Legendre Transforms and Their Application in Thermodynamics

Legendre transform theory is: (1) developed to show the relationships among the common thermodynamic potential functions (that is, energy, enthalpy, and free energy); and (2) extended to introduce other potential functions which are particularly convenient in certain applications (for example, stability and critical point phenomena of multicomponent systems). General derivative operators are employed to allow partial derivatives of a given potential function to be transformed to derivatives of other potential functions.

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SCOPE

In thermodynamics a number of potential functions are in common use, namely, internal energy, enthalpy, Gibbs and Helmholtz free energies. Few textbooks stress the underlying relationships among these functions except to point out the value of using particular functions when the system under consideration is being held under certain external restraints (for example, constant temperature, constant volume, etc.).

By employing a very simple transformation, the Legendre transform, one can easily and logically relate all the common potential functions and, in fact, introduce many others that are particularly valuable in certain applications.

This transform allows one to replace independent variables by partial derivatives of the dependent variable. Since many intensive properties in thermodynamics are actually partial derivatives, the value of the Legendre transform can be readily appreciated. (For example, temperature can be defined as the partial derivative of the internal energy with respect to variations in entropy at constant volume and mole numbers.)

Also, when delineating the criteria for stability or for critical points, depending upon the approach used, one can specify certain inequalities between partial derivatives of potential functions. Legendre transform theory allows one to relate the partial derivatives of different potential functions so that a choice may be made as to the most convenient form to employ depending upon what data or phenomenological relations are available.

CONCLUSIONS AND SIGNIFICANCE

The basic concepts of Legendre transformations are reviewed and illustrated with familiar thermodynamic functions. For example, beginning with the Fundamental Equation expressed by Gibbs, the total internal energy of a system is expressed as a function of the independent variables of total entropy, total volume, and the mole numbers (or masses) of the constituents. Then it is shown that the Helmholtz free energy is but a partial Legendre transform of the internal energy when the total entropy is replaced by the temperature as an independent variable. The transform results in no loss of information content of the original function.

The principal emphasis of the paper lies, however, in developing suitable differential operators to allow one to relate second- and third-order partial derivatives among the various Legendre transforms of energy. Applications of these relations are demonstrated in a subsequent paper which treats the stability of thermodynamic systems.

A common problem in engineering and science arises when, from theory or experiment, we have a relation expressing the dependence of a single variable on a particular set of independent variables, but for convenience or availability of data we wish to work with a different set of independent variables, using those which are partial derivatives of the original dependent variables. This problem is particularly important in the application of thermodynamics where the usual starting point is the Gibbs relation or Fundamental Equation:

$$\underline{U} = U(\underline{S}, \underline{V}, N_1, \ldots, N_n) \tag{1}$$

The partial derivatives of $\underline{U}$ with respect to the independent variables are, of course, temperature T, (negative) pressure $-P$, and the chemical potential μ_j. For reasons pointed out above, we may prefer to replace entropy by temperature and then employ as the independent set of variables $(T, \underline{V}, N_1, \ldots, N_n)$. The mathematical technique known as Legendre transforms allows us to shift between such independent variable sets without loss of any in-

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formation content in the original function (Callen, 1960; Tisza, 1966).

The purpose of the present paper is to generalize the treatment of Legendre transforms and to demonstrate techniques for relating partial derivatives of such transforms. Such techniques are of value in treating thermodynamic stability and critical point phenomena of multicomponent systems (Modell and Reid, 1974; Beegle et al., 1974).

THE LEGENDRE TRANSFORM

The Legendre transformation stems from a basic theorem in line geometry (Tisza, 1966; Aris and Amundson, 1973); although rigorous proof is no simple task, the transformation theory is conceptually easy to grasp and mechanically simple to apply. The basic principle is that a curve consisting of a locus of points can be described completely by the tangent lines which form the envelope of the curve (Callen, 1960; Modell and Reid, 1974; Tisza, 1966). Since no information is lost in shifting from one description of the curve to another, the process can be reversed. For example, the function

$$y^{(0)} = f(x_1, \ldots, x_m) \tag{2}$$

represents a locus of points in $m + 1$ space. There are m first-order partial derivatives of $y^{(0)}$ with respect to each of the m independent variables, $x_1, \ldots, x_m$. Defining these derivatives as ξ_i,

$$\xi_i \equiv \left(\frac{\partial y^{(0)}}{\partial x_i}\right)_{x_1,..[x_i]..,x_m} \tag*{(3)*}$$

or

$$\xi_i = f(x_1, \ldots, x_m) \tag{4}$$

it follows that the variation of $y^{(0)}$ with x_1 could be described by the envelope of tangents in the $y^{(0)}$-x_1 plane. If $y^{(1)}$ is the intercept of the tangent corresponding to ξ_1,

$$y^{(1)}(\xi_1, x_2, \ldots, x_m) = y^{(0)} - \xi_1 x_1 \tag{5}$$

The function $y^{(1)}(\xi_1, x_2, \ldots, x_m)$ is called the *first* Legendre transform of $y^{(0)}$ with respect to x_1. In other words, a Legendre transform results in a new function in which one or more independent variables is replaced by its slope. There are obviously m different first transforms depending upon the ordering of the variables $x_1, \ldots, x_m$.

