

Unit 1-3: The Gibbs-Duhem Relation, Entropy of the Ideal Gas, Energy Minimum Principle

The Gibbs-Duhem Relation

To recap from a previous lecture: If we regard the energy as the basic thermodynamic function, $E(S, V, N)$, then we defined the partial derivatives as:

$$\left(\frac{\partial E}{\partial S}\right)_{V,N} = T(S, V, N), \quad \left(\frac{\partial E}{\partial V}\right)_{S,N} = -p(S, V, N), \quad \left(\frac{\partial E}{\partial N}\right)_{S,V} = \mu(S, V, N) \quad (1.3.1)$$

One of our goals in this section is to show that T , p , and μ are not mutually independent quantities, but that there is a constraint that relates one to the others. This is the Gibbs-Duhem relation.

We saw already in Eq. (1.1.5) that the entropy is a 1st order homogeneous function of its variables,

$$\lambda S(E, V, N) = S(\lambda E, \lambda V, \lambda N) \quad (1.3.2)$$

Inverting this to write E in terms of S , we conclude that E is also a 1st order homogeneous function of its variables,

$$\lambda E(S, V, N) = E(\lambda S, \lambda V, \lambda N) \quad (1.3.3)$$

Now lets differentiate the above equation with respect to S .

$$\lambda \left(\frac{\partial E(S, V, N)}{\partial S}\right)_{V,N} = \left(\frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial(\lambda S)}\right)_{\lambda V, \lambda N} \left(\frac{\partial(\lambda S)}{\partial S}\right) \Rightarrow \lambda T(S, V, N) = T(\lambda S, \lambda V, \lambda N) \lambda \quad (1.3.4)$$

and so,

$$T(S, V, N) = T(\lambda S, \lambda V, \lambda N) \quad (1.3.5)$$

Similarly, if we differentiate Eq. (1.3.3) with respect to V and N , and recall that $p = -\left(\frac{\partial E}{\partial V}\right)_{S,N}$ and $\mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}$, we conclude,

$$\left. \begin{aligned} T(S, V, N) &= T(\lambda S, \lambda V, \lambda N) \\ p(S, V, N) &= p(\lambda S, \lambda V, \lambda N) \\ \mu(S, V, N) &= \mu(\lambda S, \lambda V, \lambda N) \end{aligned} \right\} T, p, \mu \text{ are homogeneous functions of the } \textit{zeroth} \text{ order} \quad (1.3.6)$$

(In general, any function that satisfies $\lambda^n f(x, y, z) = f(\lambda x, \lambda y, \lambda z)$ is said to be a homogeneous function of the n th order.)

If we now let $\lambda = 1/N$, and use that in Eqs. (1.3.6), we get

$$\left. \begin{aligned} T(S, V, N) &= T\left(\frac{S}{N}, \frac{V}{N}, 1\right) = T(s, v) \\ p(S, V, N) &= p\left(\frac{S}{N}, \frac{V}{N}, 1\right) = p(s, v) \\ \mu(S, V, N) &= \mu\left(\frac{S}{N}, \frac{V}{N}, 1\right) = \mu(s, v) \end{aligned} \right\} \text{these are called the } \textit{equations of state} \quad (1.3.7)$$

Here, as before, $s = S/N$ is the entropy per particle, and $v = V/N$ is the volume per particle.

Thus we see that T , p , and μ are really functions of only *two* intensive variables, s and v .

Since the three variables T , p , μ are all functions of the two variables s and v , there must exist a relation among them – T , p , μ are not all mutually independent.

For example, one could imagine taking the two equations $T = T(s, v)$ and $p = p(s, v)$ and solving them for s and v in terms of T and p . One could then take the third equation $\mu = \mu(s, v)$, substitute in for s and v in terms of T and p , and thus get $\mu(T, p)$. Thus μ is actually a function of T and p and can not be chosen independently of T and p .

The differential form for this constraint on T , p , μ is known as the *Gibbs-Duhem relation*. We derive it as follows.

