5

ALTERNATIVE FORMULATIONS AND LEGENDRE TRANSFORMATIONS

5-1 THE ENERGY MINIMUM PRINCIPLE

In the preceding chapters we have inferred some of the most evident and immediate consequences of the principle of maximum entropy. Further consequences will lead to a wide range of other useful and fundamental results. But to facilitate those developments it proves to be useful now to reconsider the formal aspects of the theory and to note that the same content can be reformulated in several equivalent mathematical forms. Each of these alternative formulations is particularly convenient in particular types of problems, and the art of thermodynamic calculations lies largely in the selection of the particular theoretical formulation that most incisively "fits" the given problem. In the appropriate formulation thermodynamic problems tend to be remarkably simple; the converse is that they tend to be remarkably complicated in an inappropriate formalism!

Multiple equivalent formulations also appear in mechanics—Newtonian, Lagrangian, and Hamiltonian formalisms are tautologically equivalent. Again certain problems are much more tractable in a Lagrangian formalism than in a Newtonian formalism, or vice versa. But the difference in convenience of different formalisms is enormously greater in thermodynamics. It is for this reason that *the general theory of transformation among equivalent representations is here incorporated as a fundamental aspect of thermostatistical theory.*

In fact we have already considered two equivalent representations—the energy representation and the entropy representation. But the basic extremum principle has been formulated only in the entropy representation. If these two representations are to play parallel roles in the theory we must find an extremum principle in the energy representation, analogous to the entropy maximum principle. There is, indeed, such an extremum principle; the principle of maximum entropy is equivalent to, and can be

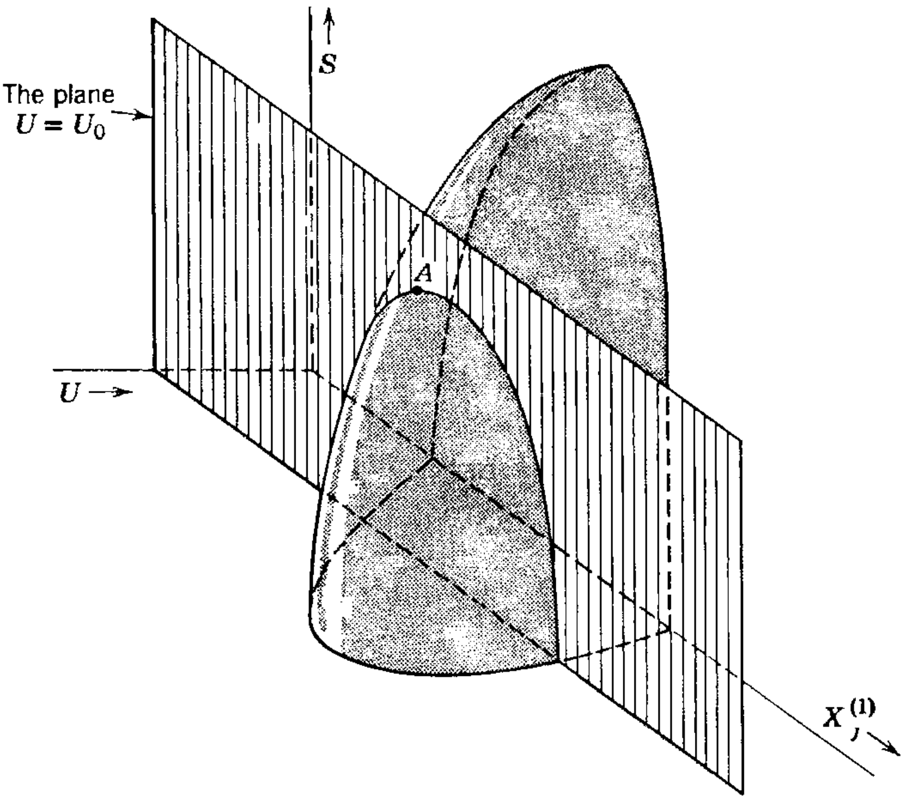

FIGURE 5.1
The equilibrium state A as a point of maximum S for constant U.

replaced by, a principle of minimum energy. Whereas the entropy maximum principle characterizes the equilibrium state as having maximum entropy for given total energy, the energy minimum principle characterizes the equilibrium state as having minimum energy for given total entropy.

Figure 5.1 shows a section of the thermodynamic configuration space for a composite system, as discussed in Section 4.1. The axes labeled S and U correspond to the total entropy and energy of the composite system, and the axis labeled $X_j^{(1)}$ corresponds to a particular extensive parameter of the first subsystem. Other axes, not shown explicitly in the figure, are $U^{(1)}$, X_j, and other pairs $X_k^{(1)}$, X_k.

The total energy of the composite system is a constant determined by the closure condition. The geometrical representation of this closure condition is the requirement that the state of the system lie on the plane $U = U_0$ in Fig. 5.1. The fundamental equation of the system is represented by the surface shown, and the representative point of the system therefore must be on the curve of intersection of the plane and the surface. If the parameter $X_j^{(1)}$ is unconstrained, the equilibrium state is the particular state that maximizes the entropy along the permitted curve; the state labeled A in Fig. 5.1.

The alternative representation of the equilibrium state A as a state of minimum energy for given entropy is illustrated in Fig. 5.2. Through the

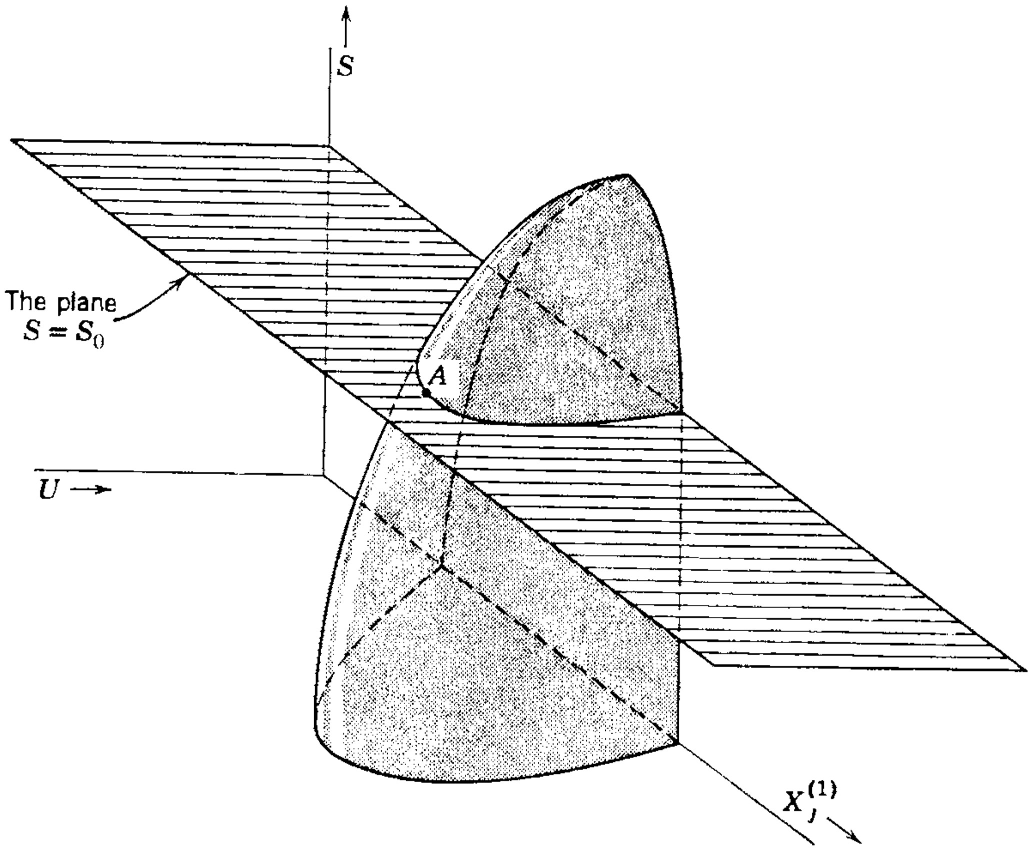

FIGURE 5.2
The equilibrium state A as a point of minimum U for constant S.

equilibrium point A is passed the plane $S = S_0$, which determines a curve of intersection with the fundamental surface. This curve consists of a family of states of constant entropy, and *the equilibrium state A is the state that minimizes the energy along this curve.*

The equivalence of the entropy maximum and the energy minimum principles clearly depends upon the fact that the geometrical form of the fundamental surface is generally as shown in Fig. 5.1 and 5.2. As discussed in Section 4.1, the form of the surface shown in the figures is determined by the postulates that $\partial S/\partial U > 0$ and that U is a single-valued continuous function of S; these analytic postulates accordingly are the underlying conditions for the equivalence of the two principles.

