

bly doing work on an external agent until it has moved to the position that equalizes the pressure on the two sides. During this process energy is withdrawn from the system, but its entropy remains constant (the process is reversible and no heat flows). This is the process suggested by the energy minimum principle. The vital fact we wish to stress, however, is that *independent of whether the equilibrium is brought about by either of these two processes, or by any other process, the final equilibrium state in each case satisfies both extremal conditions.*

Finally, we illustrate the energy minimum principle by using it in place of the entropy maximum principle to solve the problem of thermal equilibrium, as treated in Section 2.4. We consider a closed composite system with an internal wall that is rigid, impermeable, and diathermal. Heat is free to flow between the two subsystems, and we wish to find the equilibrium state. The fundamental equation in the energy representation is

$$U = U^{(1)}(S^{(1)}, V^{(1)}, N_1^{(1)}, \dots) + U^{(2)}(S^{(2)}, V^{(2)}, N_1^{(2)}, \dots) \quad (5.8)$$

All volume and mole number parameters are constant and known. The variables that must be computed are $S^{(1)}$ and $S^{(2)}$. Now, despite the fact that the system is actually closed and that the total energy is fixed, the equilibrium state can be characterized as the state that would minimize the energy *if* energy changes were permitted. The virtual change in total energy associated with virtual heat fluxes in the two systems is

$$dU = T^{(1)} dS^{(1)} + T^{(2)} dS^{(2)} \quad (5.9)$$

The energy minimum condition states that $dU = 0$, subject to the condition of fixed total entropy:

$$S^{(1)} + S^{(2)} = \text{constant} \quad (5.10)$$

whence

$$dU = (T^{(1)} - T^{(2)}) dS^{(1)} = 0 \quad (5.11)$$

and we conclude that

$$T^{(1)} = T^{(2)} \quad (5.12)$$

The energy minimum principle thus provides us with the same condition of thermal equilibrium as we previously found by using the entropy maximum principle.

Equation 5.12 is one equation in $S^{(1)}$ and $S^{(2)}$. The second equation is most conveniently taken as equation 5.8, in which the total energy U is

known and which consequently involves only the two unknown quantities $S^{(1)}$ and $S^{(2)}$. Equations 5.8 and 5.12, in principle, permit a fully explicit solution of the problem.

In a precisely analogous fashion the equilibrium condition for a closed composite system with an internal moveable adiabatic wall is found to be equality of the pressure. This conclusion is straightforward in the energy representation but, as was observed in the last paragraph of Section 2.7, it is relatively delicate in the entropy representation.

PROBLEMS

5.1-1. Formulate a proof that the energy minimum principle implies the entropy maximum principle—the “inverse argument” referred to after equation 5.7. That is, show that if the entropy were not maximum at constant energy then the energy could not be minimum at constant entropy.

Hint: First show that the permissible increase in entropy in the system can be exploited to extract heat from a reversible heat source (initially at the same temperature as the system) and to deposit it in a reversible work source. The reversible heat source is thereby cooled. Continue the argument.

5.1-2. An adiabatic, impermeable and fixed piston separates a cylinder into two chambers of volumes $V_0/4$ and $3V_0/4$. Each chamber contains 1 mole of a monatomic ideal gas. The temperatures are T_s and T_l , the subscripts s and l referring to the small and large chambers, respectively.

a) The piston is made thermally conductive and moveable, and the system relaxes to a new equilibrium state, *maximizing its entropy while conserving its total energy*. Find this new equilibrium state.

b) Consider a small virtual change in the energy of the system, maintaining the entropy at the value attained in part (a). To accomplish this physically we can reimpose the adiabatic constraint and quasistatically displace the piston by imposition of an external force. Show that the external source of this force must do work *on* the system in order to displace the piston in *either* direction. Hence *the state attained in part (a) is a state of minimum energy at constant entropy*.

c) Reconsider the initial state and specify how equilibrium can be established by decreasing the energy at constant entropy. Find this equilibrium state.

d) Describe an operation that demonstrates that the equilibrium state attained in (c) is a state of maximum entropy at constant energy.