Consider Eq. (1.3.3), $\lambda E(S, V, N) = E(\lambda S, \lambda V, \lambda N)$, and differentiate with respect to λ . One gets,

$$E(S, V, N) = \left(\frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial(\lambda S)} \right)_{\lambda V, \lambda N} \left(\frac{\partial(\lambda S)}{\partial \lambda} \right) + \left(\frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial(\lambda V)} \right)_{\lambda S, \lambda N} \left(\frac{\partial(\lambda V)}{\partial \lambda} \right) + \left(\frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial(\lambda N)} \right)_{\lambda S, \lambda V} \left(\frac{\partial(\lambda N)}{\partial \lambda} \right) \quad (1.3.8)$$

Which gives,

$$E(S, V, N) = T(\lambda S, \lambda V, \lambda N)S - p(\lambda S, \lambda V, \lambda N)V + \mu(\lambda S, \lambda V, \lambda N)N \quad (1.3.9)$$

Now take $\lambda = 1$ to get,

$$E(S, V, N) = T(S, V, N)S - p(S, V, N)V + \mu(S, V, N)N \quad (1.3.10)$$

or

$$\boxed{E = TS - pV + \mu N} \quad \text{known as the } \textit{Euler relation} \quad (1.3.11)$$

The Euler relation is a consequence of $E(S, V, N)$ being a first order homogeneous function of its variables.

In the above we regard S , V , N , as the independent variables, and T , p , μ are functions of them.

If we divide Eq. (1.3.11) by the number of particles N we get,

$$u = Ts - pv + \mu \quad \text{where } u = E/N \text{ is the energy per particle} \quad (1.3.12)$$

Now from the fundamental definitions of T , p , μ we can write,

$$dE = \left(\frac{\partial E}{\partial S} \right)_{V, N} dS + \left(\frac{\partial E}{\partial V} \right)_{S, N} dV + \left(\frac{\partial E}{\partial N} \right)_{E, V} dN \quad \Rightarrow \quad dE = TdS - pdV + \mu dN \quad (1.3.13)$$

But from the Euler relation of Eq. (1.3.11) we can write,

$$dE = TdS + SdT - pdV - Vdp + \mu dN + Nd\mu \quad (1.3.14)$$

Subtracting Eq. (1.3.13) from Eq. (1.3.14) we get

$$\boxed{SdT - Vdp + Nd\mu = 0 \quad \text{or} \quad d\mu = -sdT + vdp} \quad \text{the } \textit{Gibbs-Duhem relation} \quad (1.3.15)$$

One cannot vary T , p and μ independently. The Gibbs-Duhem relation gives the variation of one in terms of the variation of the other two. If T is varied by dT , and p is varied by dp , then we cannot vary μ independent but $d\mu$ is determined by the Gibbs-Duhem relation.

For the above derivation of the Gibbs-Duhem relation we utilized the energy formulation, where $E(S, V, N)$ if the fundamental thermodynamic potential. We can also derive a Gibbs-Duhem relation in the entropy formulation, where $S(E, V, N)$ is the fundamental thermodynamic potential.

From the Euler relation of Eq. (1.3.11) we can rearrange terms to write,

$$S = \frac{1}{T}E + \frac{p}{T}V - \frac{\mu}{T}N \quad (1.3.16)$$

Then,

$$dS = E d\left(\frac{1}{T}\right) + \frac{1}{T}dE + V d\left(\frac{p}{T}\right) + \frac{p}{T}dV - N d\left(\frac{\mu}{T}\right) - \frac{\mu}{T}dN \quad (1.3.17)$$

But from the definitions

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}, \quad \left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{p}{T}, \quad \left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{\mu}{T} \quad (1.3.18)$$

we can write

$$dS = \left(\frac{\partial S}{\partial E}\right)_{V,N} dE + \left(\frac{\partial S}{\partial V}\right)_{E,N} dV + \left(\frac{\partial S}{\partial N}\right)_{E,V} dN = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN \quad (1.3.19)$$

Subtracting Eq. (1.3.19) from (1.3.17) we then get,

$$E d\left(\frac{1}{T}\right) + V d\left(\frac{p}{T}\right) - N d\left(\frac{\mu}{T}\right) = 0 \quad \text{or, dividing by } N, \quad \boxed{d\left(\frac{\mu}{T}\right) = u d\left(\frac{1}{T}\right) + v d\left(\frac{p}{T}\right)} \quad (1.3.20)$$

