

Absolute Zero and the Third Law of Thermodynamics

ELEGANT CONNECTIONS IN PHYSICS

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1. THE THIRD LAW OF THERMODYNAMICS

A system's internal energy U and entropy S are introduced in terms of their *changes*. The First Law of Thermodynamics extends the work-energy theorem to include energy exchanged as heat besides mechanical work. The Principle does so in terms of the change in U ,

$$dU = dQ - PdV \quad (1)$$

where dQ denotes the energy put *into* the system as heat, and PdV the mechanical work done *by* the system. It took the Special Theory of relativity with $E = mc^2$ to fix the zero point for the internal energy of a system of particles.

The Second Law of Thermodynamics expresses the non-conservation of entropy S , also introduced in terms of its change:

$$S_B - S_A = \int_A^B dQ/T \quad (2)$$

where the integral may be evaluated along *any* path of successive equilibrium states that carry the system from state A to state B . If we let B denote a generic state of temperature T , and A denote some reference state, for example the state of the system at absolute zero, then

$$S(T) = S(0) + \int_0^T dQ/T \quad (3)$$

which leaves the constant $S(0)$ undetermined.

This ambiguity becomes a problem when we need to know the entropy *of* a state, not merely the entropy change *between* two states. For example, the thermodynamic potentials (introduced below) such as the Helmholtz energy F and Gibbs energy G , lead to relations for *their* changes that require the value of S *itself*, in particular,

$$dF = -SdT - PdV \quad (4)$$

and

$$dG = -SdT + VdP. \quad (5)$$

We therefore find it necessary to articulate a principle that allows the value of S to be uniquely determined for any system. A principle that fixes the integration constant in Eq. (3) is called

the "Third Law of Thermodynamics." Its simplest form was enunciated by Max Planck in 1911, who expanded on an earlier version of the principle proposed by Nernst in 1906. Nernst postulated that the entropy of any *two* states of a given system approaches the *same* value as the temperature approaches absolute zero. If states A and B denote two states of a substance, then

$$S_B - S_A \rightarrow 0 \text{ as } T \rightarrow 0 \quad (\text{Nernst}) \quad (6)$$

Let us write Eq. (3) in a form that will be useful to our purposes. When no phase changes are involved, energy transferred as heat can be represented with a heat capacity C via $dQ = CdT$, so that Eq. (3) becomes

$$S(T) = S(0) + \int_0^T C(T') dT'/T' \quad (7)$$

where a temperature dependence for C has been indicated.

As an example of a practical consequence of the Nernst postulate, and an illustration of the kinds of system to which it applies, consider system that consists of, say, N atoms of iron and N atoms of sulphur, the two species separated by a membrane. Call this "System Fe+S." Iron and sulphur may also exist together in the form of N units of FeS; call this "System FeS." Even though systems Fe+S and FeS are different states, they contain the same atoms, so according to the Nernst postulate will have the same entropy at absolute zero. Therefore, at temperature T , System Fe+S has entropy

$$S_{\text{Fe+S}}(T) = S_{\text{Fe+S}}(0) + \int_0^T C_{\text{Fe+S}}(T') dT'/T' \quad (8)$$

and for System FeS,

$$S_{\text{FeS}}(T) = S_{\text{FeS}}(0) + \int_0^T C_{\text{FeS}}(T') dT'/T' \quad (9)$$

The entropy difference between systems Fe+S and FeS is controlled by the difference in their heat capacities,

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$$S_{\text{Fe+S}}(T) - S_{\text{FeS}}(T) = \int_0^T [C_{\text{Fe+S}} - C_{\text{FeS}}] dT / T \quad (10)$$

where the Nernst postulate allows us to cancel the $S(0)$ terms:

$$S_{\text{Fe+S}}(0) = S_{\text{FeS}}(0). \quad (11)$$

Although Nernst stated this postulate for liquids and solids, it is assumed to hold for all systems that have equilibrium states in the vicinity of absolute zero (even for glasses, which are inherently disordered).