5-2 LEGENDRE TRANSFORMATIONS

In both the energy and entropy representations the extensive parameters play the roles of mathematically independent variables, whereas the intensive parameters arise as derived concepts. This situation is in direct

contrast to the practical situation dictated by convenience in the laboratory. The experimenter frequently finds that the intensive parameters are the more easily measured and controlled and therefore is likely to think of the intensive parameters as operationally independent variables and of the extensive parameters as operationally derived quantities. The extreme instance of this situation is provided by the conjugate variables entropy and temperature. No practical instruments exist for the measurement and control of entropy, whereas thermometers and thermostats, for the measurement and control of the temperature, are common laboratory equipment. The question therefore arises as to the possibility of recasting the mathematical formalism in such a way that intensive parameters will replace extensive parameters as mathematically independent variables. We shall see that such a reformulation is, in fact, possible and that it leads to various other thermodynamic representations.

It is, perhaps, superfluous at this point to stress again that thermodynamics is logically complete and self-contained within either the entropy or the energy representations and that the introduction of the transformed representations is purely a matter of convenience. This is, admittedly, a convenience without which thermodynamics would be almost unusably awkward, but in principle it is still only a luxury rather than a logical necessity.

The purely formal aspects of the problem are as follows. We are given an equation (the fundamental relation) of the form

$$Y = Y(X_0, X_1, \dots, X_n) \tag{5.13}$$

and it is desired to find a method whereby the derivatives

$$P_k \equiv \frac{\partial Y}{\partial X_k} \tag{5.14}$$

can be considered as independent variables without sacrificing any of the informational content of the given fundamental relation (5.6). This formal problem has its counterpart in geometry and in several other fields of physics. The solution of the problem, employing the mathematical technique of Legendre transformations, is most intuitive when given its geometrical interpretation; and it is this geometrical interpretation that we shall develop in this Section.

For simplicity, we first consider the mathematical case in which the fundamental relation is a function of only a single independent variable X .

$$Y = Y(X) \tag{5.15}$$

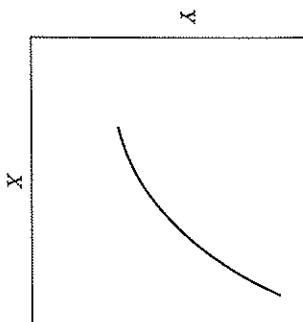


FIGURE 5.3

space (Fig. 5.3) with cartesian coordinates X and Y , and the derivative

$$P \equiv \frac{\partial Y}{\partial X} \tag{5.16}$$

is the slope of this curve. Now, if we desire to consider P as an independent variable in place of X , our first impulse might be simply to eliminate X between equations 5.15 and 5.16, thereby obtaining Y as a function of P

$$Y = Y(P) \tag{5.17}$$

A moment's reflection indicates, however, that we would sacrifice some of the mathematical content of the given fundamental relation (5.15) for, from the geometrical point of view, it is clear that knowledge of Y as a function of the slope dY/dX would not permit us to reconstruct the curve $Y = Y(X)$. In fact, each of the displaced curves shown in Fig. 5.4 corresponds equally well to the relation $Y = Y(P)$. From the analytical point of view the relation $Y = Y(P)$ is a first-order differential equation, and its integration gives $Y = Y(X)$ only to within an undetermined integration constant. Therefore we see that acceptance of $Y = Y(P)$ as a basic equation in place of $Y = Y(X)$ would involve the sacrifice of some information originally contained in the fundamental relation. Despite the

