Metric geometry of equilibrium thermodynamics. IV. Vector-algebraic evaluation of thermodynamic derivatives

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A new set of procedures is given for the systematic evaluation of thermodynamic derivatives by vector-algebraic means. The new procedures are at once simpler and more general than previously available methods, and require no special tables. General thermodynamic derivatives are evaluated for the familiar one-component homogeneous fluid (where the techniques are extensively illustrated) and for multicomponent systems of arbitrary complexity.

I. INTRODUCTION

The systematic derivation of partial thermodynamic derivatives has been a long-standing problem of considerable scientific and engineering importance. In a typical case, one desires to evaluate some partial derivative which cannot be obtained directly from experimental data, but instead must be calculated from other such derivatives which are known with sufficient precision. Unfortunately, the number of possible equations which can be written among partial derivatives of the common thermodynamic functions is exceedingly large (e.g., of the order 10^{10} for the simplest case of a homogeneous fluid, with dimension $r=2$),[1] so that some form of general and systematic procedure becomes necessary to isolate a particular thermodynamic formula of interest.

An early attack on this problem was made by Bridgman,[2] who presented comprehensive tables[3] from which many possible derivatives for a homogeneous fluid could be evaluated. Such tables subsequently became widely known and used through their incorporation into several standard texts,[4] but they lack the flexibility to deal with all thermodynamic properties which might be of interest (such as, e.g., saturation properties, or properties along any other path in phase space), and they become quite unwieldy when extended to more complex systems.[5]

A more general and elegant method was developed by Shaw[6] which makes use of algebraic properties of *Jacobian* determinants, and which has now largely supplanted the Bridgman tables.[7] The tables required for the Jacobian method are both simpler and more easily constructed than those of Bridgman, and certain possible extensions to higher dimension ($r > 2$) have been discussed.[8] Nevertheless, the available Jacobian tables for $r=3$ show[9] that such methods rapidly lose their attractive simplicity in more complex systems. In addition, these tables again lack the flexibility to deal easily with any but the most common thermodynamic properties.[10]

Several other approaches have been discussed which bring varying degrees of orderliness to thermodynamic derivations while obviating the need for special tables. Such methods may involve special algebraic[11] or procedural[12] prescriptions, the former group often taking indirect advantage of the Jacobian algebra in some simplified form.

In the present work we shall describe a new set of techniques for the evaluation of general thermodynamic derivatives, based upon a vector-algebraic representation of the thermodynamic formalism which was proposed in the preceding papers (Papers I–III).[13–15] The only mathematics required is the ordinary linear algebra of Euclidean vector spaces. It is felt that these new procedures significantly surpass previously available methods in respect to their simplicity, generality, and ease of extension to complex multicomponent systems. In particular, Shaw's method[6] will be found to arise as a special case (by no means the simplest) of the present approach. [Those readers who wish to see how the method works before studying its origins may proceed directly to Eq. (3.11) and accompanying examples.]

II. GENERAL CONSIDERATIONS

Our treatment will be based directly on the geometric representation of equilibrium thermodynamics which was described in Papers I–III.[13–15] The notation and results of those papers will therefore be adopted freely without additional comment, and specific equations will be referred to directly by means of an appropriate roman prefix, e.g., Eq. (III.2.7), etc.

The geometric representation associates an r-dimensional Euclidean vector space $\mathfrak{M}_r$ with a given equilibrium system having r "degrees of freedom" in the sense of Gibbs' phase rule. Thermodynamic variables R_i are associated with corresponding vectors $|\mathcal{R}_i\rangle$ in $\mathfrak{M}_r$ whose scalar products are evaluated in the form

$$\langle \mathcal{R}_i | \mathcal{R}_j \rangle = (\partial R_i / \partial \bar{R}_j)_{\bar{R}}, \tag{2.1}$$

where $\bar{R}_j$ denotes the variable *conjugate* to R_j [Eq. (III.3.3)]. One therefore begins by choosing some basis set of r reference variables $\{R_i\}$ whose associated vectors span the space $\mathfrak{M}_r$, and constructs therefrom the associated *biorthogonal* basis of conjugate vectors $|\bar{\mathcal{R}}_i\rangle$ (the vector representations of the $\bar{R}_i$) which satisfy [Eq. (III.3.1)]

$$\langle \mathcal{R}_i | \bar{\mathcal{R}}_j \rangle = \delta_{ij}\,, \quad i,j=1,2,\ldots,r. \tag{2.2}$$

It is assumed that the $r(r+1)/2$ independent scalar products (2.1) among the basis vectors $|\mathcal{R}_i\rangle$ are known from experiment, and that the associated Gram matrix $\mathbf{G}$,

$$(\mathbf{G})_{ij} = \langle \mathcal{R}_i | \mathcal{R}_j \rangle, \quad i,j=1,2,\ldots,r \tag{2.3}$$

is nonsingular [Eqs. (III.2.13)]. As pointed out in Paper III, $r(r+1)/2$ is the minimum number of independent thermodynamic derivatives from which one could hope to describe all the remaining thermodynamic properties; in many practical applications, the relative experimental accessibility of such derivatives will fix the convenient choice of basis variables R_i in which to carry the analysis forward.

