(37) G. A. Olah, *Acc. Chem. Res.*, **4**, 240 (1971); see also: P. Rys, P. Skrabal, and H. E. Zollinger, *Angew. Chem., Int. Ed. Engl.*, **11**, 874 (1972).

The reaction of methyl-d_3 chlorofromate with anisole is interesting because it reveals that the reaction proceeds predominantly by initial attack on the oxygen. The isotopic composition has been determined as a function of time and shown to fit the scheme shown.[38] Moreover, the intermediate methyl(methyl-d_3)phenyloxonium ion does not undergo intramolecular rearrangement to o-methylanisole. Since previous recognition of such complexes in electrophilic aromatic substitution has depended on unusual yields of ortho products, these results suggest that the intermediacy of n complexes could be much more general than previously recognized.

(38) P. Beak, J. T. Adams, P. D. Klein, P. A. Szczepanik, D. A. Simpson, and S. G. Smith, *J. Am. Chem. Soc.*, **95**, 6027 (1973).

Geometric Representation of Equilibrium Thermodynamics

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While thermodynamics continues to play a central role in chemistry and other sciences concerned with the thermal properties of matter, the basic formalism for equilibrium thermodynamics largely retains the form which it was given in the latter half of the 19th century, culminating in the work of Gibbs.[1] A recent writer reflects a widespread view in remarking, "We may be reasonably certain that a treatise on, say, thermodynamics, published in the year 2000 will not be fundamentally different from one available today …".[2]

New research[3] suggests that this prognosis may be unduly pessimistic. Examination of the formalism of equilibrium thermodynamics has revealed an unexpected facet of the theory, a *geometrical* character which provides a new set of tools for the solution of practical thermodynamic problems. This geometric character is quite distinct from that known to thermodynamicists since the time of Gibbs, but is instead more reminiscent of that of modern gravitation theory, or of quantum theory in Hilbert space.

Because these new developments are of an abstract and mathematical character, it may clarify their significance to refer initially to a quite different area of science—that of quantum mechanics. In quantum theory, certain formal features (by now widely familiar) may be identified which are found to have counterparts in the context of a general theory of thermodynamic equilibrium. The nature of the new thermodynamic work can therefore be suggested by reference to the analogous features of the quantum theory,[4] in particular to the central role of the abstract "scalar products" between abstract "vectors," and the implied geometrical structure. The empirical basis of the Gibbsian formalism will be summarized in a form which reveals how the thermodynamic laws imply, and are implied by, an underlying geometric structure of the theory. Some general features of the resulting geometric formalism of equilibrium thermodynamics will be noted in conclusion.

Quantum Theory and Thermodynamics

Modern quantum theory is known to depend in a fundamental sense on the mathematical properties of Hilbert space, whose intrinsic role in a proper formulation of the theory was stressed particularly by von Neumann.[5] In Schrödinger's wave mechanics, each state

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(1) J. W. Gibbs, "Collected Works", Vol. I, Longmans, Green, and Co., New York, N.Y., 1928.
(2) *Phys. Today*, **27**, 57 1974).
(3) (a) F. Weinhold, *J. Chem. Phys.*, **63**, 2479 (1975); (b) *ibid.*, **63**, 2484 (1975); (c) *ibid.*, **63**, 2488 (1975); (d) *ibid.*, **63**, 2496 (1975); (e) *ibid.*, to be published.
(4) Such similarities allow one, for example, to draw an analogy between the stability conditions of thermodynamics (such as Le Châtelier's principle) and variational inequalities of quantum theory; see, e.g., F. Weinhold, *Adv. Quantum Chem.*, **6**, 299 (1972).

function $\Psi_i(x_1, x_2, \ldots)$ is an ordinary differentiable function of the spatial coordinates, but von Neumann emphasized that Ψ_i should be regarded more generally as a "vector" $|i\rangle$ of an abstract Hilbert space.