To recapitulate, we have made plausible, though we have not yet proved, that the following two principles are equivalent:

Entropy Maximum Principle. *The equilibrium value of any unconstrained internal parameter is such as to maximize the entropy for the given value of the total internal energy.*

Energy Minimum Principle. *The equilibrium value of any unconstrained internal parameter is such as to minimize the energy for the given value of the total entropy.*

The proof of the equivalence of the two extremum criteria can be formulated either as a physical argument or as a mathematical exercise. We turn first to the physical argument, to demonstrate that if the energy were *not* minimum the entropy could not be maximum in equilibrium, and inversely.

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 ($dQ = T\,dS$), 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.

The inverse argument, that minimum energy implies maximum entropy, is similarly constructed (see Problem 5.1-1).

In a more formal demonstration we assume the entropy maximum principle

$$\left(\frac{\partial S}{\partial X}\right)_U = 0 \quad \text{and} \quad \left(\frac{\partial^2 S}{\partial X^2}\right)_U < 0 \tag{5.1}$$

where, for clarity, we have written X for $X_j^{(1)}$, and where it is implicit that all other X's are held constant throughout. Also, for clarity, we temporarily denote the first derivative $(\partial U/\partial X)_S$ by P. Then (by equation A.22 of Appendix A)

$$P \equiv \left(\frac{\partial U}{\partial X}\right)_S = -\frac{\left(\frac{\partial S}{\partial X}\right)_U}{\left(\frac{\partial S}{\partial U}\right)_X} = -T\left(\frac{\partial S}{\partial X}\right)_U = 0 \tag{5.2}$$

We conclude that U has an extremum. To classify that extremum as a maximum, a minimum, or a point of inflection we must study the sign of the second derivative $(\partial^2 U/\partial X^2)_S \equiv (\partial P/\partial X)_S$. But considering P as a function of U and X we have

$$\left(\frac{\partial^2 U}{\partial X^2}\right)_S = \left(\frac{\partial P}{\partial X}\right)_S = \left(\frac{\partial P}{\partial U}\right)_X\left(\frac{\partial U}{\partial X}\right)_S + \left(\frac{\partial P}{\partial X}\right)_U = \left(\frac{\partial P}{\partial U}\right)_X P + \left(\frac{\partial P}{\partial X}\right)_U \tag{5.3}$$

$$= \left(\frac{\partial P}{\partial X}\right)_U \quad \text{at } P = 0 \tag{5.4}$$

$$= \frac{\partial}{\partial X}\left[-\frac{\left(\frac{\partial S}{\partial X}\right)_U}{\left(\frac{\partial S}{\partial U}\right)_X}\right]_U \tag{5.5}$$

$$= -\frac{\dfrac{\partial^2 S}{\partial X^2}}{\dfrac{\partial S}{\partial U}} + \frac{\partial S}{\partial X}\frac{\dfrac{\partial^2 S}{\partial X \partial U}}{\left(\dfrac{\partial S}{\partial U}\right)^2} \tag{5.6}$$

$$= -T\frac{\partial^2 S}{\partial X^2} > 0 \quad \text{at } \frac{\partial S}{\partial X} = 0 \tag{5.7}$$

so that U is a minimum. The inverse argument is identical in form.

As already indicated, the fact that precisely the same situation is described by the two extremal criteria is analogous to the isoperimetric problem in geometry. Thus a circle may be characterized either as the two dimensional figure of maximum area for given perimeter or, alternatively, as the two dimensional figure of minimum perimeter for given area.

The two alternative extremal criteria that characterize a circle are completely equivalent, and each applies to every circle. Yet they suggest two different ways of generating a circle. Suppose we are given a square and we wish to distort it continuously to generate a circle. We may keep its area constant and allow its bounding curve to contract as if it were a rubber band. We thereby generate a circle as the figure of minimum perimeter for the given area. Alternatively we might keep the perimeter of the given square constant and allow the area to increase, thereby obtaining a (different) circle, as the figure of maximum area for the given perimeter. However, after each of these circles is obtained *each satisfies both extremal conditions for its final values of area and perimeter.*

The physical situation pertaining to a thermodynamic system is very closely analogous to the geometrical situation described. Again, any equilibrium state can be characterized either as a state of maximum entropy for given energy or as a state of minimum energy for given entropy. But these two criteria nevertheless suggest two different ways of attaining equilibrium. As a specific illustration of these two approaches to equilibrium, consider a piston originally fixed at some point in a closed cylinder. We are interested in bringing the system to equilibrium without the constraint on the position of the piston. We can simply remove the constraint and allow the equilibrium to establish itself spontaneously; the entropy increases and the energy is maintained constant by the closure condition. This is the process suggested by the entropy maximum principle. Alternatively, we can permit the piston to move very slowly, reversibly 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

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

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

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

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

$$Y = Y(X_0, X_1, \ldots, X_t) \tag{5.13}$$

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(5.13). 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.

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

Geometrically, the fundamental relation is represented by a curve in a

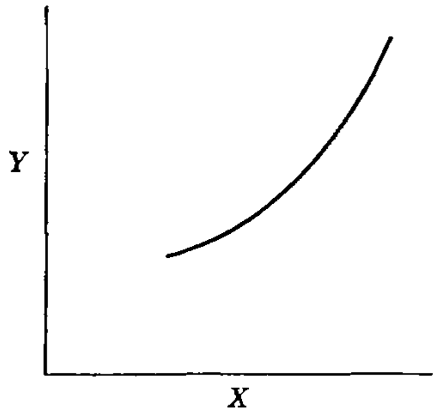

FIGURE 5.3

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

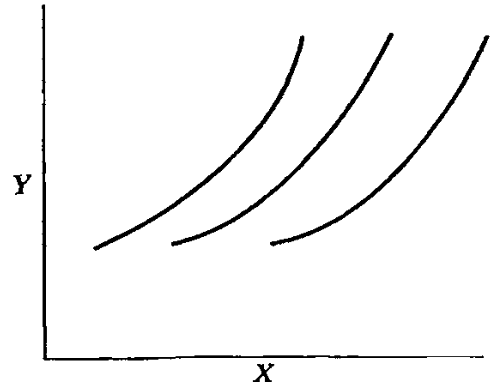

FIGURE 5.4

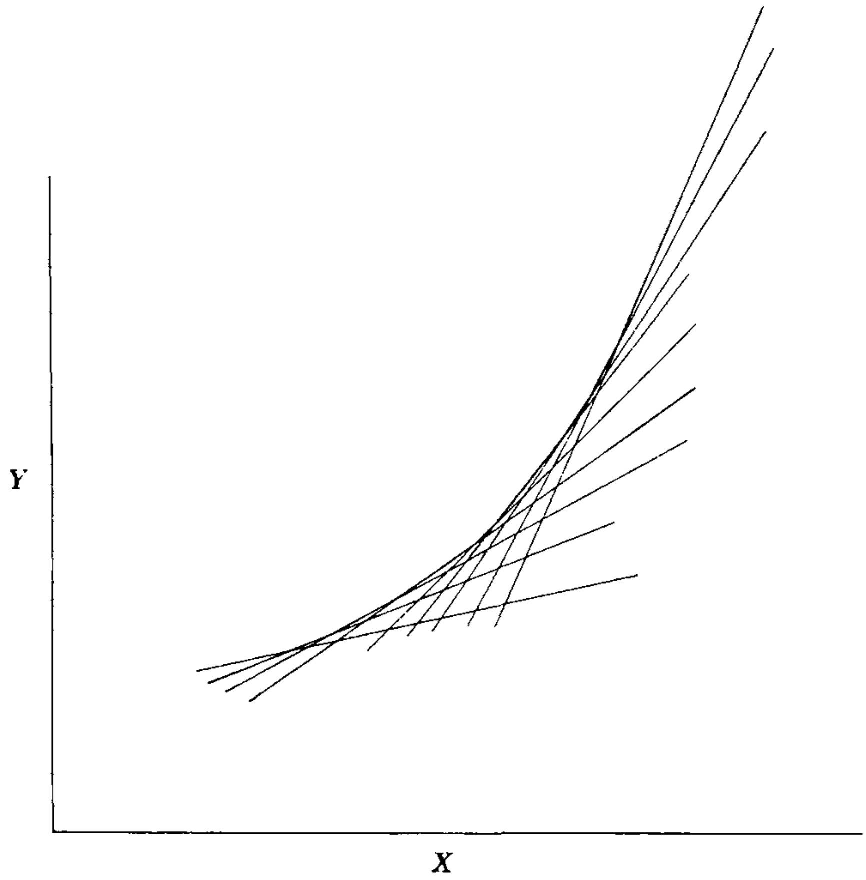

FIGURE 5.5

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

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

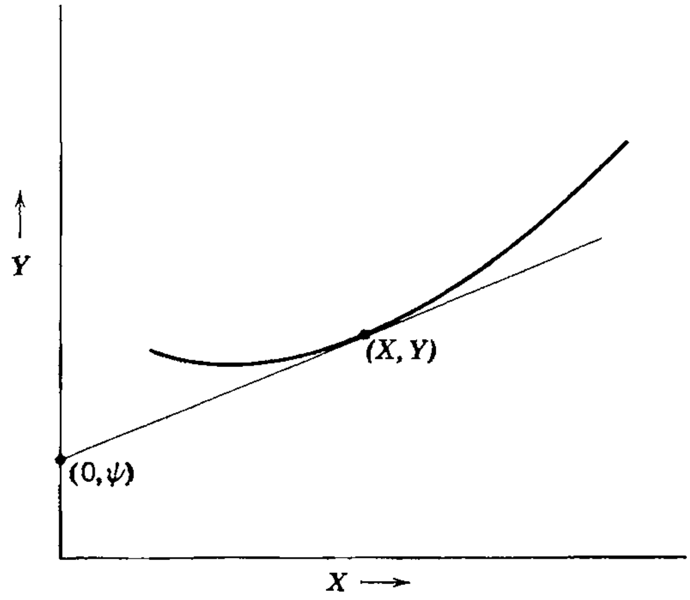

FIGURE 5.6

and by differentiation we find

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

Then by elimination[1] 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 eliminated[2] 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:

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

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

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[1] This 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

[2] The condition that this be possible is that $d^2\psi/\partial P^2 \neq 0$, which will, in the thermodynamic application, be guaranteed by the stability of the system under consideration

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

$$Y = Y(X_0, X_1, \ldots, X_t) \tag{5.25}$$

represents a hypersurface in a $(t + 2)$-dimensional space with cartesian coordinates $Y, X_0, X_1, \ldots, X_t$. 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 $P_0, P_1, \ldots, P_t$. 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 $Y = Y(X_0, X_1, \ldots, X_t)$, the set of equations 5.26, and equation 5.27. The inverse transformation is effected by eliminating ψ and the P_k from $\psi = \psi(P_1, P_2, \ldots, P_t)$, 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 $(t + 2)$-dimensional space of the relation $Y = Y(X_0, X_1, \ldots, X_t)$. Of course the subspace must contain the Y-coordinate but may involve any choice of $n + 1$ coordinates from the set $X_0, X_1, \ldots, X_t$. 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 $X_{n+1}, X_{n+2}, \ldots, X_t$ are left untransformed. Such a partial Legendre transformation is effected merely by considering the variables $X_{n+1}, X_{n+2}, \dots, X_t$ 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 $Y(X_0, X_1, \dots, X_t)$. Thus $Y[P_0, P_1, \dots, P_n]$ is a function of the independent variables $P_0, P_1, \dots, P_n, X_{n+1}, \dots, X_t$. The various relations involved in a partial Legendre transformation and its inverse are indicated in the following table.

$Y = Y(X_0, X_1, \dots, X_t)$	$Y[P_0, P_1, \dots, P_n]$ = function of $P_0, P_1, \dots, P_n, X_{n+1}, \dots, X_t$ (5.30)
$P_k = \dfrac{\partial Y}{\partial X_k}$	$-X_k = \dfrac{\partial Y[P_0, \dots, P_n]}{\partial P_k} \quad k \le n$ (5.31) $P_k = \dfrac{\partial Y[P_0, \dots, P_n]}{\partial X_k} \quad k > n$
The partial differentiation denotes constancy of all the natural variables of Y other than X_k (i.e., of all X_j with $j \neq k$)	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.
$dY = \sum_0^t P_k dX_k$	$dY[P_0, \dots, P_n] = -\sum_0^n X_k dP_k + \sum_{n+1}^t P_k dX_k$ (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)
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.	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.

In this section we have divorced the mathematical aspects of Legendre transformations from the physical applications. Before proceeding to the 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

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

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 by[3]

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

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

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

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.

a) Find the equation of this parabola in the "line geometry representation" $\psi = \psi(P)$.

b) On a sheet of graph paper (covering the range roughly from $x \simeq -15$ to $x \simeq +15$ and from $y \simeq -25$ to $y \simeq +25$) draw straight lines with slopes $P = 0$,

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[3] In our usage the Legendre transform of the Lagrangian is the *negative* Hamiltonian Actually, the accepted mathematical convention agrees with the usage in mechanics, and the function $-\psi$ would be called the Legendre transform of Y

± 0.5, ± 1, ± 2, ± 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 $y = Ae^{Bx}$.

a) Find $\psi(P)$.

b) Calculate the inverse Legendre transform of $\psi(P)$ and corroborate that this result is $y(x)$.

c) 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 $Y = Y(X_0, X_1, \ldots)$ can be interpreted as the energy-language fundamental relation $U = U(S, X_1, X_2, \ldots, X_t)$ or $U = U(S, V, N_1, N_2, \ldots)$. The derivatives $P_0, P_1, \ldots$ correspond to the intensive parameters $T, -P, \mu_1, \mu_2, \ldots$. 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 $T, V, N_1, N_2, \ldots$. That is, the functional relation $F = F(T, V, N_1, N_2, \ldots)$ constitutes a fundamental relation. In the systematic notation introduced in Section 5.2

$$F \equiv U[T] \tag{5.38}$$

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

$U = U(S, V, N_1, N_2, \ldots)$	$F = F(T, V, N_1, N_2, \ldots)$	(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	
$F = F(T, V, N_1, N_2, \ldots)$	$U = U(S, V, N_1, N_2, \ldots)$	

The complete differential dF is

$$dF = -S\,dT - P\,dV + \mu_1\,dN_1 + \mu_2\,dN_2 + \cdots \tag{5.42}$$

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 $S, P, N_1, N_2, \ldots$ and

$$H \equiv U[P] \tag{5.43}$$

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

$U = U(S, V, N_1, N_2, \ldots)$	$H = H(S, P, N_1, N_2, \ldots)$	(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	
$H = H(S, P, N_1, N_2, \ldots)$	$U = U(S, V, N_1, N_2, \ldots)$	

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

$$dH = T\,dS + V\,dP + \mu_1\,dN_1 + \mu_2\,dN_2 + \cdots \tag{5.47}$$

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 $T, P, N_1, N_2, \ldots$. We thus have

$$G \equiv U[T, P] \tag{5.48}$$

and

$U = U(S, V, N_1, N_2, \ldots)$	$G = G(T, P, N_1, N_2, \ldots)$	(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	
$G = G(T, P, N_1, N_2, \ldots)$	$U = U(S, V, N_1, N_2, \ldots)$	

The complete differential dG is

$$dG = -S\,dT + V\,dP + \mu_1\,dN_1 + \mu_2\,dN_2 + \cdots \tag{5.53}$$

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 $U[T, \mu]$ as a function of T, V, μ	Elimination of $U[T, \mu]$, T, and μ yields $U = U(S, V, N)$	

and

$$dU[T, \mu] = -S\,dT - P\,dV - N\,d\mu \tag{5.58}$$

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 $U[T, P, \mu_1, \mu_2, \ldots, \mu_r]$. The fact that $U(S, V, N_1, N_2, \ldots, N_r)$ is a homogeneous first-order function of its arguments causes this latter function to vanish identically. For

$$U[T, P, \mu_1, \ldots, \mu_r] = U - TS + PV - \mu_1 N_1 - \mu_2 N_2 - \cdots - \mu_r N_r \tag{5.59}$$

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

$$U[T, P, \mu_1, \ldots, \mu_r] \equiv 0 \tag{5.60}$$

PROBLEMS

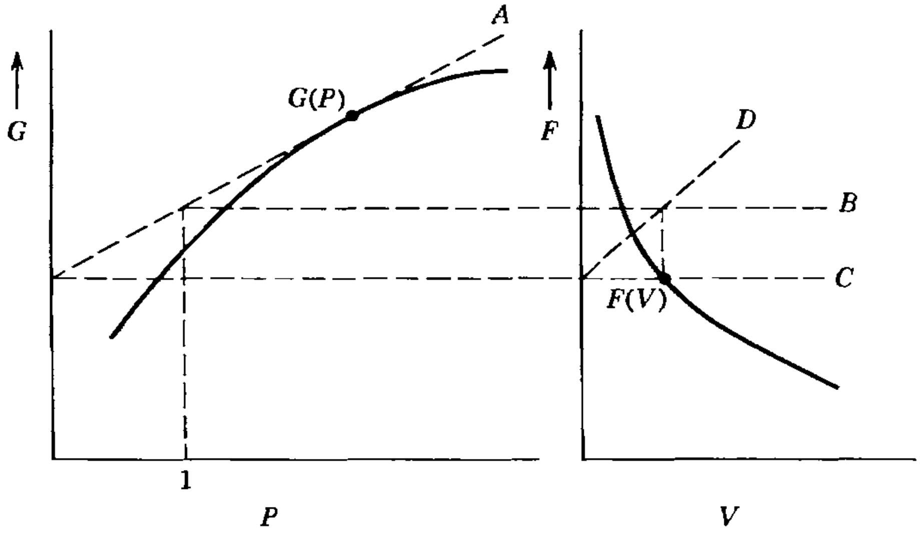
5.3-1. Find the fundamental equation of a monatomic ideal gas in the Helmholtz representation, in the enthalpy representation, and in the Gibbs representation. Assume the fundamental equation computed in Section 3.4. In each case find the equations of state by differentiation of the fundamental equation.