From the $r(r+1)/2$ independent elements of **G**, a further set of $r(r+1)/2$ scalar products (and associated thermodynamic derivatives) among the conjugate vectors $|\bar{\mathcal{R}}_i\rangle$ are found by inverting the Gram matrix **G** [Eq. (III.3.10)],

$$(\mathbf{G}^{-1})_{ij} = \langle \bar{\mathcal{R}}_i | \bar{\mathcal{R}}_j \rangle = (\partial \bar{R}_i / \partial R_j)_{\mathbf{R}} \ , \tag{2.4}$$

to get derivatives in which the R_i (rather than the $\bar{R}_i$) have the role of independent variables. However, from the $2r$ variables $\{R_i\}$ and $\{\bar{R}_j\}$, one could form as many as $(2r)!/r!(r-2)!$ possible partial derivatives having various combinations of the R_i and $\bar{R}_j$ held constant. Thus, even if attention is restricted to only those derivatives which can be formed from the conjugate R_i and $\bar{R}_j$ alone, the $r(r+1)/2$ known elements of (2.3) must serve to determine a larger number of thermodynamic properties which may be wanted.[16] If one seeks derivatives involving *other* functions of the R_i and $\bar{R}_i$ (thermodynamic potentials, coexistence coordinates, etc.) from the few known elements of **G**, the magnitude of the task increases accordingly.

The flexibility to deal with this latter situation is, of course, extremely important. In the geometric formalism, these more general variables enter by way of ordinary basis set expansions and the accompanying matrix transformations of **G**. For example, an arbitrary thermodynamic function X with associated vector $|\mathcal{X}\rangle$ can be expanded in the chosen basis set $\{|\mathcal{R}_i\rangle\}$,

$$|\mathcal{X}\rangle = \sum_{i=1}^{r} c_i |\mathcal{R}_i\rangle \ , \tag{2.5}$$

with coefficients c_i given by[17]

$$c_i = \langle \bar{\mathcal{R}}_i | \mathcal{X}\rangle = (\partial X/\partial R_i)_{\mathbf{R}} \ . \tag{2.6}$$

Expansions of the form (2.5) will allow one to easily transform thermodynamic derivatives from one set of functions to another by the matrix transformation methods of Paper III.

III. THERMODYNAMIC DERIVATIVES OF A SIMPLE FLUID

We shall first confine attention to the simplest case $r=2$ (e.g., a homogeneous, one-component fluid of fixed mass), which is treated in the Bridgman and Shaw tables. We seek to evaluate a general partial derivative $\mathcal{D}$ of the form

$$\mathcal{D} = (\partial X/\partial Y)_Z \ , \tag{3.1}$$

where X, Y, and Z are some chosen set of state properties. In order to obtain a general expression for such derivatives, we suppose that a pair of basis fields R_1 and R_2 with associated conjugates $\bar{R}_1$ and $\bar{R}_2$ have been chosen. Because of the mutual nature of the conjugacy relation [Eq. (III.3.6)], we can write the conjugate of each $\bar{R}_i$ as

$$\overline{(\bar{R}_i)} = R_i \ . \tag{3.2}$$

In this two-dimensional space, we can furthermore describe the chosen fields R_1 and R_2 as *complementary*, and let the tilde symbol on $\tilde{R}_i$ serve to designate the *complement* of R_i, so that

$$\tilde{R}_1 = R_2, \quad \tilde{R}_2 = R_1 . \tag{3.3}$$

Similarly, the conjugate variables $\bar{R}_1$ and $\bar{R}_2$ are mutually complementary, so that

$$\tilde{\bar{R}}_1 = \bar{R}_2, \quad \tilde{\bar{R}}_2 = \bar{R}_1 \ . \tag{3.4}$$

With these notational conventions, we can uniquely identify the state variables $\tilde{Z}$, $\bar{Z}$, and $\tilde{\bar{Z}}$ $(=\bar{\tilde{Z}})$ for any chosen variable Z. For example, when temperature T and (negative) pressure $-P$ are the chosen R_i's,

$$\begin{pmatrix} R_1 \\ R_2 \end{pmatrix} = \begin{pmatrix} T \\ -P \end{pmatrix} \ , \tag{3.5a}$$

with entropy S and volume V the corresponding conjugate $\bar{R}_i$'s,

$$\begin{pmatrix} \bar{R}_1 \\ \bar{R}_2 \end{pmatrix} = \begin{pmatrix} S \\ V \end{pmatrix} \ , \tag{3.5b}$$

then Z, $\bar{Z}$, $\tilde{Z}$, and $\tilde{\bar{Z}}$ have the significance shown in Table I. This choice of notation also allows us to express the biorthogonality condition (2.2) in the form

$$\langle \mathfrak{z} | \bar{\mathfrak{z}} \rangle = 1 \ , \tag{3.6a}$$

$$\langle \mathfrak{z} | \tilde{\bar{\mathfrak{z}}} \rangle = 0 \ , \tag{3.6b}$$

for a general variable Z.

The standard scalar products among vectors $|\mathcal{T}\rangle$, $|-\mathcal{P}\rangle$, $|\mathcal{S}\rangle$, and $|\mathcal{V}\rangle$ are gathered in Table II, expressed in terms of the standard response functions [see Eqs. (III.3.15)–(III.3.18) for definitions] C_P, C_V, β_T, β_S, α_P, and Γ_V. As remarked above, scalar products involving $|\mathcal{S}\rangle$ and $|\mathcal{V}\rangle$ (e.g., involving the properties C_P, β_T, and α_P) are obtained by matrix inversion from those for $|\mathcal{T}\rangle$ and $|-\mathcal{P}\rangle$ (e.g., from C_V, β_S, and Γ_V); the vector-algebraic procedure will automatically express any desired derivative in terms of the six properties in Table II, and these expressions may subsequently be reduced (if desired) to involve only three independent properties by the identities implied in Eq. (2.4).