Higher order transforms are defined in a similar manner, thus, $y^{(k)}(\xi_1, \ldots, \xi_k, x_{k+1}, \ldots, x_m)$ is the kth Legendre transform:

$$y^{(k)} = y^{(0)} - \sum_{i=1}^{k} \xi_i x_i \tag{6}$$

and $y^{(m)}(\xi_1, \ldots, \xi_m)$ is the total Legendre transform of $y^{(0)}$:

$$y^{(m)} = y^{(0)} - \sum_{i=1}^{m} \xi_i x_i \tag{7}$$

The differential of $y^{(0)}$ can be expressed as

$$dy^{(0)} = \sum_{i=1}^{m} \xi_i dx_i \tag{8}$$

and the differential of the kth transform can be obtained by differentiating Equation (6) and substituting Equation (8) into the result.

$$dy^{(k)} = -\sum_{i=1}^{k} x_i d\xi_i + \sum_{i=k+1}^{m} \xi_i dx_i \tag{9}$$

Since $y^{(k)}$ is a function of $\xi_1, \ldots, \xi_k, x_{k+1}, \ldots, x_m$, it follows from Equation (9) that for the transformed variables $(1 \leq i \leq k)$,

$$\left(\frac{\partial y^{(k)}}{\partial \xi_i}\right)_{\xi_1,..[\xi_i]..,\xi_k,x_{k+1},\ldots,x_m} = -x_i \tag{10}$$

whereas for the untransformed variables $(k < i \leq m)$,

$$\left(\frac{\partial y^{(k)}}{\partial x_i}\right)_{\xi_1,\ldots,\xi_k,x_{k+1},..[x_i]..,x_m} = \xi_i \tag{11}$$

Equation (10) is sometimes called the *inverse* Legendre transform. Equation (11) is applicable for all cases where $i > k$, and thus one may generalize the result as

$$\frac{\partial y^{(i-1)}}{\partial x_i} = \frac{\partial y^{(i-2)}}{\partial x_i} = \ldots \frac{\partial y^{(0)}}{\partial x_i} = \xi_i \tag{12}$$

The partial derivatives in Equation (12) were expressed without indicating the set of variables to be held constant. However, it is clear from the discussion above that the degree of the transform determines the set, and the only exception would be that variable used in the actual differentiation. For example, the restraints on the term $(\partial y^{(i-1)}/\partial x_i)$ would be that $\xi_1, \ldots, \xi_{i-1}, x_{i+1}, \ldots, x_m$ would be held constant.

To illustrate the application of these relations, let $y^{(0)}$ be the total internal energy of a system $\underline{U}$; then the Fundamental Equation of classical thermodynamics would be given in Equation (1). Suppose we desired the transform $y^{(2)}$ where

$$y^{(2)} = f(\xi_S, \xi_V, N_1, \ldots, N_n) \tag{13}$$

with

$$\xi_S \equiv (\partial \underline{U}/\partial \underline{S})_{\underline{V},N} = T \tag{14}$$

$$\xi_V \equiv (\partial \underline{U}/\partial \underline{V})_{\underline{S},N} = -P \tag{15}$$

then, with Equation (6)

$$y^{(2)} = \underline{U} - T\underline{S} - (-P\underline{V}) \equiv \underline{G} \tag{16}$$

where $\underline{G}$ is the total Gibbs free energy. The analogs of Equations (8) and (9) follow immediately:

$$d\underline{U} = Td\underline{S} - Pd\underline{V} + \sum_{i=1}^{n} \mu_i dN_i \tag{17}$$

$$dy^{(2)} = d\underline{G} = -\underline{S}dT + \underline{V}dP + \sum_{i=1}^{n} \mu_i dN_i \tag{18}$$

where the chemical potential μ_i is defined as

$$\mu_i \equiv (\partial \underline{U}/\partial N_i)_{\underline{S},\underline{V},N_1,\ldots[N_i]\ldots,N_n} \tag{19}$$

$$= (\partial \underline{G}/\partial N_i)_{T,P,N_1,\ldots[N_i]\ldots,N_n} \tag{20}$$

The significance of the Legendre transform is thus evident. The important thermodynamic property $\underline{G}$ is simply a partial Legendre transform of the energy $\underline{U}$ from $(\underline{S}, \underline{V}, N_1, \ldots, N_n)$ space to $(T, P, N_1, \ldots, N_n)$ space. Equation (18) is also a Fundamental Equation and no loss in information content has resulted in the transform from the $\underline{U}$ to the $\underline{G}$ representation.*

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* The symbol $[x_i]$ in the subscript of the partial derivative indicates that x_i is not held constant.

* The interested reader can readily apply the total transform, Equation (7) to Equation (1) and show that the well-known Gibbs-Duhem equation results.

Ordering of Variables and Conjugate Coordinates

It is important to note certain generalities in the use of Legendre transformations. We began with a general functional equation [Equation (2)] with an arbitrary ordering of $x_1, \ldots, x_m$. We noted that for each x_i there was a conjugate coordinate variable, ξ_i [Equation (3)]. We then illustrated that one could readily derive a functional relation with the same information content wherein we replaced independent variables $x_1, \ldots, x_k$ by $\xi_1, \ldots, \xi_k$. This was the kth Legendre transform defined in Equation (6) and shown in differential form in Equation (9).

The point of interest here is that one may now redefine this kth Legendre transform as the $y^{(0)}$ basic function if care is given in defining the correct independent variables and conjugate coordinates. For example, we have shown above that beginning with Equation (1), we obtained the Gibbs free energy potential function by a Legendre transform of $\underline{U}$ into $T, P, N_1, \ldots, N_n$ space. We could now use the Gibbs free energy function as our basic function $y^{(0)}$, but the independent variable set $(x_1, \ldots, x_m)$ would be $(T, P, N_1, \ldots, N_n)$ with arbitrary ordering. The conjugate coordinate variables $\xi_1, \ldots, \xi_m$ would still be defined by Equation (3), for example, for the variable T, $\xi_T = (\partial \underline{G}/\partial T)_{P,N} = -\underline{S}$; for P, $\xi_P = \underline{V}$, and for N_j, $\xi_j = \mu_j$.