Summary

The fundamental thermodynamic function, which determines all thermodynamic behavior, is the *entropy*,

$$S(E, V, N) \quad \text{as function of the extensive variables } E, V, N$$

We can invert S to get an equivalent formulation in which the internal energy is the fundamental thermodynamic function,

$$E(S, V, N) \quad \text{as a function of the extensive variables } S, V, N$$

The partial derivatives of E give the *equations of state*,

$$\left(\frac{\partial E}{\partial S}\right)_{V,N} = T(S, V, N), \quad -\left(\frac{\partial E}{\partial V}\right)_{E,N} = p(S, V, N), \quad \left(\frac{\partial E}{\partial N}\right)_{E,V} = \mu(S, V, N), \quad (1.3.21)$$

If one knows the three equations of state, then one can use them to construct the fundamental thermodynamic function using Euler's relation,

$$E = TS - pV + \mu N$$

If one knows any two of the three equations of state, one can find the third by using the Gibbs-Duhem relation,

$$Nd\mu = -SdT + Vdp \quad (1.3.22)$$

Example: The ideal monatomic gas

From experiment we know the following,

$$pV = Nk_B T \quad \Rightarrow \quad \frac{p}{T} = \frac{N}{V}k_B = \frac{k_B}{v} \quad (1.3.23)$$

$$E = \frac{3}{2}Nk_B T \quad \Rightarrow \quad \frac{1}{T} = \frac{3}{2}k_B \frac{N}{E} = \frac{3}{2} \frac{k_B}{u} \quad (1.3.24)$$

where k_B is Boltzmann's constant. The above (p/T) and $(1/T)$ are two of the three equations of state in the entropy formulation. If we can find the third equation of state, (μ/T) , then we will have the entropy S via the Euler relation in the entropy formulation,

$$S = \frac{1}{T}E + \frac{p}{T}V - \frac{\mu}{T}N \quad (1.3.25)$$

We can get (μ/T) from the Gibbs-Duhem relation in the entropy formulation,

$$d\left(\frac{\mu}{T}\right) = u d\left(\frac{1}{T}\right) + v d\left(\frac{p}{T}\right) = u d\left(\frac{3}{2} \frac{k_B}{u}\right) + v d\left(\frac{k_B}{v}\right) = -\frac{3}{2} \frac{k_B}{u} du - \frac{k_B}{v} dv \quad (1.3.26)$$

We can then integrate to get,

$$\left(\frac{\mu}{T}\right) - \left(\frac{\mu}{T}\right)_0 = -\frac{3}{2}k_B \ln\left(\frac{u}{u_0}\right) - k_B \ln\left(\frac{v}{v_0}\right) \quad (1.3.27)$$

where u_0 and v_0 are some reference state, and $(\mu/T)_0$ is an unknown constant of integration.

Having found μ/T , we can return to the Euler relation, $S = \frac{1}{T}E + \frac{p}{T}V - \frac{\mu}{T}N$.

Using $E = \frac{3}{2}Nk_B T \Rightarrow \frac{E}{T} = \frac{3}{2}Nk_B$ and $pV = Nk_B T \Rightarrow \frac{pV}{T} = Nk_B$, and the result of Eq. (1.3.27) for μ/T , we get,

$$S = \frac{E}{T} + \frac{pV}{T} - \frac{\mu}{T}N = \frac{3}{2}Nk_B + Nk_B + \frac{3}{2}Nk_B \ln\left(\frac{u}{u_0}\right) + Nk_B \ln\left(\frac{v}{v_0}\right) - \left(\frac{\mu}{T}\right)_0 N \quad (1.3.28)$$

$$S = \frac{5}{2}Nk_B - \left(\frac{\mu}{T}\right)_0 N + Nk_B \ln\left[\left(\frac{u}{u_0}\right)^{3/2} \left(\frac{v}{v_0}\right)\right] \quad (1.3.29)$$

Now use $u = E/N$, $v = V/N$, $u_0 = E_0/N_0$, and $v_0 = V_0/N_0$, and one finally gets,

$$S(E, V, N) = \frac{N}{N_0} S_0 + Nk_B \ln\left[\left(\frac{E}{E_0}\right)^{3/2} \left(\frac{V}{V_0}\right) \left(\frac{N}{N_0}\right)^{-5/2}\right] \quad (1.3.30)$$

where $S_0 = \frac{5}{2}N_0k_B - \left(\frac{\mu}{T}\right)_0 N_0$ is a constant.