In order to evaluate a partial derivative (3.1), one might attempt to express dZ in the form

$$dZ = \lambda dX + \mu dY \ , \tag{3.7}$$

so that the desired derivative is

$$\mathcal{D} = \left(\frac{\partial X}{\partial Y}\right)_Z = -\frac{\mu}{\lambda} \ . \tag{3.8}$$

In the geometric representation, Eq. (3.7) is repre-

TABLE I. "Standard" variables.

Z	$\bar{Z}$	$\tilde{Z}$	$\tilde{\bar{Z}}$
T	S	$-P$	V
$-P$	V	T	S
S	T	V	$-P$
V	$-P$	S	T

TABLE II. "Standard" scalar products.

	$\vert\mathcal{T}\rangle$	$\vert-\mathcal{P}\rangle$	$\vert\mathcal{S}\rangle$	$\vert\mathcal{V}\rangle$
$\langle\mathcal{T}\vert$	T/C_V	$-T/\Gamma_V$	1	0
$\langle-\mathcal{P}\vert$	$-T/\Gamma_V$	$1/V\beta_S$	0	1
$\langle\mathcal{S}\vert$	1	0	C_P/T	$V\alpha_P$
$\langle\mathcal{V}\vert$	0	1	$V\alpha_P$	$V\beta_T$

sented as a relationship among vectors [cf. Eq. (III.2.4)],

$$|\mathfrak{z}\rangle=\lambda|\mathfrak{X}\rangle+\mu|\mathfrak{Y}\rangle\ , \tag{3.9}$$

and the coefficients λ and μ are readily evaluated by ordinary vector methods. For example, if we take the scalar product of Eq. (3.9) with the conjugate complement vector $|\bar{\bar{\mathfrak{z}}}\rangle$ and use Eq. (3.6b), the result is

$$0=\lambda\langle\mathfrak{X}|\bar{\bar{\mathfrak{z}}}\rangle+\mu\langle\mathfrak{Y}|\bar{\bar{\mathfrak{z}}}\rangle\ , \tag{3.10}$$

so that $\mathfrak{D}$ is evaluated simply as a ratio of projections of vector $|\bar{\bar{\mathfrak{z}}}\rangle$ onto the vectors $|\mathfrak{X}\rangle$ and $|\mathfrak{Y}\rangle$,

$$\left(\frac{\partial X}{\partial Y}\right)_Z=\frac{\langle\mathfrak{X}|\bar{\bar{\mathfrak{z}}}\rangle}{\langle\mathfrak{Y}|\bar{\bar{\mathfrak{z}}}\rangle}\ . \tag{3.11}$$

The applications of this equation, which is to be used in conjunction with Tables I and II, may be illustrated by some simple examples.

Example: "Mixed" derivatives

Equation (3.11) may be employed to evaluate the derivatives

$$\left(\frac{\partial S}{\partial V}\right)_T,\ \left(\frac{\partial S}{\partial V}\right)_P,\ \left(\frac{\partial P}{\partial T}\right)_S,\ \left(\frac{\partial P}{\partial T}\right)_V, \tag{3.12}$$

in which mixtures of field and extensive quantities serve as independent variables. Noting from Table I that $\bar{\bar{T}}=V$, and using the "standard" scalar products defined in Table II, we obtain

$$\left(\frac{\partial S}{\partial V}\right)_T=\frac{\langle\mathcal{S}|\bar{\bar{\mathcal{T}}}\rangle}{\langle\mathcal{V}|\bar{\bar{\mathcal{T}}}\rangle}=\frac{\langle\mathcal{S}|\mathcal{V}\rangle}{\langle\mathcal{V}|\mathcal{V}\rangle}=\frac{V\alpha_P}{V\beta_T}=\frac{\alpha_P}{\beta_T}\ . \tag{3.13a}$$

Similarly, since $\bar{\bar{S}}=-P$,

$$\left(\frac{\partial P}{\partial T}\right)_S=-\frac{\langle-\mathcal{P}|\bar{\bar{\mathcal{S}}}\rangle}{\langle\mathcal{T}|\bar{\bar{\mathcal{S}}}\rangle}=-\frac{\langle-\mathcal{P}|-\mathcal{P}\rangle}{\langle\mathcal{T}|-\mathcal{P}\rangle}=-\frac{(1/V\beta_S)}{(-T/\Gamma_V)}=\frac{\Gamma_V}{TV\beta_S}\ . \tag{3.13b}$$

The reader may verify in an analogous manner the identities

$$\left(\frac{\partial S}{\partial V}\right)_P=\frac{C_P}{TV\alpha_P}\ , \tag{3.13c}$$

$$\left(\frac{\partial P}{\partial T}\right)_V=\frac{C_V}{\Gamma_V}\ . \tag{3.13d}$$

Example: Saturation properties

The application of Eq. (3.11) to variables other than the standard S, V, T, and $-P$ can be illustrated with the saturation properties C_σ and α_σ [see Eq. (III.4.18) and following],

$$C_\sigma=T\left(\frac{\partial S}{\partial T}\right)_\sigma\ , \tag{3.14a}$$

$$\alpha_\sigma=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_\sigma\ , \tag{3.14b}$$

which involve the "coexistence coordinate" σ [Eq. (III.4.23)],

$$|\sigma\rangle=\gamma_\sigma|\mathcal{T}\rangle+|-\mathcal{P}\rangle\ , \tag{3.15}$$

where γ_σ is the slope of the coexistence curve. With T and σ as reference fields, the conjugate variables were found to be [Eq. (III.4.25)]

$$|\bar{\mathcal{T}}\rangle=|\mathcal{S}\rangle-\gamma_\sigma|\mathcal{V}\rangle\ , \tag{3.16a}$$

$$|\bar{\sigma}\rangle=|\mathcal{V}\rangle\ , \tag{3.16b}$$

from which we recognize, for example,

$$|\bar{\bar{\sigma}}\rangle=|\bar{\mathcal{T}}\rangle=|\mathcal{S}\rangle-\gamma_\sigma|\mathcal{V}\rangle\ . \tag{3.17}$$

