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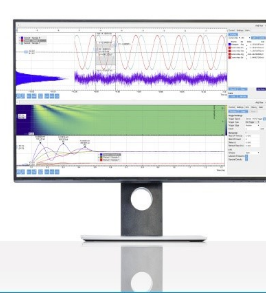

Families of Thermodynamic Equations. II. The Case of Eight Characteristic Functions

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The geometrical methods of Koenig and of Prins for resolving into families a certain class of thermodynamic equations involving four characteristic functions, are extended to the next higher case, of eight characteristic functions. The extension consists of operations upon a regular octahedron analogous to those upon a square ("the thermodynamic square") in the former case. In the present case, the number of distinct equations in a family may be 48, 24, 12, 8, 6, 3, 1. Some examples of physical interest are described.

INTRODUCTION

In 1935 the present author published in this journal a method for resolving an important class of thermodynamic equations into families.[1] This method consists in writing any equation of the class in a so-called "standard form" (a device for generating the correct algebraic signs) and thereupon transforming it by the elements of a certain substitution group of order 8, derivable from geometrical operations upon a square. The class of equations thus resolvable pertains to a single phase of $k\geq 1$ components in equilibrium, and consists of all the equations deducible from the familiar equations[2]

$$A=U-TS,$$
$$G=U-TS+PV,$$
$$H=U+PV, \tag{1}$$

$$dU=TdS-PdV+\sum_{i=1}^{k}\mu_i dn_i \tag{2}$$

by mathematical operations, in conjunction with only the assumption that of the $2k+8$ variables appearing in (1) and (2), any $k+2$ may be taken as independent, that fulfill the following two conditions: The set of $k+2$ may *not* (i) include a set whose members are interrelated through (1) (e.g., A, U, T, S; or U, A, G, H; etc.); (ii) be of the type A, B, μ_i, where A and B are respectively members of the pairs T, S and P, V.[3]

The subject thus initiated has been further developed by, chiefly, McKay,[4] Buckley,[5] Hayes,[6] Prins,[7,8] and Callen.[9] To set the present paper in proper perspective we shall summarize the contributions of these authors. For this purpose it will be convenient to note that of the four characteristic functions in (1) and (2) (i.e., U, A, G, H) any three (as here A, G, H) are the Legendre transforms—constructed from the two conjugate pairs of variables T, S, and P, V—of the remaining fourth (here U).[10]

McKay[4] in 1935 treated, for the one-phase system mentioned above, the general case in which, in addition to the pairs T, S, and P, V, one or more of the pairs μ_i, n_i ($i=1\cdots k$) may enter into the Legendre transformations acting upon U. The number of characteristic functions then arising is 2^{2+n}, where n is the number of the pairs μ_i, n_i so entering (whence $0\leq n\leq k$). McKay's method depends upon a generalized notation requiring distinction between extensive and intensive variables, and loses sight of the geometrical and group-theoretical aspects that have concerned the other authors in the field and will concern us here.

Buckley[5] in 1944 contributed a derivation, based in part on Lie's theory of contact transformations, of the substitution group discovered by Koenig.[1]

Hayes[6] in 1946 enlarged the picture by showing that the families found by Koenig can be generated by a certain group of 32 substitutions, and moreover without recourse to the above-mentioned standard form. This is possible through the fact that Hayes's 32 substitutions are not limited, as are Koenig's 8, to pure permutations, but, on the contrary, allow changes of sign.

In 1947 Prins,[7] without knowledge of the previous work just reviewed,[11] rediscovered Hayes's group of 32 substitutions, and listed a subset of 8 (not a group) which generates Koenig's families without recourse to the standard form. In a further paper, of 1948, Prins,[8] now with knowledge of Koenig's and McKay's work (but apparently not of Hayes's), derived his subset of 8 substitutions by geometrical operations upon a square similar to that put forward by Koenig.[12] Hereby the correct signs are generated by requiring the "extensive variables V and S" (respectively attached to two adjacent vertices of the square) to change sign[13] in crossing the line connecting the midpoints of the two (opposite) sides belonging initially to U and G and remaining fixed as the square is rotated. We shall refer to this derivation as the "Prins method."

Callen[9] in his text of 1960 introduced the term "thermodynamic square" for a diagram equivalent to Koenig's,[14] and pointed out that such diagrams are not limited to the four characteristic functions U, A, G, H with the associated conjugate pairs T, S, and P, V, but are indeed applicable to any four characteristic functions whatever, linked through Legendre transformations constructed from two conjugate pairs of variables. Among Callen's examples of this extension are cases pertaining to elasticity and to magnetic and electric fields.