In fact we may select any Legendre transform as the basic $y^{(0)}$ function by redefining the independent variable set. This very useful technique is utilized later when relating partial derivatives of different transforms.

RELATIONSHIPS BETWEEN PARTIAL DERIVATIVES OF LEGENDRE TRANSFORMS

Single Variable Transforms

Starting with Equation (2), we wish to investigate the relations between derivatives of $y^{(0)}$ and the first transform $y^{(1)}$, where

$$y^{(1)} = f(\xi_1, x_2, \ldots, x_m) \tag{21}$$

$$\xi_1 = (\partial y^{(0)}/\partial x_1)_{x_2,\ldots,x_m} \tag{22}$$

There are several ways to obtain the desired results but the most expeditious involves the use of the derivative operators $(\partial/\partial x_i)_{\xi_1, x_2, \ldots [x_i] \ldots, x_m}$, $i > 1$, and $(\partial/\partial \xi_1)_{x_2,\ldots,x_m}$

As proved in Appendix I,[*]

$$\left(\frac{\partial}{\partial x_i}\right)_{\xi_1, x_2, \ldots [x_i] \ldots, x_m} = \left(\frac{\partial}{\partial x_i}\right)_{x_1, \ldots [x_i] \ldots, x_m} - \left[\frac{y^{(0)}_{1i}}{y^{(0)}_{11}}\right]\left(\frac{\partial}{\partial x_1}\right)_{x_2,\ldots,x_m} \quad (i \neq 1) \tag{23}$$

and

$$\left(\frac{\partial}{\partial \xi_1}\right)_{x_2,\ldots,x_m} = \frac{1}{y^{(0)}_{11}}\left(\frac{\partial}{\partial x_1}\right)_{x_2,\ldots,x_m} \tag{24}$$

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[*] Appendices I and II have been deposited as Document No. 02493 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 305 E. 46 St., N. Y., N. Y. 10017 and may be obtained for $1.50 for microfiche or $5.00 for photocopies.

TABLE 1. SECOND- AND THIRD-ORDER DERIVATIVES OF $y^{(1)}$ IN TERMS OF $y^{(0)}$

Derivative in $y^{(1)}$ system	Derivative in $y^{(0)}$ system	Quantity operated upon	Equation used
$y^{(1)}_{11}$	$-\dfrac{1}{y^{(0)}_{11}}$	$y^{(1)}_{1}$	24
$y^{(1)}_{1i}$	$\dfrac{y^{(0)}_{1i}}{y^{(0)}_{11}} \quad (i \neq 1)$	$y^{(1)}_{i}$	24
$y^{(1)}_{ij}$	$y^{(0)}_{ij} - \dfrac{y^{(0)}_{1i} y^{(0)}_{1j}}{(y^{(0)}_{11})} \quad (i, j \neq 1)$	$y^{(1)}_{j}$	23
$y^{(1)}_{111}$	$\dfrac{y^{(0)}_{111}}{(y^{(0)}_{11})^3}$	$y^{(1)}_{11}$	24
$y^{(1)}_{11i}$	$\dfrac{y^{(0)}_{11i}}{(y^{(0)}_{11})^2} - \dfrac{y^{(0)}_{111} y^{(0)}_{1i}}{(y^{(0)}_{11})^3} \quad (i > 1)$	$y^{(1)}_{1i}$	24
$y^{(1)}_{1ij}$	$\dfrac{y^{(0)}_{1ij}}{y^{(0)}_{11}} - \left\{\dfrac{y^{(0)}_{11i} y^{(0)}_{1j} + y^{(0)}_{11j} y^{(0)}_{1i}}{(y^{(0)}_{11})^2}\right\} + \dfrac{y^{(0)}_{111} y^{(0)}_{1i} y^{(0)}_{1j}}{(y^{(0)}_{11})^3} \quad (i, j \neq 1)$	$y^{(1)}_{ij}$	24
$y^{(1)}_{ijk}$	$y^{(0)}_{ijk} - \dfrac{(y^{(0)}_{1i} y^{(0)}_{1jk} + y^{(0)}_{1j} y^{(0)}_{1ik} + y^{(0)}_{1k} y^{(0)}_{1ij})}{y^{(0)}_{11}}$ $+ \dfrac{(y^{(0)}_{1i} y^{(0)}_{1j} y^{(0)}_{11k} + y^{(0)}_{1i} y^{(0)}_{1k} y^{(0)}_{11j} + y^{(0)}_{1j} y^{(0)}_{1k} y^{(0)}_{11i})}{(y^{(0)}_{11})^2}$ $- \dfrac{y^{(0)}_{1i} y^{(0)}_{1j} y^{(0)}_{1k} y^{(0)}_{111}}{(y^{(0)}_{11})^3} \quad (i, j, k \neq 1)$	$y^{(1)}_{jk}$	23