$$|i\rangle \leftrightarrow \Psi_i(x_1, x_2, \ldots) \tag{1a}$$

In this space, the physical predictions ("probability amplitudes") of the theory are associated with *scalar products* $\langle i|j\rangle$ among abstract state vectors. To make contact with Schrödinger's wave mechanics, it is necessary to exhibit a definition for the symbol $\langle i|j\rangle$ which has the properties of a Euclidean scalar product; such a definition is

$$\langle i|j\rangle = \int_{\text{all space}} \Psi_i^*(x_1, x_2, \ldots)\Psi_j(x_1, x_2, \ldots)$$
$$dx_1 dx_2 \ldots \tag{1b}$$

The importance of this perception is to suggest how other representations of the theory might be constructed in quite different mathematical languages. For example, if the abstract $|i\rangle$'s are identified with one-dimensional matrices (column arrays), $\mathbf{c}_i$

$$|i\rangle \leftrightarrow \mathbf{c}_i = \begin{pmatrix} c_{1i} \\ c_{2i} \\ \vdots \end{pmatrix} \tag{2a}$$

a scalar product having the appropriate Euclidean properties can be defined in terms of (column) matrix multiplication as

$$\langle i|j\rangle = \mathbf{c}_i^\dagger \mathbf{c}_j = \sum_k c_{ki}^* c_{kj} \tag{2b}$$

Historically, the (Heisenberg) matrix representation (eq 2a,b) of quantum theory preceded Schrödinger's wave representation (eq 1a,b); only later were these apparently dissimilar theories recognized to be different facets of a single underlying theory in Hilbert space.

Because the definitions 1b, 2b make possible an easy "translation" from one formalism to the other, it might appear that nothing has been gained. However, the practicing quantum chemist is well aware of the advantage of using special techniques of one formalism or the other to solve particular problems; he may, for example, in one moment draw inferences from nodes, phases, and other wave properties of molecular orbitals which were in the previous moment calculated by the techniques of matrix algebra. Moreover, it is known that the wave mechanical representation cannot consistently treat degrees of freedom (e.g., spin) which have no expression as functions of the spatial coordinates, so that resort to an alternative representation may be a matter of necessity as well as convenience.

These general features of quantum theory have an interesting parallel in the general theory of equilibrium thermodynamics. In the Gibbsian formalism, the state of the system is described by a differentiable function of the thermodynamic coordinates X_i

$$U = U(X_1, X_2, \ldots) \tag{3}$$

where each X_i denotes one of the extensive state vari-

ables—such as entropy, S, volume, V, and the mole numbers, $N_1, N_2, \ldots$, of the independent chemical components (or independent linear combinations of these variables)—and U is the internal energy ("thermodynamic potential") of the system. Of special interest are the partial derivatives of U, the "field"[6] variables R_i

$$R_i = (\partial U/\partial X_i)_{X_1 \ldots X_{i-1} X_{i+1} \ldots} \tag{4}$$

Because eq 4 resembles the equations of classical mechanics which define "conjugate" coordinates and momenta (with the thermodynamic potential U taking the place of the mechanical Lagrangian function), each R_i is referred to as the (thermodynamic) *conjugate* of the corresponding X_i. These R_i's are themselves state variables, and can be identified as the temperature, T, the (negative) pressure, $-P$, and the chemical potentials $\mu_1, \mu_2, \ldots$, when X_i is taken to be S, V, and $N_1, N_2, \ldots$, respectively.

$$T = (\partial U/\partial S)_{V,N_1,N_2 \ldots}$$
$$-P = (\partial U/\partial V)_{S,N_1,N_2 \ldots}$$
$$\mu_1 = (\partial U/\partial N_1)_{S,V,N_2 \ldots} \text{ (etc.)} \tag{5}$$

In analyzing thermal properties of a system, one seeks to determine how the state variables R_i, X_i may be affected by various disturbances, and how the responses to one type of disturbance (e.g., addition of heat) must be related to those of other types (e.g., volume changes, addition of reagents, etc.) according to the dictates of the empirical laws of thermodynamics.