The saturation heat capacity C_σ is therefore found from

$$\frac{C_\sigma}{T}=\left(\frac{\partial S}{\partial T}\right)_\sigma=\frac{\langle\mathcal{S}|\bar{\bar{\sigma}}\rangle}{\langle\mathcal{T}|\bar{\bar{\sigma}}\rangle}=\frac{\langle\mathcal{S}|\mathcal{S}\rangle-\gamma_\sigma\langle\mathcal{S}|\mathcal{V}\rangle}{\langle\mathcal{T}|\mathcal{S}\rangle-\gamma_\sigma\langle\mathcal{T}|\mathcal{V}\rangle}=\frac{(C_P/T)-\gamma_\sigma(V\alpha_P)}{(1)-\gamma_\sigma(0)}\ ,$$

which is the identity

$$C_\sigma=C_P-TV\gamma_\sigma\alpha_P\ . \tag{3.18}$$

The reader may verify the analogous calculation for the thermal expansion coefficient α_σ

$$\alpha_\sigma=\alpha_P-\gamma_\sigma\beta_T\ . \tag{3.19}$$

If the scalar products appearing in (3.11) are somehow inconvenient (for example, because vector $|\bar{\bar{\mathfrak{z}}}\rangle$ is not readily available), one can return to solve Eq. (3.9) in other forms.[18] For instance, if we take the scalar product of Eq. (3.9) successively with the vectors $|\bar{\bar{\mathfrak{X}}}\rangle$ and $|\bar{\bar{\mathfrak{Y}}}\rangle$, the result is

$$\langle\bar{\bar{\mathfrak{X}}}|\mathfrak{z}\rangle=\lambda\cdot 0+\mu\langle\bar{\bar{\mathfrak{X}}}|\mathfrak{Y}\rangle\ , \tag{3.20a}$$

$$\langle\bar{\bar{\mathfrak{Y}}}|\mathfrak{z}\rangle=\lambda\langle\bar{\bar{\mathfrak{Y}}}|\mathfrak{X}\rangle+\mu\cdot 0\ , \tag{3.20b}$$

so that (3.8) becomes

$$\left(\frac{\partial X}{\partial Y}\right)_Z=-\frac{\langle\mathfrak{X}|\bar{\bar{\mathfrak{Y}}}\rangle\langle\bar{\bar{\mathfrak{X}}}|\mathfrak{z}\rangle}{\langle\mathfrak{Y}|\bar{\bar{\mathfrak{X}}}\rangle\langle\bar{\bar{\mathfrak{Y}}}|\mathfrak{z}\rangle}\ , \tag{3.21}$$

which is again rather easily remembered or rederived as the occasion warrants.

Example: Identities among basic response functions

Equation (3.21) is useful in recovering various identities which connect the entries of Table II. For example, from the definition $C_V=T(\partial S/\partial T)_V$, we deduce

$$\frac{C_V}{T}=\left(\frac{\partial S}{\partial T}\right)_V=-\frac{\langle\mathcal{S}|\bar{\bar{\mathcal{T}}}\rangle\langle\bar{\bar{\mathcal{S}}}|\mathcal{V}\rangle}{\langle\mathcal{T}|\bar{\bar{\mathcal{S}}}\rangle\langle\bar{\bar{\mathcal{T}}}|\mathcal{V}\rangle}$$

$$=-\frac{\langle\mathcal{S}|\mathcal{V}\rangle\langle-\mathcal{P}|\mathcal{V}\rangle}{\langle\mathcal{T}|-\mathcal{P}\rangle\langle\mathcal{V}|\mathcal{V}\rangle}=-\frac{(V\alpha_P)(1)}{(-T/\Gamma_V)(V\beta_T)}\ ,$$

which is the identity [cf. Eq. (III.3.28)]

$$C_V\beta_T=\alpha_P\Gamma_V\ , \tag{3.22}$$

and so forth.

Example: Saturation properties

In treating saturation properties $(\partial X/\partial Y)_\sigma$ with Eq. (3.21), we note that only σ itself (but not $\bar{\sigma}$ or $\bar{\bar{\sigma}}$) is needed. Hence, we can return to the "standard" choice of basis variables from Table I,

$$\begin{pmatrix} R_1 \\ R_2 \end{pmatrix} = \begin{pmatrix} T \\ -P \end{pmatrix}, \quad \begin{pmatrix} \bar{R}_1 \\ \bar{R}_2 \end{pmatrix} = \begin{pmatrix} S \\ V \end{pmatrix} = \begin{pmatrix} \bar{T} \\ -\bar{P} \end{pmatrix}, \tag{3.23}$$

instead of the special set

$$\begin{pmatrix} R_1 \\ R_2 \end{pmatrix} = \begin{pmatrix} T \\ \sigma \end{pmatrix}, \quad \begin{pmatrix} \bar{R}_1 \\ \bar{R}_2 \end{pmatrix} = \begin{pmatrix} S - \gamma_\sigma V \\ V \end{pmatrix} = \begin{pmatrix} \bar{T} \\ \bar{\sigma} \end{pmatrix}, \tag{3.24}$$