So from experimental knowledge of two of the three equations of state $(1/T)$ and (p/T) as functions of E , N , and V , we have derived the entropy $S(E, V, N)$ of the ideal gas. All behaviors of the ideal gas can now be deduced from our knowledge of S .

It is always good to see the same thing different ways! So, as an alternative approach, we could derive $s = S/N$ as follows.

From the Euler relation,

$$E = TS - pV + \mu N \quad \Rightarrow \quad S = \frac{E}{T} + \frac{p}{T}V - \frac{\mu}{T}N \quad \Rightarrow \quad s = \frac{u}{T} + \frac{p}{T}v - \frac{\mu}{T} \quad (1.3.31)$$

where as before, $u = E/N$ and $v = V/N$.

We then have,

$$ds = \frac{1}{T}du + \frac{p}{T}dv + u d\left(\frac{1}{T}\right) + v d\left(\frac{p}{T}\right) - d\left(\frac{\mu}{T}\right) \quad (1.3.32)$$

But the last three terms cancel due to the Gibbs-Duhem relation in the entropy formulation, Eq. (1.3.20). So we have,

$$ds = \frac{1}{T} du + \frac{p}{T} dv \quad (1.3.33)$$

Substitute in the experimental equations of state for $(1/T) = (3/2)(k_B/u)$ and $(p/T) = (k_B/v)$ and we get

$$ds = \frac{3}{2} \frac{k_B}{u} du + \frac{k_B}{v} dv \quad (1.3.34)$$

Now integrate to get,

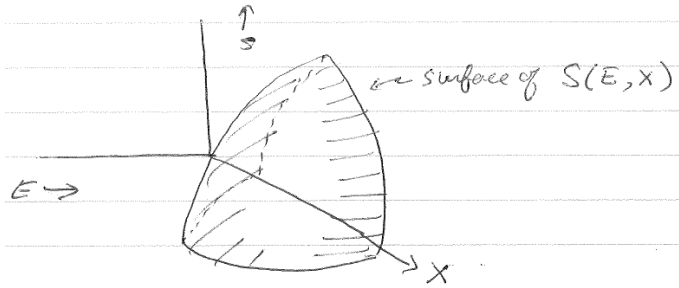
$$s - s_0 = \frac{3}{2} k_B \ln \left(\frac{u}{u_0} \right) + k_B \ln \left(\frac{v}{v_0} \right) \quad \Rightarrow \quad s = s_0 + k_B \ln \left[\left(\frac{u}{u_0} \right)^{3/2} \left(\frac{v}{v_0} \right) \right] \quad (1.3.35)$$

Substitute in $S = Ns$, $E = Nu$, $V = Nv$, $S_0 = N_0 s_0$, $E_0 = N_0 u_0$, and $V_0 = N_0 v_0$ and we recover the same result for $S(E, V, N)$ as we found before.

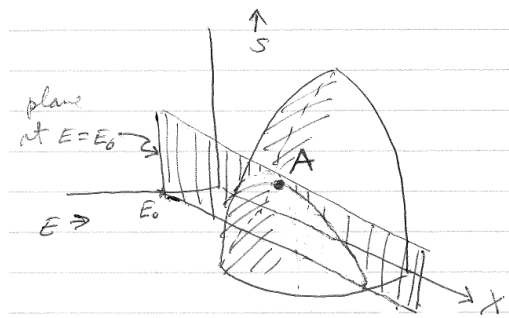
Energy Minimum Principle

Postulate II stated that when constraints are removed, the equilibrium state will be the one that maximizes the entropy $S(E, V, N)$.

We saw that the entropy is a concave function of its variables. Let us denote the macroscopic variables as E and X , where X stands for all other variables, but in order to draw pictures, we will assume X is a scalar quantity. The concave surface $S(E, X)$ is sketched below.



Consider the situation where the total E is held fixed at the value E_0 . Then if X is an *unconstrained* degree of freedom, it will take in equilibrium that value X_0 that maximizes S for the given fixed E_0 . This is determined by the intersection of the surface $S(E, X)$ with the plane at fixed $E = E_0$, as in the sketch below (see Callen Fig. 5.1).