TABLE 2. RELATIONS BETWEEN DERIVATIVES IN THE ENERGY AND HELMHOLTZ FREE ENERGY SYSTEMS

Derivatives in the energy system

$y^{(0)}$		$\underline{U}$
$y^{(0)}_1$	U_S	$= T$
$y^{(0)}_2$	U_V	$= -P$
$y^{(0)}_3$	U_N	$= \mu$
$y^{(0)}_{11}$	U_{SS}	$= (\partial T/\partial \underline{S})_{\underline{V},N}$
$y^{(0)}_{12} = y^{(0)}_{21}$	U_{SV}	$= (\partial T/\partial \underline{V})_{\underline{S},N} = -(\partial P/\partial \underline{S})_{\underline{V},N}$
$y^{(0)}_{13} = y^{(0)}_{31}$	U_{SN}	$= (\partial T/\partial N)_{\underline{S},\underline{V}} = (\partial \mu/\partial \underline{S})_{\underline{V},N}$
$y^{(0)}_{22}$	U_{VV}	$= -(\partial P/\partial V)_{\underline{S},\underline{N}}$
$y^{(0)}_{23} = y^{(0)}_{32}$	U_{VN}	$= -(\partial P/\partial N)_{\underline{S},\underline{V}} = (\partial \mu/\partial \underline{V})_{\underline{S},N}$
$y^{(0)}_{33}$	U_{NN}	$= (\partial \mu/\partial N)_{\underline{S},\underline{V}}$
$y^{(0)}_{111}$	U_{SSS}	$= (\partial^2 T/\partial \underline{S}^2)_{\underline{V},N}$
$y^{(0)}_{112} = y^{(0)}_{121} = y^{(0)}_{211}$	U_{SSV}	$= (\partial^2 T/\partial \underline{S}\partial \underline{V}) = -(\partial^2 P/\partial \underline{S}^2)_{\underline{V},N}$
$y^{(0)}_{122} = y^{(0)}_{212} = y^{(0)}_{221}$	U_{SVV}	$= (\partial^2 T/\partial \underline{V}^2)_{\underline{S},N} = -(\partial P/\partial \underline{S}\partial \underline{V})$
$y^{(0)}_{222}$	U_{VVV}	$= -(\partial^2 P/\partial \underline{V}^2)_{\underline{S},N}$
$y^{(0)}_{113} = y^{(0)}_{131} = y^{(0)}_{311}$	U_{SSN}	$= (\partial^2 T/\partial \underline{S}\partial N) = (\partial^2 \mu/\partial \underline{S}^2)_{\underline{V},N}$
$y^{(0)}_{133} = y^{(0)}_{313} = y^{(0)}_{331}$	U_{SNN}	$= (\partial^2 T/\partial N^2)_{\underline{S},\underline{V}} = (\partial^2 \mu/\partial \underline{S}\partial N)$
$y^{(0)}_{333}$	U_{NNN}	$= (\partial^2 \mu/\partial N^2)_{\underline{S},\underline{V}}$
$y^{(0)}_{223} = y^{(0)}_{232} = y^{(0)}_{322}$	U_{VVN}	$= -(\partial^2 P/\partial \underline{V}\partial N) = (\partial^2 \mu/\partial \underline{V}^2)_{\underline{S},N}$
$y^{(0)}_{233} = y^{(0)}_{323} = y^{(0)}_{332}$	U_{VNN}	$= -(\partial^2 P/\partial N^2)_{\underline{S},\underline{V}} = (\partial^2 \mu/\partial \underline{V}\partial N)$

Derivatives in the Helmholtz free energy system

$y^{(1)}$		$\underline{A}$
$y^{(1)}_1$	A_T	$= -\underline{S}$
$y^{(1)}_2$	A_V	$= -P$
$y^{(1)}_3$	A_N	$= \mu$
$y^{(1)}_{11}$	A_{TT}	$= -(\partial \underline{S}/\partial T)_{\underline{V},N}$
$y^{(1)}_{12} = y^{(1)}_{21}$	A_{TV}	$= -(\partial \underline{S}/\partial \underline{V})_{T,N} = -(\partial P/\partial T)_{\underline{V},N}$
$y^{(1)}_{13} = y^{(1)}_{31}$	A_{TN}	$= -(\partial \underline{S}/\partial N)_{T,\underline{V}} = (\partial \mu/\partial T)_{\underline{V},N}$
$y^{(1)}_{22}$	A_{VV}	$= -(\partial P/\partial \underline{V})_{T,N}$
$y^{(1)}_{23} = y^{(1)}_{32}$	A_{VN}	$= -(\partial P/\partial N)_{T,\underline{V}} = (\partial \mu/\partial \underline{V})_{T,N}$
$y^{(1)}_{33}$	A_{NN}	$= (\partial \mu/\partial N)_{T,\underline{V}}$
$y^{(1)}_{111}$	A_{TTT}	$= -(\partial^2 \underline{S}/\partial T^2)_{\underline{V},N}$
$y^{(1)}_{112} = y^{(1)}_{121} = y^{(1)}_{211}$	A_{TTV}	$= -(\partial^2 \underline{S}/\partial T\partial \underline{V}) = -(\partial^2 P/\partial T^2)_{\underline{V},N}$
$y^{(1)}_{122} = y^{(1)}_{212} = y^{(1)}_{221}$	A_{TVV}	$= -(\partial^2 \underline{S}/\partial \underline{V}^2)_{T,N} = -(\partial^2 P/\partial T\partial \underline{V})$
$y^{(1)}_{222}$	A_{VVV}	$= -(\partial^2 P/\partial \underline{V}^2)_{T,N}$
$y^{(1)}_{113} = y^{(1)}_{131} = y^{(1)}_{311}$	A_{TTN}	$= -(\partial^2 \underline{S}/\partial T\partial N) = (\partial^2 \mu/\partial T^2)_{\underline{V},N}$
$y^{(1)}_{133} = y^{(1)}_{313} = y^{(1)}_{331}$	A_{TNN}	$= -(\partial^2 S/\partial N^2)_{T,\underline{V}} = (\partial^2 \mu/\partial T\partial N)$
$y^{(1)}_{333}$	A_{NNN}	$= (\partial^2 \mu/\partial N^2)_{T,\underline{V}}$
$y^{(1)}_{223} = y^{(1)}_{232} = y^{(1)}_{322}$	A_{VVN}	$= -(\partial^2 P/\partial \underline{V}\partial N) = (\partial^2 \mu/\partial \underline{V}^2)_{T,N}$
$y^{(1)}_{233} = y^{(1)}_{323} = y^{(1)}_{332}$	A_{VNN}	$= -(\partial^2 P/\partial N^2)_{T,\underline{V}} = (\partial^2 \mu/\partial \underline{V}\partial N)$