The object of the present paper is to show that the geometrical methods of Koenig and Prins for four characteristic functions linked through two conjugate pairs of variables can be extended to the next higher case, namely that of eight characteristic functions linked through three conjugate pairs. The extension comes about through operations upon a regular octahedron analogous to those upon a square in the previous case. The feasibility of this extension was pointed out by the present author in 1937.[15] Its value lies less in the technique it supplies for generating formulas than in its revelation of "the symmetry of the equations of thermodynamics, a keen sense of which is helpful to any student of the subject."[16]

We shall treat in detail not the most general case of eight characteristic functions, but only what we shall call the "leading case." This will be recognized as the nearest analogue of the familiar case of the four characteristic functions U, A, G, H, and to include the physically most interesting cases of eight characteristic functions. To show that our treatment is easily extended to other cases we shall do it for the set of eight consisting of the entropy S and its seven Legendre transforms (Massieu-type functions) derivable from the leading case.

THE LEADING CASE

Definition and Examples

By the "leading case" we shall mean the class of cases of eight characteristic functions for which two of the associated three conjugate pairs of variables are T, S, and P, V, and the third consists (like the two mentioned) of one extensive and one intensive variable, and beyond this is determined by the nature of the class member. This third pair we shall denote in general by Y, X. It will be expedient to assign these letters in a particular way, as follows. We note that of the Gibbsian equations for the eight characteristic functions, four will contain a term of the form $\pm YdX$ and the other four a term of the form $\mp XdY$. We shall choose Y and X such that these terms in fact appear as $+YdX$ and $-XdY$. This choice still permits *either* of the two variables Y, X to be the extensive one, and we shall see examples of both kinds shortly.

Of the eight characteristic functions, any seven are, of course, the Legendre transforms—constructed from the three conjugate pairs mentioned—of the remaining eighth. As this eighth it will be expedient to choose the particular one whose total differential is given by $TdS-PdV+YdX+\sum_i\mu_i dn_i$, and thereupon to refer to it as the "primitive" characteristic function. We shall see from examples that this primitive characteristic function usually turns out to be the energy of the system (as one might expect), but not always. If it *is* the energy, we shall denote this (as before) by U and so shall have the Gibbsian equation

$$dU=TdS-PdV+YdX+\sum_i \mu_i dn_i, \qquad (3)$$

where in the last term i runs from 1 to k save when the pair Y, X is taken to be μ_1, n_1, in which case, if $k>1$, we shall have $i=2\cdots k$. And hereupon we shall denote the seven characteristic functions based on U by A, G, H, U', A', G', H' and define these according to

$$\begin{aligned} & & U'&=U-YX,\\ A&=U-TS, & A'&=A-YX,\\ G&=U-TS+PV, & G'&=G-YX,\\ H&=U+PV, & H'&=H-YX. \end{aligned} \qquad (4)$$

If on the other hand the primitive characteristic function is *not* the energy, we shall denote that function by U^* and the characteristic functions based on it by A^*, G^*, H^*, $U^{*\prime}$, etc. And then we shall have equations derivable from (3) and (4) by adding asterisks.

The class of equations resolvable into families by the methods to be set forth consists of all the equations deducible from Eqs. (3) and (4)—or from their analogues in U^*, etc.—by mathematical operations, in conjunction with only the assumption that of the $2k+14$ variables involved (or $2k+12$ in the special case that Y, X is μ_1, n_1; see Example 4 below), any $k+3$ (or $k+2$) may be taken as independent, that fulfill the following two conditions: the set of $k+3$ (or $k+2$) may *not* (i) include a set whose members are interrelated through (4); (ii) be of the type A, B, C, μ_i where A, B, C are respectively members of the three pairs T, S; P, V; Y, X. The function of condition (ii) is to exclude the sets T, P, Y, μ_i and T, P, X, μ_i from use as independent variables. This is necessary because, according as Y or X is intensive, independent variation of T, P, Y, μ_i or T, P, X, μ_i is impossible physically, as may be seen from the Gibbs–Duhem equation implied by (3), which, if Y is intensive reads

$$SdT-VdP+XdY+\sum_i n_i d\mu_i=0 \qquad (5)$$

and if X is intensive, has $-YdX$ in place of $+XdY$.

We shall now illustrate the leading case by four examples of physical interest.