which was employed in Eqs. (3.16) and following. For example α_σ is found from

$$\begin{aligned} V\alpha_\sigma = \left(\frac{\partial V}{\partial T}\right)_\sigma &= -\frac{\langle \mathcal{V}|\bar{\bar{\mathcal{T}}}\rangle\langle \bar{\bar{\mathcal{V}}}|\sigma\rangle}{\langle \mathcal{T}|\bar{\bar{\mathcal{V}}}\rangle\langle \bar{\bar{\mathcal{T}}}|\sigma\rangle} = -\frac{\langle \mathcal{V}|\mathcal{V}\rangle\langle \mathcal{T}|\sigma\rangle}{\langle \mathcal{T}|\mathcal{T}\rangle\langle \mathcal{V}|\sigma\rangle} \\ &= -\frac{\langle \mathcal{V}|\mathcal{V}\rangle[\gamma_\sigma\langle \mathcal{T}|\mathcal{T}\rangle + \langle \mathcal{T}|-\mathcal{P}\rangle]}{\langle \mathcal{T}|\mathcal{T}\rangle[\gamma_\sigma\langle \mathcal{V}|\mathcal{T}\rangle + \langle \mathcal{V}|-\mathcal{P}\rangle]} \\ &= -\frac{(V\beta_T)[\gamma_\sigma(T/C_V) + (-T/\Gamma_V)]}{(T/C_V)[\gamma_\sigma(0) + (1)]} \\ &= -V\beta_T(\gamma_\sigma - C_V/\Gamma_V) , \end{aligned}$$

which, in conjunction with (3.22) above, is again Eq. (3.19). Equation (3.18) for C_σ is recovered in an analogous manner. Note that α_σ could have been evaluated as easily in the special basis set (3.24) [since V is a "natural" variable in both (3.23) and (3.24)], but C_σ could not.

Equations (3.11) and (3.21) retain their validity even when X, Y, and Z do not belong to a single set of fields and conjugates (for example, each might be expressed as a linear combination of two other reference variables). In such cases, one can choose the complementary variables rather arbitrarily, and it often convenient, for example, to define X and Y to be complementary variables,

$$\tilde{X} = Y , \quad \tilde{Y} = X , \tag{3.25a}$$

so that Eq. (3.21) reduces to [in view of (3.6a)]

$$\left(\frac{\partial X}{\partial Y}\right)_Z = -\frac{\langle \bar{\mathfrak{Y}}|\mathfrak{Z}\rangle}{\langle \bar{\mathfrak{X}}|\mathfrak{Z}\rangle} , \tag{3.25b}$$

which is again a compact and easily remembered form. Of course, the conjugate variables $\bar{X}$ and $\bar{Y}$ of Eq. (3.25b) must now be defined specifically with respect to the choice of complementary fields implied by (3.25a), since, e.g., $\bar{X}$ is wholly arbitrary until $\tilde{X}$ has been defined.

Example: More identities

Since S and V are complementary variables in Table I, we can use Eq. (3.25b) to evaluate

$$\left(\frac{\partial S}{\partial V}\right)_T = -\frac{\langle \bar{\mathcal{V}}|\mathcal{T}\rangle}{\langle \bar{\mathcal{S}}|\mathcal{T}\rangle} = -\frac{\langle -\mathcal{P}|\mathcal{T}\rangle}{\langle \mathcal{T}|\mathcal{T}\rangle} = -\frac{(-T/\Gamma_V)}{(T/C_V)} = \frac{C_V}{\Gamma_V} ,$$

which, in conjunction with Eq. (3.13a), is again the identity (3.22). Analogous saturation properties such as $(\partial S/\partial V)_\sigma$ are also dealt with easily by Eq. (3.25b).

Example: Joule-Thomson coefficient $(\partial T/\partial P)_H$

Analysis of the Joule–Thomson "porous plug" experiment requires evaluation of the derivative $(\partial T/\partial P)_H$ at constant *enthalpy* $H(=U+PV)$. Since

$$dH = TdS + VdP , \tag{3.26}$$

the vector $|\mathcal{H}\rangle$ associated with enthalpy H is simply

$$|\mathcal{H}\rangle = T|\mathcal{S}\rangle - V|-\mathcal{P}\rangle . \tag{3.27}$$

In terms of the standard variables of Table I, T and $-P$ are already complementary variables, so the Joule–Thomson coefficient is evaluated most conveniently from Eq. (3.25b):

$$\begin{aligned} \left(\frac{\partial T}{\partial P}\right)_H &= +\frac{\langle -\bar{\mathcal{P}}|\mathcal{H}\rangle}{\langle \bar{\mathcal{T}}|\mathcal{H}\rangle} = \frac{\langle \mathcal{V}|\mathcal{H}\rangle}{\langle \mathcal{S}|\mathcal{H}\rangle} = \frac{T\langle \mathcal{V}|\mathcal{S}\rangle - V\langle \mathcal{V}|-\mathcal{P}\rangle}{T\langle \mathcal{S}|\mathcal{S}\rangle - V\langle \mathcal{S}|-\mathcal{P}\rangle} \\ &= \frac{T(V\alpha_P) - V(1)}{T(C_P/T) - V(0)} = \frac{V}{C_P}(T\alpha_P - 1) . \end{aligned} \tag{3.28}$$

Other thermodynamic potentials, such as the Gibbs or Helmholtz free energies, or the internal energy U itself, can be similarly manipulated as ordinary variables when expansion analogous to (Eq. (3.27) are introduced.