Example: Relation of A_{TTV} to derivatives of $\underline{U}$

A_{TTV} is of the form of $y^{(1)}_{112}$. From Table 1,

$$y^{(1)}_{112} = \frac{y^{(0)}_{112}}{(y^{(0)}_{11})^2} - \frac{y^{(0)}_{111}y^{(0)}_{12}}{(y^{(0)}_{11})^3}$$

From the relations given above:

$$A_{TTV} = \frac{U_{SSV}}{U^2_{SS}} - \frac{U_{SSS}U_{SV}}{U^3_{SS}}$$

or

$$-(\partial^2 \underline{S}/\partial T\partial \underline{V}) = -(\partial^2 P/\partial T^2) = \frac{(\partial^2 T/\partial \underline{S}\partial \underline{V})}{(\partial T/\partial \underline{S})^2} - \frac{(\partial^2 T/\partial \underline{S}^2)(\partial T/\partial \underline{V})}{(\partial T/\partial \underline{S})^3}$$

The terms $y^{(0)}_{1i}$ and $y^{(0)}_{11}$ are second-order derivatives:

$$y^{(0)}_{1i} \equiv (\partial^2 y^{(0)}/\partial x_1 \partial x_i) \tag{25}$$

$$y^{(0)}_{11} = (\partial^2 y^{(0)}/\partial x_1^2) \tag{26}$$

Equations (23) and (24) are of little value to obtain first derivatives since, in view of Equations (10) and (11),

$$\left(\frac{\partial y^{(1)}}{\partial \xi_1}\right)_{x_2,\ldots,x_m} \equiv y_1^{(1)} = -x_1 \tag{27}$$

$$\left(\frac{\partial y^{(1)}}{\partial x_i}\right)_{\xi_1,x_2\ldots[x_i]\ldots,x_m} = y_i^{(1)} = y_i^{(0)} = \xi_i \quad (i > 1) \tag{28}$$

However, to relate, for example, $y^{(1)}_{1i}$, to second-order derivatives of $y^{(0)}$, one can employ the operator equation [Equation (24)] on $y_i^{(1)}$.

$$\left(\frac{\partial y_i^{(1)}}{\partial \xi_1}\right)_{x_2,\ldots,x_m} \equiv y^{(1)}_{1i} = \frac{1}{y^{(0)}_{11}}\left(\frac{\partial y_i^{(1)}}{\partial x_1}\right)_{x_2,\ldots,x_m}$$

$$= \frac{1}{y^{(0)}_{11}}\left(\frac{\partial y_i^{(0)}}{\partial x_1}\right)_{x_2,\ldots,x_m} = \frac{y^{(0)}_{1i}}{y^{(0)}_{11}} \quad (i \neq 1) \tag{29}$$

where Equation (12) was used to simplify the third step. In a similar manner, other second- and third-order derivatives may be readily transformed. A list of these is presented in Table 1.

To illustrate the use of the relations in Table 1, let

$$y^{(0)}(x_1, x_2, x_3) = U(\underline{S}, \underline{V}, N)$$

where $\underline{U}$, $\underline{S}$, $\underline{V}$, N are, respectively, the *total* energy, entropy, volume, and moles in a one-component system. Then, if we make a single transformation of x_1 to ξ_1, that is, $\underline{S}$ to T,

$$y^{(1)}(\xi_1, x_2, x_3) = y^{(0)} - \xi_1 x_1 = U - T\underline{S} = \underline{A}(T, \underline{V}, N) \tag{30}$$

where, of course, $\underline{A}$ is the total Helmholtz free energy. The various derivatives of $\underline{U}$ and $\underline{A}$ are shown on Table 2. Also, to illustrate the combination of Tables 1 and 2, one example is shown, that is, how A_{TTV} is related to derivatives of $\underline{U}$.

MULTIPLE VARIABLE TRANSFORMS

The development shown above was, of course, limited to the case where only a single variable was transformed. Should one wish to transform more than a single variable, it is always possible to proceed a step-at-a-time and transform each variable separately as was shown above. It is, however, not difficult to develop a more general technique to allow one to express the partial derivatives of a Legendre transform $y^{(j)}(\xi_1, \ldots, \xi_j, x_{j+1}, \ldots, x_m)$ in terms of $y^{(0)}$. We indicate the final equations in Table 3 and show the derivations of the relations in Appendix II. Only second-order partial derivatives are considered. Extending the method to third-order terms is not difficult, but it is somewhat tedious.

Should we desire to relate derivatives of $y^{(j)}$ to a lower order transform $y^{(r)}$, $0 < r < j$, we may use the technique discussed earlier, that is, we define $y^{(r)}$ as the basic function $y^{(0)}$ and examine which variables are to be transformed between $y^{(j)}$ and $y^{(r)}$. These are, obviously $(j - r)$ in number. An example would best illustrate the idea. Suppose $y^{(j)}$ were the Legendre transform of Equation (1)