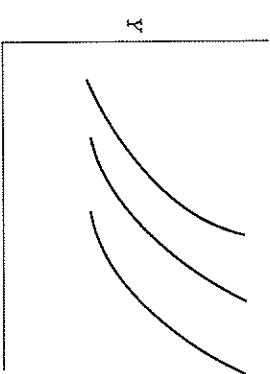


FIGURE 5.4

Geometrically the fundamental relation is represented by a curve in a

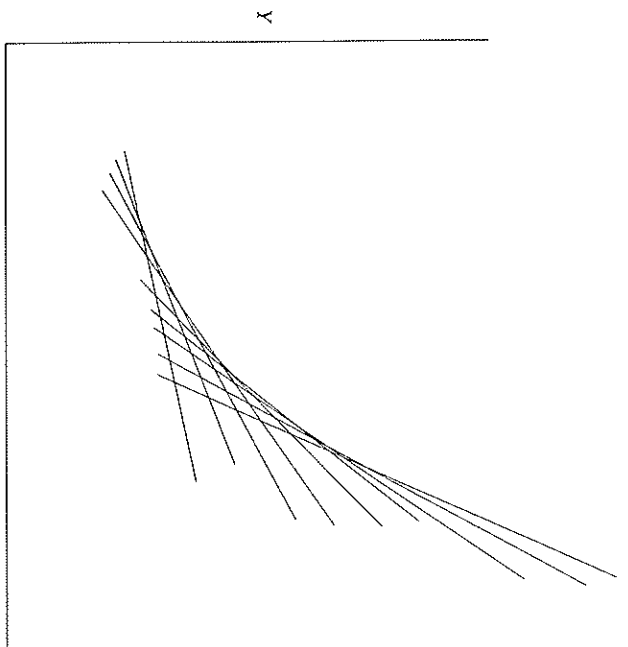


FIGURE 5.5

desirability of having P as a mathematically independent variable, this sacrifice of the informational content of the formalism would be completely unacceptable.

The practicable solution to the problem is supplied by the duality between conventional *point geometry* and the Pluecker *line geometry*. The essential concept in line geometry is that a given curve can be represented equally well either (a) as the envelope of a family of tangent lines (Fig. 5.5), or (b) as the locus of points satisfying the relation $Y = Y(X)$. Any equation that enables us to construct the family of tangent lines therefore determines the curve equally as well as the relation $Y = Y(X)$.

Just as every point in the plane is described by the two numbers X and Y , so every straight line in the plane can be described by the two numbers P and ψ , where P is the slope of the line and ψ is its intercept along the Y -axis. Then just as a relation $Y = Y(X)$ selects a subset of all possible points (X, Y) , a relation $\psi = \psi(P)$ selects a subset of all possible lines (P, ψ) . A knowledge of the intercepts ψ of the tangent lines as a function of the slopes P enables us to construct the family of tangent lines and thence the curve of which they are the envelope. Thus the relation

$$\psi = \psi(P) \tag{5.18}$$

is completely equivalent to the fundamental relation $Y = Y(X)$. In this

relation the independent variable is P , so that equation 5.18 provides a complete and satisfactory solution to the problem. As the relation $\psi = \psi(P)$ is mathematically equivalent to the relation $Y = Y(X)$, it can also be considered a fundamental relation; $Y = Y(X)$ is a fundamental relation in the “ Y -representation”; whereas $\psi = \psi(P)$ is a fundamental relation in the “ ψ -representation.”

The reader is urged at this point actually to draw a reasonable number of straight lines, of various slopes P and of various Y -intercepts $\psi = -P^2$. The relation $\psi = -P^2$ thereby will be seen to characterize a parabola (which is more conventionally described as $Y = \frac{1}{4}X^2$). In ψ -representation the fundamental equation of the parabola is $\psi = -P^2$, whereas in Y -representation the fundamental equation of this same parabola is $Y = \frac{1}{4}X^2$.

The question now arises as to how we can compute the relation $\psi = \psi(P)$ if we are given the relation $Y = Y(X)$. The appropriate mathematical operation is known as a Legendre transformation. We consider a tangent line that goes through the point (X, Y) and has a slope P . If the intercept is ψ , we have (see Fig. 5.6)