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[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

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

---

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

where A is a positive constant. Calculate the molar heat capacity at constant volume c_v as a function of T and P.

5.3-8. In Chapter 15 it is shown by a statistical mechanical calculation that the fundamental equation of a system of $\tilde{N}$ "atoms" each of which can exist in an atomic state with energy ε_u or in an atomic state with energy ε_d (and in no other state) is

$$F = -\tilde{N}k_B T^{\ln}\left(e^{-\beta\varepsilon_u} + e^{-\beta\varepsilon_d}\right)$$

Here k_B is Boltzmann's constant and $\beta = 1/k_B T$. Show that the fundamental equation of this system, in entropy representation, is

$$S = NR\ln\left(\frac{1 + Y^{\varepsilon_d/\varepsilon_u}}{Y^Y}\right)$$

where

$$Y \equiv \frac{U - \tilde{N}\varepsilon_u}{\tilde{N}\varepsilon_d - U}$$

Hint: Introduce $\beta = (k_B T)^{-1}$, and show first that $U = F + \beta\partial F/\partial\beta = \partial(\beta F)/\partial\beta$. Also, for definiteness, assume $\varepsilon_u < \varepsilon_d$, and note that $\tilde{N}k_B = NR$ where $\tilde{N}$ is the number of atoms and N is the number of moles.

5.3-9. Show, for the two-level system of Problem 5.3-8, that as the temperature increases from zero to infinity the energy increases from $\tilde{N}\varepsilon_u$ to $\tilde{N}(\varepsilon_u + \varepsilon_d)/2$. Thus, at zero temperature all atoms are in their "ground state" (with energy ε_u), and at infinite temperature the atoms are equally likely to be in either state. Energies higher than $N(\varepsilon_u + \varepsilon_d)/2$ are inaccessible in thermal equilibrium! (This upper bound on the energy is a consequence of the unphysical oversimplification of the model; it will be discussed again in Section 15.3.)
Show that the Helmholtz potential of a mixture of simple ideal gases is the sum of the Helmholtz potentials of each individual gas:

5.3-10.
a) Show that the Helmholtz potential of a mixture of simple ideal gases is the sum of the Helmholtz potentials of each individual gas:

$$F(T, V, N_1, \ldots, N_r) = F(T, V, N_1) + \cdots + F(T, V, N_r)$$

Recall the fundamental equation of the mixture, as given in equation 3.40.
An analogous additivity does not hold for any other potential expressed in terms of its natural variables.

5.3-11. A mixture of two monatomic ideal gases is contained in a volume V at temperature T. The mole numbers are N_1 and N_2. Calculate the chemical potentials μ_1 and μ_2. Recall Problems 5.3-1 and 5.3-10.

Assuming the system to be in contact with a reservoir of given T and μ_1, through a diathermal wall permeable to the first component but not to the second, calculate the pressure in the system.

5.3-12. A system obeys the fundamental relation

$$(s - s_0)^4 = Avu^2$$

Calculate the Gibbs potential $G(T, P, N)$.

5.3-13. For a particular system it is found that

$$u = \left(\tfrac{3}{2}\right)Pv$$

and

$$P = AvT^4$$

Find a fundamental equation, the molar Gibbs potential, and the Helmholtz potential for this system.

5.3-14. For a particular system (of 1 mole) the quantity $(v + a)f$ is known to be a function of the temperature only ($= Y(T)$). Here v is the molar volume, f is the molar Helmholtz potential, a is a constant, and $Y(T)$ denotes an unspecified function of temperature. It is also known that the molar heat capacity c_v is

$$c_v = b(v)T^{\frac{1}{2}}$$

where $b(v)$ is an unspecified function of v.

a) Evaluate $Y(T)$ and $b(v)$.

b) The system is to be taken from an initial state (T_0, v_0) to a final state (T_f, v_f). A thermal reservoir of temperature T_r is available, as is a reversible work source. What is the maximum work that can be delivered to the reversible work source? (Note that the answer may involve constants unevaluated by the stated conditions, but that the answer should be fully explicit otherwise.)

5-4 GENERALIZED MASSIEU FUNCTIONS

Whereas the most common functions definable in terms of Legendre transformations are those mentioned in Section 5.3, another set can be defined by performing the Legendre transformation on the entropy rather than on the energy. That is, the fundamental relation in the form $S = S(U, V, N_1, N_2, \ldots)$ can be taken as the relation on which the transformation is performed. Such Legendre transforms of the entropy were invented by Massieu in 1869 and actually predated the transforms of the energy introduced by Gibbs in 1875. We refer to the transforms of the entropy as *Massieu functions*, as distinguished from the *thermodynamic potentials* transformed from the energy. The Massieu functions will turn out to be particularly useful in the theory of irreversible thermodynamics, and they also arise naturally in statistical mechanics and in the theory of thermal fluctuations. Three representative Massieu functions are $S[1/T]$, in which the internal energy is replaced by the reciprocal temperature as independent variable; $S[P/T]$, in which the volume is replaced by P/T as independent variable; and $S[1/T, P/T]$, in which both replacements are made simultaneously. Clearly

$$S\left[\frac{1}{T}\right] \equiv S - \frac{1}{T}U = -\frac{F}{T} \tag{5.61}$$

$$S\left[\frac{P}{T}\right] \equiv S - \frac{P}{T} \cdot V \tag{5.62}$$

and

$$S\left[\frac{1}{T}, \frac{P}{T}\right] = S - \frac{1}{T}U - \frac{P}{T} \cdot V = -\frac{G}{T} \tag{5.63}$$

Thus, of the three, only $S[P/T]$ is not trivially related to one of the previously introduced thermodynamic potentials. For this function

$S = S(U, V, N_1, N_2, \ldots)$	$S[P/T] =$ function of $U, P/T, N_1, N_2, \ldots,$ (5.64)
$P/T = \partial S/\partial V$	$-V = \partial S[P/T]/\partial(P/T)$ (5.65)
$S[P/T] = S - (P/T)V$	$S = S[P/T] + (P/T)V$ (5.66)
Elimination of S and V yields $S[P/T]$ as a function of $U, P/T, N_1, N_2, \ldots$	Elimination of $S[P/T]$ and P/T yields $S = S(U, V, N_1, N_2, \ldots)$

and

$$dS[P/T] = (1/T)\,dU - V\,d(P/T) - (\mu_1/T)\,dN_1 - \frac{\mu_2}{T}\,dN_2 \ldots \tag{5.67}$$

Other Massieu functions may be invented and analyzed by the reader as a particular need for them arises.

PROBLEMS

5.4-1. Find the fundamental equation of a monatomic ideal gas in the representation

$$S\left[\frac{P}{T}, \frac{\mu}{T}\right]$$

Find the equations of state by differentiation of this fundamental equation.

5.4-2. Find the fundamental equation of electromagnetic radiation (Section 3.6)
a) in the representation $S[1/T]$
b) in the representation $S[P/T]$

5.4-3. Find the fundamental equation of the ideal van der Waals fluid in the representation $S[1/T]$. Show that $S[1/T]$ is equal to $-F/T$ (recall that F was computed in Problem 5.3-2).

6

THE EXTREMUM PRINCIPLE IN THE LEGENDRE TRANSFORMED REPRESENTATIONS

6-1 THE MINIMUM PRINCIPLES FOR THE POTENTIALS

We have seen that the Legendre transformation permits expression of the fundamental equation in terms of a set of independent variables chosen to be particularly convenient for a given problem. Clearly, however, the advantage of being able to write the fundamental equation in various representations would be lost if the extremum principle were not itself expressible in those representations. We are concerned, therefore, with the reformulation of the basic extremum principle in forms appropriate to the Legendre transformed representations.

For definiteness consider a composite system in contact with a thermal reservoir. Suppose further that some internal constraint has been removed. We seek the mathematical condition that will permit us to predict the equilibrium state. For this purpose we first review the solution of the problem by the energy minimum principle.

In the equilibrium state the total energy of the composite system-plus-reservoir is minimum:

$$d(U + U^r) = 0 \tag{6.1}$$

and

$$d^2(U + U^r) = d^2U > 0 \tag{6.2}$$

subject to the isentropic condition

$$d(S + S^r) = 0 \tag{6.3}$$

The quantity d^2U^r has been put equal to zero in equation 6.2 because d^2U^r is a sum of products of the form

$$\frac{\partial^2 U^r}{\partial X_j^r \, \partial X_k^r} \, dX_j^r \, dX_k^r$$

which vanish for a reservoir (the coefficient varying as the reciprocal of the mole number of the reservoir).