Example 1

The system of interest consists of two fluid phases and a plane interface formed by their contact, all in equilibrium. The energy U of this system is subject to a Gibbsian equation which reads

$$dU=TdS-PdV+\sigma d\Omega+\sum_i \mu_i dn_i, \qquad (6)$$

where σ and Ω denote, respectively, the tension, and the area of the interface, and the other letters on the right refer (like U) to the entire system. Eq. (6) is a special case of (3) with

$$Y=\sigma, \qquad X=\Omega. \qquad (7)$$

Hence, U is the primitive member of a set of eight characteristic functions of which the seven others are obtained by inserting (7) into (4). Note that here X is *extensive.*

Example 2

The system of interest consists of a homogeneous portion of a dielectric fluid α in equilibrium, and arranged as follows (i) α lies between the plates of a plane electrostatic condenser of variable charge, and of plate area very great compared with the plate separation, which are both fixed; (ii) α touches both plates; and that part of the surface of α not touching either plate—call this the "free surface" of α—is normal to both plates and relatively distant from their rims; (iii) between the plates all the space not filled with α has the permittivity of empty space; (iv) the volume V of α can be varied only by moving the free surface of α. Under these constraints the electric field strength has the same value $\mathcal{E}$ at all points between the plates, while the electric displacement has the value $\epsilon\mathcal{E}$ or $\epsilon_0\mathcal{E}$ according as the point (between the plates) lies inside or outside of α—where ϵ and ϵ_0 denote the permittivities of α and empty space respectively. The energy U of this system is subject to a Gibbsian equation which reads

$$dU=TdS-PdV+Jd\mathfrak{D}+\sum_i \mu_i dn_i. \tag{8}$$

In this equation, $\mathfrak{D}$ denotes the electric displacement in α (equal to $\epsilon\mathcal{E}$ as just noted); J is defined by

$$J=\mathcal{E}V/4\pi, \tag{9}$$

and P is a "pressure" defined by

$$P=P_{pa}-\mathcal{E}\mathfrak{D}/4\pi+\epsilon_0\mathcal{E}^2/8\pi, \tag{10}$$

where P_{pa} denotes the force per unit area on the free surface of α.[17] Eq. (8) is a special case of (3) with

$$Y=J, \qquad X=\mathfrak{D}. \tag{11}$$

Hence, U is the primitive member of a set of eight characteristic functions of which the seven others are obtained by inserting (11) into (4). Note that here X is *intensive*. But there is a further possibility. Obviously useful would be a set of characteristic functions for which, in the conjugate pair P, V, the member P would be simply P_{pa} rather than the quantity defined by (10). It turns out that the primitive member U^* of such a set is defined by

$$U^*=U-\epsilon_0\mathcal{E}^2V/8\pi. \tag{12}$$

For from (12), (8), (9), and (10) we find

$$dU^*=TdS-PdV+\mathcal{E}dI+\sum_i \mu_i dn_i, \tag{13}$$

where

$$P=P_{pa}, \tag{14}$$

$$I=(\mathfrak{D}V-\epsilon_0\mathcal{E}V)/4\pi=(\epsilon-\epsilon_0)J. \tag{15}$$

And so, the seven remaining characteristic functions are obtained by inserting

$$Y=\mathcal{E}, \qquad X=I, \tag{16}$$

into the Eqs. (4) taken with asterisks. Note that here X is *extensive*.

Example 3

The system of interest consists of a homogeneous portion of fluid α in equilibrium, and arranged as follows (i) α forms a cylindrical core within a uniformly wound solenoid of variable current, and of length very great compared to the cross section, which are both fixed; (ii) the cross section of α is smaller than that of the solenoid; (iii) within the solenoid, all the space not filled by α has the permeability of empty space; (iv) the volume of α can be varied only by moving the mantel of its (cylindrical) surface normal to itself. Under these constraints the magnetic field strength has the same value $\mathcal{H}$ at all points within the solenoid, while the magnetic induction has the value $\eta\mathcal{H}$ or $\eta_0\mathcal{H}$ according as the point (within the solenoid) lies inside or outside of α—where η and η_0 denote the permeabilities of α and of empty space respectively (we use η instead of the more customary μ because we use μ_i for chemical potential). This system is the magnetic analogue of the electrostatic system of Example 2, and is subject to equations obtainable from (8) to (16) by replacing $\mathcal{E}$, $\mathfrak{D}$, ϵ, ϵ_0 by $\mathcal{H}$, $\mathcal{B}$, η, η_0—where $\mathcal{B}$ denotes the magnetic induction in α (equal to $\eta\mathcal{H}$ as just noted), and P_{pa} now denotes the force per unit area on the cylinder-mantel of α. And so we have again two sets of eight characteristic functions: U, A, etc. and U^*, A^*, etc.[18]