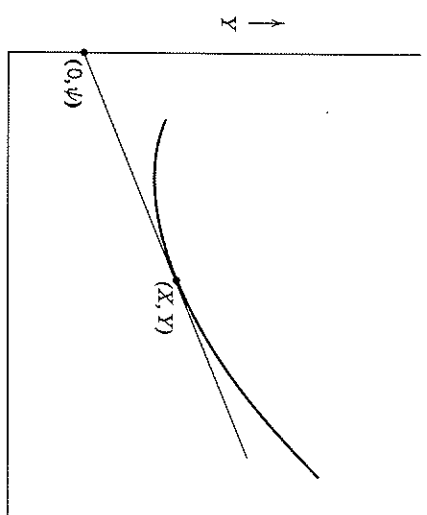
$$P = \frac{Y - \psi}{X - 0} \tag{5.19}$$

or

$$\psi = Y - PX \tag{5.20}$$

Let us now suppose that we are given the equation

$$Y = Y(X) \tag{5.21}$$



and by differentiation we find

$$P = P(X) \tag{5.22}$$

Then by elimination¹ of X and Y among equations 5.20, 5.21, and 5.22 we obtain the desired relation between ψ and P . The basic identity of the Legendre transformation is equation 5.20, and this equation can be taken as the analytic definition of the function ψ . The function ψ is referred to as a *Legendre transform* of Y .

The inverse problem is that of recovering the relation $Y = Y(X)$ if the relation $\psi = \psi(P)$ is given. We shall see here that the relationship between (X, Y) and (P, ψ) is symmetrical with its inverse, except for a sign in the equation of the Legendre transformation. Taking the differential of equation 5.20 and recalling that $dY = P dX$, we find

$$\begin{aligned} d\psi &= dY - P dX - X dP \\ &= -X dP \end{aligned} \tag{5.23}$$

or

$$-X = \frac{d\psi}{dP} \tag{5.24}$$

If the two variables ψ and P are eliminated² from the given equation $\psi = \psi(P)$ and from equations 5.24 and 5.20, we recover the relation $Y = Y(X)$. The symmetry between the Legendre transformation and its inverse is indicated by the following schematic comparison:

| | |
|-----------------------------------|--------------------------------------|
| $Y = Y(X)$ | $\psi = \psi(P)$ |
| $P = \frac{dY}{dX}$ | $-X = \frac{d\psi}{dP}$ |
| $\psi = -PX + Y$ | $Y = XP + \psi$ |
| Elimination of X and Y yields | Elimination of P and ψ yields |
| $\psi = \psi(P)$ | $Y = Y(X)$ |

The generalization of the Legendre transformation to functions of more than a single independent variable is simple and straightforward. In three dimensions Y is a function of X_0 and X_1 , and the fundamental equation represents a surface. This surface can be considered as the locus of points

¹This elimination is possible if P is not independent of X , that is, if $d^2Y/dX^2 \neq 0$. In the thermodynamic application this criterion will turn out to be identical to the criterion of stability. The criterion fails only at the "critical points," which are discussed in detail in Chapter 10.

²The condition that this be possible is that $d^2\psi/dP^2 \neq 0$, which will, in the thermodynamic

satisfying the fundamental equation $Y = Y(X_0, X_1)$, or it can be considered as the envelope of tangent planes. A plane can be characterized by its intercept ψ on the Y -axis and by the slopes P_0 and P_1 of its traces on the $Y - X_0$ and $Y - X_1$ planes. The fundamental equation then selects from all possible planes a subset described by $\psi = \psi(P_0, P_1)$.

In general the given fundamental relation

$$Y = Y(X_0, X_1, \dots, X_n) \tag{5.25}$$

represents a hypersurface in a $(n + 2)$ -dimensional space with cartesian coordinates Y, X_0, X_1, \dots, X_n . The derivative

$$P_k = \frac{\partial Y}{\partial X_k} \tag{5.26}$$

is the partial slope of this hypersurface. The hypersurface may be equally well represented as the locus of points satisfying equation 5.25 or as the envelope of the tangent hyperplanes. The family of tangent hyperplanes can be characterized by giving the intercept of a hyperplane, ψ , as a function of the slopes P_0, P_1, \dots, P_n . Then

$$\psi = Y - \sum_k P_k X_k \tag{5.27}$$

Taking the differential of this equation, we find

$$d\psi = -\sum_k X_k dP_k \tag{5.28}$$

whence

$$-X_k = \frac{\partial \psi}{\partial P_k} \tag{5.29}$$

A Legendre transformation is effected by eliminating Y and the X_k from $Y = Y(X_0, X_1, \dots, X_n)$, the set of equations 5.26, and equation 5.27. The inverse transformation is effected by eliminating ψ and the P_k from $\psi = \psi(P_1, P_2, \dots, P_n)$, the set of equations 5.29, and equation 5.27.