The other closure conditions depend upon the particular form of the internal constraints in the composite system. If the internal wall is movable and impermeable, we have

$$dN_j^{(1)} = dN_j^{(2)} = d\left(V^{(1)} + V^{(2)}\right) = 0 \qquad (\text{for all } j) \tag{6.4}$$

whereas, if the internal wall is rigid and permeable to the kth component, we have

$$d\left(N_k^{(1)} + N_k^{(2)}\right) = dN_j^{(1)} = dN_j^{(2)} = dV^{(1)} = dV^{(2)} = 0 \qquad (j \neq k) \tag{6.5}$$

These equations suffice to determine the equilibrium state.

The differential dU in equation 6.1 involves the terms $T^{(1)}dS^{(1)} + T^{(2)}dS^{(2)}$, which arise from heat flux among the subsystems and the reservoir, and terms such as $-P^{(1)}dV^{(1)} - P^{(2)}dV^{(2)}$ and $\mu_k^{(1)}dN_k^{(1)} + \mu_k^{(2)}dN_k^{(2)}$, which arise from processes within the composite system. The terms $T^{(1)}dS^{(1)} + T^{(2)}dS^{(2)}$ combine with the term $dU^r = T^r dS^r$ in equation 6.1 to yield

$$\begin{aligned} T^{(1)}dS^{(1)} + T^{(2)}dS^{(2)} + T^r dS^r &= T^{(1)}dS^{(1)} + T^{(2)}dS^{(2)} - T^r d\left(S^{(1)} + S^{(2)}\right) \\ &= 0 \end{aligned} \tag{6.6}$$

whence

$$T^{(1)} = T^{(2)} = T^r \tag{6.7}$$

Thus one evident aspect of the final equilibrium state is the fact that the reservoir maintains a constancy of temperature throughout the system. The remaining conditions of equilibrium naturally depend upon the specific form of the internal constraints in the composite system.

To this point we have merely reviewed the application of the energy minimum principle to the composite system (the subsystem plus the reservoir). We are finally ready to recast equations 6.1 and 6.2 into the language of another representation. We rewrite equation 6.1

$$d(U + U^r) = dU + T^r dS^r = 0 \tag{6.8}$$

or, by equation 6.3

$$dU - T^r dS = 0 \tag{6.9}$$

or, further, since T^r is a constant

$$d(U - T^r S) = 0 \tag{6.10}$$

Similarly, since T^r is a constant and S is an independent variable, equation 6.2 implies[1]

$$d^2U = d^2(U - T^r S) > 0 \tag{6.11}$$

Thus the quantity $(U - T^r S)$ is minimum in the equilibrium state. Now the quantity $U - T^r S$ is suggestive by its form of the Helmholtz potential $U - TS$. We are therefore led to examine further the extremum properties of the quantity $(U - T^r S)$ and to ask how these may be related to the extremum properties of the Helmholtz potential. We have seen that an evident feature of the equilibrium is that the temperature of the composite system (i.e., of each of its subsystems) is equal to T^r. If we accept that part of the solution, we can immediately restrict our search for the equilibrium state among the manifold of states for which $T = T^r$. But over this manifold of states $U - TS$ is identical to $U - T^r S$. Then we can write equation 6.10 as

$$dF = d(U - TS) = 0 \tag{6.12}$$

subject to the auxiliary condition that

$$T = T^r \tag{6.13}$$

That is, the equilibrium state minimizes the Helmholtz potential, not absolutely, but over the manifold of states for which $T = T^r$. We thus arrive at the equilibrium condition in the Helmholtz potential representation.

Helmholtz Potential Minimum Principle. *The equilibrium value of any unconstrained internal parameter in a system in diathermal contact with a heat reservoir minimizes the Helmholtz potential over the manifold of states for which $T = T^r$.*

---

[1] d^2U represents the second-order terms in the expansion of U in powers of dS, the linear term $-T^r S$ in equation 6.11 contributes to the expansion only in first order (see equation A.9 of Appendix A)

The intuitive significance of this principle is clearly evident in equations 6.8 through 6.10. The energy of the system plus the reservoir is, of course, minimum. But the statement that the Helmholtz potential of the system alone is minimum is just another way of saying this, for $dF = d(U - TS)$, and the term $d(-TS)$ actually represents the change in energy of the reservoir (since $T = T^r$ and $-dS = dS^r$). It is now a simple matter to extend the foregoing considerations to the other common representations.

Consider a composite system in which all subsystems are in contact with a common pressure reservoir through walls nonrestrictive with respect to volume. We further assume that some internal constraint within the composite system has been removed. The first condition of equilibrium can be written

$$d(U + U^r) = dU - P^r dV^r = dU + P^r dV = 0 \tag{6.14}$$

or

$$d(U + P^r V) = 0 \tag{6.15}$$

Accepting the evident condition that $P = P^r$, we can write

$$dH = d(U + PV) = 0 \tag{6.16}$$

subject to the auxiliary restriction

$$P = P^r \tag{6.17}$$

Furthermore, since P^r is a constant and V is an independent variable

$$d^2H = d^2(U + P^r V) = d^2U > 0 \tag{6.18}$$

so that the extremum is a minimum.

Enthalpy Minimum Principle. *The equilibrium value of any unconstrained internal parameter in a system in contact with a pressure reservoir minimizes the enthalpy over the manifold of states of constant pressure (equal to that of the pressure reservoir).*

Finally, consider a system in simultaneous contact with a thermal and a pressure reservoir. Again

$$d(U + U^r) = dU - T^r dS + P^r dV = 0 \tag{6.19}$$

Accepting the evident conditions that $T = T^r$ and $P = P^r$, we can write

$$dG = d(U - TS + PV) = 0 \tag{6.20}$$

subject to the auxiliary restrictions

$$T = T^r \qquad P = P^r \tag{6.21}$$

Again

$$d^2G = d^2(U - T^rS + P^rV) = d^2U > 0 \tag{6.22}$$

We thus obtain the equilibrium condition in the Gibbs representation.

Gibbs Potential Minimum Principle. *The equilibrium value of any unconstrained internal parameter in a system in contact with a thermal and a pressure reservoir minimizes the Gibbs potential at constant temperature and pressure (equal to those of the respective reservoirs).*

If the system is characterized by other extensive parameters in addition to the volume and the mole numbers the analysis is identical in form and the general result is now clear:

The General Minimum Principle for Legendre Transforms of the Energy. *The equilibrium value of any unconstrained internal parameter in a system in contact with a set of reservoirs (with intensive parameters* $P_1^r, P_2^r, \ldots$*) minimizes the thermodynamic potential* $U[P_1, P_2, \ldots]$ *at constant* $P_1, P_2, \ldots$ *(equal to* $P_1^r, P_2^r, \ldots$*).*

6-2 THE HELMHOLTZ POTENTIAL

For a composite system in thermal contact with a thermal reservoir the equilibrium state minimizes the Helmholtz potential over the manifold of states of constant temperature (equal to that of the reservoir). In practice many processes are carried out in rigid vessels with diathermal walls, so that the ambient atmosphere acts as a thermal reservoir; for these the Helmholtz potential representation is admirably suited.

The Helmholtz potential is a natural function of the variables $T, V, N_1, N_2, \ldots$. The condition that T is constant reduces the number of variables in the problem, and F effectively becomes a function only of the variables V and $N_1, N_2, \ldots$. This is in marked contrast to the manner in which constancy of T would have to be handled in the energy representation: there U would be a function of $S, V, N_1, N_2, \ldots$ but the auxiliary condition $T = T^r$ would imply a relation among these variables. Particularly in the absence of explicit knowledge of the equation of state $T = T(S, V, N)$ this auxiliary restriction would lead to considerable awkwardness in the analytic procedures in the energy representation.

