partial \lambda^2}\right)_U < 0. \quad (33)$$

Keep in mind that S and U are properties of the combined system, while λ is generally related to some property of one of the subsystems, such as its energy.

Variational principle for the energy

Recall that the function $S = S(U, V, N)$ is a relation among four variables that contains all the thermodynamic information about the system. It can be solved for the alternative function $U = U(S, V, N)$, which contains all the same information. It should not be surprising then that the equilibrium condition can equally well be stated in an alternative form using this function, instead of the entropy.

Imagine that instead of fixing the total energy U and asking what value of λ maximizes S , we fix S and look for the appropriate variational principle

satisfied by U , now allowed to vary. While it is easy to envision isolating the combined system in order to fix its total energy, fixing its entropy may be physically trickier. Entry of any heat must be prevented, since that would raise the entropy, and any work that is done must be done quasistatically. Nevertheless, we can easily handle that mathematically.

Since S is fixed, its total differential, given small changes in U and λ , must vanish:

$$dS = \left(\frac{\partial S}{\partial U}\right)_\lambda dU + \left(\frac{\partial S}{\partial \lambda}\right)_U d\lambda = 0. \quad (34)$$

This implies that the derivative of the energy with respect to λ can be expressed in terms of derivatives of S :

$$\left(\frac{\partial U}{\partial \lambda}\right)_S = -\frac{(\partial S/\partial \lambda)_U}{(\partial S/\partial U)_\lambda}. \quad (35)$$

At equilibrium, the partial derivative of S with respect to U gives the inverse of the temperature:

$$\left(\frac{\partial S}{\partial U}\right)_\lambda = \left(\frac{\partial S}{\partial U}\right)_{\lambda, V, N} = \frac{1}{T}. \quad (36)$$

Thus, the derivatives of U and S with respect to λ are proportional:

$$\left(\frac{\partial U}{\partial \lambda}\right)_S = -T \left(\frac{\partial S}{\partial \lambda}\right)_U = 0, \quad (37)$$

where the last equality follows from the equilibrium condition stated in terms of entropy.

So we have found that the energy of the combined system with specified entropy is, like the entropy with specified energy, extremal in the equilibrium state. But what kind of extremum is it? To find out, we'll need to look at the second derivative. To simplify the notation, let's define

$$f(U, \lambda) = \left(\frac{\partial U}{\partial \lambda}\right)_S. \quad (38)$$

Then the second derivative of the energy is

$$\begin{aligned}
\left(\frac{\partial^2 U}{\partial \lambda^2}\right)_S &= \left(\frac{\partial f}{\partial \lambda}\right)_S \\
&= \left(\frac{\partial f}{\partial U}\right)_\lambda \underbrace{\left(\frac{\partial U}{\partial \lambda}\right)_S}_{0 \text{ in equilibrium}} + \left(\frac{\partial f}{\partial \lambda}\right)_U \\
&= \frac{\partial}{\partial \lambda} \left[-\frac{(\partial S / \partial \lambda)_U}{(\partial S / \partial U)_\lambda} \right]_U \\
&\qquad\qquad\qquad 0 \text{ in equilibrium} \\
&= -\frac{(\partial^2 S / \partial \lambda^2)_U}{(\partial S / \partial U)_\lambda} + \frac{\overbrace{(\partial S / \partial \lambda)_U}^0 (\partial^2 S / \partial \lambda \partial U)}{(\partial S / \partial U)_\lambda^2} \\
&= -T \underbrace{\left(\frac{\partial^2 S}{\partial \lambda^2}\right)_U}_{< 0 \text{ in equilibrium}} \\
&> 0.
\end{aligned} \tag{39}$$

Thus, in the equilibrium state U is minimized over all values of λ at fixed S . This is the variational principle satisfied by U for a system with S fixed, and it is completely equivalent to the variational principle satisfied by S for fixed U , in the sense that both determine the same equilibrium state. That is, if we find the equilibrium value of S by maximizing S subject to fixed U , then the minimization of U when S is fixed at the equilibrium value found by the entropic variational principle, the value of U found matches the fixed value used to maximize the entropy. And, the values of the parameter λ are the same in both cases.