What is surprising is that the Gibbsian formalism can be regarded as but one mathematical representation of an underlying abstract theory (in a Euclidean space of finite dimensionality) which permits a quite different representation based on matrix algebra. The key to this alternative viewpoint is a suitable scalar product $\langle i|j\rangle$ of abstract thermodynamic "vectors", namely[3a]

$$\langle i|j\rangle = (\partial R_i/\partial X_j)_{X_1 \ldots X_{j-1} X_{j+1} \ldots} \tag{6}$$

Unlike the corresponding quantum-mechanical definitions 1b, 2b of ordinary Hilbert space, the thermodynamic definition 6 does *not* obviously possess the (distributive, symmetric, and positive) qualities of a Euclidean scalar product. Indeed, many possible mathematical functions $U(X_1, X_2, \ldots)$ could be imagined for which (6) is quite meaningless. Nevertheless, we shall show that nature (as represented by the empirical "laws of thermodynamics") exhibits only such functions U as conform with (6) in a fully Euclidean sense. Indeed, eq 6 could be regarded as a rigorous, if unconventional, summary of the laws of thermodynamics on which the Gibbsian formalism rests, in a sense we shall shortly describe.

Empirical Laws of Thermodynamics

The empirical principles which govern the behavior of thermodynamic systems are traditionally stated in the form of "laws",[7] from which the characteristics of specific systems should subsequently be derived. The

(5) J. von Neumann, "Mathematical Foundations of Quantum Mechanics", Princeton University Press, Princeton, N.J., 1955.

(6) R. B. Griffiths and J. C. Wheeler, *Phys. Rev. A*, **2**, 1047 (1970). The "fields" are essentially those intensive variables which, at equilibrium, assume the same numerical value in every portion of the system.

(7) It is interesting that Gibbs altogether refrained from speaking of "laws of thermodynamics" in his monumental paper (ref 1, p 55), preferring instead to refer to the "criteria of equilibrium and stability".

objective is thereby to distinguish the empirical (inductive) elements of the theory from those which are purely deductive and mathematical. Yet the proper statement of such laws has been a matter of persistent ambiguity. Koenig[8] identified no fewer than 13 distinct forms of the second law, and additional controversy surrounds the content or number of other possible laws. However, empirical "laws" whose primary purpose is to *define* thermodynamic variables (e.g., to lay a basis for experimental thermometry, or for definitions of thermal and mechanical variables) can be distinguished from those which govern the characteristic *relationships* among these variables. Following Gibbs, we therefore assume that it is meaningful to associate properties P, V, S, T, etc. with each equilibrium state, and seek now to describe the relationships among such properties which are characteristic of a chosen state.

The key empirical observations which a formal theory of equilibrium thermodynamics must undertake to incorporate can be expressed succinctly in terms of the thermodynamic potential (eq 3) and its low-order derivatives:

(*I*) *Existence of thermodynamic potentials,* e.g., the observation that an equilibrium system can be completely characterized for thermodynamic purposes in terms of a mathematical function,[9] the internal energy $U = U(X_1, X_2, \ldots, X_r)$, which (a) depends on only some small determinate number (fixed by the Gibbs phase rule) of independent state properties, and (b) is sufficiently "smooth" to possess low-order derivatives[10] satisfying the usual rules of the partial differential calculus.

(*II*) *The first law,* e.g., the observation that the internal energy is a state property, and therefore satisfies the requirement for an exact differential

$$\frac{\partial^2 U}{\partial X_i \partial X_j} = \frac{\partial^2 U}{\partial X_j \partial X_i} \qquad (7)$$

(*III*) *The second law,* e.g., the observation that the internal energy is minimized at constant entropy (or, equivalently, that the entropy is maximized at constant energy) in an isolated equilibrium state, and hence

$$\frac{\partial^2 U}{\partial X_i{}^2} \geq 0 \qquad (8)$$

In these latter equations, it is understood that the variables X_i may represent *any possible* nonsingular linear transformation of the basic extensive variables S, V, N_1, N_2, ...