In 1911 Planck extended the Nernst statement of the Third Law to postulate that any equilibrium state has zero entropy as the temperature approaches absolute zero:

$$S \rightarrow 0 \text{ as } T \rightarrow 0 \quad (\text{Planck}). \quad (12)$$

Therefore, $S(0) = 0$ and a system's entropy at any other temperature $T > 0$ can be uniquely determined from the integral of Eq. (3).

We will demonstrate the connection between the Nernst and Planck statements, and see how the Third Law can be reconciled with statistical mechanics in Section 4. In the meantime we accept the Third Law and in Section 3 examine some of its consequences.

Before we can develop those consequences we must back up to recall the thermodynamic potentials that are necessary for connecting the Nernst-Planck postulate to the rest of thermodynamics. These potentials are all developed from U via the Legendre transformation. Section 2 therefore takes us on a digression into the generic Legendre transformation, which is subsequently applied to the thermodynamic potentials. This leads us to the so-called Maxwell relations between state variables, that will be useful to our program.

2. LEGENDRE TRANSFORMATIONS AND THE MAXWELL RELATIONS

Consider some function W of two independent variables x and y , $W = W(x,y)$. It's differential is

$$dW = (\partial W / \partial x)_y dx + (\partial W / \partial y)_x dy \quad (13a)$$

Let

$$P = (\partial W / \partial x)_y \quad (13b)$$

and

$$Q = (\partial W / \partial y)_x \quad (13c)$$

where the subscripts on the partial derivatives remind us which variable is being held fixed. Therefore, Eq. (13) may also be written

$$dW = P dx + Q dy \quad (13d)$$

P is "canonically conjugate" to x , and Q is "canonically conjugate" to y . If x and y are called "space coordinates," then P

and Q might be called their corresponding "momenta." If we picture $W(x,y)$ as a surface, like a roof over the xy plane, then P and Q measure the slope of this surface's local tangent line, parallel to the x axis and the y axis respectively, as in Fig. 1. It should be well noted that the "coordinates" and their "momenta" come coupled in pairs, like some kind of mathematically married couple. In our example there are two of these couples,

(x,P) and (y,Q)

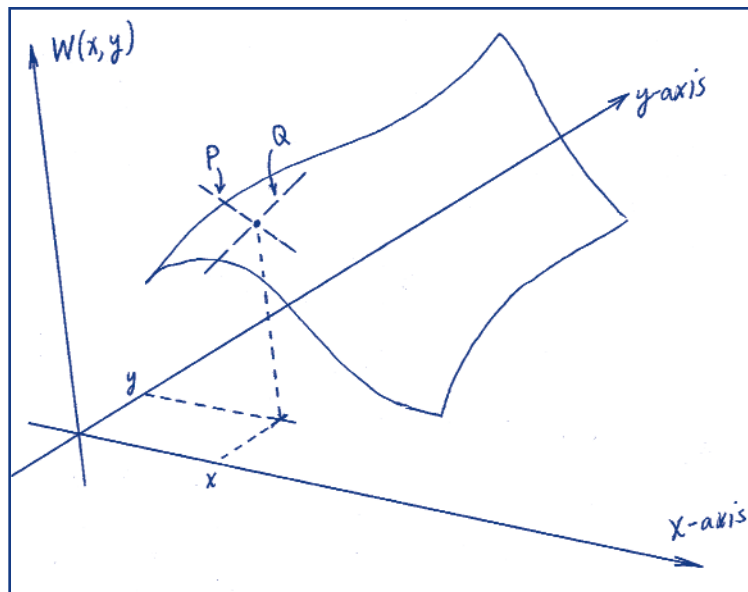


Fig. 1. The xy plane, the surface $W(x,y)$, and the conjugate slopes P (conjugate to x) and Q (conjugate to y).