Variational principle for the free energy

To find the appropriate variational principle satisfied by the Helmholtz free energy, $F = U - TS$, we consider a system in thermal contact with a reservoir whose temperature determines the equilibrium temperature. An appropriate parameter that characterizes the macrostate of the combined system plus reservoir is the energy of the system, U . The total differential of the total entropy of the system plus reservoir is

$$dS_{\text{tot}} = dS + dS_R, \tag{40}$$

where S is the entropy of the system, and S_R is that of the reservoir. The thermodynamic identity for the entropy of the reservoir is

$$dS_R = \frac{1}{T_R} dU_R + \frac{P_R}{T_R} dV_R - \frac{\mu_R}{T_R} dN_R, \tag{41}$$

but the reservoir can only exchange energy with the system, so the last two terms vanish. Since any energy change of the reservoir is the negative of the energy change of the system, and the temperature T of the system at equilibrium is the same as the temperature T_R of the reservoir, the total differential of S_{tot} can be written entirely in terms of variables the system:

$$\begin{aligned}
 dS_{\text{tot}} &= dS + \frac{1}{T_R} dU_R \\
 &= dS - \frac{1}{T} dU \\
 &= -\frac{1}{T}(dU - T dS) \\
 &= -\frac{1}{T} dF.
 \end{aligned}
 \tag{42}$$

In the last step, we've made use of the fact that $dF = dU - T dS - S dT = dU - T dS$, since the reservoir fixes the temperature, so that $S dT = 0$.

This proportionality between the total differential of the total entropy of the combined system plus reservoir and the total differential of the free energy of the system alone tells us two things. The first is that S_{tot} is extremal if and only if F is extremal. That is, either both of their total differentials vanish, or both do not. The second is that the differentials have opposite sign—if S_{tot} decreases a little, then F increases a little, and vice versa. In fact, S_{tot} can only decrease from its equilibrium value, so the free energy of the system can only increase from its equilibrium value. Thus, the free energy of the system is minimized in equilibrium.

[EOC, Mon. 3/6/2006, #24; HW07 closed, due Mon. 3/13/2006]

Similar arguments can be developed to show that the other thermodynamic potentials also satisfy minimum principles as conditions for equilibrium.

HW Problem. Schroeder problem 5.20, p. 163.

0.1.4 Extensive vs intensive variables

The basic variables, S , U , V , and N are all proportional to system size in the thermodynamic limit. They are said to be *extensive variables*. For example, recall that the entropy of the combination of two systems is the sum of the entropies of the subsystems:

$$S_{\text{tot}}(U_{\text{tot}}, V_{\text{tot}}, N_{\text{tot}}) = S_1(U_1, V_1, N_1) + S_2(U_2, V_2, N_2). \tag{43}$$

So, if the subsystems are identical,

$$S_{\text{tot}}(2U, 2V, 2N) = 2S(U, V, N). \tag{44}$$

A more precise, as well as more general way to state this is to note that if the variables on which S depends are all multiplied by a factor λ , then

$$S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N). \tag{45}$$

For example, in the Sackur-Tetrode entropy of a monatomic ideal gas:

$$S(U, V, N) = Nk \left\{ \ln \left[\frac{V}{N} \left(\frac{4\pi m U}{3h^2 N} \right)^{3/2} \right] + \frac{5}{2} \right\}. \quad (46)$$

If $U \rightarrow \lambda U$, $V \rightarrow \lambda V$, and $N \rightarrow \lambda N$, then the ratios V/N and U/N are unchanged, and the N out front becomes λN , so that $S \rightarrow \lambda S$. In fact, that's why I always write it in terms of V/N and U/N —it makes the extensivity obvious.

In general, a function that satisfies

$$f(\lambda x_1, \lambda x_2, \dots) = \lambda^n f(x_1, x_2, \dots) \quad (47)$$

is said to be a *homogeneous function of degree n* . Extensive variables are homogeneous functions of degree 1.

Derivatives of extensive quantities with respect to extensive quantities, like

$$T = \left(\frac{\partial U}{\partial S} \right)_{V,N}, \quad P = - \left(\frac{\partial U}{\partial V} \right)_{S,N}, \quad \text{and} \quad \mu = \left(\frac{\partial U}{\partial N} \right)_{S,V} \quad (48)$$

are independent of system size in the thermodynamic limit. They are called *intensive variables* and are *homogeneous functions of degree zero*. In general, ratios of extensive quantities are intensive, like V/N and U/N in the Sackur-Tetrode equation.

Note that any purported entropy function $S(U, V, N)$ that violates extensivity is bogus. This provides a quick and easy check on the validity of any such function.

