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Families of Thermodynamic Equations. I

The Method of Transformations by the Characteristic Group

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Attention is called to the fact that certain important equations of thermodynamics such as the two Gibbs-Helmholtz equations may be grouped into families, but that a precise definition of such families has hitherto been lacking. For the case of a single phase of k components in equilibrium a method is given for splitting a certain class of equations, the "$f_1{}^1$-equations," into families in a precise manner as follows. The $f_1{}^1$-class of equations is defined by means of four "basic" equations and two "basic" assumptions, and involves the $2k+8$ variables E, H, F, A, V, S, P, T, μ_i, n_i. For the $f_1{}^1$-equations there is in turn defined a number of "standard forms" which depend upon the introduction of absolute value signs in a certain way. Then the "characteristic group," a substitution group of the eighth order on the letters E, H, F, A, V, $-S$, $-P$, T, μ_i, n_i is generated by a series of geometrical operations on a square. The theorem is stated that the transformation of any $f_1{}^1$-equation in standard form by any element of the characteristic group yields an $f_1{}^1$-equation in standard form. No formal proof of this theorem is given, but its correctness is sufficiently demonstrated by systematic verification. The theorem leads immediately to the definition of a family of $f_1{}^1$-equations as the totality of distinct $f_1{}^1$-equations resulting from the transformation of a given $f_1{}^1$-equation in standard form by all the elements of the characteristic group. It is found that every $f_1{}^1$-equation is a member of one and only one $f_1{}^1$-family. The method increases the number of fundamental equations readily available and emphasizes the symmetry of these equations.

A. INTRODUCTION

1. The existence of families of thermodynamic equations

It has been recognized since the work of Gibbs that many of the important equations of thermodynamics fall into families of marked algebraical symmetry. Of this the Gibbs-Helmholtz equations are a well known example:

$$E=A-T(\partial A/\partial T)_{V,\, n_i}, \qquad (1.1)$$

$$H=F-T(\partial F/\partial T)_{P,\, n_i}.[1] \qquad (1.2)$$

Hitherto the recognition of these families seems to have been more intuitive than explicit, in that it has to the author's knowledge never been exactly stated what constitutes such a family. Thus no immediate answer suggests itself to the question whether the family to which Eqs. (1.1) and (1.2) belong has any further members, and, if so, how the latter may be found.

2. Method of the present paper

This paper (communication I) gives a method for splitting an important class (defined below and referred to as the "$f_1{}^1$-class") of thermodynamic equations into families. The method consists in deducing the family to which a particular equation of the class in question belongs, by writing the equation in a certain form (the "standard form") and then transforming it by the elements of a certain substitution group (the "characteristic group"). This group in turn can be generated geometrically.

3. The thermodynamic system to be considered

The definitions of the class of equations in question and of the corresponding substitution group depend somewhat upon the type of thermodynamic system considered. In this paper only one type of system will be dealt with, namely an open system made up of an arbitrary number $k (k \geq 1)$ of components in a single phase (volume phase) in internal equilibrium. An open system is one in which the amounts of the components and consequently the total mass are freely variable. For simplicity it is assumed that the pressure is the same at each point within the phase, i.e., that gravity is absent. External electric and magnetic fields are also assumed to be absent or of negligible influence.

The treatment of certain other types of systems will be given in a later paper.

[1] The meaning of all symbols is given below.

B. The Fundamental Thermodynamic Equations (f_1^1- and f_2^1-Equations) of the System

1. Necessity of defining the f^1-class of equations

The class of thermodynamic equations which can be resolved into families by the group method developed in this paper is part of a larger class of equations which are properly regarded as the fundamental thermodynamic equations of the system and which for reasons apparent in a later paper (communication II) will be referred to as the "fundamental equations of the first order of generality" or abbreviated, as the f^1-equations. It is expedient to define first the larger class of the f^1-equations and then the subclass which can be treated by the group method in question.