Example 4

The system of interest consists of a single phase in equilibrium, just as in the case of the four characteristic functions in Eqs. (1) and (2). But now we transcribe (2) to the form

$$dU=TdS-PdV+\mu_1 dn_1+\sum_i \mu_i dn_i \tag{17}$$

with i running from 2 to k—and so indicate that we mean to have the conjugate pair μ_1, n_1 enter into the Legendre transformations upon U. Then (17) is a special case of (3) with

$$Y=\mu_1, \qquad X=n_1. \tag{18}$$

Hence, we have eight characteristic functions consisting of U and the seven obtained by inserting (18) into (4). Note that here X is *extensive.*

The Thermodynamic Octahedron

Figure 1 shows the octahedron we shall use for the present leading case. We shall call it the "thermodynamic octahedron," in analogy to the term "thermodynamic square" mentioned above. The six vertices of the octahedron are assigned to the six variables T, S, P, V, Y, X in such wise that the two variables, respectively, at the ends of each diagonal, are conjugate. Thereupon the eight faces are assigned to the eight characteristic functions in such wise that each of the latter is framed by the variables "natural" to it; that is, when the primitive function is U we assign the faces

$$\begin{aligned} &SVX \text{ to } U, && SVY \text{ to } U', \\ &VTX \text{ to } A, && VTY \text{ to } A', \\ &TPX \text{ to } G, && TPY \text{ to } G', \\ &PSX \text{ to } H, && PSY \text{ to } H', \end{aligned} \tag{19}$$

and when the primitive function is U^* we assign the faces similarly to U^*, A^*, etc. This labeling is indicated in Fig. 1 by the eight arrows. The center of the octahedron is assigned to the $2k$ variables (or $2k-2$ for Example 4 above) μ_i, n_i. The hexagon within the octahedron indicates the plane which passes through the midpoints of the edges SV, VX, XT, TP, PY, YS, and so, cuts the octahedron into two congruent halves. We shall call this plane the "Prins boundary" because it constitutes the extension to the thermodynamic octahedron of the line introduced by Prins as described above to obtain the correct signs from the thermodynamic square. Note that on removing the diagonal YX from Fig. 1, the octahedron and its Prins boundary collapse to give the square and line just mentioned.

From the thermodynamic octahedron we shall now derive first the substitutions of the Prins type,[8] and then those of the Koenig type.[1] We adopt this order because the latter substitutions are briefly describable in terms of the former, but not vice versa.

Extension of the Prins Method

In Fig. 1, disregard the Prins boundary until further notice, and suppose all the letters to be rigidly attached to their respective parts (vertices, faces, center) of the octahedron. Consider then all the distinct figures generated from Fig. 1 by rotation, and coinciding with it in respect of vertices (and so of faces and center) but not of all the attached letters. The number of figures so derivable from Fig. 1 is evidently 23. Next, generate 24 further figures by subjecting all of the 24 now on hand (Fig. 1 and the 23 derived from it by rotation) to reflection in one and the same plane normal to one of the diagonals of the octahedron in Fig. 1, e.g., a plane normal to the diagonal VP. Hereupon modify the 48 figures *now* on hand by using the Prins boundary as follows: Require the Prins boundary *not* to take part in the rotations and reflections mentioned, but rather to lie, in each of the 47 figures generated, parallel to the Prins boundary in Fig. 1; then in each figure *either* leave each of the three letters S, P, X with an implicit plus sign (as in Fig. 1), *or* give it a minus sign, according as the letter lies, in that figure, on the same side of the Prins boundary as in Fig. 1, or on the opposite side. For example, in the figure obtained by rotating Fig. 1 about the diagonal XY clockwise by 90°, the three letters will read $-S$, P, X; and in the figure obtained by reflecting Fig. 1 in a plane normal to the

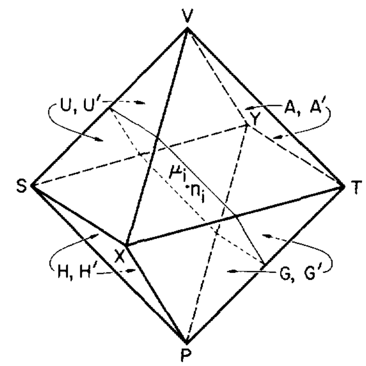

FIG. 1. "Thermodynamic octahedron" with "Prins boundary," to generate substitutions appropriate to eight characteristic functions.

diagonal VP, the three letters will read S, $-P$, X. Finally, generate a set of 48 substitutions by superposing upon Fig. 1, in turn, each of the 48 figures as they now stand. The order in which the figures are taken is of course immaterial. We have chosen an order which produces regularities in Table I. This table gives substitution no. n ($n=1\cdots 48$) as the substitution of Row 1 by Row n. It applies to the usual case that the primitive characteristic function is U. If that function is U^* the first eight columns will have asterisks.

Any equation based, as above described, on Eqs. (3) and (4), when transformed by the 48 substitutions of Table I, yields the corresponding family of equations. Four further features of the Prins method as here extended deserve mention.