To build some intuition that will inspire us to rediscover for ourselves the significance of Legendre transformations, let's temporarily suppress the x dimension (with its P) by holding x fixed, and consider W as a function of only y . Now $W = W(y)$ describes a curve above the y -axis. At some value of y , the slope of the local tangent line has some value Q . If we extend this tangent line to cross the W -axis where the intercept is N , as in Fig. 2, the equation of this tangent line is [1]

$$Q = (W - N) / (y - 0) \quad (14a)$$

which we can transpose to the standard form of a Legendre transformation,

$$N = W - Qy. \quad (14b)$$

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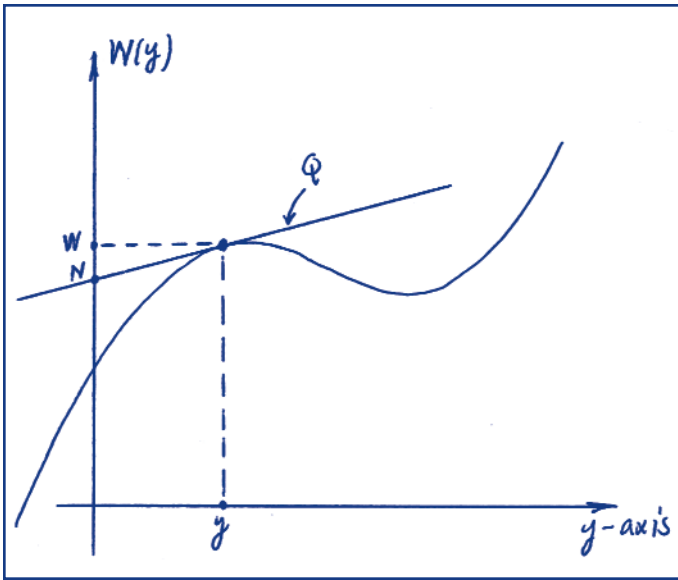


Fig. 2. The curve $W(y)$ and one its tangent lines, described by the equation $W = Qy + N$.

The differential of N yields

$$dN = dW - Qdy - ydQ \quad (15a)$$

and using Eqs. (13d) for dW , and restoring Pdx , the Qdy cancels, leaving

$$dN = Pdx - ydQ \quad (15b)$$

If we say that $N = N(x, Q)$ then we may also write its differential as

$$dN = (\partial N / \partial x)_Q dx + (\partial N / \partial Q)_x dQ . \quad (15c)$$

Even though N is a function of x and Q , P and y can still be extracted from it, for comparing Eq. (15b) to (15c) requires

$$P = (\partial N / \partial x)_Q \quad (15d)$$

and

$$y = -(\partial N / \partial Q)_x . \quad (15e)$$

We now have two ways of describing the information carried in the W -surface above the xy plane: we can use either $W(x, y)$ itself, or we can trade one of the coordinates for its conjugate slope, as we just did for $N(x, Q)$, where we traded y for its conjugate slope, the “momentum” Q . Such trades can be done in a variety of ways that preserves the “ x -ness” and “ y -ness” of the dependent function, where we have a function of *one* element from *each* pair of a coordinate and its conjugate slope. Our options will therefore be functions of:

$$(x, y), (x, Q), (P, y), \text{ and } (P, Q) .$$

The functions of these variables considered so far are $W(x, y)$ and $N(x, Q) = W - Qy$; functions of the other two pairings can be derived from W by further Legendre transformations, where the old function is turned into a new one by subtracting the product of a conjugate pair. Thus, we can form a function $M = M(P, Q)$ by subtracting from N the conjugate pair Px ,

$$\begin{aligned} M &= N - Px \\ &= W - Qy - Px \end{aligned} \quad (16a)$$

whose differential, when compared to

$$dM = (\partial M / \partial P)_Q dP + (\partial M / \partial Q)_P dQ , \quad (16b)$$