2. The basic equations

The definition of the f^1-class of equations depends upon four equations which will be known as the basic equations. These are conveniently taken to be:

$$E=H-VP, \tag{2.1}$$

$$H=F+ST, \tag{2.2}$$

$$F=A+PV, \tag{2.3}$$

$$dE=-PdV+TdS+\sum_i \mu_i dn_i. \tag{3}$$

E, H, F and A denote, respectively, the energy, heat content, Gibbs free energy and Helmholtz free energy of the system, and are called the characteristic functions. V, S, P, T, μ_i and n_i denote, respectively, the volume, entropy, pressure, temperature, chemical potential of the ith component and amount of the ith component.

3. The basic assumptions

In addition to the basic equations there are necessary for the definition of the f^1-equations two physically valid assumptions, to be known as the basic assumptions. They are the following: (i) The $k+3$ differentials appearing in Eqs. (3) are total differentials. (ii) E is a homogeneous function of the first order in the $k+2$ capacity factors V, S, n_i.

4. The f^1-equations

Such equations in any or all of the $2k+8$ variables E, H, F, A, V, S, P, T, μ_i, n_i as can by mathematical operations be obtained from the four basic equations and no physical assumptions other than the two basic assumptions will be known as the f^1-equations. The four basic equations are evidently members of the class of f^1-equations because any equation can be obtained from itself, e.g., through multiplication by unity. It is furthermore evident that the particular Eqs. (2), (3) do not represent the only possible choice of basic equations: any set of three equations defining three of the characteristic functions in terms of the fourth and of V, S, P, T will serve as well as the particular set (2), and Eq. (3) may be replaced by any one of the other three general Gibbsian equations (see Eqs. (13) below) of the system.

5. Division of the f^1-class into the f_1^1- and the f_2^1-classes

The thermodynamic equations subject to the group method described in this paper form a subclass of the f^1-class comprising only such f^1-equations as do not depend upon basic assumption (ii) above. This subclass will be known as the "f^1-equations of the first kind," or abbreviated, as the f_1^1-equations. The basic Eqs. (2), (3) and the Gibbs-Helmholtz Eqs. (1) are examples of f_1^1-equations.

Such f^1-equations on the other hand as depend upon basic assumption (ii) will be known as the "f^1-equations of the second kind," or f_2^1-equations. An example is the equation:

$$E=-PV+TS+\sum_i \mu_i n_i \tag{4}$$

obtained by applying Euler's theorem to (3). The f_2^1-class cannot be split into families by the group method of this paper. A method less elegant but powerful enough to resolve the entire f^1-class will be given in a later paper (communication II).

C. The f_1^1-Equations in Standard Form

The method described below (Parts E and F) necessitates writing the f_1^1-equations in certain forms to be known as "standard." These standard forms yield no new information: they are merely a mathematical device. For any given $f_1{}^1$-equation the standard forms are defined by the following two rules: (i) If the equation contains both P and V then *either* the letter P wherever it occurs *or* the letter V wherever it occurs is to be enclosed in an absolute value sign, thus: $|P|$ or $|V|$. Which of the two letters is so enclosed is immaterial. If the equation contains only P without V, or *vice versa*, the letter present is to be left unchanged. (ii) A procedure similar to (i) is to be applied to the letters T and S. Eq. (2.1) for example has two standard forms:

$$E=H-|V|P, \quad E=H-V|P|. \qquad (5.1), (5.2)$$

It is clear that as regards standard forms there are only three types of $f_1{}^1$-equations, characterized by one, two and four standard forms and illustrated by Eqs. (1), (2) and (3), respectively

If any given $f_1{}^1$-equation is written in any one of its standard forms, the resulting $f_1{}^1$-equation will be said to be "in standard form," and if every equation of the $f_1{}^1$-class is imagined to be written in every one of its standard forms, the result will be referred to as the "$f_1{}^1$-class in standard form."

Since for any system in thermodynamic equilibrium (Part A) the quantities P, V, T, S are essentially positive, writing the $f_1{}^1$-equations in standard form incurs no loss of generality.