As an illustration of the use of the Helmholtz potential we first consider a composite system composed of two simple systems separated by a

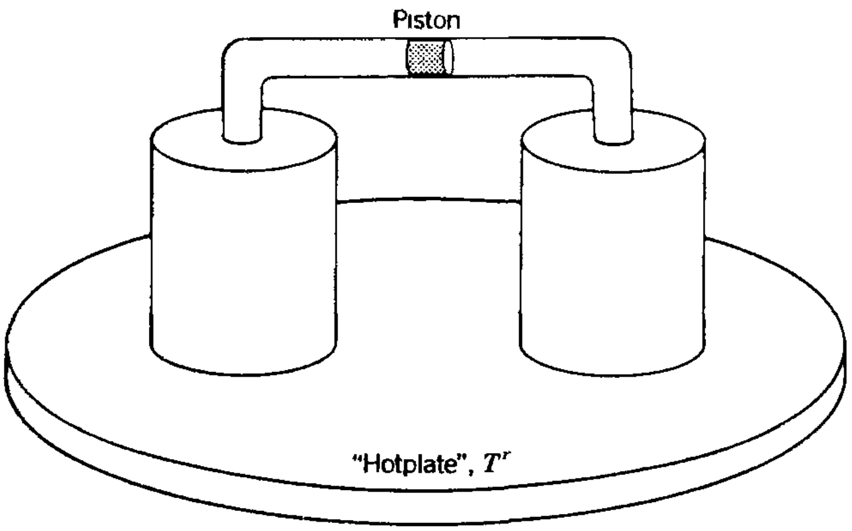


FIGURE 6.1

movable, adiabatic, impermeable wall (such as a solid insulating piston). The subsystems are each in thermal contact with a thermal reservoir of temperature T^r (Fig. 6.1). The problem, then, is to predict the volumes $V^{(1)}$ and $V^{(2)}$ of the two subsystems. We write

$$P^{(1)}\left(T^r, V^{(1)}, N_1^{(1)}, N_2^{(1)}, \ldots\right) = P^{(2)}\left(T^r, V^{(2)}, N_1^{(2)}, N_2^{(2)}, \ldots\right) \qquad (6.23)$$

This is one equation involving the two variables $V^{(1)}$ and $V^{(2)}$; all other arguments are constant. The closure condition

$$V^{(1)} + V^{(2)} = V, \text{ a constant} \qquad (6.24)$$

provides the other required equation, permitting explicit solution for $V^{(1)}$ and $V^{(2)}$.

In the energy representation we would also have found equality of the pressures, as in equation 6.23, but the pressures would be functions of the entropies, volumes, and mole numbers. We would then require the equations of state to relate the entropies to the temperature and the volumes; the two simultaneous equations, 6.23 and 6.24, would be replaced by four.

Although this reduction of four equations to two may seem to be a modest achievement, such a reduction is a very great convenience in more complex situations. Perhaps of even greater conceptual value is the fact that the Helmholtz representation permits us to focus our thought processes exclusively on the subsystem of interest, relegating the reservoir only to an implicit role. And finally, for technical mathematical reasons to be elaborated in Chapter 16, statistical mechanical calculations are *enormously* simpler in Helmholtz representations, permitting calculations that would otherwise be totally intractable.

For a system in contact with a thermal reservoir the Helmholtz potential can be interpreted as the *available work at constant temperature*.

Consider a system that interacts with a reversible work source while being in thermal contact with a thermal reservoir. In a reversible process the work input to the reversible work source is equal to the decrease in energy of the system and the reservoir

$$dW_{\mathrm{RWS}} = -dU - dU^r = -dU - T^r dS^r \tag{6.25}$$

$$= -dU + T^r dS = -d(U - T^r S) \tag{6.26}$$

$$= -dF \tag{6.27}$$

Thus *the work delivered in a reversible process, by a system in contact with a thermal reservoir, is equal to the decrease in the Helmholtz potential of the system.* The Helmholtz potential is often referred to as the Helmholtz "free energy," though the term *available work at constant temperature* would be less subject to misinterpretation.

Example 1

A cylinder contains an internal piston on each side of which is one mole of a monatomic ideal gas. The walls of the cylinder are diathermal, and the system is immersed in a large bath of liquid (a heat reservoir) at temperature 0°C. The initial volumes of the two gaseous subsystems (on either side of the piston) are 10 liters and 1 liter, respectively. The piston is now moved reversibly, so that the final volumes are 6 liters and 5 liters, respectively. How much work is delivered?

Solution

As the reader has shown in Problem 5.3-1, the fundamental equation of a monatomic ideal gas in the Helmholtz potential representation is

$$F = NRT\left\{\frac{F_0}{N_0 R T_0} - \ln\left[\left(\frac{T}{T_0}\right)^{3/2} \frac{V}{V_0}\left(\frac{N}{N_0}\right)^{-1}\right]\right\}$$

At constant T and N this is simply

$$F = \text{constant} - NRT \ln V$$

The change in Helmholtz potential is

$$\Delta F = -NRT[\ln 6 + \ln 5 - \ln 10 - \ln 1] = -NRT \ln 3 = -2.5\ \mathrm{kJ}$$

Thus 2.5 kJ of work are delivered in this process.

It is interesting to note that all of the energy comes from the thermal reservoir. The energy of a monatomic ideal gas is simply $\frac{3}{2}NRT$ and therefore it is constant at constant temperature. The fact that we withdraw heat from the temperature reservoir and deliver it *entirely* as work to the reversible work source does not, however, violate the Carnot efficiency principle because the gaseous subsystems are not left in their initial state. Despite the fact that the energy of these subsystems remains constant, their *entropy* increases.

PROBLEMS

6.2-1. Calculate the pressure on each side of the internal piston in Example 1, for arbitrary position of the piston. By integration then calculate the work done in Example 1 and corroborate the result there obtained.

6.2-2. Two ideal van der Waals fluids are contained in a cylinder, separated by an internal moveable piston. There is one mole of each fluid, and the two fluids have the same values of the van der Waals constants b and c; the respective values of the van der Waals constant "a" are a_1 and a_2. The entire system is in contact with a thermal reservoir of temperature T. Calculate the Helmholtz potential of the composite system as a function of T and of the total volume V. If the total volume is doubled (while allowing the internal piston to adjust), what is the work done by the system? Recall Problem 5.3-2.

6.2-3. Two subsystems are contained within a cylinder and are separated by an internal piston. Each subsystem is a mixture of one mole of helium gas and one mole of neon gas (each to be considered as a monatomic ideal gas). The piston is in the center of the cylinder, each subsystem occupying a volume of 10 liters. The walls of the cylinder are diathermal, and the system is in contact with a thermal reservoir at a temperature of 100°C. The piston is permeable to helium but impermeable to neon.

Recalling (from Problem 5.3-10) that the Helmholtz potential of a mixture of simple ideal gases is the sum of the individual Helmholtz potentials (each expressed as a function of temperature and volume), show that in the present case

$$F = N\frac{T}{T_0}f_0 - \frac{3}{2}NRT\ln\frac{T}{T_0} - N_1RT\ln\left(\frac{V}{V_0}\frac{N_0}{N_1}\right)$$
$$-N_2^{(1)}RT\ln\frac{V^{(1)}N_0}{V_0N_2^{(1)}} - N_2^{(2)}RT\ln\frac{V^{(2)}N_0}{V_0N_2^{(2)}}$$

where T_0, f_0, V_0, and N_0 are attributes of a standard state (recall Problem 5.3-1), N is the total mole number, $N_2^{(1)}$ is the mole number of neon (component 2) in subsystem 1, and $V^{(1)}$ and $V^{(2)}$ are the volumes of subsystems 1 and 2, respectively.

How much work is required to push the piston to such a position that the volumes of the subsystems are 5 liters and 15 liters? Carry out the calculation both by calculating the change in F and by a direct integration (as in Problem 6.2-1).

Answer:
work = $RT\ln(\frac{4}{3}) = 893$ J

6-3 THE ENTHALPY: THE JOULE–THOMSON OR "THROTTLING" PROCESS

For a composite system in interaction with a pressure reservoir the equilibrium state minimizes the enthalpy over the manifold of states of constant pressure. The enthalpy representation would be appropriate to processes carried out in adiabatically insulated cylinders fitted with adiabatically insulated pistons subject externally to atmospheric pressure, but this is not a very common experimental design. In processes carried out in open vessels, such as in the exercises commonly performed in an elementary chemistry laboratory, the ambient atmosphere acts as a pressure reservoir, but it also acts as a thermal reservoir: for the analysis of such processes only the Gibbs representation invokes the full power of Legendre transformations. Nevertheless, there are particular situations uniquely adapted to the enthalpy representation, as we shall see shortly.

More immediately evident is the interpretation of the enthalpy as a "potential for heat." From the differential form

$$dH = T\,dS + V\,dP + \mu_1\,dN_1 + \mu_2\,dN_2 + \cdots \tag{6.28}$$

it is evident that for a system in contact with a pressure reservoir and enclosed by impermeable walls

$$dH = đQ \qquad (\text{where } P, N_1, N_2, \ldots \text{ are constant}) \tag{6.29}$$

That is, *heat added to a system at constant pressure and at constant values of all the remaining extensive parameters* (other than S and V) *appears as an increase in the enthalpy.*

This statement may be compared to an analogous relation for the energy

$$dU = đQ \qquad (\text{where } V, N_1, N_2, \ldots \text{ are constant}) \tag{6.30}$$

and similar results for any Legendre transform in which the entropy is not among the transformed variables.

Because heating of a system is so frequently done while the system is maintained at constant pressure by the ambient atmosphere, the enthalpy is generally useful in discussion of heat transfers. The enthalpy accordingly is sometimes referred to as the "heat content" of the system (but it should be stressed again that "heat" refers to a mode of energy *flux* rather than to an attribute of a state of a thermodynamic system).