1. A substitution given by two rows of Table I of which neither is the first (corresponding to superposition of two figures both different from Fig. 1) may be one of the 48 substitutions in question (e.g., Row 2 by Row 3 gives Row 1 by Row 2) or may not be (e.g., Row 3 by Row 4; but we shall see shortly that such substitutions generate correct family members). This implies that the 48 substitutions in question do not form a group—a feature in which they resemble Prins's 8 substitutions for the case of 4 characteristic functions. But, as in the latter case, this aesthetic lack is compensated by the practical advantage of direct applicability.

2. In using the thermodynamic octahedron to obtain substitutions of the Prins type we are not restricted to taking Fig. 1 as that upon which the 48 figures are to be superposed: We may on the contrary replace Fig. 1 for this purpose by any of the other 47. This means that if we rearrange Table I so that each of its Rows 2 to 48 becomes in turn the first row, the 47 further sets of substitutions so defined, though not identical with those of Table I, will be valid in that they generate the same families.

3. We are not restricted to the above choice of S, P, X for the variables undergoing change of sign on crossing the Prins boundary (cf. Ref. 13). With the latter located as in Fig. 1 any of the *other* seven triples

TABLE I. Substitutions of the Prins type for the leading case.

Row No.															
1	U	A	G	H	H'	G'	A'	U'	S	V	X	T	P	Y	$\mu_i n_i$
2	H	U	A	G	G'	A'	U'	H'	P	$-S$	X	V	T	Y	$\mu_i n_i$
3	G	H	U	A	A'	U'	H'	G'	T	$-P$	X	$-S$	V	Y	$\mu_i n_i$
4	A	G	H	U	U'	H'	G'	A'	V	T	X	$-P$	S	Y	$\mu_i n_i$
5	U'	A'	A	U	H	G	G'	H'	S	Y	V	T	X	$-P$	$\mu_i n_i$
6	U	U'	A'	A	G	G'	H'	H	X	$-S$	V	Y	T	$-P$	$\mu_i n_i$
7	A	U	U'	A'	G'	H'	H	G	T	$-X$	V	$-S$	Y	$-P$	$\mu_i n_i$
8	A'	A	U	U'	H'	H	G	G'	Y	T	V	$-X$	S	$-P$	$\mu_i n_i$
9	H'	U'	U	H	G	A	A'	G'	P	Y	S	V	X	T	$\mu_i n_i$
10	H	H'	U'	U	A	A'	G'	G	X	$-P$	S	Y	V	T	$\mu_i n_i$
11	U	H	H'	U'	A'	G'	G	A	V	$-X$	S	$-P$	Y	T	$\mu_i n_i$
12	U'	U	H	H'	G'	G	A	A'	Y	V	S	$-X$	P	T	$\mu_i n_i$
13	G'	A'	U'	H'	H	U	A	G	P	T	Y	V	S	$-X$	$\mu_i n_i$
14	H'	G'	A'	U'	U	A	G	H	S	$-P$	Y	T	V	$-X$	$\mu_i n_i$
15	U'	H'	G'	A'	A	G	H	U	V	$-S$	Y	$-P$	T	$-X$	$\mu_i n_i$
16	A'	U'	H'	G'	G	H	U	A	T	V	Y	$-S$	P	$-X$	$\mu_i n_i$
17	G	G'	H'	H	U	U'	A'	A	X	T	P	Y	S	V	$\mu_i n_i$
18	H	G	G'	H'	U'	A'	A	U	S	$-X$	P	T	Y	V	$\mu_i n_i$
19	H'	H	G	G'	A'	A	U	U'	Y	$-S$	P	$-X$	T	V	$\mu_i n_i$
20	G'	H'	H	G	A	U	U'	A'	T	Y	P	$-S$	X	V	$\mu_i n_i$
21	A	A'	G'	G	H	H'	U'	U	X	V	T	Y	P	$-S$	$\mu_i n_i$
22	G	A	A'	G'	H'	U'	U	H	P	$-X$	T	V	Y	$-S$	$\mu_i n_i$
23	G'	G	A	A'	U'	U	H	H'	Y	$-P$	T	$-X$	V	$-S$	$\mu_i n_i$
24	A'	G'	G	A	U	H	H'	U'	V	Y	T	$-P$	X	$-S$	$\mu_i n_i$
25	A	G	G'	A'	U'	H'	H	U	V	$-X$	T	$-P$	Y	$-S$	$\mu_i n_i$
26	A'	A	G	G'	H'	H	U	U'	Y	V	T	$-X$	P	$-S$	$\mu_i n_i$
27	G'	A'	A	G	H	U	U'	H'	P	Y	T	V	X	$-S$	$\mu_i n_i$
28	G	G'	A'	A	U	U'	H'	H	X	$-P$	T	Y	V	$-S$	$\mu_i n_i$
29	G	H	H'	G'	A'	U'	U	A	T	$-X$	P	$-S$	Y	V	$\mu_i n_i$
30	G'	G	H	H'	U'	U	A	A'	Y	T	P	$-X$	S	V	$\mu_i n_i$
31	H'	G'	G	H	U	A	A'	U'	S	Y	P	T	X	V	$\mu_i n_i$
32	H	H'	G'	G	A	A'	U'	U	X	$-S$	P	Y	T	V	$\mu_i n_i$
33	G'	H'	U'	A'	A	U	H	G	T	$-P$	Y	$-S$	V	$-X$	$\mu_i n_i$
34	A'	G'	H'	U'	U	H	G	A	V	T	Y	$-P$	S	$-X$	$\mu_i n_i$
35	U'	A'	G'	H'	H	G	A	U	S	V	Y	T	P	$-X$	$\mu_i n_i$
36	H'	U'	A'	G'	G	A	U	H	P	$-S$	Y	V	T	$-X$	$\mu_i n_i$
37	H'	H	U	U'	A'	A	G	G'	Y	$-P$	S	$-X$	V	T	$\mu_i n_i$
38	U'	H'	H	U	A	G	G'	A'	V	Y	S	$-P$	X	T	$\mu_i n_i$
39	U	U'	H'	H	G	G'	A'	A	X	V	S	Y	P	T	$\mu_i n_i$
40	H	U	U'	H'	G'	A'	A	G	P	$-X$	S	V	Y	T	$\mu_i n_i$
41	U'	U	A	A'	G'	G	H	H'	Y	$-S$	V	$-X$	T	$-P$	$\mu_i n_i$
42	A'	U'	U	A	G	H	H'	G'	T	Y	V	$-S$	X	$-P$	$\mu_i n_i$
43	A	A'	U'	U	H	H'	G'	G	X	T	V	Y	S	$-P$	$\mu_i n_i$
44	U	A	A'	U'	H'	G'	G	H	S	$-X$	V	T	Y	$-P$	$\mu_i n_i$
45	U	H	G	A	A'	G'	H'	U'	V	$-S$	X	$-P$	T	Y	$\mu_i n_i$
46	A	U	H	G	G'	H'	U'	A'	T	V	X	$-S$	P	Y	$\mu_i n_i$
47	G	A	U	H	H'	U'	A'	G'	P	T	X	V	S	Y	$\mu_i n_i$
48	H	G	A	U	U'	A'	G'	H'	S	$-P$	X	T	V	Y	$\mu_i n_i$