TABLE 3. RELATIONS BETWEEN SECOND-ORDER DERIVATIVES OF THE *j*-TH LEGENDRE TRANSFORM AND THE BASIC FUNCTION

$$y_{ik}^{(j)} = \frac{\begin{vmatrix} y_{11}^{(0)} & \cdots & y_{1j}^{(0)} & y_{1k}^{(0)} \\ \vdots & & \vdots & \vdots \\ y_{j1}^{(0)} & \cdots & y_{jj}^{(0)} & y_{jk}^{(0)} \\ y_{i1}^{(0)} & \cdots & y_{ij}^{(0)} & y_{ik}^{(0)} \end{vmatrix}}{\Theta_j} \quad \begin{matrix} i > j \\ k > j \end{matrix} \qquad (31)^{*}$$

$$y_{ik}^{(j)} = \frac{\begin{vmatrix} y_{11}^{(0)} & \cdots & y_{1(i-1)}^{(0)} & y_{1(i+1)}^{(0)} & \cdots & y_{1j}^{(0)} & y_{1k}^{(0)} \\ \vdots & & \vdots & \vdots & & \vdots & \vdots \\ y_{(i-1)1}^{(0)} & \cdots & y_{(i-1)(i-1)}^{(0)} & y_{(i-1)(i+1)}^{(0)} & \cdots & y_{(i-1)j}^{(0)} & y_{(i-1)k}^{(0)} \\ y_{(i+1)1}^{(0)} & \cdots & y_{(i+1)(i-1)}^{(0)} & y_{(i+1)(i+1)}^{(0)} & \cdots & y_{(i+1)j}^{(0)} & {}_{(i+1)k} \\ \vdots & & \vdots & \vdots & & \vdots & \vdots \\ y_{j1}^{(0)} & \cdots & y_{j(i-1)}^{(0)} & y_{j(i+1)}^{(0)} & \cdots & y_{jj}^{(0)} & y_{jk}^{(0)} \\ y_{i1}^{(0)} & \cdots & y_{i(i-1)}^{(0)} & y_{i(i+1)}^{(0)} & \cdots & y_{ij}^{(0)} & y_{ik}^{(0)} \end{vmatrix}}{\Theta_j} \quad \begin{matrix} i \leq j \\ k > j \end{matrix} \qquad (32)^{*}$$

$$y_{ii}^{(j)} = -\frac{\begin{vmatrix} y_{11}^{(0)} & \cdots & y_{1(i-1)}^{(0)} & y_{1(i+1)}^{(0)} & \cdots & y_{1j}^{(0)} \\ \vdots & & \vdots & \vdots & & \vdots \\ y_{(i-1)1}^{(0)} & \cdots & y_{(i-1)(i-1)}^{(0)} & y_{(i-1)(i+1)}^{(0)} & \cdots & y_{(i-1)j}^{(0)} \\ y_{(i+1)1}^{(0)} & \cdots & y_{(i+1)(i-1)}^{(0)} & y_{(i+1)(i+1)}^{(0)} & \cdots & y_{(i+1)j}^{(0)} \\ \vdots & & \vdots & \vdots & & \vdots \\ y_{j1}^{(0)} & & y_{j(i-1)}^{(0)} & y_{j(i+1)}^{(0)} & & y_{jj}^{(0)} \end{vmatrix}}{\Theta_j} \quad j \geq i \qquad (33)^{*}$$

$$y_{ik}^{(j)} = \frac{\begin{vmatrix} y_{11}^{(0)} & & y_{1(i-1)}^{(0)} & y_{1(i+1)}^{(0)} & \cdots & y_{1(k-1)}^{(0)} & y_{1(k+1)}^{(0)} & \cdots & y_{1j}^{(0)} & y_{1k}^{(0)} \\ \vdots & & \vdots & \vdots & & \vdots & \vdots & & \vdots & \vdots \\ y_{(i-1)1}^{(0)} & \cdots & y_{(i-1)(i-1)}^{(0)} & y_{(i-1)(i+1)}^{(0)} & \cdots & y_{(i-1)(k-1)}^{(0)} & y_{(i-1)(k+1)}^{(0)} & \cdots & y_{(i-1)j}^{(0)} & y_{(i-1)k}^{(0)} \\ y_{(i+1)1}^{(0)} & \cdots & y_{(i+1)(i-1)}^{(0)} & y_{(i+1)(i+1)}^{(0)} & \cdots & y_{(i+1)(k-1)}^{(0)} & y_{(i+1)(k+1)}^{(0)} & \cdots & y_{(i+1)j}^{(0)} & y_{(i+1)k}^{(0)} \\ \vdots & & \vdots & \vdots & & \vdots & \vdots & & \vdots & \vdots \\ y_{(k-1)1}^{(0)} & \cdots & y_{(k-1)(i-1)}^{(0)} & y_{(k-1)(i+1)}^{(0)} & \cdots & y_{(k-1)(k-1)}^{(0)} & y_{(k-1)(k+1)}^{(0)} & \cdots & y_{(k-1)j}^{(0)} & y_{(k+1)k}^{(0)} \\ y_{(k+1)1}^{(0)} & \cdots & y_{(k+1)(i-1)}^{(0)} & y_{(k+1)(i+1)}^{(0)} & \cdots & y_{(k+1)(k-1)}^{(0)} & y_{(k+1)(k+1)}^{(0)} & \cdots & y_{(k+1)j}^{(0)} & y_{(k+1)k}^{(0)} \\ \vdots & & \vdots & \vdots & & \vdots & \vdots & & \vdots & \vdots \\ y_{j1}^{(0)} & \cdots & y_{j(i-1)}^{(0)} & y_{j(i+1)}^{(0)} & \cdots & y_{j(k-1)}^{(0)} & y_{j(k+1)}^{(0)} & \cdots & y_{jj}^{(0)} & y_{jk}^{(0)} \\ y_{i1}^{(0)} & \cdots & y_{i(i-1)}^{(0)} & y_{i(i+1)}^{(0)} & \cdots & y_{i(k-1)}^{(0)} & y_{i(k+1)}^{(0)} & \cdots & y_{ij}^{(0)} & y_{ik}^{(0)} \end{vmatrix}}{\Theta_j} \quad j \geq k > i$$

$$(34)^{*}$$

$$\Theta_j = \begin{vmatrix} y_{11}^{(0)} & y_{12}^{(0)} & \cdots & y_{1j}^{(0)} \\ y_{21}^{(0)} & y_{22}^{(0)} & \cdots & y_{2j}^{(0)} \\ \vdots & \vdots & & \vdots \\ y_{j1}^{(0)} & y_{j2}^{(0)} & & y_{jj}^{(0)} \end{vmatrix} \qquad (35)$$