To illustrate the significance of the enthalpy as a "potential for heat," suppose that a system is to be maintained at constant pressure and its volume is to be changed from V_i to V_f. We desire to compute the heat absorbed by the system. As the pressure is constant, the heat flux is equal to the change in the enthalpy

$$Q_{i \to f} \equiv \int đQ = H_f - H_i \tag{6.31}$$

If we were to know the fundamental equation

$$H = H(S, P, N) \tag{6.32}$$

then, by differentiation

$$V = \frac{\partial H}{\partial P} = V(S, P, N) \tag{6.33}$$

and we could eliminate the entropy to find H as a function of V, P, and N. Then

$$Q_{i \to f} = H(V_f, P, N) - H(V_i, P, N) \tag{6.34}$$

A process of great practical importance, for which an enthalpy representation is extremely convenient, is the Joule–Thomson or "throttling" process. This process is commonly used to cool and liquify gases and as a second-stage refrigerator in "cryogenic" (low-temperature) laboratories.

In the Joule–Thomson process or "Joule–Kelvin" process (William Thomson was only later granted peerage as Lord Kelvin) a gas is allowed to seep through a porous barrier from a region of high pressure to a region of low pressure (Fig. 6.2). The porous barrier or "throttling valve" was originally a wad of cotton tamped into a pipe; in a laboratory demonstration it is now more apt to be glass fibers, and in industrial practice it is generally a porous ceramic termination to a pipe (Fig. 6.3). The process can be made continuous by using a mechanical pump to return the gas from the region of low pressure to the region of high pressure. Depending on certain conditions, to be developed in a moment, the gas is either heated or cooled in passing through the throttling valve.

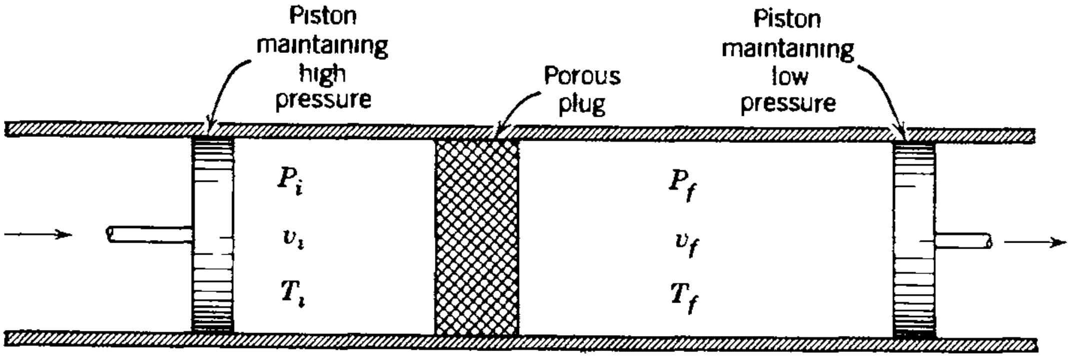


FIGURE 6.2
Schematic representation of the Joule-Thomson process.

For real gases and for given initial and final pressures, the change in temperature is generally positive down to a particular temperature, and it is negative below that temperature. The temperature at which the process changes from a heating to a cooling process is called the *inversion temperature*; it depends upon the particular gas and upon both the initial and final pressures. In order that the throttling process operate as an effective cooling process the gas must first be precooled below its inversion temperature.

To show that the Joule–Thomson process occurs at constant enthalpy consider one mole of the gas undergoing a throttling process. The piston

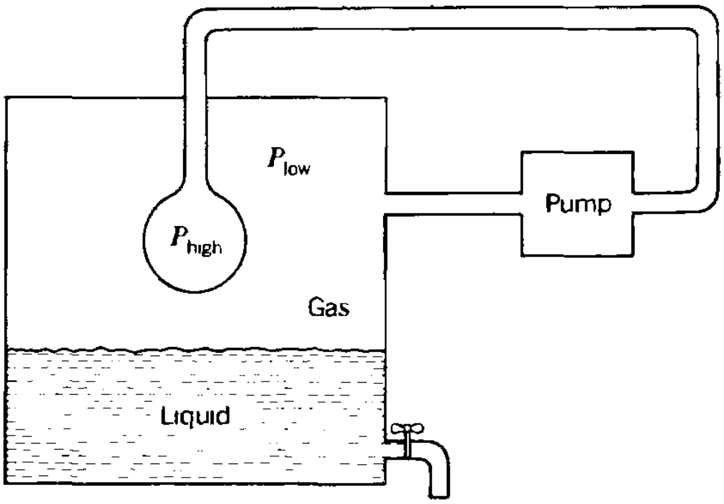


FIGURE 6.3
Schematic apparatus for liquefaction of a gas by throttling process. The pump maintains the pressure difference ($P_{\text{high}} - P_{\text{low}}$). The spherical termination of the high pressure pipe is a porous ceramic shell through which the gas expands in the throttling process.

(Fig. 6.2) that pushes this quantity of gas through the plug does an amount of work $P_i v_i$, in which v_i is the molar volume of the gas on the high pressure side of the plug. As the gas emerges from the plug, it does work on the piston that maintains the low pressure P_f, and this amount of work is $P_f v_f$. Thus the conservation of energy determines the final molar energy of the gas; it is the initial molar energy, plus the work $P_i v_i$ done on the gas, minus the work $P_f v_f$ done by the gas.

$$u_f = u_i + P_i v_i - P_f v_f \tag{6.35}$$

or

$$u_f + P_f v_f = u_i + P_i v_i \tag{6.36}$$

which can be written in terms of the molar enthalpy h as

$$h_f = h_i \tag{6.37}$$

Although, on the basis of equation 6.37, we say that the Joule–Thomson process occurs at constant enthalpy, we stress that this simply implies that the final enthalpy is equal to the initial enthalpy. We do not imply anything about the enthalpy during the process; *the intermediate states of the gas are nonequilibrium states for which the enthalpy is not defined.*

The isenthalpic curves ("isenthalps") of nitrogen are shown in Fig. 6.4 The initial temperature and pressure in a throttling process determine a particular isenthalp. The final pressure then determines a point on this same isenthalp, thereby determining the final temperature.

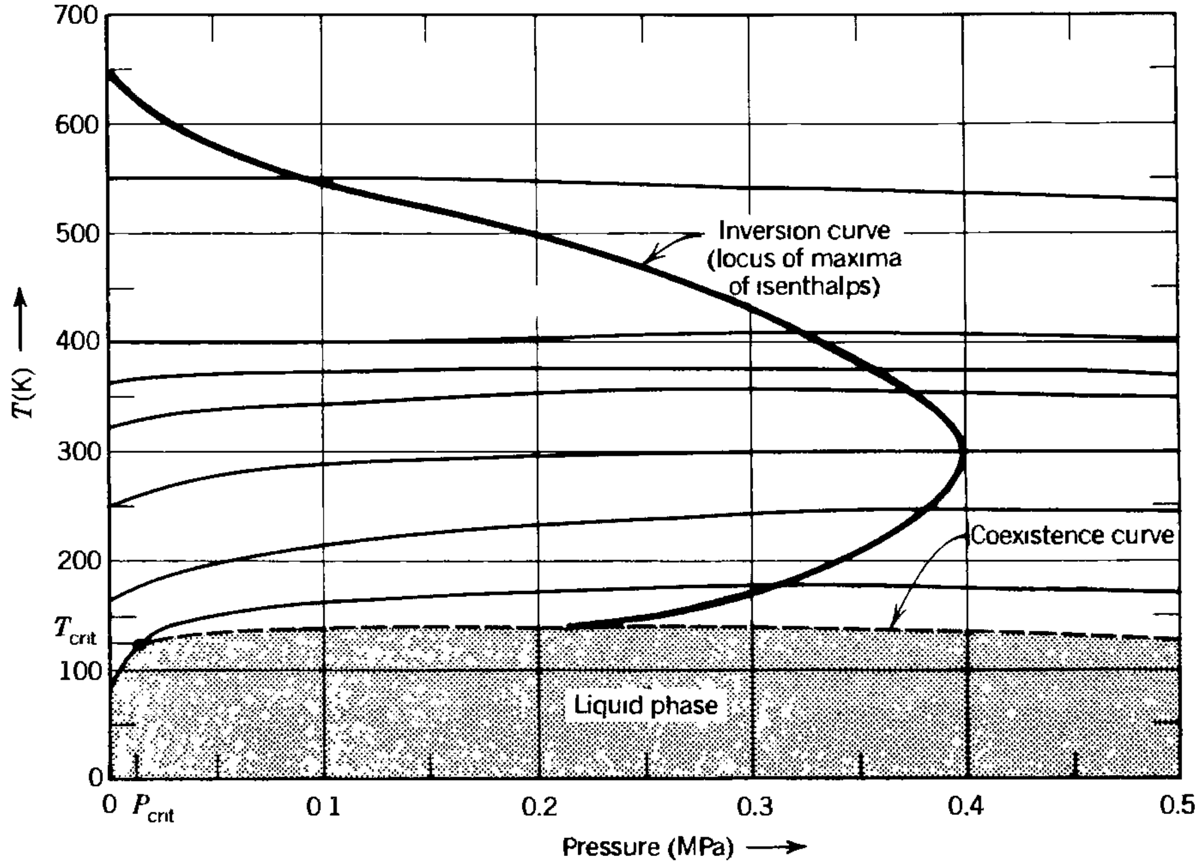


FIGURE 6.4
Isenthalps (solid), inversion temperature (dark), and coexistence curve for nitrogen; semiquantitative.