Observations II and III (the conservation of energy and its convexity with respect to each argument X_i) are well known, but observation I summarizes information whose empirical content is easily overlooked. Yet (Ia), for example, is undeniably empirical; indeed, the fact that states of a simple fluid could be described in terms of only *two* (rather than, e.g., 10^{23}) variables is, from the microscopic point of view, perhaps the *most* notable aspect of macroscopic thermodynamics. Similarly, no general principles of pure mathematics would guarantee

that an arbitrary function $U(X_1, X_2, \ldots, X_r)$ is sufficiently well behaved to possess the low-order derivatives asserted by (Ib).

The content of (II) and (III) commonly appears in other forms in textbooks. It was among Gibbs' most inspired insights to recognize that thermodynamics could be successfully formulated in terms of individual equilibrium *states,* completely by-passing the cycles, engines, perpetual-motion devices, and related "processes" on which the formalism had seemingly depended since the time of Carnot. While many Gibbsian innovations eventually found their way into the textbooks, this simple, basic change in perspective by and large did not. Yet the advantages of this "Gibbs perspective" regarding the clear formulation of principles and rigorous deduction of their consequences can scarcely be doubted. Whether or not one adopts this perspective for the conventional treatment in terms of partial differential equations, it becomes indispensable as one seeks to make contact with a *geometric* representation of the theory.

The so-called "third law" of course played no role in the Gibbsian formalism. Fowler and Guggenheim[11] concluded that the only valid form of this law asserts the inaccessibility of the absolute zero of temperature, e.g., that the internal energy function cannot correspond to states of perceptible response but imperceptibly small absolute temperature. Such a restriction (to which we return below) need not be of direct concern in describing the usual states of finite temperature.

Metric Geometry of Equilibrium Thermodynamics

An abstract metric space can be characterized by a simple set of mathematical axioms. Objects $\mathcal{R}_i$ which conform to these axioms are isomorphic to the vectors of a Euclidean space, and can be labeled as "vectors" $|\mathcal{R}_i\rangle$ and manipulated by the familiar rules of Euclidean geometry. In other words, though the objects $\mathcal{R}_i$ might initially have arisen with no reference to "geometry", they can be put into one-to-one correspondence with the elements ("vectors") of a Euclidean vector space, and their behavior (mathematical relationships, rules of combination, etc.) will be in all respects identical with the behavior of corresponding Euclidean vectors. For example, the thermodynamic temperature and pressure variables apparently have only scalar (rather than vectorial) significance, yet their relationships in states of thermal equilibrium are, for the reasons described below, precisely those which are characteristic of Euclidean vectors. Thus, one may advantageously speak of a "temperature vector" $|T\rangle$ or "pressure vector" $|\mathcal{P}\rangle$ (just as one speaks of a solution $|\Psi\rangle$ of Schrödinger's differential equation as a "vector" in abstract Hilbert space) and manipulate these objects according to the Euclidean rules which this nomenclature suggests.

The key axiomatic requirement for an abstract metric space of dimension r is that the scalar product $\langle \mathcal{R}_i | \mathcal{R}_j \rangle$ should have the Euclidean properties:[12]

(8) F. O. Koenig, *Surv. Prog. Chem.,* **7**, in press.

(9) The entropy function, with U as an argument, might alternatively be chosen; here we proceed in what has been called the "energy representation" by H. B. Callen, "Thermodynamics", Wiley, New York, N.Y., 1960, p 36.

(10) Specifically, (finite) derivatives of first and second order. It may occur that second derivatives of U are multivalued, depending on the order and direction in which the limiting procedures of differentiation are carried out (e.g., on which side of a phase boundary the property is evaluated).

(11) R. Fowler and E. A. Guggenheim, "Statistical Thermodynamics", Cambridge University Press, New York, N.Y., 1956, pp 223–229.