Finally, a Legendre transformation may be made only in some $(n + 2)$ -dimensional subspace of the full $(n + 2)$ -dimensional space of the relation $Y = Y(X_0, X_1, \dots, X_n)$. Of course the subspace must contain the Y -coordinate but may involve any choice of $n + 1$ coordinates from the set X_0, X_1, \dots, X_n . For convenience of notation, we order the coordinates so that the Legendre transformation is made in the subspace of the first $n + 1$ coordinates (and of Y); the coordinates X_0, X_1, \dots, X_n are left

untransformed. Such a partial Legendre transformation is effected merely by considering the variables $X_{n+1}, X_{n+2}, \dots, X_l$ as constants in the transformation. The resulting Legendre transform must be denoted by some explicit notation that indicates which of the independent variables have participated in the transformation. We employ the notation $Y[P_0, P_1, \dots, P_n]$ to denote the function obtained by making a Legendre transformation with respect to X_0, X_1, \dots, X_n on the function $Y(X_0, X_1, \dots, X_l)$. Thus $Y[P_0, P_1, \dots, P_n]$ is a function of the independent variables $P_0, P_1, \dots, P_n, X_{n+1}, \dots, X_l$. The various relations involved in a partial Legendre transformation and its inverse are indicated in the following table.

| | |
|---|---|
| $Y = Y(X_0, X_1, \dots, X_l)$ | $Y[P_0, P_1, \dots, P_n]$ = function of $P_0, P_1, \dots, P_n, X_{n+1}, \dots, X_l$ (5.30) |
| $P_k = \frac{\partial Y}{\partial X_k}$ | $-X_k = \frac{\partial Y[P_0, \dots, P_n]}{\partial P_k}$ $k \leq n$ (5.31) |
| <p>The partial differentiation denotes constancy of all the natural variables of Y other than X_k (i.e., of all X_j with $j \neq k$)</p> | <p>The partial differentiation denotes constancy of all the natural variables of $Y(P_0, \dots, P_n)$ other than that with respect to which the differentiation is being carried out.</p> |
| $dY = \sum_0^l P_k dX_k$ | $dY[P_0, \dots, P_n] = -\sum_0^n X_k dP_k + \sum_{n+1}^l P_k dX_k$ (5.32) |
| $Y[P_0, \dots, P_n] = Y - \sum_0^n P_k X_k$ | $Y = Y[P_0, \dots, P_n] + \sum_0^n X_k P_k$ (5.33) |
| <p>Elimination of Y and X_0, X_1, \dots, X_n from equations 5.30, 5.33, and the first $n + 1$ equations of 5.31 yields the transformed fundamental relation.</p> | <p>Elimination of $Y[P_0, \dots, P_n]$ and P_0, P_1, \dots, P_n from equations 5.30, 5.33, and the first $n + 1$ equations of 5.31 yields the original fundamental relation.</p> |

thermodynamic applications in the succeeding sections of this chapter, it may be of interest to indicate very briefly the application of the formalism to Lagrangian and Hamiltonian mechanics, which perhaps may be a more familiar field of physics than thermodynamics. The Lagrangian principle guarantees that a particular function, the Lagrangian, completely characterizes the dynamics of a mechanical system. The Lagrangian is a function of $2r$ variables, r of which are *generalized coordinates* and r of which are *generalized velocities*. Thus the equation

$$L = L(v_1, v_2, \dots, v_r, q_1, q_2, \dots, q_r) \tag{5.34}$$

plays the role of a fundamental relation. The *generalized momenta* are defined as derivatives of the Lagrangian function

$$P_k \equiv \frac{\partial L}{\partial v_k} \tag{5.35}$$

If it is desired to replace the velocities by the momenta as independent variables, we must make a partial Legendre transformation with respect to the velocities. We thereby introduce a new function, called the Hamiltonian, defined by³