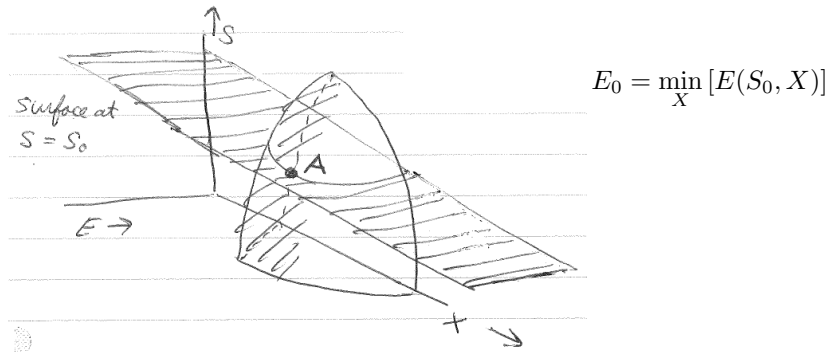


X_0 is given by the point A in the sketch, that maximizes S along this curve of intersection. The entropy at point A is given by,

$$S_0 = \max_X [S(E_0, X)]$$

Suppose now an alternative situation in which the total entropy S is held fixed at the value S_0 found in the previous sketch. Then if X is an unconstrained degree of freedom, we see that the equilibrium state at S_0 and E_0 will

correspond to *minimizing* the energy with respect to X , along the curve of intersection between the surface $S(E, X)$ and the plane of constant $S = S_0$, as in the sketch below (see Callen Fig. 5.2).



We thus have two contrasting formulations:

Entropy formulation: the fundamental thermodynamic function is $S(E, X_1, X_2, \dots)$. If a constraint on some X_i is removed, then when the system reaches equilibrium X_i will take the value that *maximizes* S at the fixed total energy E and fixed $X_j, j \neq i$. In equilibrium, $d^2S < 0$, S is concave.

Energy formulation: the fundamental thermodynamic function is $E(S, X_1, X_2, \dots)$. If a constraint on some X_i is removed, then when the system reaches equilibrium X_i will take the value that *minimizes* E at the fixed total entropy S and fixed $X_j, j \neq i$. In equilibrium $d^2E > 0$, E is convex.

Note, the goal in the above discussion is to try and characterize the *same* equilibrium point A , given by S_0 and E_0 , within the two different formulations, $S(E, X)$ and $E(S, X)$.

Within the entropy formulation $S(E, X)$, A is characterized as the point where $E = E_0$ and $(\partial S / \partial X)_E = 0$, i.e. A is an extremum of the curve $S(E_0, X)$ as a function of X ; and also $(\partial^2 S / \partial X^2)_E < 0$, i.e. the extremum at A is a *maximum* of the entropy.

Within the energy formulation $E(S, X)$, A is characterized as the point where $S = S_0$ and $(\partial E / \partial X)_S = 0$, i.e. A is an extremum of the curve $E(S_0, X)$ as a function of X ; and also $(\partial^2 E / \partial X^2)_S > 0$, i.e. the extremum at A is a *minimum* of the energy.

The above is a graphic way to show how the Energy Minimum Principle follows as a consequence of the Entropy Maximum Principle. We can also show it algebraically, as follows below.

From the Entropy Maximum Principle we have for the point A on the curve $S(E_0, X)$,

$$\left(\frac{\partial S}{\partial X} \right)_E = 0 \quad \text{and} \quad \left(\frac{\partial^2 S}{\partial X^2} \right)_E < 0 \quad (1.3.36)$$

We now wish to see what this implies for the behavior of $E(S_0, X)$ at point A . For convenience, let us define χ as the conjugate variable to X ,

$$\chi \equiv \left(\frac{\partial E}{\partial X} \right)_S \quad (1.3.37)$$

From a general result for partial derivatives given in Eq. (1.8.16), we can write,

$$\left(\frac{\partial E}{\partial X} \right)_S \left(\frac{\partial X}{\partial S} \right)_E \left(\frac{\partial S}{\partial E} \right)_X = -1 \quad (1.3.38)$$

from which we have,

$$\chi = \left(\frac{\partial E}{\partial X} \right)_S = \frac{-1}{\left(\frac{\partial X}{\partial S} \right)_E \left(\frac{\partial S}{\partial E} \right)_X} = - \frac{\left(\frac{\partial S}{\partial X} \right)_E}{\left(\frac{\partial S}{\partial E} \right)_X} \quad (1.3.39)$$