It may finally be remarked that equations such as (3.11), (3.21), and (3.25b), which represent partial derivatives as simple ratios of geometric projections, make it easy (as well as largely superfluous) to recover various identities among partial derivatives which are often taken as starting points in thermodynamic manipulations.

IV. GENERAL SOLUTION FOR $r=2$ AND RELATION TO JACOBIAN METHODS

In order to obtain the ratio $\mathfrak{D} = -\mu/\lambda$ of coefficients from the vector equation (3.9) in its most general form, let $|\mathfrak{A}\rangle$ and $|\mathfrak{B}\rangle$ (corresponding to thermodynamic variables A and B, respectively) represent arbitrary vectors in the two-dimensional space. The successive scalar products of these vectors with Eq. (3.9) then lead to the linear equations

$$\langle \mathfrak{A}|\mathfrak{Z}\rangle = \lambda\langle \mathfrak{A}|\mathfrak{X}\rangle + \mu\langle \mathfrak{A}|\mathfrak{Y}\rangle , \tag{4.1a}$$

$$\langle \mathfrak{B}|\mathfrak{Z}\rangle = \lambda\langle \mathfrak{B}|\mathfrak{X}\rangle + \mu\langle \mathfrak{B}|\mathfrak{Y}\rangle , \tag{4.1b}$$

which can be solved in the usual manner

$$\begin{pmatrix} \lambda \\ \mu \end{pmatrix} = \begin{pmatrix} \langle \mathfrak{A}|\mathfrak{X}\rangle & \langle \mathfrak{A}|\mathfrak{Y}\rangle \\ \langle \mathfrak{B}|\mathfrak{X}\rangle & \langle \mathfrak{B}|\mathfrak{Y}\rangle \end{pmatrix}^{-1} \begin{pmatrix} \langle \mathfrak{A}|\mathfrak{Z}\rangle \\ \langle \mathfrak{B}|\mathfrak{Z}\rangle \end{pmatrix} , \tag{4.2}$$

for the unknown coefficients λ and μ, provided that

$$\langle \mathfrak{A}|\mathfrak{X}\rangle\langle \mathfrak{B}|\mathfrak{Y}\rangle - \langle \mathfrak{A}|\mathfrak{Y}\rangle\langle \mathfrak{B}|\mathfrak{X}\rangle \neq 0 . \tag{4.3}$$

The desired ratio is then obtained in the form

$$\left(\frac{\partial X}{\partial Y}\right)_Z = \frac{\langle \mathfrak{X}|\mathfrak{A}\rangle\langle \mathfrak{B}|\mathfrak{Z}\rangle - \langle \mathfrak{X}|\mathfrak{B}\rangle\langle \mathfrak{A}|\mathfrak{Z}\rangle}{\langle \mathfrak{Y}|\mathfrak{A}\rangle\langle \mathfrak{B}|\mathfrak{Z}\rangle - \langle \mathfrak{Y}|\mathfrak{B}\rangle\langle \mathfrak{A}|\mathfrak{Z}\rangle} . \tag{4.4}$$

Example: Identities for C_V

From the definition $C_V = T(\partial S/\partial T)_V$, Eq. (4.4) gives

$$\frac{C_V}{T} = \frac{\langle \mathcal{S}|\mathfrak{A}\rangle\langle \mathfrak{B}|\mathcal{V}\rangle - \langle \mathcal{S}|\mathfrak{B}\rangle\langle \mathfrak{A}|\mathcal{V}\rangle}{\langle \mathcal{T}|\mathfrak{A}\rangle\langle \mathfrak{B}|\mathcal{V}\rangle - \langle \mathcal{T}|\mathfrak{B}\rangle\langle \mathfrak{A}|\mathcal{V}\rangle} ,$$

for any A and B (but note that one merely recovers the definition $C_V/T=\langle\mathcal{T}|\mathcal{T}\rangle^{-1}$ if A or B is T). With the choice $A=S$, $B=V$, this becomes

$$\frac{C_V}{T}=\frac{(C_P/T)\,(V\beta_T)-(V\alpha_P)\,(V\alpha_P)}{(1)\,(V\beta_T)-(0)\,(V\alpha_P)} \quad ,$$

which is the identity

$$C_V=C_P-TV\alpha_P^2/\beta_T \quad . \tag{4.5a}$$

Similarly, the choice $A=S$, $B=-P$ leads to

$$C_V=\frac{C_P}{1+TV\alpha_P/\Gamma_V} \quad , \tag{4.5b}$$

while the choice $A=V$ and $B=-P$ leads to

$$C_V=\alpha_P\,\Gamma_V/\beta_T \quad , \tag{4.5c}$$

which was previously obtained in (3.22). Other examples of such identities [all of which are special instances of Eqs. (III.3.28)] can be readily obtained by treating the other standard response functions in an analogous manner.

The general solution (4.4) reduces to the simpler forms obtained earlier when we introduce special choices for the variables A and B. Thus, the particular choices

$$A=\bar{Z} \quad , \quad B=\bar{\bar{Z}} \quad , \tag{4.6a}$$

$$A=\bar{\bar{X}} \quad , \quad B=\bar{\bar{Y}} \quad , \tag{4.6b}$$

$$A=\bar{Y} \quad , \quad B=\tilde{A}=\bar{X} \quad , \tag{4.6c}$$

lead to Eqs. (3.11), (3.21), and (3.25b), respectively.