$$(-H) = L - \sum_1^r P_k v_k \tag{5.36}$$

A complete dynamical formalism can then be based on the new fundamental relation

$$H = H(P_1, P_2, \dots, P_r, q_1, q_2, \dots, q_r) \tag{5.37}$$

Furthermore, by equation 5.31 the derivative of H with respect to P_k is the velocity v_k , which is one of the Hamiltonian dynamical equations. Thus, if an equation of the form 5.34 is considered as a dynamical fundamental equation in the Lagrangian representation, the Hamiltonian equation (5.37) is the equivalent fundamental equation expressed in the Hamiltonian representation.

PROBLEMS

5.2-1. The equation $y = x^2/10$ describes a parabola.

- Find the equation of this parabola in the "line geometry representation" $\psi = \psi(P)$.
- On a sheet of graph paper (covering the range roughly from $x = -15$ to $x = +15$ and from $y = -25$ to $y = +25$) draw straight lines with slopes $P = 0$,

³In our usage the Legendre transform of the Lagrangian is the *negative* Hamiltonian. Actually, the

$\pm 0.5, \pm 1, \pm 2, \pm 3$ and with intercepts ψ satisfying the relationship $\psi = \psi(P)$ as found in part (a). (Drawing each straight line is facilitated by calculating its intercepts on the x -axis and on the y -axis.)

5.2-2. Let $y = Ae^{Bx}$.

- Find $\psi(P)$.
- Calculate the inverse Legendre transform of $\psi(P)$ and corroborate that this result is $y(x)$.
- Taking $A = 2$ and $B = 0.5$, draw a family of tangent lines in accordance with the result found in (a), and check that the tangent curve goes through the expected points at $x = 0, 1$, and 2 .

5-3 THERMODYNAMIC POTENTIALS

The application of the preceding formalism to thermodynamics is self-evident. The fundamental relation $Y = Y(X_0, X_1, \dots)$ can be interpreted as the energy-language fundamental relation $U = U(S, X_1, X_2, \dots, X)$ or $U = U(S, V, N_1, N_2, \dots)$. The derivatives P_0, P_1, \dots correspond to the intensive parameters $T, -P, \mu_1, \mu_2, \dots$. The Legendre transformed functions are called *thermodynamic potentials*, and we now specifically define several of the most common of them. In Chapter 6 we continue the discussion of these functions by deriving extremum principles for each potential, indicating the intuitive significance of each, and discussing its particular role in thermodynamic theory. But for the moment we concern ourselves merely with the formal aspects of the definitions of the several particular functions.

The *Helmholtz potential* or the *Helmholtz free energy*, is the partial Legendre transform of U that replaces the entropy by the temperature as the independent variable. The internationally adopted symbol for the Helmholtz potential is F . The natural variables of the Helmholtz potential are T, V, N_1, N_2, \dots . That is, the functional relation $F = F(T, V, N_1, N_2, \dots)$ constitutes a fundamental relation. In the systematic notation introduced in Section 5.2

$$F \equiv U[T] \quad (5.38)$$

The full relationship between the energy representation and the Helmholtz representation, is summarized in the following schematic comparison:

| | | |
|--------------------------------|--------------------------------|--------|
| $U = U(S, V, N_1, N_2, \dots)$ | $F = F(T, V, N_1, N_2, \dots)$ | (5.39) |
|--------------------------------|--------------------------------|--------|

| | | |
|-------------------------------|--------------------------------|--------|
| $T = \partial U / \partial S$ | $-S = \partial F / \partial T$ | (5.40) |
|-------------------------------|--------------------------------|--------|

| | | |
|--------------|--------------|--------|
| $F = U - TS$ | $U = F + TS$ | (5.41) |
|--------------|--------------|--------|

| | |
|-----------------------------------|-----------------------------------|
| Elimination of U and S yields | Elimination of F and T yields |
| $F = F(T, V, N_1, N_2, \dots)$ | $U = U(S, V, N_1, N_2, \dots)$ |