(12) See, e.g., P. Dennery and A. Krzywicki, "Mathematics for Physicists", Harper and Row, New York, N.Y., 1967, pp 109–111. It may be noted that axioms I'–III' are essentially equivalent to the *triangle inequality* or the *Schwarz inequality* for every vector of the space. These permit somewhat different expositions of the geometrical formalism; see, e.g., F. Weinhold, *Phys. Today,* **29**, 23 (1976).

$$\langle \mathcal{R}_i | \lambda \mathcal{R}_j + \mu \mathcal{R}_k \rangle = \lambda \langle \mathcal{R}_i | \mathcal{R}_j \rangle + \mu \langle \mathcal{R}_i | \mathcal{R}_k \rangle \quad \text{(I')}$$

$$\langle \mathcal{R}_i | \mathcal{R}_j \rangle = \langle \mathcal{R}_j | \mathcal{R}_i \rangle \quad \text{(II')}$$

$$\langle \mathcal{R}_i | \mathcal{R}_i \rangle \geq 0 \; (= 0 \text{ only if } | \mathcal{R}_i \rangle = 0) \quad \text{(III')}$$

In particular, the distributive axiom I' requires that it should be meaningful to form the vector $| \lambda \mathcal{R}_i + \mu \mathcal{R}_j \rangle = \lambda | \mathcal{R}_i \rangle + \mu | \mathcal{R}_j \rangle$ from any pair of vectors $| \mathcal{R}_i \rangle, | \mathcal{R}_j \rangle$ and real scalars λ, μ.

We can now show that the thermodynamic field properties R_i of eq 4 do indeed conform to the axioms I'–III', and can be associated with abstract vector symbols $| \mathcal{R}_i \rangle$

$$| \mathcal{R}_i \rangle \leftrightarrow R_i \quad \text{(9a)}$$

if we define the scalar product $\langle \mathcal{R}_i | \mathcal{R}_j \rangle$ as in eq 6

$$\langle \mathcal{R}_i | \mathcal{R}_j \rangle = (\partial R_i / \partial X_j)_{X_1 \ldots X_{j-1} X_{j+1} \ldots X_r} \quad \text{(9b)}$$

For example, one sees that the *symmetric* property (II') of the scalar product is assured by the *first law* (II) (and conversely), since eq 7 can be written as

$$\frac{\partial R_i}{\partial X_j} = \frac{\partial R_j}{\partial X_i} \quad \text{(10)}$$

which is precisely axiom II'. Similarly, the *positivity* property III' is evidently assured by the second law (III) (and conversely), since inequality 8 is equivalent to

$$\frac{\partial R_i}{\partial X_i} \geq 0 \quad \text{(11)}$$

which is axiom III'.[13] It is not quite so evident that the distributive axiom I' ensures, and is ensured by, observation Ib. However, ref 3a details the argument by which one confirms that the rules of the partial differential calculus (the "chain rules", etc.) for differentials dR_i, dX_i are precisely the distributive property I' of the scalar product 9b. In effect, the low-order differentials have a simple *linear* behavior like that associated with linear vector spaces, and it becomes advantageous to represent these linear relationships by means of such a space rather than (less directly) by the formal rules of the partial differential calculus.

With the axiomatic properties I', II', III' guaranteed by observations Ib, II, and III, respectively, it remains for observation Ia, the Gibbs phase rule, to set the *dimensionality* r of the abstract space

$$r = c - \nu + 2 \quad \text{(12)}$$

where c and ν are the number of independent chemical components and of phases, respectively. However, as shown in ref 3a, the phase rule also plays a role in guaranteeing the portion of axiom III' which requires that $\langle \mathcal{R}_i | \mathcal{R}_i \rangle$ cannot vanish unless $| \mathcal{R}_i \rangle = 0$. Furthermore, this dimensionality limitation also precludes the occurrence of states of finite heat capacity at $T = 0$. To see this, one may note that, when $\mathcal{R}_i = \mathcal{T}$ (the "temperature vector"), eq 9 becomes

$$\langle \mathcal{T} | \mathcal{T} \rangle = \left(\frac{\partial T}{\partial S} \right)_V = T/T \left(\frac{\partial S}{\partial T} \right)_V = T/C_V \quad \text{(13)}$$

However, $| \mathcal{T} \rangle = 0$ can be recognized to be a violation of the Gibbs phase rule, as it would reduce the number of degrees of freedom (dimensions) below what is known

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(13) The proper provision for the case of equality in axiom III' is described in ref 3a, and will be seen to depend on the Gibbs phase rule, observation Ia.