where last step comes from the general result for partial derivatives given in Eq. (1.8.20). Then, since $\left(\frac{\partial S}{\partial E}\right)_X = \frac{1}{T}$, we have,

$$\chi = -T \left(\frac{\partial E}{\partial X}\right)_E \quad \text{and since from Eq. (1.3.36)} \quad \left(\frac{\partial S}{\partial X}\right)_E = 0 \quad \text{we conclude} \quad \chi = \left(\frac{\partial E}{\partial X}\right)_S = 0 \quad \text{at point A.} \quad (1.3.40)$$

So the point A is an extremum of the curve $E(S_0, X)$. Now we want to show it is a minimum. We want to know the sign of,

$$\left(\frac{\partial^2 E}{\partial X^2}\right)_S = \left(\frac{\partial \chi}{\partial X}\right)_S \quad (1.3.41)$$

Since $\chi = \left(\frac{\partial E}{\partial X}\right)_S$, and E is $E(S, X)$, we can regard χ as a function of S and X , i.e. $\chi(S, X)$. But we also have entropy as a function of E and X , i.e. $S(E, X)$. So we can then write χ as $\chi(S(E, X), X)$, and regard χ as a function of E and X . We then have by the chain rule,

$$\left(\frac{\partial \chi}{\partial X}\right)_S = \left(\frac{\partial \chi}{\partial E}\right)_X \left(\frac{\partial E}{\partial X}\right)_S + \left(\frac{\partial \chi}{\partial X}\right)_E = \left(\frac{\partial \chi}{\partial E}\right)_X \chi + \left(\frac{\partial \chi}{\partial X}\right)_E = \left(\frac{\partial \chi}{\partial X}\right)_E \quad \text{since } \chi = 0 \text{ at } A. \quad (1.3.42)$$

Now we can write, using Eq. (1.3.39), we have,

$$\left(\frac{\partial \chi}{\partial X}\right)_E = \frac{\partial}{\partial X} \left(- \frac{\left(\frac{\partial S}{\partial X}\right)_E}{\left(\frac{\partial S}{\partial E}\right)_X} \right) = - \frac{\left(\frac{\partial^2 S}{\partial X^2}\right)_E}{\left(\frac{\partial S}{\partial E}\right)_X} + \left(\frac{\partial S}{\partial X}\right)_E \frac{\left(\frac{\partial^2 S}{\partial X \partial E}\right)}{\left(\frac{\partial S}{\partial E}\right)_X^2} \quad (1.3.43)$$

But, as we used before, at point A we have from Eq. (1.3.36) that $\left(\frac{\partial S}{\partial X}\right)_E = 0$. Using also that $\left(\frac{\partial S}{\partial E}\right)_X = \frac{1}{T}$, we then have from Eqs. (1.3.41), (1.3.42), and (1.3.43),

$$\left(\frac{\partial^2 E}{\partial X^2}\right)_S = \left(\frac{\partial \chi}{\partial X}\right)_S = \left(\frac{\partial \chi}{\partial X}\right)_E = -T \left(\frac{\partial^2 S}{\partial X^2}\right)_E > 0 \quad (1.3.44)$$

where the last step follows from Eq. (1.3.36), that $\left(\frac{\partial^2 S}{\partial X^2}\right)_E < 0$.

So we conclude that $\left(\frac{\partial^2 E}{\partial X^2}\right)_S > 0$, and thus $E(S_0, X)$ is a minimum at the extremum point A .

This completes the algebraic proof of the Energy Minimum Principle.

We can also demonstrate the correctness of the Energy Minimum Principle by a physical argument. To quote from Callen, "Assume, then, that the system is in equilibrium but that the energy does *not* have its smallest possible value consistent with the given entropy. We could then withdraw energy from the system (in the form of work) maintaining the entropy constant, and we could thereafter return this energy to the system in the form of heat. The entropy of the system would increase ($dQ = TdS$), and the system would be restored to its original energy but with an increased entropy. This is inconsistent with the principle that the initial equilibrium state is the state of maximum entropy! Hence we are forced to conclude that the original equilibrium state must have had minimum energy consistent with the prescribed entropy."