The complete differential dF is

$$dF = -SdT - P dV + \mu_1 dN_1 + \mu_2 dN_2 + \dots \quad (5.42)$$

The *enthalpy* is that partial Legendre transform of U that replaces the volume by the pressure as an independent variable. Following the recommendations of the International Unions of Physics and of Chemistry, and in agreement with almost universal usage, we adopt the symbol H for the enthalpy. The natural variables of this potential are S, P, N_1, N_2, \dots and

$$H \equiv U[P] \quad (5.43)$$

The schematic representation of the relationship of the energy and enthalpy representations is as follows:

| | | |
|--------------------------------|--------------------------------|--------|
| $U = U(S, V, N_1, N_2, \dots)$ | $H = H(S, P, N_1, N_2, \dots)$ | (5.44) |
|--------------------------------|--------------------------------|--------|

| | | |
|--------------------------------|-------------------------------|--------|
| $-P = \partial U / \partial V$ | $V = \partial H / \partial P$ | (5.45) |
|--------------------------------|-------------------------------|--------|

| | | |
|--------------|--------------|--------|
| $H = U + PV$ | $U = H - PV$ | (5.46) |
|--------------|--------------|--------|

| | |
|-----------------------------------|-----------------------------------|
| Elimination of U and V yields | Elimination of H and P yields |
| $H = H(S, P, N_1, N_2, \dots)$ | $U = U(S, V, N_1, N_2, \dots)$ |

Particular attention is called to the inversion of the signs in equations 5.45 and 5.46, resulting from the fact that $-P$ is the intensive parameter associated with V . The complete differential dH is

$$dH = T dS + V dP + \mu_1 dN_1 + \mu_2 dN_2 + \dots \quad (5.47)$$

The third of the common Legendre transforms of the energy is the *Gibbs potential*, or *Gibbs free energy*. This potential is the Legendre transform that simultaneously replaces the entropy by the temperature and the volume by the pressure as independent variables. The standard notation is G , and the natural variables are T, P, N_1, N_2, \dots . We thus have

$$G \equiv U[T, P] \quad (5.48)$$

and

| | | |
|--------------------------------|--------------------------------|--------|
| $U = U(S, V, N_1, N_2, \dots)$ | $G = G(T, P, N_1, N_2, \dots)$ | (5.49) |
|--------------------------------|--------------------------------|--------|

| | | |
|-------------------------------|--------------------------------|--------|
| $T = \partial U / \partial S$ | $-S = \partial G / \partial T$ | (5.50) |
|-------------------------------|--------------------------------|--------|

| | | |
|--------------------------------|-------------------------------|--------|
| $-P = \partial U / \partial V$ | $V = \partial G / \partial P$ | (5.51) |
|--------------------------------|-------------------------------|--------|

| | | |
|-------------------|-------------------|--------|
| $G = U - TS + PV$ | $U = G + TS - PV$ | (5.52) |
|-------------------|-------------------|--------|

| | |
|--|--|
| Elimination of U, S , and V yields | Elimination of G, T , and P yields |
| $G = G(T, P, N_1, N_2, \dots)$ | $U = U(S, V, N_1, N_2, \dots)$ |

The complete differential dG is

$$dG = -S dT + V dP + \mu_1 dN_1 + \mu_2 dN_2 + \dots \quad (5.53)$$

A thermodynamic potential which arises naturally in statistical mechanics is the *grand canonical potential*, $U[T, \mu]$. For this potential we have

| | | |
|--|--|--------|
| $U = U(S, V, N)$ | $U[T, \mu]$ = function of T, V , and μ | (5.54) |
| $T = \partial U / \partial S$ | $-S = \partial U[T, \mu] / \partial T$ | (5.55) |
| $\mu = \partial U / \partial N$ | $-N = \partial U[T, \mu] / \partial \mu$ | (5.56) |
| $U[T, \mu] = U - TS - \mu N$ | $U = U[T, \mu] + TS + \mu N$ | (5.57) |
| Elimination of U, S , and N yields | Elimination of $U[T, \mu], T$, and μ yields | |
| $U[T, \mu]$ as a function of T, V, μ | $U = U(S, V, N)$ | |