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to be required empirically. Axiom III' correspondingly guarantees that $\langle \mathcal{T} | \mathcal{T} \rangle \neq 0$, and hence that the heat capacity C_v must always approach zero as rapidly as T if a violation of Gibbs' phase rule is to be averted. Consideration of other thermodynamic vectors shows that the same must be true of the isobaric heat capacity, C_p. This suggests that essential elements of the so-called "third law" are already implicit consequences of the Gibbs phase rule, when the metric significance of the latter is taken fully into account.

Some General Features of the Geometric Representation

The representation of equilibrium thermodynamics which arises from eq 9 has been outlined in ref 3b–e. As even a brief sketch of general thermodynamic theory from the geometric viewpoint would carry this Account beyond permissible bounds, we shall only remark here on some general respects in which the geometric representation differs appreciably from the familiar formalism.

Physical Interpretation. State variables appear in the form of vectors whose lengths and orientations are related to heat capacities, compressibilities, and other measurable properties of the system, as determined by eq 9b. The lengths of vectors express the extent to which a field variable will respond to a change in the associated conjugate variable, while their angles of separation express the extent to which a change in one variable will affect the field conjugate to some *other* variable (e.g., the extent to which the various modes—thermal, mechanical, chemical, etc.—of the system are "coupled"). Geometrical deductions concerning the lengths and orientations of thermodynamic vectors will in turn have direct observational consequences.[3c]

Conjugate Variables. "Conjugate" pairs R_i, X_i of variables are found to be geometrically associated with vectors $| \mathcal{R}_i \rangle, | \mathcal{X}_i \rangle$ having the *biorthogonality* property, e.g.

$$\langle \mathcal{R}_i | \mathcal{X}_j \rangle = \delta_{ij} \quad \text{(14)}$$

Just as the variables R_i (and vectors $| \mathcal{R}_i \rangle$) arise from partial derivatives of U with respect to the X_j's (as in eq 4, 9b), so are the conjugates X_i (and associated vectors $| \mathcal{X}_i \rangle$) obtained as derivatives of U with respect to the R_j's

$$| \mathcal{X}_i \rangle \leftrightarrow X_i = (\partial U / \partial R_i)_{R_1 \ldots R_{i-1} R_{i+1} \ldots R_r} \quad \text{(15a)}$$

with

$$\langle \mathcal{X}_i | \mathcal{X}_j \rangle = (\partial X_i / \partial R_j)_{R_1 \ldots R_{j-1} R_{j+1} \ldots R_r} \quad \text{(15b)}$$

e.g., with symmetric interchange of the roles of the R's and X's. The formalism thus manifests a high degree of symmetry between variables and their conjugates and permits construction of the field variables conjugate to arbitrary choices of the independent thermodynamic coordinates.[3a,c]

Normal Fields. The special set of variables which are *self*-conjugate are called "normal fields" (analogous to "normal coordinates" of a vibrating molecule) and furnish a particularly convenient orthonormal basis set to span the metric space. The orientation of these field vectors relative to the temperature, pressure, and other vectors is determined from the eigenvalues and eigenvectors of the metric matrix of the space.[3c]

"$r(r+1)/2$ Rule". The fixed dimensionality r of the space, set by Gibbs' phase rule (eq 12), limits the number of independent response functions (e.g., number of independent elements of the metric matrix) to $r(r+1)/2$. When this number of independent properties has been measured, the thermodynamic geometry is completely specified, and remaining properties can in principle be calculated from this basic set.[3c,d]

Stability Inequalities. The stability conditions of equilibrium thermodynamics can be written in the form of the Schwarz inequality, e.g., as statements of the form

$$\langle \mathcal{R}_i | \mathcal{R}_j \rangle^2 \leq \langle \mathcal{R}_i | \mathcal{R}_i \rangle \langle \mathcal{R}_j | \mathcal{R}_j \rangle \qquad (16a)$$

or

$$\cos^2 \theta \leq 1 \qquad (16b)$$

for the angles θ between thermodynamic vectors.[3c] In this form, the analogy with variational inequalities of quantum theory[4] can be seen.