* Note that the rank of the determinants in Equations (31) through (34) are, respectively, $j + 1$, j, $j - 1$, and $j - 1$.

into T, P, μ_1, N_2, ..., N_n space. No common name has been assigned this function; we shall call it $\underline{G}'$.

$$\underline{G}' = f(T, P, \mu_1, N_2, \ldots, N_n) \tag{36}$$

Suppose we wished to relate the derivatives of $\underline{G}'$ to those of the Helmholtz free energy $\underline{A}$ as given by Equation (30),

$$\underline{A} = f(T, \underline{V}, N_1, \ldots, N_n) \tag{37}$$

We note that the common independent variables are T, N_2, ..., N_n. $\underline{A}$ and $\underline{G}'$ differ only in transformations between P and $\underline{V}$ and between μ_1 and N_1. We can select either $\underline{A}$ or $\underline{G}'$ as the $y^{(0)}$ function. If we choose $\underline{A}$, then we should reorder the variables as

$$y^{(0)} = \underline{A} = f(x_1, x_2, \ldots, x_m) = f(\underline{V}, N_1, \ldots, N_n, T) \tag{38}$$

and then

$$\begin{aligned} y^{(2)} = \underline{G}' &= f(\xi_1, \xi_2, x_3, \ldots, x_m) \\ &= f(P, \mu_1, N_2, \ldots, N_n, T) \end{aligned} \tag{39}$$

where

$$\xi_1 = (\partial y^{(0)}/\partial x_1) = (\partial \underline{A}/\partial \underline{V}) = -P$$

$$\xi_2 = (\partial y^{(0)}/\partial x_2) = (\partial \underline{A}/\partial N_1) = \mu_1$$

and x_3 through x_{m-1} correspond to N_2 through N_n and x_m corresponds to T. With this formulation the partial derivatives of $y^{(j)}$, $j \doteq 2$ can be related to derivatives of $y^{(0)}$ or in the example $\underline{G}'$ to $\underline{A}$.

RESTRUCTURING OF THERMODYNAMICS TRANSFORMS

Beginning with Equation (1), we can now easily transform one or all of the independent variable set $\underline{S}$, $\underline{V}$, N_1, ..., N_n. Let us choose only the variable $\underline{V}$ and reorder so that $\underline{V}$ represents x_1. Then

$$y^{(1)} = y^{(0)} - \xi_1 x_1 = \underline{U} - (-P)\underline{V} = \underline{U} + P\underline{V} = \underline{H} \tag{40}$$

where this particular Legendre transform is usually called the *enthalpy*. We note that

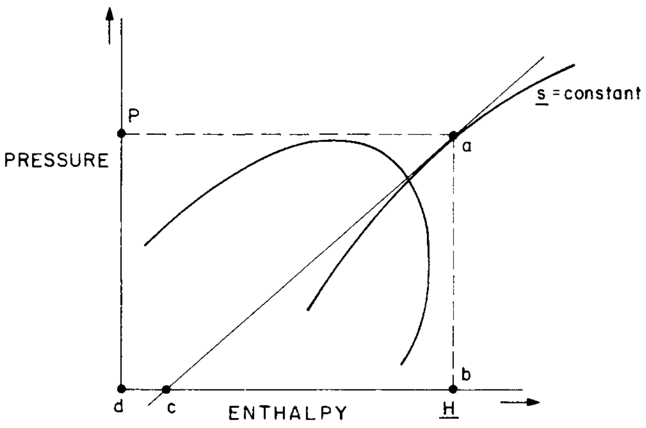
$$\underline{H} = f(P, \underline{S}, N_1, \ldots, N_n) \tag{41}$$

We call Equation (41) a Fundamental Equation in the same way we refer to Equation (1); then P is x_1, $\underline{S}$ is x_2, etc. and $\xi_1 = (\partial \underline{H}/\partial P) = \underline{V}$. We can recover Equation (1) by carrying out a Legendre transform assuming Equation (41) is the $y^{(0)}$ function, that is,

$$y^{(1)} = y^{(0)} - \xi_1 x_1 = \underline{H} - (\underline{V})P = \underline{U} \tag{42}$$

This transform can be readily shown in Figure 1 for a common pressure-enthalpy diagram. If a curve of constant entropy is considered, the slope is ξ_1^{-1} or $1/\underline{V}$. The intercept of this tangent on the enthalpy axis is, as shown, equal to the internal energy $\underline{U}$.