given in (19) will do as well, i.e., produce a valid set of substitutions. It will be expedient to call any triple selected for change of sign the "active triple."

4. The Prins boundary need not be restricted to the choice shown in Fig. 1. Any of the three analogous hexagons will do as well, provided we observe the following rule for the active triple: According as *all three* variables fall (through rotation and/or reflection of the octahedron) on *one* or on *the other* side of the Prins boundary, they have the signs possessed by the corresponding terms in the two Gibbsian equations in which all three appear respectively as *differentials* or as *derivatives* (i.e., coefficients of the differentials of their respective conjugates).[19] Note that under the (implicit) positive signs which the variables S, V, X, T, P, Y have in Fig. 1, this rule is obeyed: Thus the two possibilities S, P, X and $-S$, $-P$, $-X$ required by the rule correspond respectively to the two Gibbsian equations

$$dH=TdS+VdP+YdX+\sum_i \mu_i dn_i,$$

$$dA'=-SdT-PdV-XdY+\sum_i \mu_i dn_i. \qquad (20)$$

And if, for example, in Fig. 1, we change the Prins boundary to that defined by the midpoints of VX and VT, the triple T, P, Y, if chosen as active, must appear in the resulting figure either as $-T$, P, Y or (equally well) as T, $-P$, $-Y$.

Extension of the Koenig Method

Modify Fig. 1 by deleting the Prins boundary and giving minus signs to the three letters S, P, X. From this modified Fig. 1, generate 47 other figures by rotations and reflections the same as before. Then generate 48 substitutions by superimposing upon the modified Fig. 1, in turn, each of the 48 figures as they *now* stand. The result may be embodied in a table derivable from Table I by giving S, P, and X minus signs *throughout*. Any equation based as described on (3) and (4), when written in "standard form" and then transformed by the 48 substitutions in question, yields the corresponding family of equations.