Gibbs–Duhem Relation. The Gibbs–Duhem relation occurs as the equation of linear dependence among $r+1$ vectors in the r-dimensional space.[3b] Additional equations of linear dependence arise with each additional phase, as the spatial dimensionality is successively reduced in accordance with the Gibbs phase rule ($\nu \rightarrow \nu + 1$ implying $r \rightarrow r - 1$). Each such equation corresponds to an "invariant" (or "symmetry") of the system, e.g., to a set of changes of S, V, N_1, N_2, . . ., which leave the state of the system unchanged. Each such invariant (including the Gibbs–Duhem invariant) is associated with a null eigenvector of the thermodynamic metric matrix.[3e]

Changes of Variables. Changes of thermodynamic variables (e.g., to variables running parallel and perpendicular to a coexistence curve, etc.) correspond to changes of the basis vectors used to span the abstract space. Such changes are accommodated (as in ordinary vector algebra) by elementary matrix transformations. The thermodynamic theorems and equations can therefore be cast into a coordinate-free form in which this freedom to "rotate axes" is always manifest.[3c]

Complex Systems. In the geometric picture, thermodynamic theorems and procedures can often be phrased in a dimension-free form (as can ordinary Euclidean geometry). Because dimensionality is connected with chemical complexity through the phase rule, such theorems and procedures generalize immediately to thermodynamic systems of arbitrary chemical complexity. For example, general procedures have been given for the evaluation of thermodynamic derivatives[3d] and for determining the slopes of phase boundaries (generalized Clapeyron equations) and conditions for maxima or minima in phase diagrams (generalized Gibbs–Konowalow laws) for multicomponent systems of any complexity.[3e]

Laws of Thermodynamics. A characteristic feature of the geometric representation is that laws of thermodynamics are no longer seen explicitly, but instead are incorporated into the mathematical framework (Euclidean geometry) which is employed. Conclusions drawn within this framework must be consistent with laws of thermodynamics so long as one "does geometry" according to Euclidean rules. The directness with which implications of thermodynamic laws are taken into account will appear as an advantage in many types of applications.

Summary and Conclusions

Recognition of a geometrical quality in the underlying laws of thermodynamics has permitted development of an alternative representation of the formalism of equilibrium thermodynamics. This geometrical representation, based on the matrix algebra of a Euclidean vector space, forms an interesting complement to the usual analytical representation. The two representations, sharing a common empirical basis, are of course formally equivalent, inasmuch as eq 9 permits ready "translation" from one formalism to the other. Nevertheless, the geometric representation leads naturally to a number of new developments which are practically inaccessible to the usual methods, such as comprehensive analysis of phase equilibria (generalized Clausius–Clapeyron and Gibbs–Konowalow laws)[3e] and systematic procedures for evaluating thermodynamic derivatives,[3d] as extensively illustrated in the original references. It is interesting that many of these developments lie in the direction of making complex chemical systems susceptible to a degree of thermodynamic analysis which could not realistically be contemplated with older methods. Thus, the new representation may be of most tangible value to those interested in multicomponent, multiphase equilibria of the complexity often encountered in chemical and biological systems. Conceptually, the new representation exhibits (and exploits) the interesting relationship which unites the first and second laws with other spoken and unspoken empirical observations into a single mathematical framework of surprising simplicity and ubiquity—elementary Euclidean geometry. Its mathematical and logical simplicity suggest that the new representation is of a fundamental character.

Future research in this area may be concerned with the systematics of phase equilibria, with generalizations from the local Euclidean structure to a global Riemannian viewpoint, with the special features (metric singularities and dimensional collapse) associated with critical behavior, with possible extensions of the geometrical picture into the near-equilibrium domain of irreversible thermodynamics, and with the statistical-mechanical origin of the macroscopic metric structure.