and

$$dU[T, \mu] = -S dT - P dV - N d\mu \quad (5.58)$$

Other possible transforms of the energy for a simple system, which are used only infrequently and which consequently are unnamed, are $U[\mu_1], U[P, \mu_1], U[T, \mu_1, \mu_2]$, and so forth. The complete Legendre transform is $U[T, P, \mu_1, \mu_2, \dots, \mu_r]$. The fact that $U(S, V, N_1, N_2, \dots, N)$ is a homogeneous first-order function of its arguments causes this latter function to vanish identically. For

$$U[T, P, \mu_1, \dots, \mu_r] = U - TS + PV - \mu_1 N_1 - \mu_2 N_2 - \dots - \mu_r N_r \quad (5.59)$$

which, by the Euler relation (3.6), is identically zero

$$U[T, P, \mu_1, \dots, \mu_r] \equiv 0 \quad (5.60)$$

PROBLEMS

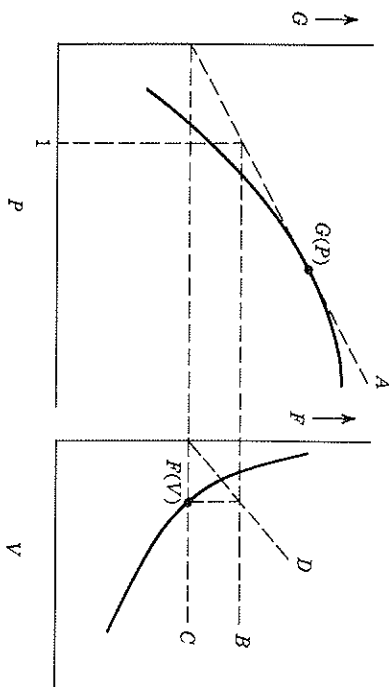
5.3-1. Find the fundamental equation of a monatomic ideal gas in the Helmholtz representation, in the enthalpy representation, and in the Gibbs representation. Assume the fundamental equation computed in Section 3.4. In each case find the equations of state by differentiation of the fundamental equation.

5.3-2. Find the fundamental equation of the ideal van der Waals fluid (Section 3.5) in the Helmholtz representation.

Perform an inverse Legendre transform on the Helmholtz potential and show that the fundamental equation in the energy representation is recovered.

5.3-3. Find the fundamental equation of electromagnetic radiation in the Helmholtz representation. Calculate the "thermal" and "mechanical" equations of state and corroborate that they agree with those given in Section 3.6.

5.3-4. Justify the following recipe for obtaining a plot of $F(V)$ from a plot of $G(P)$ (the common dependent variables T and N being notationally suppressed for convenience).



- (1) At a chosen value of P draw the tangent line A .
- (2) Draw horizontal lines B and C through the intersections of A with $P = 1$ and $P = 0$.
- (3) Draw the 45° line D as shown and project the intersection of B and D onto the line C to obtain the point $F(V)$.

Hint: Identify the magnitude of the two vertical distances indicated in the G versus P diagram, and also the vertical separation of lines B and C .

Note that the units of F and V are determined by the chosen units of G and P . Explain.

Give the analogous construction for at least one other pair of potentials.

Note that $G(P)$ is drawn as a concave function (i.e., negative curvature) and show that this is equivalent to the statement that $\kappa_T > 0$.

5.3-5. From the first acceptable fundamental equation in Problem 1.10-1 calculate the fundamental equation in Gibbs representation. Calculate $\alpha(T, P)$, $\kappa_T(T, P)$, and $c_p(T, P)$ by differentiation of G .

5.3-6. From the second acceptable fundamental equation in Problem 1.10-1 calculate the fundamental equation in enthalpy representation. Calculate $V(S, P, N)$ by differentiation.

5.3-7. The enthalpy of a particular system is

$$H = AS^2 N^{-1} \ln \left(\frac{P}{P_0} \right)$$

⁴Adapted from H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford University Press, 1971)