Another interesting special form of the solution (4.4) can be gotten if we write the general scalar product $\langle\mathfrak{X}|\mathfrak{Y}\rangle$ in the form

$$\langle\mathfrak{X}|\mathfrak{Y}\rangle=(\partial X/\partial\bar{Y})_{\bar{\bar{Y}}} \quad , \tag{4.7}$$

which is merely Eq. (2.1) written in terms of the notation established in Eqs. (3.2)–(3.4) for the two-dimensional space. Equation (4.4) thereby becomes

$$\left(\frac{\partial X}{\partial Y}\right)_Z=\frac{(\partial X/\partial\bar{A})_{\bar{\bar{A}}}\,(\partial Z/\partial\bar{B})_{\bar{\bar{B}}}-(\partial Z/\partial\bar{A})_{\bar{\bar{A}}}\,(\partial X/\partial\bar{B})_{\bar{\bar{B}}}}{(\partial Y/\partial\bar{A})_{\bar{\bar{A}}}\,(\partial Z/\partial\bar{B})_{\bar{\bar{B}}}-(\partial Z/\partial\bar{A})_{\bar{\bar{A}}}\,(\partial Y/\partial\bar{B})_{\bar{\bar{B}}}} \, . \tag{4.8}$$

If now $\bar{A}$ and $\bar{B}$ are chosen as *complementary* variables in each term,

$$\bar{\bar{A}}=\bar{B} \, , \quad \bar{\bar{B}}=\bar{A} \, , \tag{4.9}$$

Eq. (4.8) becomes simply a ratio of Jacobian determinants,

$$\left(\frac{\partial X}{\partial Y}\right)_Z=\frac{J(X,Z)}{J(Y,Z)} \, , \tag{4.10}$$

where, for example,

$$J(X,Z)=\frac{\partial(X,Z)}{\partial(\bar{A},\bar{B})}=\begin{vmatrix}\left(\frac{\partial X}{\partial\bar{A}}\right)_{\bar{B}} & \left(\frac{\partial Z}{\partial\bar{A}}\right)_{\bar{B}} \\ \left(\frac{\partial X}{\partial\bar{B}}\right)_{\bar{A}} & \left(\frac{\partial Z}{\partial\bar{B}}\right)_{\bar{A}}\end{vmatrix} \quad , \tag{4.11}$$

and $J(Y,Z)$ is defined correspondingly (the dependence on the fixed variables $\bar{A}$ and $\bar{B}$ being understood implicitly). Equation (4.10) can be recognized as the basic equation employed by Shaw[6] in his formulation of the Jacobian algebra and tables. Thus, the relative simplicity of Jacobian methods can be understood in terms of their rather close connection with the underlying thermodynamic geometry. Nevertheless, Eqs. (4.4) and (4.6), and the examples of Sec. III show that the Jacobian solution is neither the simplest nor the most general algebraic representation of a general thermodynamic derivative.

V. HIGHER DIMENSIONAL (MULTICOMPONENT) SYSTEMS

The solutions previously given for $r=2$ are specialized to the extent they depend on the notion of *mutual* complementarity of pairs of variables, a convenient notion (and notation) which cannot be carried beyond two dimensions. In a space of r dimensions, a general thermodynamic derivative $\mathfrak{D}$ will have the form

$$\mathfrak{D}=(\partial X/\partial Y)_{\mathbf{Z}} \quad , \tag{5.1}$$

where now $\mathbf{Z}=(Z_1,Z_2,\ldots,,Z_{r-1})$ enumerates the $r-1$ variables held constant during differentiation. As before, we assume that the Gram matrix $\mathbf{G}$ is known in terms of some basis set $\{R_i\}$ (with conjugate basis $\{\bar{R}_i\}$),

$$(\mathbf{G})_{ij}=\langle\mathfrak{R}_i|\mathfrak{R}_j\rangle, \quad i,j=1,2,\ldots,r \tag{5.2}$$

and that expansions are known for each variable X, Y, and Z_i in terms of the basis variables $\{R_i\}$ or $\{\bar{R}_i\}$,

$$|\mathfrak{X}\rangle=\sum_{i=1}^{r}c_i\,|\mathfrak{R}_i\rangle \quad (c_i=\langle\bar{\mathfrak{R}}_i|\mathfrak{X}\rangle) \, , \tag{5.3a}$$

$$|\mathfrak{X}\rangle=\sum_{i=1}^{r}c_i'\,|\bar{\mathfrak{R}}_i\rangle \quad (c_i'=\langle\mathfrak{R}_i|\mathfrak{X}\rangle) \, , \tag{5.3b}$$

etc. for $|\mathfrak{Y}\rangle$, $|\mathfrak{z}_i\rangle$.

It may first be observed that geometric evaluation of derivative $\mathfrak{D}$ in Eq. (5.1) would become rather simple if we had made a fortuitous choice of basis variables $\{R_i'\}$ such that the conjugate variables $\{\bar{R}_i'\}$ were

$$\begin{aligned}\bar{R}_i'&=Z_i \, , \quad i=1,2,\ldots,r-1\\ \bar{R}_r'&=Y \quad ,\end{aligned} \tag{5.4}$$

since in this case, $\mathfrak{D}$ becomes

$$\mathfrak{D}=\langle\mathfrak{X}|\mathfrak{R}_r'\rangle=\langle\mathfrak{X}|\bar{\mathfrak{Y}}_{\mathbf{Z}}\rangle \quad , \tag{5.5}$$

where $\bar{Y}_{\mathbf{Z}}$,

$$\bar{Y}_{\mathbf{Z}}=R_r' \quad , \tag{5.6}$$

is the conjugate of Y with respect to the choice of the Z_i as the complementary set of variables in (5.4). To achieve the desired simple form (5.5), we need only transform from the old conjugate basis $\{\bar{R}_i\}$ to the special conjugate basis $\{\bar{R}_i'\}$ in the usual manner,