D. The Characteristic Group and the Characteristic Array

1. The characteristic group

The central part in the resolution of the $f_1{}^1$-class into families is played by a set of eight substitutions on the ten letters E, H, F, A, V, $-S$, $-P$, T, μ_i, n_i. This set of substitutions moreover forms a group because it can be obtained by a geometrical method of a type often used to generate groups.

Fig. 1a represents a square of which each side is regarded as belonging to one of the four characteristic functions E, H, F, A in the definite order shown, and each vertex to one of the four variables V, $-S$, $-P$, T also in the definite order shown. It may be noted that corresponding intensity and capacity factors occupy opposite

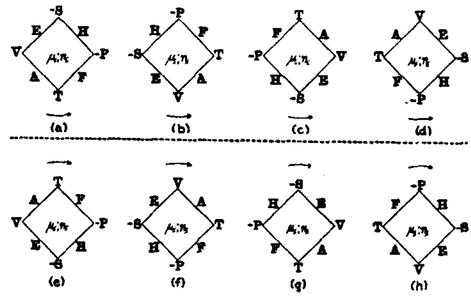

FIG. 1.

vertices and have opposite signs. The center of the square belongs to the k pairs of variables μ_i, n_i. By rotation and reflection of Fig. 1a in its plane the seven Figs. 1b, $\cdots$ 1h can be generated. The superposition of any two figures brings about a superposition of letters which is definite except for μ_i and n_i. This indefiniteness is removed by the convention that μ_i and n_i always fall upon themselves. Superposition of any particular pair of figures then becomes symbolic of the substitution of the set E, H, F, A, V, $-S$, $-P$, T, μ_i, n_i by a particular one of its permutations. It is readily verified that the superposition of Figs. 1a, $\cdots$ 1h upon themselves and upon one another in all possible pairs leads to a group of but eight distinct substitutions, s_1, $\cdots$ s_8, as follows:

$$s_1=\begin{pmatrix} E & H & F & A & V & -S & -P & T & \mu_i & n_i \\ E & H & F & A & V & -S & -P & T & \mu_i & n_i \end{pmatrix},$$
$$s_2=\begin{pmatrix} E & H & F & A & V & -S & -P & T & \mu_i & n_i \\ H & F & A & E & -S & -P & T & V & \mu_i & n_i \end{pmatrix},$$
$$s_3=\begin{pmatrix} E & H & F & A & V & -S & -P & T & \mu_i & n_i \\ F & A & E & H & -P & T & V & -S & \mu_i & n_i \end{pmatrix},$$
$$s_4=\begin{pmatrix} E & H & F & A & V & -S & -P & T & \mu_i & n_i \\ A & E & H & F & T & V & -S & -P & \mu_i & n_i \end{pmatrix}, \qquad (6)$$
$$s_5=\begin{pmatrix} E & H & F & A & V & -S & -P & T & \mu_i & n_i \\ A & F & H & E & V & T & -P & -S & \mu_i & n_i \end{pmatrix},$$
$$s_6=\begin{pmatrix} E & H & F & A & V & -S & -P & T & \mu_i & n_i \\ E & A & F & H & -S & V & T & -P & \mu_i & n_i \end{pmatrix}$$

$$s_7=\begin{pmatrix} E & H & F & A & V & -S & -P & T & \mu_i & n_i \\ H & E & A & F & -P & -S & V & T & \mu_i & n_i \end{pmatrix},$$

$$s_8=\begin{pmatrix} E & H & F & A & V & -S & -P & T & \mu_i & n_i \\ F & H & E & A & T & -P & -S & V & \mu_i & n_i \end{pmatrix}.$$

In the condensed notation used in the theory of groups the substitutions (6) become:

$$\begin{aligned} s_1&=I,\\ s_2&=(E\ H\ F\ A)(V\ -S\ -P\ T),\\ s_3&=(E\ F)(H\ A)(V\ -P)(-S\ T),\\ s_4&=(E\ A\ F\ H)(V\ T\ -P\ -S),\\ s_5&=(E\ A)(H\ F)(-S\ T),\\ s_6&=(H\ A)(V\ -S)(-P\ T),\\ s_7&=(E\cdot H)(F\ A)(V\ -P),\\ s_8&=(E\ F)(V\ T)(-S\ -P). \end{aligned} \tag{7}$$

That these substitutions form a group is readily confirmed by constructing their multiplication table, here omitted for brevity.