gives

$$y = -(\partial M / \partial Q)_P \quad (16c)$$

and

$$x = -(\partial M / \partial P)_Q . \quad (16d)$$

Similarly, we can form $R = R(P, y)$ with

$$R = W - xP . \quad (17a)$$

so that

$$Q = (\partial R / \partial y)_P \quad (17b)$$

and

$$x = -(\partial R / \partial P)_y . \quad (17c)$$

A function of just (x, P) or only (y, Q) will not describe the xy space in its entirety; therefore, no function of (x, P) and (y, Q) can be derived from $W(x, y)$ by Legendre transformations. To see this, let $Y = Y(x, P)$ and introduce some as-yet-unknown parameters A and B , according to

$$Y = W - AB . \quad (18a)$$

The differential gives

$$dY = Pdx + Qdy - AdB - BdA . \quad (18b)$$

Suppose we want Qdy to cancel. We can make that happen by setting $A = Q$ and $dB = dy$. But this also means $BdA = ydQ$, leaving

$$dY = Pdx - ydQ \quad (18c)$$

which makes Y a function of x and Q , contrary to our assumption that Y was to be a function of x and P .

In summary, Legendre transformations allows us the luxury of describing a function of x -ness and y -ness in a variety of ways, by selecting a combination of coordinates and slopes that are the most convenient for whatever data we have at hand.

APPLICATIONS TO THERMODYNAMICS

Now let's apply the Legendre transformations to the internal energy U , and generate some related energy functions, the

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“thermodynamic potentials.” These are the enthalpy H , Helmholtz energy F , and Gibbs energy G . From the combined First and Second Laws of Thermodynamics, we have $U = U(S, V)$ because

$$dU = TdS - PdV. \quad (19a)$$

so that

$$T = (\partial U / \partial S)_V \quad (19b)$$

and

$$P = -(\partial U / \partial V)_S. \quad (19c)$$

Let us now turn to the thermodynamic potentials derivable from U by Legendre transformations. We start with the enthalpy H ,

$$H = H(S, P) = U + PV \quad (20a)$$

Examining the differentials and using dU gives

$$dH = TdS + VdP \quad (20b)$$

so that

$$T = (\partial H / \partial S)_P \quad (20c)$$

$$V = (\partial H / \partial P)_S. \quad (20d)$$

Next we take up the Helmholtz energy F ,

$$F = F(T, V) = U - TS \quad (21a)$$

from whose differential, with that of dU , yields

$$dF = -SdT - PdV \quad (21b)$$

with

$$P = -(\partial F / \partial V)_T \quad (21c)$$

$$S = -(\partial F / \partial T)_V. \quad (21d)$$

We come finally to the Gibbs energy G ,

$$G = G(T, P) = U - TS - PV \quad (22a)$$

whose differential yields

$$dG = -SdT + VdP \quad (22b)$$

and

$$S = -(\partial G / \partial T)_P \quad (22c)$$

$$V = (\partial G / \partial P)_T. \quad (22d)$$

We can find several useful relations between state variables by pushing on to the second derivatives. If a function of two variables is continuous, then its second derivatives commute; generically,

$$\partial^2 f / \partial x \partial y = \partial^2 f / \partial y \partial x. \quad (23)$$

Accordingly, from the eight expressions above we have

$$\partial^2 U / \partial S \partial V = (\partial T / \partial V)_S = -(\partial P / \partial S)_V \quad (24)$$

$$\partial^2 H / \partial S \partial P = (\partial T / \partial P)_S = (\partial V / \partial S)_P \quad (25)$$

$$\partial^2 F / \partial T \partial V = -(\partial P / \partial T)_V = -(\partial S / \partial V)_T \quad (26)$$

$$\partial^2 G / \partial P \partial T = -(\partial S / \partial P)_T = (\partial V / \partial T)_P. \quad (27)$$

These equations are called the “Maxwell relations.”