$$\begin{pmatrix}\bar{R}_1'\\ \vdots\\ \bar{R}_{r-1}'\\ \bar{R}_r'\end{pmatrix}=\begin{pmatrix}Z_1\\ \vdots\\ Z_{r-1}\\ Y\end{pmatrix}=\mathbf{A}\begin{pmatrix}\bar{R}_1\\ \vdots\\ \bar{R}_{r-1}\\ \bar{R}_r\end{pmatrix} \quad , \tag{5.7}$$

where the matrix $\mathbf{A}$ is known from expansions such as Eqs. (5.3b) for $|\mathfrak{Y}\rangle$ and $|\mathfrak{z}_i\rangle$.[19] The Gram matrix $\mathbf{G}'$ for the new basis is then, as usual,

$$\mathbf{G}' = \mathbf{A}\mathbf{G}\mathbf{A}^t = \mathbf{G}_\mathbf{A} \ , \tag{5.8}$$

and the usual equation connecting the $\mathbf{R}'$ and $\overline{\mathbf{R}}'$ is accordingly

$$\mathbf{R}' = \mathbf{G}'\overline{\mathbf{R}}' = \mathbf{G}_\mathbf{A}\overline{\mathbf{R}}' \ . \tag{5.9}$$

The final entry of vector Eq. (5.9) is the desired expression for $\overline{Y}_\mathbf{Z}$,

$$|\overline{\mathcal{Y}}_\mathbf{Z}\rangle = \sum_{i=1}^{r-1} (\mathbf{G}_\mathbf{A})_{ir} \mid \mathfrak{z}_i\rangle + (\mathbf{G}_\mathbf{A})_{rr} \, |\mathcal{Y}\rangle \ , \tag{5.10}$$

so that Eq. (5.5) becomes finally

$$\left(\frac{\partial X}{\partial Y}\right)_\mathbf{Z} = (\mathbf{G}_\mathbf{A})_{rr} \langle \mathcal{X} | \mathcal{Y}\rangle + \sum_{i=1}^{r-1} (\mathbf{G}_\mathbf{A})_{ir} \langle \mathcal{X} | \, \mathfrak{z}_i\rangle \ . \tag{5.11}$$

Equation (5.11) gives the desired evaluation of the general derivative $\mathfrak{D}$ in a system of r dimensions, expressed in terms of known geometrical quantities. As in the two-dimensional case, other expressions for $\mathfrak{D}$ would be possible which involve special choices of the basis set $\mathbf{R}$. It is clear that vector-algebraic expressions such as (5.5) or (5.11) can be applied straightforwardly (for example, through machine computation) to multicomponent thermodynamic systems of arbitrary complexity.

VI. CONCLUSION

The vector-algebraic representation of equilibrium thermodynamics has been found to lead to new systematic procedures for the evaluation of thermodynamic derivatives. Like the Jacobian methods (which arise here as a special case), these procedures do not require manipulations of partial derivatives in any intermediate steps, but instead are strictly algebraic in character. The new procedures appear to enjoy distinct advantages over previously available methods (including Jacobian methods) in the following respects.

(*i*) *Simplicity*. The basic formulas are elementary consequences of vector geometry, so that when their general origin is understood, they can be easily derived from scratch in a form suited to any particular need (though they are easily memorized as well); essentially no special tables or memorization are required beyond that necessary to define the basic response functions in which the final answers are to be expressed.

(*ii*) *Generality*. Thermodynamic variables of quite general type (thermodynamic potentials, "coexistence" coordinates, other arbitrary "directions" in phase space) are systematically accomodated by general matrix transformation methods; in particular, one can work directly in terms of variables, or combinations of variables, which correspond to practical experimental demands.

(*iii*) *Ease of Extension*. The general techniques can be easily extended to complex multicomponent chemical systems, where they again lead to simple matrix-algebraic expressions which are in a convenient form, e.g., for machine computation.

The new procedures exhibit certain attractive pedagogical features as well. While they require a modest investment in linear algebra, they in turn permit one to reduce significantly the dependence on formal consequences (identities, chain rules, etc.) of the partial differential calculus. This may represent a favorable trade-off even at the elementary level.

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[16] For the simple homogeneous fluid ($r=2$), this "known/wanted" ratio is only 3/12, but for two-component ($r=3$) and three-component ($r=4$) systems it becomes 6/120 and 10/840, respectively. [We include pairs of derivatives connected by Maxwell relations, but only one member of each pair differing only by inversion, e.g., $(\partial S/\partial V)_T = (\partial V/\partial S)_T^{-1}$.]

[17] Eqs. (2.5), (2.6) are essentially the "completeness" relation,

$$1 = \sum_{i=1}^{r} |\mathcal{R}_i\rangle\langle\overline{\mathcal{R}}_i| = \sum_{i=1}^{r} |\overline{\mathcal{R}}_i\rangle\langle\mathcal{R}_i| \ ,$$

for the conjugate bases $|\mathcal{R}_i\rangle$, $|\overline{\mathcal{R}}_i\rangle$.

[18] The most general form of solution will be treated in Section IV.

[19] Explicitly, for $j=1, 2, \ldots, r$,

$$(\overline{\mathbf{A}})_{ij} = \langle\overline{\mathcal{R}}_j \mid \mathfrak{z}_i\rangle, \ i=1, 2, \ldots, r-1,$$
$$= \langle\overline{\mathcal{R}}_j \mid \mathcal{Y}\rangle, \ i=r.$$