Each individual substitution, or element, of the group (6) [or (7)] may be regarded as the product of a substitution on E, H, F, A by one on V, $-S$, $-P$, T, μ_i, n_i.[2] Because the group thus correlates certain substitutions on the characteristic functions with certain substitutions on the variables V, $-S$, $-P$, T, μ_i, n_i it will be called the "characteristic group."

2. The characteristic array

In what follows it will often be necessary to introduce the substitutions of the characteristic group into a given equation (always an $f_1{}^1$-equation in standard form), an operation known as transforming the equation by the elements of the group. For this purpose the following summary of the substitutions (6) in the form of an array of eight rows and ten columns is useful:

$$\begin{array}{cccc|cccc|cc} E & H & F & A & V & -S & -P & T & \mu_i & n_i \\ H & F & A & E & -S & -P & T & V & \mu_i & n_i \\ F & A & E & H & -P & T & V & -S & \mu_i & n_i \\ A & E & H & F & T & V & -S & -P & \mu_i & n_i \\ \hline A & F & H & E & V & T & -P & -S & \mu_i & n_i \\ E & A & F & H & -S & V & T & -P & \mu_i & n_i \\ H & E & A & F & -P & -S & V & T & \mu_i & n_i \\ F & H & E & A & T & -P & -S & V & \mu_i & n_i \end{array} . \tag{8}$$

Inspection of the four square areas marked off by the dotted lines shows plainly how the substitutions of the characteristic group are interrelated through cyclic permutation. The array (8) may be regarded as derived from its first row by superposing the eight Figs. 1, in the order 1a, ⋯ 1h, upon Fig. 1a. Because it is closely related to the characteristic group, the array (8) will be known as the "characteristic array."

The characteristic array is of interest not merely for the above-mentioned practical reason, but also because it can be used to resolve the $f_2{}^1$-class of equations, which does not yield to the group method here described, into families; this will be shown in a later paper.

E. The Method for the Deduction of Families of $f_1{}^1$-Equations

1. Relation of the $f_1{}^1$-class to the characteristic group

The property which leads to the definition of families of $f_1{}^1$-equations is expressed by the following theorem: *The transformation of any $f_1{}^1$-equation in standard form by any element of the characteristic group yields an $f_1{}^1$-equation in standard form.* A more compact statement is the following: *The $f_1{}^1$-class in standard form is invariant under the characteristic group.* The rigorous proof of these theorems transcends the scope of this paper. Their correctness may be regarded as established by the examples given below (Part F).

2. Definition of the $f_1{}^1$-families

The first of the above statements leads directly to the following definition: The totality of distinct $f_1{}^1$-equations resulting from the trans-

[2] The latter substitution is formally identical with one on V, $-S$, $-P$, T alone because μ_i and n_i always replace themselves. The group (6) [or (7)] thus defines two sets of substitutions on four letters each. The members of these sets are formally similar and moreover each set alone forms a group of the eighth order, the so-called octic group. From the formal point of view the group (7) is thus one of the simple isomorphisms between the two octic groups on the letters E, H, F, A and V, $-S$, $-P$, T, respectively.

formation of a given $f_1{}^1$-equation in standard form by all the elements of the characteristic group will be called a family of $f_1{}^1$-equations or an $f_1{}^1$-family.

This definition may be supplemented by two others: (i) The individual distinct $f_1{}^1$-equations constituting an $f_1{}^1$-family will be known as its members. (ii) Two $f_1{}^1$-equations will be regarded as distinct if they cannot be converted into each other by operations which besides the two $f_1{}^1$-equations themselves involve only algebraic identities, and they will be regarded as identical if they can be so converted. Definition (ii) regards as identical any two $f_1{}^1$-equations the differences between which are "trivial," because the operations by which such differences can be removed, e.g., transposition, rearrangement of terms in accordance with the formal laws of algebra, introduction or removal of absolute value signs, simple changes of algebraic sign, cancellation of terms by subtraction or division, etc., can be looked upon as derived from algebraic identities.