3. CONSEQUENCES OF THE THIRD LAW

The Planck statement of the Third Law says that, for any system, $S \rightarrow 0$ as $T \rightarrow 0$. With the help of the Maxwell relations we now derive some important consequences of the Third Law: As $T \rightarrow 0$, we find (1) that the heat capacity of any substance scales with temperature as T^s where $s \geq 1$; (2) the coefficient of thermal expansion of any substance approaches zero; and (3) no system can be cooled to precisely $T = 0$ in a finite number of steps, which means that absolute zero can be approached, at best, only asymptotically.

The first of these statements, that the heat capacity approaches zero *as fast or faster than* T as $T \rightarrow 0$, follows at once: with the Third Law, in the absence of phase changes the entropy of a system at temperature T follows from Eq. (7),

$$S(T) = S(0) + \int_0^T C(T') dT' / T' \quad (28)$$

(typically, C is the heat capacity at constant pressure). As $T \rightarrow 0$, by the Third Law the left-hand side vanishes, so the $1/T$ in the integrand on the right-hand side demands that $C(T) \sim T^s$ where $s \geq 1$.

The coefficient of thermal expansion α is, by definition, the fractional change of the system’s volume with respect to a change in temperature at constant pressure:

$$\alpha \equiv (1/V)(\partial V / \partial T)_P. \quad (29)$$

By virtue of the Maxwell Relation of Eq. (27), α may be written

$$\alpha = -(1/V)(\partial S / \partial P)_T \quad (30)$$

which by the Nernst statement of the Third Law vanishes as $T \rightarrow 0$. Because both αV and the heat capacity C vanish at absolute zero, it requires some care to show that the Third Law implies that their ratio be finite, in particular,

$$\alpha V / C \rightarrow \text{const as } T \rightarrow 0. \quad (31)$$

This result provides a crucial link in demonstrating the impossibility of a system’s temperature actually *reaching* absolute zero in a *finite* number of steps. So let us first demonstrate the claim about $\alpha V / C$. From Eq. (30) we have

$$\alpha V = -(\partial S / \partial P)_V$$

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$$= -(\partial/\partial P) \int_0^T C(T^s) dT^s / T^s \quad (32)$$

Expanding the heat capacity in a Taylor series about $T = 0$, after factoring out its low-temperature behavior $C(T) \sim T^s$, we may write

$$C = T^s (a + bT + \dots) \quad (33)$$

for some a, b, \dots . This step allows us to evaluate the integral term by term, after which we take the derivative with respect to P to find

$$\alpha V = -T^s [a'/s + b' T/(s+1) + \dots] \quad (34)$$

where the primes denote derivatives with respect to pressure. Therefore,

$$\alpha V/C = -[a'/s + b' T/(s+1) + \dots] (a + bT + \dots)^{-1} \quad (35)$$

which gives a constant value as $T \rightarrow 0$, as asserted in Eq. (31). To show that absolute zero can only be approached asymptotically, we now appeal to one of the so-called TdS equations that can be derived from the Second Law of Thermodynamics (see the Appendix),

$$TdS = -\alpha VT dP + C_p dT \quad (36)$$

where C_p denotes the system's isobaric heat capacity. Let us examine the behavior of dT as $T \rightarrow 0$. We have already seen that, in this limit, $C_p \rightarrow aT^s$ where $s \geq 1$, and $\alpha V/C_p \rightarrow \text{const.} \equiv \mu$. So for temperatures approaching absolute zero, the TdS equation says

$$dT = dS/aT^{s-1} + \mu T dP. \quad (37)$$

Now we know that temperature is a state variable, so its change is path-independent. So consider a decrease in temperature by using an adiabatic process for which $dS = 0$. Then our TdS equation collapses to

$$dT = \mu T dP. \quad (38)$$

This innocent-looking equation holds a strong message about the impossible: To achieve any *finite* decrease in temperature, however infinitesimal, the closer T is to absolute zero the greater the pressure change required: in other words, to have a *finite* $|dT|$ requires *infinite* $|dP|$ for $T = 0$. Therefore, a system cannot actually *reach* absolute zero in a finite number of steps!