The isenthalps in Fig. 6.4 are concave, with maxima. If the initial temperature and pressure lie to the left of the maximum the throttling process necessarily cools the gas. If the initial temperature lies to the right of the maximum a small pressure drop heats the gas (though a large pressure drop may cross the maximum and can either heat or cool the gas). The maximum of the isenthalp therefore determines the inversion temperature, at which a small pressure change neither heats nor cools the gas.

The dark curve in Fig. 6.4 is a plot of inversion temperature as a function of pressure, obtained by connecting the maxima of the isenthalpic curves. Also shown on the figure is the curve of liquid–gas equilibrium. Points below the curve are in the liquid phase and those above are in the gaseous phase. This coexistence curve terminates in the "critical point." In the region of this point the "gas" and the "liquid" phases lose their distinguishability, as we shall study in some detail in Chapter 9.

If the change in pressure in a throttling process is sufficiently small we can employ the usual differential analysis.

$$dT = \left(\frac{\partial T}{\partial P}\right)_{H, N_1, N_2,} dP \tag{6.38}$$

The derivative can be expressed in terms of standard measurable quantities (c_p, α, κ_T) by a procedure that may appear somewhat complicated on first reading, but that will be shown in Chapter 7 to follow a routine and straightforward recipe. By a now familiar mathematical identity (A.22),

$$dT = -\left[\left(\frac{\partial H}{\partial P}\right)_T \Big/ \left(\frac{\partial H}{\partial T}\right)_P\right] dP \tag{6.39}$$

where we suppress the subscripts $N_1, N_2, \dots$ for simplicity, noting that the mole numbers remain constant throughout. However, $dH = T\,dS + V\,dP$ at constant mole numbers, so that

$$dT = -\frac{T(\partial S/\partial P)_T + V}{T(\partial S/\partial T)_P}\, dP \tag{6.40}$$

The denominator is Nc_P. The derivative $(\partial S/\partial P)_T$ is equal to $-(\partial V/\partial T)_P$ by one of the class of "Maxwell relations," analogous to equations 3.62 or 3.65 (in the present case the two derivatives can be corroborated to be the two mixed second derivatives of the Gibbs potential). Identifying $(\partial S/\partial P)_T = -(\partial V/\partial T)_P = -V\alpha$ (equation 3.67) we finally find

$$dT = \frac{v}{c_P}(T\alpha - 1)\, dP \tag{6.41}$$

This is a fundamental equation of the Joule–Thomson effect. As the change in pressure dP is negative, the sign of dT is opposite that of the quantity in parentheses. Thus if $T\alpha > 1$, a small decrease in pressure (in transiting the "throttling valve") cools the gas. The inversion temperature is determined by

$$\alpha T_{\text{inversion}} = 1 \tag{6.42}$$

For an ideal gas the coefficient of thermal expansion α is equal to $1/T$, so that there is no change in temperature in a Joule–Thomson expansion. All gases approach ideal behavior at high temperature and low or moderate pressure, and the isenthalps correspondingly become "flat," as seen in Fig. 6.4. It is left to Example 2 to show that for real gases the temperature change is negative below the inversion temperature and positive above, and to evaluate the inversion temperature.

Example 2

Compute the inversion temperature of common gases, assuming them to be described by the van der Waals equation of state (3.41).

Solution

We must first evaluate the coefficient of expansion α. Differentiating the van der Waals equation of state (3.41) with respect to T, at constant P

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P = \left[\frac{Tv}{v-b} - \frac{2a(v-b)}{Rv^2}\right]^{-1}$$

To express the right-hand side as a function of T and P is analytically difficult. An approximate solution follows from the recognition that molar volumes are on the order of 0.02 m^3,[1] whence b/v is on the order of 10^{-3} and a/RTv is on the order of $10^{-3} - 10^{-4}$ (see Table 3.1). Hence a series expansion in b/v and a/RTv can reasonably be terminated at the lowest order term. Let

$$\varepsilon_1 \equiv \frac{b}{v} \qquad \varepsilon_2 \equiv \frac{a}{RTv}$$

Then

$$\alpha = \left[\frac{T}{1-\varepsilon_1} - \frac{2T}{v}(v-b)\,\varepsilon_2\right]^{-1}$$

$$= \frac{1}{T}\left[\frac{1}{1-\varepsilon_1} - 2(1-\varepsilon_1)\,\varepsilon_2\right]^{-1}$$

Returning to equation 6.41

$$dT = \frac{v}{c_p}(T\alpha - 1)\,dP$$

from which we recall that

$$T_{\text{inv.}}\,\alpha = 1$$

It then follows that at the inversion temperature

$$[1 - \varepsilon_1 + 2\varepsilon_2 + \cdots] = 1$$

or

$$\varepsilon_1 = 2\varepsilon_2$$

The inversion temperature is now determined by

$$T_{\text{inv}} \simeq \frac{2a}{bR}$$

with cooling of the gas for temperature below T_{inv}, and heating above. From Table 3.1, we compute the inversion temperature of several gases: $T_{\text{inv}}(H_2) = 224$ K, $T_{\text{inv}}(\text{Ne}) = 302$ K, $T_{\text{inv}}(N_2) = 850$ K, $T_{\text{inv}}(O_2) = 1020$ K, $T_{\text{inv}}(CO_2) = 2260$ K. In fact the inversion temperature empirically depends strongly on the pressure —a dependence lost in our calculation by the neglect of higher-order terms. The observed inversion temperature at zero pressure for H_2 is 204 K, and for neon it is 228 K—in fair agreement with our crude calculation. For polyatomic gases the agreement is less satisfactory; the observed value for CO_2 is 1275 K whereas we have computed 2260 K.

PROBLEMS

6.3-1. A hole is opened in the wall separating two chemically identical single-component subsystems. Each of the subsystems is also in interaction with a pressure reservoir of pressure P^r. Use the enthalpy minimum principle to show that the conditions of equilibrium are $T^{(1)} = T^{(2)}$ and $\mu^{(1)} = \mu^{(2)}$.

6.3-2. A gas has the following equations of state

$$P = \frac{U}{V} \qquad T = 3B\left(\frac{U^2}{NV}\right)^{1/3}$$

where B is a positive constant. The system obeys the Nernst postulate ($S \to 0$ as $T \to 0$). The gas, at an initial teperature T_i and initial pressure P_i, is passed through a "porous plug" in a Joule–Thomson process. The final pressure is P_f. Calculate the final temperature T_f.

6.3-3. Show that for an ideal van der Waals fluid

$$h = -\frac{2a}{v} + RT\left(c + \frac{v}{v-b}\right)$$

where h is the molar enthalpy. Assuming such a fluid to be passed through a porous plug and thereby expanded from v_i to v_f (with $v_f > v_i$), find the final temperature T_f in terms of the initial temperature T_i and the given data.

Evaluate the temperature change if the gas is CO_2, the mean temperature is 0°C, the mean pressure is 10^7 Pa, and the change in pressure is 10^6 Pa. The molar heat capacity c_P of CO_2 at the relevant temperature and pressure is 29.5 J/mole-K. Carry calculation only to first order in b/v and a/RTv.

6.3-4. One mole of a monatomic ideal gas is in a cylinder with a movable piston on the other side of which is a pressure reservoir with $P_r = 1$ atm. How much heat must be added to the gas to increase its volume from 20 to 50 liters?

6.3-5. Assume that the gas of Problem 6.3-4 is an ideal van der Waals fluid with the van der Waals constants of argon (Table 3-1), and again calculate the heat required. Recall Problem 6.3-3.

6-4 THE GIBBS POTENTIAL; CHEMICAL REACTIONS

For a composite system in interaction with both thermal and pressure reservoirs the equilibrium state minimizes the Gibbs potential over the manifold of states of constant temperature and pressure (equal to those of the reservoirs).

The Gibbs potential is a natural function of the variables $T, P, N_1, N_2, \ldots$, and it is particularly convenient to use in the analysis of problems involving constant T and P. Innumerable processes of common experience occur in systems exposed to the atmosphere, and thereby maintained at constant temperature and pressure. And frequently a process of interest occurs in a small subsystem of a larger system that acts as both a thermal and a pressure reservoir (as in the fermentation of a grape in a large wine vat).

The Gibbs potential of a multicomponent system is related to the chemical potentials of the individual components, for $G = U - TS + PV$,