0.1.5 Chemical potential revisited

From our handy table of thermodynamic identities for the common thermodynamic potentials, we find several expressions for μ :

$$\mu = \left(\frac{\partial U}{\partial N} \right)_{S,V} = \left(\frac{\partial H}{\partial N} \right)_{S,P} = \left(\frac{\partial F}{\partial N} \right)_{T,V} = \left(\frac{\partial G}{\partial N} \right)_{T,P}. \quad (49)$$

That is, μ is the change in energy when a particle is added at constant S and V , etc. Of all these expressions, the one involving the Gibbs free energy G is special, in that the variables being held fixed are both intensive. This means that

$$G = G(T, P, N) \quad (50)$$

has an especially simple expression in terms of N . If N is increased by a factor λ , increasing the system's size, with T and P remaining fixed, the only thing that causes G to change is the explicit change in N . So the derivative

$$\left(\frac{\partial G}{\partial N} \right)_{T,P} = \mu \quad (51)$$

remains unchanged as particles are added. Thus, G is actually proportional to μ :

$$G = N\mu. \quad (52)$$

Thus, the chemical potential can be characterized as the Gibbs free energy per particle, if the system contains only one type of particle.

We can state this argument more rigorously by making explicit use of extensivity. That the Gibbs free energy is an extensive function can be seen from its definition

$$G = U - TS + PV, \quad (53)$$

in which every term contains either an extensive variable or the product of an intensive variable multiplied by an extensive variable. Every term is extensive, so their sum must be.

If we scale the system size by λ , the effect on G and its arguments is

$$G(T, P, \lambda N) = \lambda G(T, P, N). \quad (54)$$

Now differentiate both sides of this with respect to the scale factor λ :

$$\frac{dG(T, P, \lambda N)}{d\lambda} = \left[\frac{\partial G(T, P, \lambda N)}{\partial(\lambda N)} \right]_{T, P} \underbrace{\frac{d(\lambda N)}{d\lambda}}_N = G(T, P, N). \quad (55)$$

Now let $\lambda \rightarrow 1$ and make use of the definition of the chemical potential as $\mu = (\partial G / \partial N)_{T, P}$ to get

$$G(T, P, N) = \mu N. \quad (56)$$

In contrast,

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T, V} \quad (57)$$

does change as particles are added, because increasing N while the temperature and volume are held fixed requires changing the pressure and density. We know the chemical potential depends on the concentration of particles, so it must change as the density changes.

Recall from previous notes that for the ideal gas

$$U = TS - PV + \mu N. \quad (58)$$

I claimed it was true generally, but offered no proof. In fact, the proof is properly done by the same technique we used above to show that $G = \mu N$. That technique, or the expression for U above together with the definitions of the potentials, can also be used to obtain the corresponding expressions for the enthalpy and free energy:

$$H = TS + \mu N \quad \text{and} \quad F = -PV + \mu N. \quad (59)$$

HW Problem. Schroeder problem 5.23, p. 166.

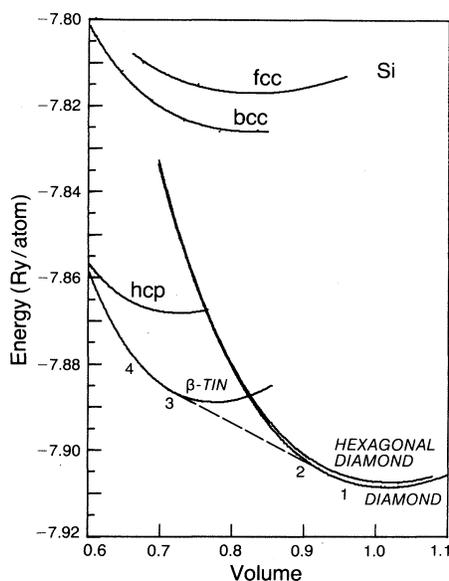
0.1.6 Phase transformations of pure substances

Generally, substances can exist in any of several *phases*, distinguished from each other macroscopically by their physical properties and microscopically by the structural arrangement of their particles. Some common phases of matter and their typical characteristics are:

- Gas: low density, high compressibility, little interaction between particles, no significant order, hence high entropy.
- Liquid: high density; low compressibility; strong interaction between particles; possibly some short-range order, such as temporary clustering; no long-range order. There may be multiple liquid phases, such as in liquid helium.
- Solid: high density; low compressibility; strong interaction between particles; long-range order is common, as in crystalline solids. There may be multiple solid phases.

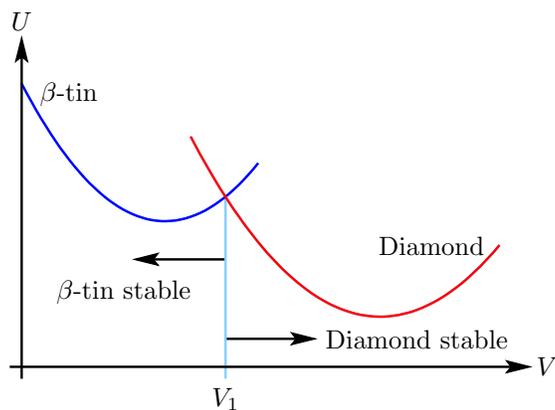
In each phase, there is a function $S(U, V, N)$ or $U(S, V, N)$ that characterizes that phase, but the form of that function, which determines the macroscopic properties, is generally quite different in each phase.