4. STATISTICAL MECHANICS AND THE EQUIVALENCE OF THE NERNST AND PLANCK STATEMENTS

Thermodynamics tells us *relations* between macroscopic state variables, such as internal energy and temperature, entropy and volume. Internal energy and entropy, and thus the First and Second Laws of Thermodynamics, receive their ultimate inter-

pretation—we find out what internal energy and entropy *are* in terms of atoms—from statistical mechanics. In particular, we learn that the internal energy measures the average energy of the population of atoms, and entropy measures the logarithm of the number of ways the microscopic atoms can be arranged to give the macroscopic state. What is the statistical mechanics foundation of the Third Law? To answer this question—which will also demonstrate in what sense the Nernst and Planck statements are equivalent—we must examine the entropy, as it's described in statistical mechanics, in the limit as $T \rightarrow 0$. From the Helmholtz energy we see that

$$S = (U - F)/T, \quad (39)$$

and from statistical mechanics we recall that when the macroscopic system can be partitioned into N identical microscopic subsystems (“atoms”) in thermal equilibrium at temperature T ,

$$F = -(N/\beta) \ln Z \quad (40)$$

and

$$U = -N \partial \ln Z / \partial \beta \quad (41)$$

where $\beta \equiv 1/kT$ and $k = 1.4 \times 10^{-23}$ J/K denotes Boltzmann's constant. Z stands for the “partition function,” the *Zustandssumme*, or “sum over states,”

$$Z = \sum_n \exp(-\beta E_n) \quad (42)$$

with E_n the energy of a microsystem in its microscopic state n . Therefore Eq. (39) becomes

$$S = Nk [-\beta \partial \ln Z / \partial \beta + 1] \ln Z \quad (43)$$

As the macroscopic system's temperature approaches absolute zero (so that $\beta \rightarrow \infty$), the overwhelming majority of the microscopic atoms will drop down into their state of lowest energy. Let that ground state have energy ϵ , perhaps with a g -fold degeneracy, viz., there are g states in each atom that have the lowest energy ϵ . Then the partition function is dominated by the ground state energy term and Z becomes approximately $Z \approx g e^{-\beta \epsilon}$. When we put this into Eq. (43), we find $S \approx Nk \ln g$. Because all terms on the right-hand side are independent of T , we can go to the limit $T = 0$ and say that

$$S(0) = Nk \ln g. \quad (44)$$

If $g = 1$ (e.g., the quantum ground state is nondegenerate) then $S(0) = 0$, and we have the Planck statement of the Third Law right away. But even if $g \neq 1$ then we have the crucial result, the foundation of the Nernst insight, that the specific entropy, $S(0)/N = k \ln g$, is *independent of any macroscopic state variables*. [2] For a given collection of atoms, such as our iron and sulphur atoms in the earlier example, the specific entropy at absolute zero does not depend on the thermodynamics state variables at all; it depends only on the degeneracy of the atom's ground state,

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and that's a property of the microscopic atom, not of thermodynamics. Therefore the zero for the entropy of a given collection of atoms can be shifted, the $Nk \ln g$ subtracted off. In this sense the Nernst statement is equivalent to the Planck statement, atomic species by atomic species (if not universally so across the board with the *same* shift for *all* atomic species).