3. Theorems on $f_1{}^1$-families

It is readily verified that: (i) The $f_1{}^1$-families arising from a given $f_1{}^1$-equation in its various standard forms are all identical, i.e., from a given $f_1{}^1$-equation one and only one $f_1{}^1$-family can arise. (ii) The $f_1{}^1$-families arising from all the members of a given $f_1{}^1$-family are all identical, i.e., every $f_1{}^1$-family is invariant under the characteristic group. It follows that: (iii) Every $f_1{}^1$-equation is a member of one and only one $f_1{}^1$-family.

4. Consideration of a particular case

The above principles may be illustrated by examining in some detail the deduction of the family corresponding to the $f_1{}^1$-equation:

$$(\partial T/\partial V)_{S,\,n_i} = -(\partial P/\partial S)_{V,\,n_i}. \tag{9}$$

This equation evidently has four standard forms. If the particular form chosen is:

$$(\partial|T|/\partial V)_{S,\,n_i} = -(\partial|P|/\partial S)_{V,\,n_i}, \tag{10}$$

the substitutions of the characteristic group, as summarized in the characteristic array (8), yield:

$$\begin{aligned}
\left(\frac{\partial|T|}{\partial V}\right)_{S,\,n_i} &= -\left(\frac{\partial|P|}{\partial S}\right)_{V,\,n_i},\\
-\left(\frac{\partial|V|}{\partial S}\right)_{P,\,n_i} &= -\left(\frac{\partial|T|}{\partial P}\right)_{S,\,n_i},\\
-\left(\frac{\partial|S|}{\partial P}\right)_{-T,\,n_i} &= +\left(\frac{\partial|V|}{\partial T}\right)_{-P,\,n_i},\\
\left(\frac{\partial|P|}{\partial T}\right)_{-V,\,n_i} &= +\left(\frac{\partial|S|}{\partial V}\right)_{-T,\,n_i},\\
\left(\frac{\partial|S|}{\partial V}\right)_{-T,\,n_i} &= +\left(\frac{\partial|P|}{\partial T}\right)_{V,\,n_i},\\
-\left(\frac{\partial|P|}{\partial S}\right)_{-V,\,n_i} &= +\left(\frac{\partial|T|}{\partial V}\right)_{-S,\,n_i},\\
-\left(\frac{\partial|T|}{\partial P}\right)_{S,\,n_i} &= -\left(\frac{\partial|V|}{\partial S}\right)_{-P,\,n_i},\\
\left(\frac{\partial|V|}{\partial T}\right)_{P,\,n_i} &= -\left(\frac{\partial|S|}{\partial P}\right)_{T,\,n_i}.
\end{aligned} \tag{11}$$

The eight equations of this set are readily shown to be $f_1{}^1$-equations in standard form. The set is seen to contain only four distinct $f_1{}^1$-equations, i.e., it constitutes a four membered $f_1{}^1$-family, to which moreover (9) belongs. This family may if desired be obtained in the usual form by dropping from the first four equations of the set (11) the absolute value signs and the minus signs in the subscripts. It can be verified that the three remaining standard forms of (9) as well as the three other members of the $f_1{}^1$-family in question in any of their standard forms all yield the same family.

F. Survey of Some $f_1{}^1$-Families of Physical Interest

Any $f_1{}^1$-equation can be treated by the same method as Eq. (9) above. The results for a number of $f_1{}^1$-equations of physical interest[3] are summarized below. In every case the theorems on which the method is based have been confirmed.

[3] For proof that the equations to be considered are $f_1{}^1$-equations, i.e., for their derivation from the basic equations (without the basic assumption (ii) above) see E. A. Guggenheim, *Modern Thermodynamics by the Methods of Willard Gibbs*, Methuen, London, 1933.