With internal energy as the basic function, there are $n + 2$ permutations of first Legendre transforms: the two common functions, $H(P, \underline{S}, N_1, \ldots, N_n)$ and $A(T, \underline{V}, N_1, \ldots, N_n)$, and n other functions for the independent variable set of $\underline{S}$, $\underline{V}$, N_1, ..., N_{i-1}, μ_i, N_{i+1}, ..., N_n. Since the ordering of components is arbitrary, we shall refer to the n functions as $U'(\underline{S}, \underline{V}, \mu_1, N_2, \ldots, N_n)$. In a similar manner, there are $(n + 2)(n + 1)/2$ second Legendre transforms: one is the Gibbs free energy, $G(T, P, N_1, \ldots, N_n)$; there are n of the form $A'(T, \mu_1, \underline{V}, N_2, \ldots, N_n)$ and n of the form $H'(P, \mu_1, \underline{S}, N_2, \ldots, N_n)$, and $(n)(n - 1)/2$ of the form $U''(\mu_1, \mu_2, \underline{S}, \underline{V}, N_3, \ldots, N_n)$. Third Legendre transforms would involve G', A'', H'', and U''' potential functions.



$$(\partial \underline{H}/\partial P)_{\underline{S}} = \underline{V} = \overline{cb}/\overline{ab} \; ; \; \overline{ab} = P$$

$$\therefore \; \overline{cb} = P\underline{V}$$

$$\overline{dc} = \overline{db} - \overline{cb} = \underline{H} - P\underline{V} = \underline{U}$$

Fig. 1. An example of a Legendre transform for a pure material.

CONCLUDING REMARKS

Legendre transform theory relates the useful thermodynamic potential functions such as free energy, enthalpy, etc. The definition of these functions is unique and necessary in order to work in the desired set of variables. The power of the Fundamental Equation, $\underline{U} = U(\underline{S}, \underline{V}, N_1, \ldots, N_n)$ is not diluted when Legendre transforms are employed since each contains the same information content.

It has also been demonstrated that partial derivatives of a potential function can be expressed in terms of derivatives of the various transforms. These relations between partial derivatives are useful when it is necessary or expedient to switch from one set of independent variables to another. They will also be shown to be of considerable value when, in subsequent papers, we develop generalized thermodynamic relations to describe stable, metastable, unstable, and critical states.

NOTATION

$\underline{A}$ = total Helmholtz free energy
$\underline{C}_p$ = heat capacity at constant pressure
$\underline{G}$ = total Gibbs free energy
$\underline{H}$ = total enthalpy
$\underline{N}$ = total moles (or mass)
N_j = moles of component j
P = pressure $\equiv -(\partial \underline{U}/\partial \underline{V})_{\underline{S},N}$
$\underline{S}$ = total entropy
T = temperature $\equiv (\partial \underline{U}/\partial \underline{S})_{\underline{V},N}$
$\underline{U}$ = total internal energy
$\underline{V}$ = total volume
x_j = independent variable in the Fundamental Equation
$y^{(0)}$ = dependent variable in the basic Fundamental Equation $= f(x_1, \ldots, x_m)$

$y^{(j)}$ = jth Legendre transform of the Fundamental Equation $= f(\xi_1, \ldots, \xi_j, x_{j+1}, \ldots, x_m)$

$y_k^{(j)}$ = first-order partial derivative of the jth Legendre transform with respect to x_k (if $k > j$) or ξ_k (if $k \leq j$)

$y^{(j)}_{ik}$ = second-order partial derivative of $y^{(j)}$ with respect to either $x_i (i > j)$ or $\xi_i (i \leq j)$ and $x_k (k > j)$ or $\xi_k (k \leq j)$

μ_j = chemical potential of component j $\equiv (\partial \underline{U}/\partial N_j)_{\underline{S},\underline{V},N_1,..[N_j]..,N_n}$

ξ_k = $(\partial y^{(0)}/\partial x_k)_{x_1,..[x_k]..,x_m}$ or $(\partial y^{(j)}/\partial x_k)_{\xi_1,\ldots,\xi_j,x_{j+1},..[x_k]..,x_m}$ if $k > j$

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Thermodynamic Stability Criterion for Pure Substances and Mixtures

Criteria are derived to specify the limit of stability for pure material and multicomponent thermodynamic systems. Through the use of Legendre transforms, the criteria may be expressed in a very simple form that only involves the determination of positiveness of a single second-order partial derivative of a potential function. Alternate and equivalent criteria are shown to result from a simple reordering of the independent variables in the Fundamental Equation of Gibbs. Certain criteria that are often stated as necessary conditions of stability (for example, $C_v > 0$) are shown to be insufficient for specifying the *limit* of stability; that is, a system will always become unstable for other reasons before C_v can attain a negative value.

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SCOPE

Thermodynamic systems are often categorized as being stable or unstable. The latter, by definition, cannot exist and must undergo a change to one or more stable phases. Of interest here are the criteria (or criterion) which one may use to track a stable system as it approaches an unstable state, the cross-over condition being defined as the limit of stability.

The basic concept is that an isolated system in stable equilibrium possesses the maximum possible entropy or, equivalently, the least energy (at constant entropy). By a series expansion around the state variables, inequalities can be developed to indicate whether or not a system is indeed in stable equilibrium or, more importantly, under what conditions would a given system be expected to reach the stability limit.

These inequalities are developed in their general form and use is made of Legendre transform theory to simplify the resulting inequalities.

CONCLUSIONS AND SIGNIFICANCE

For a n-component system, it is shown that a single criterion sufficies to define the stability limit. This criterion is

$$y^{(n)}_{(n+1)(n+1)} \begin{cases} > 0 & \text{(stable systems)} \\ = 0 & \text{(at the limit of stability)} \end{cases}$$

Here, $y^{(n)}$ is the nth Legendre transform and $y^{(n)}_{(n+1)(n+1)}$ represents the second-order partial derivative of $y^{(n)}$ with respect to the $n + 1$ variable (see Beegle et al., 1974). For a pure component system ($n = 1$), the energy is a function of the entropy, volume, and mass. Depending upon the ordering of these variables, six equivalent criteria can be written from the relation given above (see Table 1). The most common of these is $-(\partial P/\partial \underline{V})_{T,N} > 0$. It is shown that other cited criteria (for example, $C_v > 0$), although necessary for stable states, are not sufficient criteria to determine the limit of stability.

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