The necessary standard form is given by the following three directives: (i) Define the operator $\ulcorner\ \urcorner$ by the condition

$$\ulcorner x\urcorner=\ulcorner -x\urcorner=x, \qquad (21)$$

where x stands for any of the symbols T, S, P, V, Y, X. (ii) If the equation to be transformed contains both T and S, then enclose *either* the letter T wherever it occurs, *or* the letter S wherever it occurs, in the operator $\ulcorner\ \urcorner$; but if the equation contains only T without S, or *vice versa*, leave that letter unchanged. (iii) Treat similarly each of the pairs P, V, and Y, X.[20] After transformation of an equation in standard form has been carried out, removal of the symbols $\ulcorner\ \urcorner$ yields the equation in ordinary form. Two further features of the Koenig method as here extended deserve mention.

1. In the table derived from Table I as just described, the substitution given by any two rows whatever (corresponding to the superposition of any two of the 48 modified figures) is one of the 48 substitutions in question. The latter therefore form a group, as do Koenig's eight substitutions for the case of four characteristic functions. But, as in the latter case, this aesthetically pleasing feature entails the practical inconvenience of the need for the standard form for transformation.

2. Instead of giving minus signs to S, P, X in Fig. 1, we may give them to their conjugates T, V, Y. The resulting table is then to be derived from Table I by deleting the minus signs there present, and giving minus signs to T, V, Y throughout.

The Number of Members in a Family

The equations of greatest physical interest belong to families having 48, 24, 12, or 8 members. The remaining possibilities for the number of members per family are 6, 4, 3, 1. We give one example of each kind:

48 members:

$$(\partial U/\partial V)_{T,X,n_i}=T(\partial P/\partial T)_{V,X,n_i}-P, \qquad (22)$$

24 members:

$$(\partial T/\partial V)_{S,X,n_i}=-(\partial P/\partial S)_{V,X,n_i}, \qquad (23)$$

12 members:

$$A=U-TS, \qquad (24)$$

8 members:

$$dU=TdS-PdV+YdX+\sum_i \mu_i dn_i, \qquad (25)$$

6 members:

$$U-A+G-H=0, \qquad (26)$$

4 members:

$$U-G'=TS-PV+YX, \qquad (27)$$

3 members:

$$U+A+G+H-H'-G'-A'-U'=4YX, \qquad (28)$$

1 member:

$$U-A+G-H+H'-G'+A'-U'=0. \qquad (29)$$

THE MASSIEU CASE

The foregoing treatment of the leading case is readily extended to other cases. For illustration we shall take the entropy S and its seven Legendre transforms derivable from Eq. (3). We may call this the "Massieu case" corresponding to the leading case.

We solve (3) for dS and note that the result can be written in the following form analogous to (3)

$$dS=(1/T)dU-(Y/T)dX+(P/T)dV+\sum_i (-\mu_i/T)dn_i. \qquad (30)$$

Then in analogy to (4) we define the seven further characteristic functions $J_2, J_3, J_4, J_1', J_2', J_3', J_4'$ according to

$$\begin{aligned} & & J_1' &= S-(P/T)V, \\ J_2 &= S-(1/T)U, & J_2' &= J_2-(P/T)V, \\ J_3 &= S-(1/T)U+(Y/T)X, & J_3' &= J_3-(P/T)V, \\ J_4 &= S+(Y/T)X, & J_4' &= J_4-(P/T)V. \end{aligned} \tag{31}$$

We consider then, the substitution

$$\begin{pmatrix} U & A & G & H & H' & G' & A' & U' & S & V & X & T & P & Y & \mu_i & n_i \\ S & J_2 & J_3 & J_4 & J_4' & J_3' & J_2' & J_1' & U & X & V & 1/T & Y/T & P/T & -\mu_i/T & n_i \end{pmatrix}. \tag{32}$$

From the analogy of (30) and (31) to (3) and (4) respectively, it follows that the substitution (32) will transform (i) any family of the leading case into a corresponding family for the Massieu case; (ii) the above Table I into a table of Prins type for the Massieu case; (iii) the table of Koenig type for the leading case (derived from Table I as described) into a table of that type for the Massieu case. The latter table is of course to be used in conjunction with a standard form based on (21) with x now standing for any of the symbols $1/T$, U, Y/T, X, P/T, V.

CONCLUDING REMARK

In accord with its intention declared at the outset, the foregoing discussion centers on the *geometrical* features of the case of 8 characteristic functions. Beyond this, it suggests two questions concerning the associated *group-theoretical* features. (i) Since the original Prins substitutions are a subset of a group of 32 substitutions,[6,7,8] of what group are the extended Prins substitutions given in our Table I a subset? (ii) Can the group-theoretical features exhibited by the cases of four and eight characteristic functions be extended to the higher cases (the corresponding geometrical features would then occur in hyperspaces of $n \geq 4$ dimensions), and if so, how? The author hopes that others more knowledgeable than he in group theory will answer these questions.