1. The basic families

The basic Eqs. (2) are found to belong to the following four membered $f_1{}^1$-family:

$$E=H-VP, \quad F=A+PV, \qquad H=F+ST, \quad A=E-TS, \tag{12}$$

and the basic Eq. (3) yields the four general Gibbsian equations of the system:

$$\begin{aligned} dE&=-PdV+TdS+\sum_i \mu_i dn_i,\\ dH&=\quad TdS+VdP+\sum_i \mu_i dn_i,\\ dF&=\quad VdP-SdT+\sum_i \mu_i dn_i,\\ dA&=-SdT-PdV+\sum_i \mu_i dn_i. \end{aligned} \tag{13}$$

The $f_1{}^1$-families (12) and (13) may be called the "basic families."

2. Partial derivatives of the characteristic functions

(i) *With respect to* V, S, P, T. The equation:

$$(\partial F/\partial T)_{P,\, n_i}=-S \tag{14}$$

yields an $f_1{}^1$-family of eight members, which may be written in condensed form as:

$$\begin{aligned} \left(\frac{\partial E}{\partial V}\right)_{S,\, n_i}&=-P=\left(\frac{\partial A}{\partial V}\right)_{T,\, n_i},\\ \left(\frac{\partial H}{\partial S}\right)_{P,\, n_i}&=\quad T=\left(\frac{\partial E}{\partial S}\right)_{V,\, n_i},\\ \left(\frac{\partial F}{\partial P}\right)_{T,\, n_i}&=\quad V=\left(\frac{\partial H}{\partial P}\right)_{S,\, n_i},\\ \left(\frac{\partial A}{\partial T}\right)_{V,\, n_i}&=-S=\left(\frac{\partial F}{\partial T}\right)_{P,\, n}. \end{aligned} \tag{15}$$

(ii) *With respect to* n_i. The equation:

$$(\partial F/\partial n_i)_{P,\, T,\, n_i'}=\mu_i, \tag{16}$$

where the subscript n_i' indicates the constancy of all the n_i except the particular one with respect to which the differentiation is carried out, yields the four membered $f_1{}^1$-family:

$$\left.\begin{aligned} &(\partial E/\partial n_i)_{V,\, S,\, n'}\\ &(\partial H/\partial n_i)_{S,\, P,\, n_i'}\\ &(\partial F/\partial n_i)_{P,\, T,\, n_i'}\\ &(\partial A/\partial n_i)_{T,\, V,\, n_i'} \end{aligned}\right\}=\mu_i. \tag{17}$$

The particularly simple relations of the families (15) and (17) to the geometrical Figs. 1 are worth noting.

3. The Gibbs-Helmholtz type

Either one of the Eqs. (1) yields the following eight membered $f_1{}^1$-family:

$$\begin{array}{l|l} E=H-P\left(\dfrac{\partial H}{\partial P}\right)_{S,\, n_i}, & A=F-P\left(\dfrac{\partial F}{\partial P}\right)_{T,\, n_i},\\ H=F-T\left(\dfrac{\partial F}{\partial T}\right)_{P,\, n_i}, & E=A-T\left(\dfrac{\partial A}{\partial T}\right)_{V,\, n_i},\\ F=A-V\left(\dfrac{\partial A}{\partial V}\right)_{T,\, n_i}, & H=E-V\left(\dfrac{\partial E}{\partial V}\right)_{S,\, n_i},\\ A=E-S\left(\dfrac{\partial E}{\partial S}\right)_{V,\, n_i}, & F=H-S\left(\dfrac{\partial H}{\partial S}\right)_{P,\, n_i}. \end{array} \tag{18}$$

4. Partial derivatives of μ_i with respect to V, S, P, T

The equation:

$$(\partial \mu_i/\partial T)_{P,\, n_i}=-(\partial S/\partial n_i)_{T,\, P,\, n_i'} \tag{19}$$

is found to yield an $f_1{}^1$-family of eight members.