As an example, let's take a look at some possible phases of solid silicon. The following figure, from Yin and Cohen, *Phys. Rev. Lett.* **45**, 1004 (1980), shows the results of calculations of the energy $U(0, V, N)/N$ at zero temperature for several different hypothetical crystal structures that one could suppose silicon might adopt, depending on conditions. Actually, the volume axis shows V/N normalized to the measured volume under standard conditions.

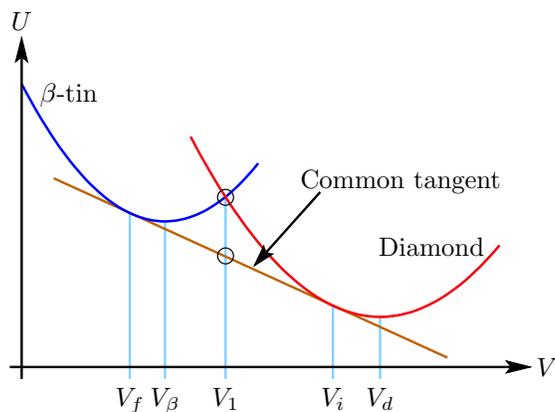


There are a number of insights we can glean from analysis of this figure and of the general notion of two competing solid phases, each of which is more stable than the other under some conditions.

First, it's clear that some of these crystal structures are simply too energetic to be competitive at any of the volumes shown on the graph. The fcc and bcc structures fall into that category, and the hcp structure does as well, though it seems to become competitive at sufficiently low volumes. The hexagonal diamond structure lies close in energy to the diamond structure, so it would not be surprising to see some of it present at finite temperature, but the diamond structure clearly has the lowest energy globally. The graphite structure is actually a bit lower in energy, but it is not shown. The β -tin structure lies higher in energy globally than the diamond structure, but it becomes more stable than the diamond structure under sufficiently high pressure:

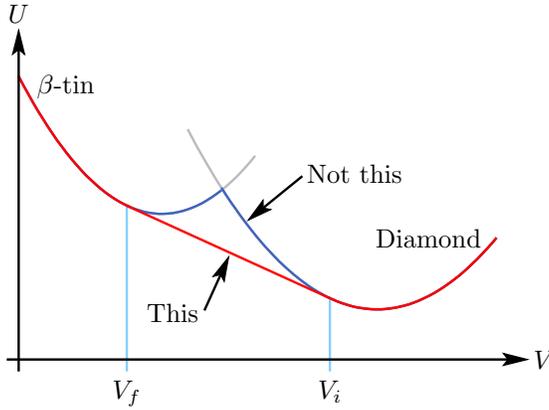


The transformation from the diamond structure to the β -tin structure doesn't take place suddenly at the volume V_1 , however. The energies of both structures lie above the energy of a mixture of the two structures:



It is energetically favorable for the system to *phase separate* into regions having the diamond structure and regions having the β -tin structure. Within each of these, the volume is that appropriate to the local structure, either V_i or V_f , and the average volume is an intermediate value, possibly V_1 , depending on how much work is done after the onset of the phase transformation. The common tangent to the two energy curves gives the energy of a mixture of the two phases as a function of the average volume, and that energy is lower than that of either a uniform diamond structure or a uniform β -tin structure between the points of tangency at V_i and V_f .

Thus, the thermodynamically relevant global function $U(V)$, encompassing the volumes at which each phase is individually stable and the region where a mixture is stable, includes the parts of the energy curves of the uniform phases outside the region where $V_f < V < V_i$, together with the common tangent within that volume range. The portions of the energy curves of the uniform phases lying within the range of the phase separation are thermodynamically inaccessible, in the sense that they represent nonequilibrium structures of the system:



Recall now that the pressure can be expressed as

$$P = - \left(\frac{\partial U}{\partial C} \right)_{S,N}, \quad (60)$$

which is just the slope of the $U(V)$ curve. This means we can view the compression-driven phase transition of silicon from the diamond structure to the β -tin structure as beginning when the volume reaches V_i or the pressure reaches

$$P = - \left(\frac{\partial U}{\partial V} \right)_{S,N} \Big|_{V_i}. \quad (61)$$

The pressure remains at that value while the system moves along the common tangent line, with decreasing volume and increasing amounts of the β -tin structure.