[1] F. O. Koenig, J. Chem. Phys. **3**, 29 (1935). In our further footnotes we shall refer to this paper as Ko.

[2] The present quantities U, A, G, H were denoted in Ko as E, A, F, H and there called "characteristic functions." We shall retain this term here despite the fact that today it is used less often than "thermodynamic potentials."

[3] Two remarks: (a) In Ko the class of equations resolvable into families is called the "f_1^1-class." We shall not need this term here. (b) The definition given in Ko of the class in question is too weak. It becomes correct if the first of the two "basic assumptions" on p. 30 of Ko is replaced by the above assumption on independent variables. In this assumption condition (ii) has the function of barring the set T, P, μ_i from use as independent variables.

[4] H. A. C. McKay, J. Chem. Phys. **3**, 715 (1935).

[5] F. Buckley, J. Res. Natl. Bur. Std. **33**, 213 (1944).

[6] W. D. Hayes, Quart. of Appl. Math. **4**, 227 (1946).

[7] J. A. Prins, Physica **13**, 417 (1947).

[8] J. A. Prins, J. Chem. Phys. **16**, 65 (1948).

[9] H. B. Callen, *Thermodynamics* (Wiley, Inc., New York, 1960), pp. 119, 121, 194, 224, 246, 247.

[10] This fact is not stated in Ko but has been made familiar by subsequent discussions e.g., that of H. B. Callen in *Thermodynamics* (Wiley, New York, London, 1960), pp. 90–101.

[11] That Prins's 1947 paper represents independent discovery is proved by its Footnote 2.

[12] In Footnote 1 of his 1948 paper Prins cites Ko and adds: "Professor M. Born informs me that the subject was also treated in his lectures at Göttingen and that a poem was made for memorizing the substitutions." The history here traced therefore exhibits two cases of independent multiple discovery, Prins's rediscovery of Hayes's 32-group, and Koenig's rediscovery of Born's method based on the square. Born, however, never published anything on the subject. This has not prevented the square from becoming known as the "Born diagram"; see for instance W. W. Bowley, Am. J. Phys. **37**, 1066 (1969).

[13] The extensivity of V and S is, however, irrelevant here, since any of the other three pairs V, T, or T, P, or P, S may also be elected for change of sign. We shall enlarge on this fact later.

[14] A footnote attached by Callen to his diagram shows it to be the version used by Born. This version has been adopted in a number of later texts, e.g., S. M. Blinder, *Advanced Physical Chemistry* (Macmillan, Collier–Macmillan Ltd., London, 1969), p. 341; P. A. Rock, *Chemical Thermodynamics, Principles and Applications* (Macmillan, Collier–Macmillan Ltd., London, 1969), p. xv. On the other hand, the versions of Koenig and of Prins are featured in C. E. Reid, *Principles of Chemical Thermodynamics* (Rheinhold, New York; Chapman and Hall, Ltd., London, 1960), pp. 261–264.

[15] F. O. Koenig, J. Phys. Chem. **41**, 608 (1937).

[16] Ko, p. 35.

[17] F. O. Koenig, Footnote 15, Eq. (29). The deductions there assume $\epsilon_0 = 1$, which is true only in cgs units. Here we have dropped that restriction.

[18] For a careful discussion of the thermodynamics of this and other magnetic systems see E. A. Guggenheim, Proc. Roy. Soc. (London) **155**, 70 (1936). Guggenheim's equations for the present system differ from those indicated above [by analogy to our Eqs. (7)–(15)] in that they apply to the *entire* content of the solenoid (fluid α *and* vacuum), and are restricted to constant composition. Cf. F. O. Koenig, Footnote 15, pp. 597–598.

[19] Likewise in the thermodynamic square the Prins boundary is not restricted to that connecting initially the midpoints of the sides SV and TP; we may take the other possibility if we observe the rule analogous to that just given.

[20] In Ko, p. 31, I used, instead of the above operator $\ulcorner\ \urcorner$, the *absolute value sign* denoted as usual by $|\ \ |$, and justified this by the remark that "the quantities P, V, T, S are essentially positive," which is weak because, for one thing, P may in certain circumstances be negative. The definition (21) frees our discussion of this difficulty. I am indebted for it to R. J. Bearman. Let me emphasize that we must adhere strictly to the interpretation of x as one of the *symbols* specified, and that in particular we may *not* take x to be a *number*, since this would lead to absurdities such as $1 = -1$.