5. PHYSICS PRINCIPLES SEEM TO STATE WHAT'S IMPOSSIBLE

The Third Law of Thermodynamics joins a list of fundamental physics principles that tell us what nature *cannot* do. The Third Law implies that a system can only approach absolute zero asymptotically; it cannot actually *reach* absolute zero in a finite number of steps (the temperature to beat these days lies in the nanoKelvin scale, achieved in the last steps by the laser cooling of atoms). Similarly, Special Relativity tells us that material particles may, in principle, approach the speed of light asymptotically but will never actually reach light speed. Quantum theory tells us that the precision to which conjugate variables can be measured simultaneously must exceed the tolerance of the quantum. The Second Law of Thermodynamics observes that the efficiency of an engine can never achieve unity; as a consequence, the entropy of an isolated system cannot decrease.

Such articulations of the impossible stake out the boundaries of reality. While heroic virtue in human affairs may follow from the maxim that "anything is possible if you try hard enough," knowing where limits are in reality is valuable knowledge.

APPENDIX: DERIVATION OF A TdS EQUATION

Start with the combined First and Second Law, Eq. (19), which shows that $U = U(S, V)$. When the system is in thermal equilibrium, equations of state relates the entropy to the temperature and volume, and the volume to the pressure and temperature. This is readily illustrated with the monatomic ideal gas of N atoms, for which

$$S = (3/2)Nk \ln T + Nk \ln V + \text{const.} \quad (45)$$

and

$$V = NkT/P. \quad (46)$$

Presumably we can suppose that, in general, we may write both S and V , and therefore U , in terms of T and P . Therefore Eq. (1) may be expanded in terms of dT and dP : [3]

$$\begin{aligned} (\partial U/\partial P)_T dP + (\partial U/\partial T)_P dT \\ = TdS - P[(\partial V/\partial P)_T dP + (\partial V/\partial T)_P dT]. \end{aligned} \quad (47)$$

Solving for TdS gives

$$\begin{aligned} TdS = [(\partial U/\partial P)_T + P(\partial V/\partial P)_T] dP \\ + [(\partial U/\partial T)_P + P(\partial V/\partial T)_P] dT. \end{aligned} \quad (48)$$

Recall the definition of the coefficient of thermal expansion α , Eq. (29), and note that the definition of isothermal compressibility κ_T is the fractional decrease in volume per change in temperature,

$$\kappa_T \equiv -(1/V)(\partial V/\partial P)_T \quad (49)$$

(α and κ_T are readily measurable in the laboratory). The TdS equation becomes

$$\begin{aligned} dS = (1/T)[(\partial U/\partial P)_T - \kappa_T PV] dP \\ + (1/T)[(\partial U/\partial T)_P + \alpha PV] dT. \end{aligned} \quad (50)$$

which can be denoted temporarily as

$$dS = AdP + BdT \quad (51)$$

where $A = (1/T)[(\partial U/\partial P)_T - \kappa_T PV]$ and $B = (1/T)[(\partial U/\partial T)_P + \alpha PV]$. Because dS is an exact (path-independent) differential, we may write

$$(\partial A/\partial T)_P = (\partial B/\partial P)_T \quad (52)$$

which yields

$$(\partial U/\partial P)_T = -\alpha VT + \kappa_T PV. \quad (53)$$

Placing this in Eq. (50), recall that $H = U + PV$, and that $dH = C_p dT$, and using Eq. (29), one finds

$$TdS = -\alpha VT dP + C_p dT. \quad (54)$$

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 Erwin Schrödinger, *Statistical Thermodynamics*, Cambridge Univ. Press (1967), Ch. III.

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- [1] Ashley Carter's text (see Bibliography) includes a beautiful description of Legendre transformations in terms of slopes.
 [2] This argument is adapted from Schrödinger. For classical systems, such as an ideal gas, the entropy acquires a $\ln V$ term, where V denotes the volume of the gas container. This is analogous to the degeneracy g of a quantum microsystem because the classical gas particle can be anywhere inside the volume V . However, quantum mechanics teaches us that the smallest "pixel" of phase space (momentum and spatial coordinates) is that of the quantum. Therefore the number of "pixels" in phase space is countable.
 [3] See Huang, Section 1.5.