5. The equations of the type:

$$(\partial E/\partial V)_{T,\, n_i}=T(\partial P/\partial T)_{V,\, n_i}-P. \tag{20}$$

This equation, useful in the theory of constant volume thermometry, is found to belong to an eight membered $f_1{}^1$-family.

6. The equations of the type:

$$\left(\frac{\partial T}{\partial V}\right)_{E,\, n_i}=P-T\left(\frac{\partial P}{\partial T}\right)_{V,\, n_i}\Big/\left(\frac{\partial E}{\partial T}\right)_{V,\, n_i}. \tag{21}$$

These equations are found to constitute an eight membered $f_1{}^1$-family.

7. The equations of the type:

$$(\partial H/\partial T)_{P,\, n_i}=T(\partial S/\partial T)_{P,\, n_i}. \tag{22}$$

This equation, important in the determination of entropy from heat capacity, yields an f_1^1-family of eight members.

8. The equations of the type:

$$(\partial H/\partial T)_{P,\ n_i}-(\partial E/\partial T)_{V,\ n_i} = T(\partial P/\partial T)_{V,\ n_i}\cdot(\partial V/\partial T)_{P,\ n_i}. \quad (23)$$

Eq. (23) is the familiar relation between the two heat capacities written as an f_1^1-equation. It is found to belong to an f_1^1-family of four members.

9. Remark on the number of members in an f_1^1-family

The number of members in an f_1^1-family evidently cannot exceed eight. All the families mentioned above have either eight or four members. These are however not the only possibilities because the two f_1^1-equations:

$$E-F=TS-PV, \quad (24)$$

$$E-H+F-A=0, \quad (25)$$

are seen to belong to f_1^1-families of two members and one member, respectively. Some theorems concerning the number of members in a family will be given in a later paper (communication II).

10. Concluding remarks

It is evident that the method here described greatly increases the number of fundamental equations which are readily available. The method can however scarcely be regarded as an alternative to P. W. Bridgman's[4] condensed summary of differential coefficients because it differs too much from the latter both in requirements and in results. It may perhaps find some use as a supplement to the method of Bridgman.

More valuable than the proliferation of formulae seems the way in which the above considerations reveal the symmetry of the equations of thermodynamics, a keen sense of which is helpful to any student of the subject.

The author is indebted to Dr. C. F. Luther of the Department of Mathematics, Stanford University, for much valuable advice.

[4] P. W. Bridgman, Phys. Rev. [2] 3, 273 (1914); see also G. N. Lewis and M. Randall, *Thermodynamics, etc.* pp. 163–165 (1923).

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The Compressibility of Solutions of Three Amino Acids

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The compressibility of aqueous solutions of glycine, α-amino butyric acid, and ϵ-amino caproic acid have been measured over the concentration range up to 2.5 N at 25° and 75°C and up to a maximum pressure of 8000 kg/cm². The results are exhibited in tables giving the volume in cm³ as a function of pressure, temperature, and concentration of that amount of solution which contains one gram of water, and in figures showing the apparent molal volume at 25° as a function of pressure and concentration. The general character of the results is complicated; the most striking result is that at low pressures the apparent compressibility of the acid in solution is positive, which is opposite in sign from all other known solutes. A connection is probable with the high dielectric constant. Other qualitative aspects of the phenomena are discussed.

A NUMBER of the physical properties of that very interesting group of highly polar substances known as Zwitterions have been studied during the last few years. Dr. E. J. Cohn,[1] of the Harvard Medical School, who has contributed so much to our knowledge of these substances suggested that a study of the compressibility at high pressures might be expected to be of interest, and he very kindly undertook to provide the materials from his highly purified stock. It was desired to study the compressibility over as wide a range of concentration as possible, which demanded that the substance have high solubility, and also over as wide a range of composition as possible. The following representatives of the class of Zwitterions were therefore

[1] Edwin J. Cohn, *Die Physikalische Chemie der Eiweisskörper*, Ergebnisse der Physiologie 33, 782–882 (1931).